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METALS AND CERAMICS DIVISION

METALS AND CERAMICS DIVISION MATERIALS SCIENCE PROGRAM
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Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

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INTRODUCTION

The progress and current status of the Materials Sciences Program (Office of Basic Energy Sciences) conducted in the Metals and Ceramics Division are reported herein. These activities represent between one-fifth and one-fourth of the research and development carried out in that division. An overview of the Division's program and the role of the Materials Sciences Program in it are given in the *Metals and Ceramics Division Annual Progress Report for the Period Ending June 30, 1980*, ORNL-5670.

The shift in emphasis from support of nuclear technologies to non-nuclear energy systems has continued. Because the Oak Ridge National Laboratory has emerged as a lead national laboratory in the fossil energy area, we have reoriented or initiated a number of tasks to address the long-range problems associated with this energy source.

Two major changes have occurred in the Materials Science Program during this reporting period. The studies on oxidation of zirconium and refractory metals, diffusion in metals, and tritium diffusion in oxides were replaced by research on the attack of metals by sulfur. The level of effort on solidification of eutectics containing metals and metal oxides was decreased and a structural ceramics program was initiated. The initial emphasis of the latter program is on the processing, structure, and properties of hard ceramics. Consideration of the supply of strategic materials and the needs of energy systems determine the specific systems chosen for study.

Interactions with universities and other laboratories have continued to be an important function of this program. Progress in establishing users groups and collaborative research programs is described in Chap. 7.

A section has been included on the progress made toward establishing a High Temperature Materials Program at ORNL. This program is conducted in several divisions and includes applied as well as basic activities.

1. STRUCTURE OF METALS

1.1 THEORETICAL STUDIES OF METALS AND ALLOYS — J. S. Faulkner

The unifying feature of this program is a mutual interest in certain *theoretical techniques* for studying the electronic states in condensed matter and in relating the properties of solids and surfaces to the electronic states. Techniques that have been invented by this group or that we have played a leading role in developing are multiple-scattering theory, constant-energy-search KKR band theory, discrete-variational-method band theory, theories of disordered solids, coherent potential approximation for substitutional alloys, cluster calculations, and layer calculations for surfaces. We are also involved heavily in investigating the applicability of the local density approach in one-electron calculations of total energies as well as other properties.

These and other techniques are used to investigate certain *phenomenological areas* that are sufficiently diverse that it is useful to describe them separately. The ones that we are presently looking at follow.

Electron-Phonon Interactions — Our studies in this area are based on our constant-energy-search KKR band theory techniques and also the rigid-muffin-tin approximation that was proposed by one of our collaborators. They lead to specific predictions that are used to explain and organize experimental measurements in the areas of superconductivity, high-temperature electrical and thermal conductivity, and neutron diffraction.

Alloy Theory — We have been contributing to the theory of disordered solids since the inception of the theory group. Much of the theoretical data on the electronic states in real alloy systems that is presently available to the scientific community is generated here. This work is used to explain the results of photoemission, soft x-ray, and positron annihilation experiments.

Surface Theory — This program is directed to the theoretical study of the interaction of gases with metal surfaces. The goal is understanding the mechanisms operative in such surface phenomena as corrosion and catalysis on the basis of the underlying electronic structure. A thin-film energy band approach allows us to investigate the effects of electron

delocalization in the surface plane. Cluster programs of various levels of sophistication give us the capability of studying the interactions between surface and gas atoms for a wide range of configurations.

Band Theory — This group has been known for many years for its work on the multiple-scattering theory approach to band theory known as the KKR method. A recent trend in band theory is the development of linearized methods, which speed up the computational process enough to significantly alter the kind of properties for which calculations are feasible. Most of these linearized band theories are based on a hybrid multiple-scattering-variational approach, but we have shown that even more useful equations can be obtained from a pure multiple scattering approach. We are presently investigating the possibility that a quadraticized band theory would have significant advantages over a linearized one.

Our progress in these phenomenological areas is described in more detail below.

1.1.1 Alloy Theory — G. M. Stocks and J. S. Faulkner

The major theoretical advance of this reporting period is a new method for calculating the properties of random alloys from the solutions of the KKR-CPA equations. The method is based on newly derived formulas for the average Green's function and was proved to be necessary by the discovery of unphysical behavior in a Bloch spectral density function, which was calculated according to the formula currently available. The new method provides the necessary theoretical framework for calculating many observables that had previously been impossible to deal with. We are presently calculating the momentum density $N(\vec{p})$, which is used to interpret positron annihilation studies of the Fermi surfaces of random alloys. The new method provides the basis for a critical review of existing formulas for calculating total and component densities of states in the muffin-tin version of the average t -matrix approximation, and they have all turned out to be incorrect.

We calculated the concentration dependence of the residual resistivity of $\text{Ag}_c\text{Pd}_{(1-c)}$ alloys entirely from first principles (Fig. 1.1). The calculations reproduce the large asymmetry in the experimental data and

Fig. 1.1. Residual Resistivity of $\text{Ag}_c\text{Pd}_{(1-c)}$ Alloys. The experimental results were taken variously from B. R. Coles and J. C. Taylor, *Proc. R. Soc. London Ser. A* 267: 139 (1962); W.R.G. Kemp et al., *Proc. R. Soc. London Ser. A* 233: 480 (1956); and R. Fletcher and D. Greig, *Philos. Mag.* 17: 21 (1968).

are off by only about 30% for the magnitude. The concentrations dependence of the residual resistivity in $\text{Ag}_c\text{Pd}_{(1-c)}$ alloys was one of the cornerstones on which Mott's "rigid band" model of electronic states in random alloys and his "sd" model of electrical transport in random alloys were built. Both these models have had enormous influence on the thinking of metallurgists and solid state physicists over the last 45 years. Our calculations show "rigid band" model and the "sd" model to be invalid even for the system for which they were first developed.

Although both lithium and magnesium belong to the class of "simple" metals, the effects of alloying on the densities of states, as monitored by soft x-ray studies, are quite dramatic. The magnesium *L* emission suggests¹ that as the concentration of magnesium is reduced the density of states on the magnesium sites is increasingly peaked at low energies. We

¹J. A. Tagle, E. T. Arkawa, and T. A. Calcott, *Physical Review* (in press).

have calculated the densities of states shown in Fig. 1.2 using the KKR-CPA method and find that the total density of states in the alloy is rather free-electron-like. However, the s -density of states on the magnesium sites (which is being probed in the magnesium L spectrum) is peaked at the bottom of the lithium band. This low-energy peaking results from an incipient s -wave resonance in the magnesium muffin-tin potential. In Fig. 1.3 we compare our calculated Li K and Mg L soft x-ray spectra with experiment. This good agreement could never have been obtained with pseudopotential theory, which has hitherto been suggested as the best way to treat simple metals.

Fig. 1.2. Total and Component Densities of States of an $\text{Li}_{0.8}\text{Mg}_{0.2}$ Alloy. The outer curve gives the total density of states; the various species and symmetry decomposed densities of states are marked in a self-explanatory notation.

Fig. 1.3 Calculated and Measured Soft X-Ray Spectra of an $\text{Li}_{0.8}\text{Mg}_{0.2}$ Alloy. The solid line gives the theoretical prediction, the dots give the measured spectra. The dash line gives the theoretical curve before broadening with a 0.5-eV Gaussian to account for core hole lifetimes.

1.1.1.1 Calculating Properties with the Coherent-Potential Approximation² — J. S. Faulkner and G. M. Stocks

It is demonstrated that the expression that has hitherto been used for calculating the Bloch spectral-density function $A^B(E, \vec{k})$ in the Korringa-Kohn-Rostoker coherent-potential-approximation theory of alloys

²Abstract of paper published in *Phys. Rev. B* 21: 3222-44 (April 1980).

leads to manifestly unphysical results. No manipulation of the expression can eliminate this behavior. We develop an averaged Green's-function formulation and from it derive a new expression for $A^B(E, \vec{k})$, which does not contain unphysical features. The earlier expression for $A^B(E, \vec{k})$ was suggested as plausible on the basis that it is a spectral decomposition of the Lloyd formula. Expressions for many other properties of alloys have been obtained by manipulations of the Lloyd formula, and it is now clear that all such expressions must be considered suspect. It is shown by numerical and algebraic comparisons that some of the expressions obtained in this way are equivalent to the ones obtained from a Green's function, while others are not. In addition to studying these questions, the averaged Green's function formulation developed in this paper is shown to furnish an interesting new way to approach many problems in alloy theory. The method is described in such a way that the aspects of the formulation that arise from the single-site approximation can be distinguished from those that depend on a specific choice for the effective scatterer.

1.1.1.2 First-Principles Band Theory for Random Metallic Alloys³ — B. L. Gyorffy⁴ and G. M. Stocks

We describe and advocate a first-principles approach to the problem of calculating electronic states in random substitutional alloys. We begin by reviewing the three major elements in the band-theory program for pure metals and alloys; that is, specification of the one-electron potential function, solution of the Schrödinger equation, and calculation of observables. The coherent-potential approximation (CPA) as a method for dealing with Hamiltonians having random potentials is motivated through the analogous problem of the conductivity of an inhomogeneous conductor. We then give a detailed description of the CPA for the case of interest,

³Prologue to lecture notes published in *Electrons in Disordered Metals and at Metallic Surfaces*, P. Phariseau, B. L. Gyorffy, and L. Scheire, eds., Plenum Press, New York and London, 1979, pp. 89-192.

⁴University of Bristol, Bristol, U.K.

namely, the calculation of the electronic states of random substitutional alloys for a muffin-tin model of the crystal potential function. For this so-called KKR-CPA (Korringa-Kohn-Rostoker-CPA) we describe the specification of the muffin-tin potential functions appropriate to the alloying species, the evolution of the methods used to solve the KKR-CPA equations, the nature of the solutions, and the calculation of certain observables. Results for the $\text{Cu}_c\text{Ni}_{1-c}$ alloy system illustrate the physical content of the theory. Using the Bloch spectral density, we show how the effects of alloying manifest themselves in the band structure of the alloy. Again using the Bloch spectral density function, the evolution of the alloy Fermi surface as a function of concentration is followed. In order to illustrate the detailed contact that can be made between the *ab-initio* KKR-CPA alloy theory and experiment, we focus on soft x-ray spectroscopy. The one-electron theory of soft x-ray emission and absorption in a random alloy is presented. Calculations of the L_{23} emission spectra for $\text{Cu}_c\text{Ni}_{1-c}$ are compared with the recent experimental results of Durham et al.⁵ In conclusion, some possible future developments are speculated upon, including the implementation of charge self-consistency, development of a spin polarized theory, calculation of total energies, and calculation of electron-phonon coupling.

1.1.1.3 Aspects of the Numerical Solution of the KKR-CPA Equations⁶ — G. M. Stocks, W. M. Temmerman,⁴ and B. L. Gyorffy⁴

We review some of the difficulties encountered in the solution of the KKR-CPA equations and the numerical techniques developed to overcome them. We begin by setting out the KKR-CPA and briefly reviewing the band theory program for random alloys. The nature of the difficulties encountered in solving the KKR-CPA equations is detailed. The numerical techniques

⁵P. J. Durham, D. Chaleb, B. L. Gyorffy, C. F. Hague, J-M. Mariot, G. M. Stocks, and W. M. Temmerman, "Soft X Ray Emission and the Local Densities of States in Cu-Ni Alloys," *J. Phys. P.* 9(8): 1719-30 (August 1979).

⁶Abstract from lecture notes published in *Electrons in Disordered Metals and at Metallic Surfaces*, P. Phariseau, B. L. Gyorffy, and L. Scheire, eds., Plenum Press, New York and London, 1979, pp. 193-222.

developed for the efficient evaluation of the KKR structure constants required in the calculation, for performing the necessary Brillouin zone integrations, and for iterating the KKR-CPA equation are presented.

1.1.1.4 New Formulas for Calculating Properties with the KKR-CPA:
Algebraical⁷ - J. S. Faulkner and G. M. Stocks

The expression that has hitherto been used for calculating the Bloch spectral density function $A^B(E, \vec{k})$ has been found to lead to manifestly unphysical results. We develop an averaged Green's function formulation and from it derive a new expression for $A^B(E, \vec{k})$, which eliminates the unphysical features. The earlier expression for $A^B(E, \vec{k})$ was derived by manipulating the Lloyd formula. Many other expressions for properties have been obtained in this way, and they must be considered suspect. It is shown algebraically that the Gyorffy-Stocks formula for the density of states is equivalent to the Green's-function formula, but most other expressions derived from the Lloyd formula are not equivalent. The expressions obtained from our averaged Green's function are easier to apply for most purposes.

1.1.1.5 New Formulas for Calculating Properties with the KKR-CPA:
Numerical⁷ - G. M. Stocks and J. S. Faulkner

We show that for the $\text{Cu}_c\text{Pd}_{(1-c)}$ alloy system, the existing formula for the Bloch spectral density $A^B(E, \vec{k})$ within the KKR-CPA gives negative values over a range of energies E and wave vectors $\vec{k}$. It is shown that this is not a numerical convergence problem; rather, it is a general problem associated with singularities of the inverse of the single-site t -matrices of the constituent species. We show that the new formula for $A^B(E, \vec{k})$ of Faulkner and Stocks does not have this unphysical behavior and that all the structures in $A^B(E, \vec{k})$ can be understood in terms of states of

⁷Abstract of a paper presented at the March Meeting of the American Physical Society, New York, March 24-28, 1980.

the disordered alloy. Results for the total densities of states of $\text{Cu}_c\text{Ni}_{(1-c)}$ alloys are shown, which support our algebraic conclusion that the Green's-function formulas and the Gyorffy-Stocks formula are equivalent. We also show component densities of states based on our Green's-function formulas. We believe this to be the first totally satisfactory KKR-CPA calculation of component densities of states.

1.1.1.6 Momentum Distribution of Electrons in Random Alloys: The Fermi Surface of $\text{Ag}_c\text{Pd}_{(1-c)}$ Alloys⁷ - G. M. Stocks and B. L. Gyorffy⁴

We derive an expression for calculating the momentum distribution function, $N(\vec{p})$, in random substitutional alloys within the framework of the first-principles KKR-CPA (Korringa-Kohn-Rostoker Coherent-Potential-Approximation) method. The formula is derived by using the methods of calculating observables in the KKR-CPA proposed by Faulkner and Stocks (Sect. 1.1.1.1) and involves no approximations beyond those inherent in the KKR-CPA. We show calculations of $N(\vec{p})$ for an $\text{Ag}_{0.2}\text{Pd}_{0.8}$ random alloy, which show structure resulting from a well defined " Γ -centered" sheet of Fermi surface and from incipient X -centered "ellipses" and a multiply connected "jungle-gym." The implications of these results for positron annihilation experiments in random alloys are discussed.

1.1.1.7 Total and Component Densities of States in the KKR-CPA and Average t -Matrix Approximation⁷ - A. Gonis⁸ and G. M. Stocks

We use the one-dimensional muffin-tin Korringa-Kohn-Rostoker model of Butler to investigate the equivalence or otherwise of various formulas that have been proposed for calculating properties within the KKR-CPA and within the average t -matrix approximation. The previously proposed formulas for component densities of states based on Lloyd formula derivations and those based on a proper Green's function formulation are not equivalent. For the ATA, all the Lloyd-formula-based equations for calculating densities of states that are currently in use can lead to pathological results, while the corresponding Green's-function-based formulas lead to physically sensible results.

⁸Argonne National Laboratory, Argonne, Illinois.

1.1.1.8 Residual Resistivity of AgPd Alloys⁷ — G. M. Stocks and W. H. Butler

We have calculated the residual resistivities of $\text{Ag}_c\text{Pd}_{(1-c)}$ alloys for $0 < c < 1$ from first principles using no adjustable parameters. In these alloys, the Γ -centered sheet of the Fermi surface maintains its integrity throughout the concentration range. Since this sheet provides the dominant contribution to the current, the residual resistivity is determined by the impurity lifetimes and the velocities of the electrons on this sheet. We have calculated these lifetimes and velocities using the *ab-initio* KKR-CPA band theory method for random alloys. Results for $\text{Ag}_{0.8}\text{Pd}_{0.2}$ and $\text{Ag}_{0.2}\text{Pd}_{0.8}$ agree with experiment.

1.1.1.9 Soft X-Ray Emission from Li-Mg and Li-Al Alloys and Comparisons with KKR-CPA Calculations⁹ — T. A. Callcott,^{10,11} J. A. Tagle^{10,12} E. T. Arakawa¹⁰ and G. M. Stocks

The K-emission band of Li and the L_{23} emission bands of Mg and Al have been measured for Li-Mg and Li-Al prepared in a range of concentrations by either coevaporation or by evaporating thin films of Li on Mg(Al) substrates or Mg(Al) on Li substrates. The Li K spectrum is nearly unchanged at all alloy concentrations in the Li-Mg system but broadens and develops a low-energy shoulder for large Al concentrations in the Li-Al system. Both Mg and Al L_{23} spectra are narrower and more peaked at low energy in the equilibrium alloys than in the pure metals. The "many-body" threshold peaks on the Al and Mg L_{23} spectra are generally suppressed by alloying with Li, except for low-temperature coevaporated Li-Al samples, where the peak persists to very Li-rich alloys. Data for a Li-20 at. % Mg alloy are compared with KKR-CPA calculations, and good agreement is found for both the Li K spectrum and the Mg L spectrum.

⁹Abstract of invited paper for Sixth International Conference on Vacuum Ultraviolet Physics. To be published in *Journal of Applied Physics*.

¹⁰Health and Safety Research Division.

¹¹Department of Physics, University of Tennessee, Knoxville.

¹²Departamento de Física Fundamental and Instituto de Física del Estado Sólido (SCIC), Universidad Autónoma, Madrid, Spain.

1.1.2 Electron-Phonon Interactions — W. H. Butler

During the past two years, we have made substantial progress in understanding the electrical and thermal resistivities of transition metals. Extensions of the theoretical and computational techniques that we earlier applied to superconductivity in the transition metals have enabled us to solve the Boltzmann equation (which governs transport) taking full account of the anisotropy of the Fermi surface and of the electron-phonon matrix elements. We obtain good agreement between theory and experiment without having to resort to adjustable parameters, as our results for niobium and palladium in Fig. 1.4 illustrate. This agreement gives us added confidence in the techniques that we use to generate the electron-phonon matrix elements, which are central to the calculation of the superconducting transition temperature.

We expect our work to have a significant impact on the way experimentalists analyze transport data. Typically, a simple model of the electronic structure is used to explain the low-temperature resistivity of transition metals. This model assumes that there are two types of electronic states at the Fermi energy, "s" states, which have a high velocity and carry most of the current, and "d" states, which have a

Fig. 1.4. Electrical Resistivity of Niobium and of Palladium. The solid lines are results of first-principles calculations using no adjustable parameters. The circles and squares are experimental values for niobium and palladium, respectively.

relatively low velocity. The low-temperature experimental resistivity is fit to an expression of the form $\rho(T) = A + \beta T^2 + CT^3 + DT^5$, where the four terms are assumed to arise from: A , impurity scattering; βT^2 , electron-electron scattering; CT^3 , "s to d" electron-phonon scattering (where the electron is scattered between an s state and a d state; DT^5 , "s to s" electron-phonon scattering. The particular power law dependences of the various scattering processes result from further assumptions about the nature of the solution to the Boltzmann equation. Our work shows these assumptions to be seriously in error at the typical analysis of the data to be misleading. The electron-phonon contribution to the resistivity is much more complicated than had been supposed. It is, however, amenable to theoretical analysis and provides much useful information if properly analyzed. Our research program has benefitted from interactions with P. B. Allen of the State University of New York at Stony Brook and from the assignment to ORNL of F. J. Pinski and T. P. Beaulac of that university. It has also benefited from interactions with members of several experimental groups, especially R. K. Williams of the Physical Properties group.

1.1.2.1 Upper Critical Field of Pure Niobium: Calculated Temperature Dependence and Anisotropy^{7,13} — W. H. Butler

The upper critical field, H_{c2} , of niobium was calculated as a function of field direction and temperature taking into account Fermi velocity anisotropy, finite mean free path effects, and strong coupling effects. The calculations use an accurate niobium Fermi surface and no adjustable parameters. Agreement with experiment is excellent for the magnitude, temperature dependence, and anisotropy of H_{c2} , and the deviation of its temperature dependence from that calculated by Hohenberg and Werthamer is due primarily to the anisotropy of the Fermi velocity. Anisotropies in H_{c2} previously ascribed to gap anisotropy are found to result from Fermi velocity anisotropy instead. Strong coupling effects enhance H_{c2} in niobium by a factor that is approximately independent of temperature and is approximately 1.10. Implications of this work for the H_{c2} of A-15 materials is briefly discussed.

¹³A paper on this subject has been published by W. H. Butler, *Phys. Rev. Lett.* 44: 1516 (1980).

1.1.2.2 Electronic Structure and the Electron-Phonon Interaction¹⁴ — W. H. Butler

The electron-phonon interaction affects the physical properties of metals in many ways. It causes, for example, electrical resistivity, electronic mass enhancement, superconductivity, phonon lifetimes, and phonon frequency shifts. Part I of this article relates all these physical effects to the basic electron-phonon interaction and emphasizes their interrelationships. Part II of the article discusses the theory of the electron-phonon matrix element for simple metals, transition metals, and transition metal compounds. The large variation in the electron-phonon interaction between different materials is explained qualitatively.

1.1.2.3 Solutions to the Boltzmann Equation for Electrons in a Metal: Energy Dependence¹⁵ — F. J. Pinski¹⁶

The solution to the Boltzmann equation for electrons in a metal is a distribution function that depends on energy and wave vector. This paper solves the energy dependence by expanding the distribution function in sets of orthogonal functions: (1) energy polynomials, (2) Legendre polynomials in $\tanh(\epsilon_k/2k_B T)$, or (3) a combination of these two choices. To study *only* the effects of the energy dependence, the electrical and thermal conductivities were calculated for a class of isotropic models. For one of these models, the electrical resistivity is 37% lower than the Bloch-Grüneisen result at a temperature of 0.15 (in units of the Debye temperature, θ_D). For thermal resistivity, this method is consistent with the result of Klemens; that is, at very low temperature the correction to the lowest order result is 51%. Corrections are important at temperatures as high as 0.3 θ_D . These results show that the standard — that is, simple

¹⁴Abstract of a review article to be published in *Electronic Structure and Properties*, F. Y. Fradin, ed., Academic Press.

¹⁵Abstract of a paper published in *Phys. Rev. B* 21: 4380-88 (1980).

¹⁶On assignment from the Department of Physics, State University of New York, Stony Brook.

variational — results for the temperature dependence of transport coefficients make significant errors. However, the methods of this paper can obtain accurate results quite easily by computer, not only for simple isotropic models but also for realistic metals. Results for transition metals are briefly mentioned; more complete calculations will be presented elsewhere.

1.1.2.4 Calculation of the Anisotropic Electron-Phonon Mass Enhancement in Copper and Niobium⁷ — F. J. Pinski¹⁶ and W. H. Butler

We have calculated the electron-phonon mass enhancement λ_k in copper and niobium. We used accurate KKR wave functions calculated on a dense mesh of points on the Fermi surfaces. Phonon frequencies and polarizations were obtained from Born-von Kármán force constant fits to neutron data. Electron-phonon matrix elements were calculated in the rigid-muffin-tin approximation. For copper we find $\lambda = \langle \lambda_k \rangle = 0.11$ with an rms deviation of 14%. The enhancement is highest near the necks, in qualitative agreement with interpretations of cyclotron-mass data. For niobium we find $\lambda = 1.11$ with an rms deviation of 5%. The calculated enhancements for niobium differ substantially from those inferred from de Haas-van Alphen measurements.

1.1.2.5 Calculation of the Low-Field Hall Coefficient in Copper and Niobium⁷ — T. P. Beaulac,¹⁶ P. B. Allen,¹⁷ and F. J. Pinski¹⁶

We have solved the linearized Boltzmann equation for electrons in a metal and in the presence of uniform electric and magnetic fields. In lowest order, the low-field Hall coefficient is given as a ratio of quantities that are expressible as averages over the Fermi surface. We used exact KKR wave functions on a dense mesh of about 500 wave vectors on the irreducible 1/48 of the Fermi surface. Results for copper are within 5% of experimental data at room temperature. Similar results are obtained for niobium, for example, within 8% of experiment. These calculations are free of all adjustable parameters.

¹⁷Department of Physics, State University of New York, Stony Brook.

1.1.2.6 Ideal Thermal Conductivity of Palladium and Niobium¹⁸ —
F. J. Pinski,¹⁶ W. H. Butler, and P. B. Allen¹⁷

We have calculated the electron-phonon contribution to the thermal conductivity of palladium and niobium. The Boltzmann equation describes the electronic distribution function in the presence of a thermal gradient. We solved the Boltzmann equation within the rigid-muffin-tin approximation, using a very dense mesh of first-principles Korringa-Kohn-Rostoker wave vectors on the Fermi surface. Phonon frequencies and polarizations were obtained from Born-von Kármán force-constant fits of neutron scattering data. The electron-phonon matrix elements were calculated by using the rigid-muffin-tin approximation. Our calculation is free of adjustable parameters. Agreement with experiment is at the 15% level at room temperature.

1.1.2.7 Exotic Pairing in Metals: Formalism and Application to Niobium and Palladium¹⁹ — W. H. Butler

In all known superconductors the pair-wave function is a singlet (antisymmetric in the electron spins and spatially symmetric). More complicated pairing can occur in principle and has been predicted in palladium. In this paper, a general formalism of $l > 0$ pairing is developed, including the influence of impurities. Previous treatments of $l > 0$ pairing assumed a spherically symmetric Fermi surface, which we find gives large errors in a metal like palladium. Previous treatments also overestimated the depression of T_c due to impurities. Calculations of the electron-phonon Γ_{15} ("p-wave") coupling constants for niobium and palladium suggest that exotic pairing will be hard to observe in metals.

1.1.3 Surface Theory — G. S. Painter

Our major effort during the year has been to develop refined theoretical techniques for carrying out studies within a cluster framework,

¹⁸Abstract of a paper presented at the International Thermal Conductivity Conference, proceedings to be published.

¹⁹Extended abstract of a paper presented at the La Jolla Conference on "Superconductivity in d - and f -Band Metals," June 1980, proceedings to be published by Academic Press.

which focuses on the *local* bonding within a cluster of atoms. Our capabilities in this area are unique in that our discrete variation method (DVM) cluster techniques are directly related to those of our DVM energy band method so that localization effects can be obtained by correlating results from our energy-band and cluster studies of a given system.

We are continuing our studies of the precursor stages of aluminum oxidation (the molecular dissociation of O_2) in order to determine the basic mechanisms of surface-induced dissociation. There is an increasing amount of experimental data²⁰⁻²² on well-characterized single crystal samples (Al 2p-core shifts, EXAFS determination of oxygen bond site, etc.), and our program will focus on relating the one-electron features for various bond sites to experiment in order to assess the capabilities of the surface probe for identifying surface species. In this work an efficient "self-consistent-charge" procedure is used in which self-consistency is established in the charge density as determined through a Mulliken population analysis of the occupied states. While full self-consistency is not attained (as in our localized muffin-tin orbital approach, below), we have a commensurate increase in capability to treat larger clusters. Thus, we are using this scheme for problems where higher accuracy is not required.

A major project carried out in collaboration with J. Harris²³ was brought to a successful stage of completion this year. Our localized muffin-tin-orbital cluster approach represents a new level of completeness for carrying out fully self-consistent electronic structure and total energy calculations for atomic clusters. Our present efforts involve completing calculations for selected dimers, investigating the accuracy of

²⁰L. I. Johansson and J. Stohr, "Bonding of Oxygen on Al(111): A Surface Extended X-Ray Absorption Fine-Structure Study." *Phys. Rev. Lett.* 43: 1882-85 (1979).

²¹W. Eberhardt and F. J. Himpsel, "Dispersion and Symmetry of Oxygen-Induced Bands on Al(111)." *Phys. Rev. Lett.* 42: 1375-78 (1979).

²²S. A. Flodström et al., "Ordered Oxygen Overlayer Associated with Chemisorption State on Al(111)." *Phys. Rev. Lett.* 40: 907-10 (1978) and references therein.

²³Permanent address: Institut für Festkörperforschung der Kernforschungsanlage, Jülich, FRG.

various exchange-correlation functionals, and further refining the accuracy of the approach (a paper describing one such refinement is summarized in Sect. 1.1.3.2). Our goal in constructing this theoretical technique has been to optimize efficiency and accuracy in order to calculate reliably total energies. Our future studies will exploit this capability and allow us to ascertain the predictive aspects of the density functional formalism. In another development, carried out in collaboration with F. W. Averill,²⁴ we have constructed a cluster approach based on Gaussian orbitals. This approach is currently being used to study various density functionals in applications to dimers. We plan to extend our more elaborate cluster methods to treat the *energetics* in our oxygen-aluminum chemisorption studies. A. T. Fromhold, Jr.,²⁵ is an authority on the theory of metal oxidation, and he has joined this program with the goal of establishing a better link between quantum theoretical calculations, in which we have expertise, and the phenomenological oxidation theories used in materials science.

1.1.3.1 Localized Muffin-Tin Orbital Basis for Atomic Cluster Calculations Within the Local Density Formalism²⁶ — J. Harris²³ and G. S. Painter

A new approach for solving the Hohenberg-Kohn-Sham density functional equations for atomic clusters of moderate size and arbitrary symmetry is described. A basis set is introduced in the spirit of the LCMT0 (linear combination of muffin-tin orbitals) method of Andersen with a $(\phi, \dot{\phi})$ form inside each atomic sphere. However, advantageous features of the conventional LCAO method are brought in by introducing only atomic-like orbital tails in the region outside the spheres. The "common- κ " approximation and cellular partitioning of the LCMT0 approach are abandoned; with this approach it becomes necessary to carry out some three-dimensional integrations. Techniques are introduced to allow all integrals contributing to the secular matrix and total energy to be evaluated either

²⁴ORAU Visiting Professor from Judson College, Elgin, Illinois.

²⁵NSF Visiting Professor from Physics Department, Auburn University, Auburn, Alabama.

²⁶Abstract of a paper to be published in *Physical Review B*.

semianalytically or by the Gaussian integration of smooth functions. Preliminary results for H_2 and O_2 demonstrate the practicality of the scheme.

1.1.3.2 Calculation of the Multipole Potential from an Arbitrary Localized Charge Distribution²⁷ — G. S. Painter

A method for solving Poisson's equation as a set of finite-difference equations is described for an arbitrary localized charge distribution expanded in a partial wave representation. The procedure is an extension of the widely used technique developed by Loucks for spherically symmetric charge densities. In the present development, the higher partial wave components of the density lead to an l -dependence in the boundary conditions and the finite-difference equations. The potential components for $l > 0$ can be calculated recursively with the same degree of accuracy and efficiency as for the $l = 0$ case. This procedure requires the additional computational step of evaluating a one-dimensional integral of each density component to determine the multipole moment, required by the boundary condition at large r . Specific modifications required to adapt the Loucks technique for this more general charge density are described, and illustrative results are given for a model density with components $\rho_L(r) = C_L r^L \exp(-\alpha_L r)$, which can also be treated analytically.

1.2 X-RAY SCATTERING RESEARCH — R. W. Hendricks

The x-ray scattering research task has focused on small-angle x-ray scattering (SAXS) studies. During this reporting period a substantial effort was devoted to the study of polymers. These studies were carried out in large part by collaboration with guest scientists attached to our group or by visitors participating in the Users Group of the National Center for Small-Angle Scattering Research.

²⁷Abstract of a paper submitted to *Physical Review B*.

1.2.1 Polymer Research

1.2.1.1 Temperature-Dependent Small-Angle X-Ray Scattering From Poly(Vinylidene Fluoride)²⁸ — J. M. Schultz,²⁹ J. S. Lin, R. W. Hendricks, R. R. Lagasse,³⁰ and R. G. Kepler³⁰

X-ray scattering measurements over the angular range 2 to 30 mrad are reported for a uniaxially oriented poly(vinylidene fluoride) film containing the phase I crystal polymorph. Each intensity profile exhibits at about 10 mrad an interference peak arising from quasi-periodic variation in electron density between crystalline and amorphous phases of the polymer. Over the temperature range 25 to 72°C, reversible changes of 23% in peak intensity and 6% in peak position are observed. These reversible changes in x-ray scattering are analyzed in terms of a one-dimensional stack of alternating crystalline and amorphous layers. These model calculations show that the observed changes in the interference peak cannot be explained solely by thermal expansion within the two phases. In accordance with previous studies on other semicrystalline polymers, this discrepancy between observed scattering results and the predictions for thermal expansion is taken to be evidence that the crystallinity changes reversibly over the investigated temperature range. This evidence for reversible crystal melting is consistent with a hypothesis proposed by Kepler and Anderson to explain the pyroelectric response of polarized phase I poly(vinylidene fluoride) films.

1.2.1.2 Small-Angle X-Ray Scattering From Polybutene-1 Films Crystallized from a Highly Extended Melt³¹ — J. Peterman,³² J. M. Schultz,²⁹ R. W. Hendricks, and J. S. Lin

In an experimental analog to many industrial processes, very thin (0.1–0.2 μm) polymer films have been produced under elongational strain

²⁸Summary of a paper to be published in *Journal of Applied Physics*.

²⁹On Assignment to ORNL during a leave from the University of Delaware, Newark.

³⁰Sandia Laboratories, Albuquerque, New Mexico.

³¹Abstract of a paper to be published in *Journal of Materials Science*.

³²Universität des Saarlandes, Saarbrücken, FRG.

rates of more than $10^4/s$. The microstructure of these films is thus of considerable technological importance. As is the case in most materials science research, it is essential to characterize such films with a variety of physical techniques. These films are sufficiently thin to permit transmission electron microscopy, and the results of such an investigation have been reported previously. In this companion paper, we present results of a small-angle x-ray scattering (SAXS) investigation of the same films.

1.2.1.3 Annealing of Polypropylene Films Crystallized From a Highly Extended Melt³³ — J. M. Schultz,²⁹ J. S. Lin, R. W. Hendricks, J. Petermann,³² and R. M. Gohil³²

Thin films of isotactic polypropylene were drawn from the melt at a very high rate of extension. Transmission electron micrographs of this material reveal fibrous crystals lying along the draw direction. The chain axis and fiber axis are identical. Dark-field micrographs show a dark-light modulation along the fiber axis. Annealing at temperatures below 110°C produces no qualitative change in the electron microscope observations. Annealing between 110 and 150°C produces the gradual dominance of lamellar crystals oriented normal to the draw direction. Data by SAXS exhibit a strong streaking normal to the fiber axis, in broad agreement with the observed fibrosity. A Bragg peak along the draw directions shows that the modulation observed microscopically is a density modulation. The absence of second-order maxima and the dependence of the SAXS peak on treatment temperature strongly suggest that the axial modulation is a spinodal decomposition of the material into crystalline and amorphous regions.

³³Abstract of a paper to be published in *Journal of Polymer Science - Polymer Physics Edition*.

1.2.1.4 The Kinetics of Defect Clustering in Fibrillar Polypropylene Crystals,³⁴ — J. Peterman,³² J. M. Schultz,²⁹ R. M. Gohil,³² R. W. Hendricks, and J. S. Lin

Polypropylene films were produced by solidification during high-rate ($>10^4/s$) melt drawing. Small-angle x-ray scattering (SAXS) data were collected during interruptions of the annealing of these films. Fibrillar crystallization took place during the melt-drawing process. The fibrils exhibit an axial density modulation. Results of SAXS and transmission electron microscopy show that annealing increases the amplitude of the density modulation. Detailed examination of the SAXS curves shows that the modulation is approximately sinusoidal and that the amplification of the density modulation occurs with no change in periodicity. Comparison of SAXS curves taken at different times during annealing suggests a process similar to spinodal decomposition. It is proposed that the microstructural change within a fibril takes place by the axial motion and clustering of chain defects.

1.2.2 Irradiation Effects in Metals

1.2.2.1 The Use of Small-Angle X-Ray and Neutron Scattering for Characterizing Voids in Neutron-Irradiated Metals and Alloys³⁵ — R. W. Hendricks

Small-angle x-ray and neutron scattering techniques are powerful analytical tools for investigating long-range fluctuations in electron (x-rays) or magnetic moment (neutron) densities in materials. In recent years they have yielded valuable information about voids, void size distributions, and swelling in Al, Al alloys, Cu, Mo, Ni, Ni-Al alloys, Nb, Nb alloys, stainless steels, graphite, and SiC. In the case of aluminum information concerning the shape of the voids and the ratio of

³⁴Summary of paper to be submitted to *Polymer*.

³⁵Summary of a paper to be published in TMS-AIME Conference Proceedings, *Advanced Techniques for the Characterization of Microstructure*. Conference held at Las Vegas, Nevada, February 24-28, 1980.

specific surface energies was obtained. The technique of small-angle scattering and its application to the study of voids are reviewed in the paper. Emphasis is placed on the conditions that limit the applicability of the technique, the interpretation of the data, and a comparison of the results obtained with companion techniques such as transmission electron microscopy and bulk density.

1.2.2.2 A Small-Angle X-Ray Study of Neutron-Irradiation Effects in Molybdenum and Molybdenum Alloys³⁵ — J. S. Lin, R. W. Hendricks, J. Bentley, and F. W. Wiffen

Small-angle x-ray scattering (SAXS) has been employed to study voids that were created by neutron irradiation in molybdenum and molybdenum alloys. Specimens of unalloyed molybdenum and TZM (titanium-zirconium-molybdenum alloy) were irradiated in the EBR-II at temperatures between 425 and 1000°C to fluences of 2.5×10^{26} neutrons/m² (>0.1 MeV) or higher in one group, and in another group at temperatures between 600 and 1500°C with fluence of about 4.0×10^{25} neutrons/m². The SAXS studies were performed on the ORNL 10-m camera using Mo K α radiation. Companion transmission electron microscopy (TEM) was performed on the same specimens. Void sizes in the range from 5 to 20 nm, size distributions, and swelling were determined from both the x-ray and TEM data. After correction for the fact that SAXS and TEM measure different moments of the void size distribution, the results from the two techniques were in general agreement; however, in some cases dislocation loops contributed significant x-ray scattering, which obscured void scattering. In two bicrystal samples the diffraction maxima from an ordered void lattice were observed. The void lattice parameters (23 and 30.2 nm, respectively) are in good agreement with the values obtained from the small-angle electron scattering in an electron microscope.

1.2.3 Facility Development

1.2.3.1 An Intelligent CAMAC I/O Module Based on the Signetics 8X300 Microcontroller³⁶ — G. W. Turner³⁷ and R. W. Hendricks

An intelligent CAMAC I/O module based on the Signetics 8X300 microcontroller has been developed. Sixteen 8-bit I/O ports have been utilized; eight are dedicated to data transfers with external devices and/or processes and eight are dedicated to communication with the CAMAC dataway. Separate status and data registers are provided. The input status port (SIN) can receive up to seven individual signals from external devices or the host computer, while the output status port (SOUT) can be used to provide up to seven internally graded LAMs, and one bit can be used to generate a Q-response for termination of block transfers. Diagnostic software has been developed to operate on the host computer and fully tests all implemented instructions. In our application the device is used in a high-speed memory mapping scheme for data acquisition with a two-dimensional position-sensitive detector system.

1.2.3.2 The LASL-ORNL Fast Digital Data Acquisition System³⁸ — R. W. Hendricks, P. A. Seeger,³⁹ J. W. Scheer,³⁹ and S. Suehiro⁴⁰

A data acquisition system for recording multiparameter digital data into a large memory array at 1 MHz is described. The system consists of a MOSTEK MK8600 2048K × 24-bit memory system, I/O ports to various external devices including the CAMAC dataway, a memory incrementer, and a daisy chain of experiment-specific modules that calculate the memory address that is to be incremented. The design of the daisy chain permits multiple modules and provides for easy modification as experimental needs change. Several specific examples are described.

³⁶Abstract of *Nucl. Instrum. Methods* 169: 373-80 (1980).

³⁷Instrumentation and Controls Division.

³⁸Abstract of ORNL/TM-7325 and LASL-8260-MS.

³⁹Los Alamos Scientific Laboratory, New Mexico.

⁴⁰Polymer Research Institute, University of Massachusetts, Amherst, and on assignment to ORNL. Permanent address: Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.

1.2.3.3 A CAMAC Modular Programmable Function Generator⁴¹ — G. W. Turner,³⁷ S. Suehiro,⁴⁰ and R. W. Hendricks

A CAMAC modular programmable function generator has been developed. The device contains a 1024-word by 12-bit memory, a 12-bit digital-to-analog converter with a 600-ns settling time, an 18-bit programmable frequency register, and two programmable trigger output registers. The trigger registers can produce programmed output logic transitions at various (binary) points in the output function curve and are used to synchronize various other data acquisition devices with the function curve.

1.3 SYNTHESIS AND CHARACTERIZATION OF STRUCTURAL CERAMICS — V. J. Tennery

A major part of this year's effort has been devoted to the preparation and characterization of hard ceramics based on TiB_2 or $\text{TiB}_2\text{-CrB}_2$ solid solutions as model systems. This work has included fabrication studies in which nickel powder is blended with the diboride and hot-pressed at temperatures near its melting point to accomplish liquid-phase sintering. Reactions between the nickel and the boride result in a hard, erosion-resistant material. Particulate and coal slurry erosion test data on our first samples, obtained by the Albany Research Center (ARC) and the Battelle Columbus Laboratories (BCL), indicate that under certain conditions some of our experimental compositions have an erosion resistance comparable to or better than cobalt-bonded tungsten carbide. Additionally, specimens of these materials have been prepared as experimental cutting tools for use on steels and special alloys.

In another area, work has been done on the directional solidification of oxide-metal eutectics in the system $\text{ZrO}_2(\text{Y}_2\text{O}_3)\text{-Al}_2\text{O}_3(\text{Cr}_2\text{O}_3)\text{-Mo}$, and arrangements were completed for evaluation of these materials as abrasive grains for metal grinding.

Fayalite (Fe_2SiO_4) crystals were grown and distributed to various laboratories for property measurements. Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) crystal-growth work was completed, and flux growth of monazite (LaPO_4) crystals

⁴¹Abstract of ORNL/TM-7363.

containing Np, Pu, Am, and Cm was performed as part of an effort to evaluate this crystal as a possible radioactive waste host. Quartz crystals were also grown under a variety of conditions to determine whether crystals of significantly higher electrical Q can be produced.

1.3.1 Borides and Other Hard Ceramics — V. J. Tennery

During this period, a significant part of our effort was devoted to the synthesis, fabrication, characterization, and evaluation of hot-pressed boride ceramics of the molar composition $(1 - y)(\text{Ti}_{1-\alpha}\text{Cr}_\alpha\text{B}_2) + y\text{Ni}$ with $y = 0.10, 0.15, \text{ and } 0.20$ and $\alpha = 0, 0.2, \text{ and } 0.4$. These materials constitute a model system enabling study of the relationships between the microcomposition and microstructure of hard, erosion-resistant ceramic materials in which liquid-phase sintering plays an active role in densification.

1.3.1.1 Synthesis, Characterization, and Properties of Diboride Ceramics — V. J. Tennery, G. W. Clark, C. B. Finch, J. D. Holder, and C. S. Yust

The transition metal diborides TiB_2 and CrB_2 are each characterized by a high hardness and high melting point. Because of their refractory nature, it is generally necessary to densify them under pressure at temperatures near 2000°C before a dense, polycrystalline body of potential application is produced. Liquid-phase sintering has previously been shown to permit densification at much lower temperatures.

Studies of the densification of TiB_2 and $\text{TiB}_2\text{-CrB}_2$ solid solutions by liquid-phase sintering are employing nickel as the fluidizing medium. This choice was based on the eutectic temperature of 1180°C reported for the $\text{TiB}_2\text{-Ni}$ system and the conclusion that liquid-phase sintering should be possible at relatively low temperatures. The microstructure and properties of compositions from this system are being determined as a function of nickel content up to 20 mol %. Studies were also made on the hot-pressing parameters required to achieve high densities, as well as processes for synthesizing solid solutions of TiB_2 and CrB_2 .

Scanning electron microscope (SEM) data had shown that the commercial TiB_2 powders contained a significant fraction of particles large relative to the average particle diameter. This coarse particle fraction results in a wide variation of grain size in the fabricated body and could adversely affect the strength and other properties. A study was completed with personnel at the Oak Ridge Gaseous Diffusion Plant to determine the particle-size distributions in the as-received TiB_2 powders and in the TiB_2 powder subjected to several classification regimes. A Vortec C-13 classifier was employed, and optimum operating parameters were determined for maximizing the fine-fraction yield. The particle-size distributions are shown in Fig. 1.5 for the as-received powder, the classified fine fraction, and the coarse reject fraction. The mean particle size decreased from 7.2 μm for the as-received powder to 5.6 μm for the fine fraction. The fine-fraction distribution was also considerably narrower after classification, ranging from 0.5 to 13.5 μm . Scanning electron micrographs of some of the powders are shown in Figs. 1.6 and 1.7. In Fig. 1.6 it is apparent that the as-received powder contains a coarse particle population having a mean diameter 5 or more times that of the fines.

Fig. 1.5. Particle Size Distributions of Commercial TiB_2 Powders as Received and After Classification by Vortec Classifier.

Fig. 1.6. Scanning Electron Micrographs of As-Received Commercial TiB_2 Powder. ORGDP photographs.

(a)

20 μm

(b)

5 μm

Fig. 1.7. Scanning Electron Micrographs of the Fine Fraction of Classified Commercial TiB_2 Powder. ORGDP photographs.

As shown in Fig. 1.7, the classified powder consists of a population devoid of large particles and shows many particles with the sharp angular corners desirable in the microstructure of a cutting tool. Nickel-bonded diboride bodies are being hot-pressed from the size-classified powders, and their properties are compared with bodies fabricated from the as-received (nonclassified) powders.

Previous results had indicated that the substitution of chromium for titanium (up to about 40% in TiB_2) could produce a more fracture-resistant material than TiB_2 alone. Experiments were conducted to identify a process whereby homogeneous TiB_2 - CrB_2 solid solutions could be synthesized. Two values of Cr/(Ti + Cr) mole ratio, 0.20 and 0.40, were selected. Because of the refractory nature of these compounds and their sluggish diffusion behavior at moderate temperatures, powdered mixtures of TiB_2 and CrB_2 have to be annealed at temperatures well above 1800°C for prolonged periods (~24 h) before interdiffusion begins. We explored reactions with Ti-Cr-B mixtures and reactions with TiO_2 , Cr_2O_3 , B_4C , and C for synthesizing the (Ti,Cr) B_2 solid solutions. Initial results indicate that reaction of Ti, Cr, and B produces the best solid-solution product. Fabrication and characterization of materials in the series $(1 - y)(Ti_{0.8}Cr_{0.2}B_2) + yNi$ and $(1 - y)(Ti_{0.6}Cr_{0.4}B_2) + yNi$ are under way.

During this year, a new hot-press facility was obtained. The unit is capable of temperatures up to 2200°C in vacuum or inert gas environments with pressing loads up to 88 kN.

X-ray diffraction studies of several experimental compositions were completed and many are still under way. Significant amounts of reaction occur between the nickel and the diboride phase at the relatively low hot-pressing temperature of about 1450°C. In the compositions having $y = 0.10, 0.15$, and 0.20 in the series $(1 - y)TiB_2 + yNi$, the secondary phases (those other than TiB_2) present after fabrication vary in an orderly way with increasing value of y . In most cases the fabricated body contains at least two secondary phases. Also, crystalline nickel is not present to any extent after hot-pressing, nor are any of the four reported nickel borides clearly identifiable. Optical microscopy results indicate that significant grain boundary motion occurs during densification; the

nickel appears to facilitate eutectic formation and liquid-phase sintering and is finally incorporated on solidification into complex phases whose identities are presently unknown.

Observation of the optical microstructure of our TiB_2 -based specimens has in the past been complicated by the inability to etch chemically the grain boundary regions between the TiB_2 grains while simultaneously developing observable structure within the TiB_2 phase. We developed a technique using an evaporated tin oxide film on the polished specimen surface. This technique including examination under polarized light overcomes the previous problems. The various phases or different orientations of the same phase are distinguished by means of an optical phase shift at the film-specimen interface. This shift depends upon the optical constants of the film and the underlying compound or phase of interest. This technique has been referred to in the literature as "deposition etch." Using this technique we have determined that standard polished sections of our diboride ceramics often appear to exhibit relatively high porosity because the optical field consists of the relatively bright TiB_2 phase and smaller dark angular areas, which were previously assumed to be voids. These observations were inconsistent with immersion density measurements, which indicated densities greater than 95% of the expected theoretical density. The deposition etch technique has shown that in most cases the areas previously presumed to be pores were in fact a phase having much lower reflectivity than the primary TiB_2 phase. An example of the microstructure of one of these materials is shown in Fig. 1.8. Figure 1.8(a) displays a field in a polished specimen TiB_2 -10 mol % Ni under bright-field oil immersion conditions. Figure 1.8(b) shows the same field with the tin oxide film, using polarized light and oil immersion. In Fig. 1.8(b), the TiB_2 grains are clearly delineated, as are secondary phases that initially appeared in Fig. 1.8(a) to be porosity (for example, at point A). In addition, Fig. 1.8(b) reveals numerous curved grain boundaries between TiB_2 grains, as well as several examples of grain triple points with angles near 120° . These observations suggest that significant mass transport had occurred during the 1450°C hot-pressing.

We also performed hot microhardness measurements on several diboride specimens, and Fig. 1.9 compares the diamond pyramid hardness (DPH) as a

(a)

(b)

20 μm

Fig. 1.8. Optical Micrographs of Hot-Pressed Diboride Ceramic Having Initial Composition TiB_2 -10 mol % Ni with Tin Oxide Coating. (a) Bright field. (b) Polarized light.

Fig. 1.9. Hot Microhardness of Hot-Pressed Diboride Ceramic Having the Initial Composition TiB_2 -10 mol % Ni Compared with Commercial Cemented Carbide (WC-8 wt % Co). Tungsten carbide data from R. H. Wentorf, R. C. DeVries, and F. P. Bundy, "Sintered Superhard Materials," *Science*, 208: 873-80 (May 23, 1980).

function of temperature for a specimen of the initial composition TiB_2 -10 mol % Ni with that of a commercial, cobalt-bonded tungsten carbide product. These data indicate that the diborides are quite hard, retaining their hardness to temperatures in the range 500 to 600°C.

We are also characterizing these materials by transmission electron microscopy, seeking to determine the grain boundary structure and the identity of the primary and secondary phases. Electron diffraction analyses are anticipated to supplement the x-ray diffraction data and aid in identification of secondary phases. In addition, analytical electron microscopy has just been started with the goal of determining the elemental distributions within the secondary phases. Figure 1.10 illustrates a grain boundary region observed in a specimen of the initial composition TiB_2 -15 mol % Ni, revealing a triple point junction between three TiB_2 grains and a grain boundary in which crystals appear to have grown.

Fig. 1.10. Transmission Electron Micrograph of Hot-Pressed Diboride Ceramic Having Initial Composition TiB_2 -15 mol % Ni.

During this year, certain properties of our diboride materials have been determined by investigators at other laboratories, and arrangements have been completed for the performance of other measurements. This work includes particulate erosion tests at the Albany Research Center (ARC), coal-oil slurry erosion tests at Battelle Columbus Laboratories (BCL), engineering wear tests at Vanderbilt University, flash thermal diffusivity measurements at Virginia Polytechnic Institute and State University, and machine-cutting-tool tests at the Y-12 facility of Union Carbide, Oak Ridge. Some results are available from the ARC and BCL test facilities, and these will be briefly reviewed. The ARC test is designed to determine the erosion resistance of hard materials for use as valve components in a high-velocity particulate-laden gas stream, such as may be experienced in coal gasification systems. The BCL test is designed to evaluate hard materials in a high-velocity jet of anthracene oil containing dissolved solvent refined coal products (SRC-I). This test simulates the environment of a pressure letdown valve trim in a coal liquefaction plant.

Diboride samples from the compositional series $(1 - y)\text{TiB}_2 + y\text{Ni}$ having y values of 0.10, 0.15, and 0.20 were tested in both the ARC and BCL facilities. The results are given in Tables 1.1 and 1.2. In the ARC facility materials are classified according to a Relative Erosion Factor (REF) parameter with Stellite 6B having a defined value of unity. From Table 1.1, it is apparent that our diboride ceramics have a particulate erosion resistance at 25°C that is comparable to that of the cemented carbides. This property is valid for both 20 and 90° impingement angles. The specimen designated as NT-80B had the highest erosion resistance. In the BCL facility materials are characterized according to the maximum depth of the erosion pit formed in the material by a jet that impinges the sample at 20° from the surface. Table 1.2 shows that the boride samples were not quite as erosion resistant as the best cemented carbides. Again the NT-80B specimen exhibited the highest erosion resistance. In this case, the pit depth was 3.9 times that for K-701 cemented tungsten carbide. According to these results, the erosion rate of these materials appears to be sensitive to the initial composition, that is, the initial nickel content. The x-ray diffraction data show that the specific constitution of the secondary phases in these materials depends strongly upon

Table 1.1. Erosion properties of ORNL boride ceramics (ARC test facility)^a

Material Designation	Major Phase	Initial Nickel Content (mol %)	REF ^b	
			20°	90°
NT-80B	TiB ₂	20	0.008	0.036
NT-85B	TiB ₂	15	0.017	0.046
NT-90B	TiB ₂	10	0.013	0.108
K-602 ^c	WC		0.01	0.11
K-701 ^c	WC		0.02	0.25
K-801 ^c	WC	6	<i>d</i>	0.32

^aTest conditions: 25°C, 27- μ m-diam Al₂O₃ particles, velocity = 170 m/s, 180 s.

^bREF calculated by dividing volume loss of sample by volume loss of Stellite 6B tested under identical conditions.

^cKennametal cemented tungsten carbide products — shown for comparison.

^dNot available.

Table 1.2. Erosion characteristics of ORNL boride ceramics (BCL test facility)^a

Material Designation	Major Phase	Initial Nickel Content (mol %)	Maximum Depth of Erosion Pit (μ m)
NT-80B	TiB ₂	20	17.8
NT-85B	TiB ₂	15	35.6
NT-90B	TiB ₂	10	30.5
K-701 ^b	WC		4.6

^aTest conditions: 343°C, oil jet containing 24 wt % dissolved SRC-I (Wilsonville product, Run 4b), impingement angle = 20°, H₂/Ar carrier gas, 3.6 ks.

^bKennametal cemented tungsten carbide product — shown for comparison.

the volume fraction of nickel originally present, the hot-pressing parameters, and probably the boride particle size distribution since this distribution will initially control available interfacial contact area between the TiB_2 and the nickel phase during densification.

1.3.2 Eutectics — G. W. Clark

Studies in the directional solidification of high-temperature eutectic systems by the internal zone growth (IZG) technique have formed the central theme. We continue to devise and improve the methods of directional solidification and crystal growth, to develop an increased understanding of crystal-growth processes and kinetics, and to provide materials needed in research. It is satisfying to point out that the mathematical modeling of our IZG technique has been selected by the 1980 Gordon Conference on Crystal Growth for the session entitled "Fundamental Considerations in Crystal Growth." This talk will be presented by R. F. Sekerka, Carnegie-Mellon University. J. D. Holder, Structural Ceramics Group, presented an invited review of our work at a symposium sponsored by the German Metallurgical Society in Konstanz, Germany, and three seminars in Germany and the Netherlands. This program has shifted emphasis towards the design considerations of high-strength, toughened eutectics. The first success was the growth of the eutectic ZrO_2 - ZrB_2 .

1.3.2.1 Mathematical Modeling of Internal Zone Growth (IZG) and Electrical Conductivity Tailoring of Compacts — G. W. Clark and J. D. Holder

The directional solidification of many high-melting eutectics by crucible techniques is severely limited by the lack of compatible crucible materials. Our IZG technique circumvents the problem by balancing the heating effect with large radiant heat losses at the sample surface, producing an unmelted skin, which serves as the crucible. This is proving to be an important technique for both laboratory studies and technology in general.

One can devise a mathematical model for the above process by using two partial differential equations, which describe the heat flow and electrical conductivity. However, the variables in these two equations are interrelated, and the mathematics becomes very complex. We sought the assistance of R. F. Sekerka (Carnegie-Mellon University). Working with one of his students, R. A. Hartzell, Sekerka described the growth process theoretically. As a result, Sekerka and Hartzell were able to predict a temperature instability related to the rf coupling and heat transfer at various frequencies, sample diameters, and sample electrical conductivities. The instability had been observed in our own laboratory, although not recognized, during our experiments with the system $\text{Cr}_2\text{O}_3\text{-Mo}$. Often, as we approached the melting temperature the surface temperature would increase rapidly, the surface would melt, and the molten sample would be lost. This work by Sekerka and Hartzell is one of three topics selected by the 1980 Gordon Conference on Crystal Growth for the session entitled "Fundamental Considerations in Crystal Growth."

In our annual report last year, we based much emphasis on the electrical conductivity tailoring of oxide-metal compacts. This new technique circumvented the occurrence of the above instability during initial sample heat to the melting temperature.

Electrical conductivity tailoring has also been extended to our new investigation of eutectic solidification in metal oxide-metal boride systems. In this case, the technique appears to work equally well. However, the metal oxide-metal boride experiments have only recently been started.

1.3.2.2 Oxygen Partial Pressure and Regular Solution Model for Phase Equilibrium in Oxide-Metal Eutectic Systems — J. D. Holder and G. W. Clark

The application of the phase rule to $\text{M}_2\text{O}_3\text{-M'}$ ($\text{M'} \neq \text{M}$) oxide-metal eutectic systems shows that in an atmosphere buffered to maintain a constant oxygen pressure only pseudobinary (i.e., two-phase, three-component) eutectic composites can be grown. The thermodynamic regular solution model has been used to calculate the variation

of activity coefficient with oxygen pressure in oxide melts produced from a mixture of Cr_2O_3 and Mo. The calculations indicate that the metallic phase would be a Mo-Cr alloy and that the Cr content should increase as the oxygen pressure is reduced.

Composite growth experiments by IZG and cold-crucible skull melting techniques were performed to test the predictions; Fig. 1.11 gives the results. The melting techniques did not permit reaching equilibrium in gas mixtures with low CO_2 contents. However, as the melt was held for longer times, the chromium content of the molybdenum-chromium fiber approached the predicted composition.

The regular solution model has been shown to be an adequate treatment to predict the pseudobinary composition of high-temperature oxide-metal eutectic composites. Also, it has been demonstrated that oxygen pressure and starting composition (i.e., oxide-metal mixture) are the critical parameters in controlling the oxide-metal eutectic composite composition.

Fig. 1.11. Dependence of Chromium Content in Mo-Cr Fibers in a Cr_2O_3 -Mo Eutectic upon CO_2 Concentration in the Growth Atmosphere. "Calculated" curve is fitted to calculated closed points. Dashed line is fitted to experimental open points.

1.3.2.3 Chemical and Structural Considerations for Design of High-Strength Toughened Eutectics — G. W. Clark and J. D. Holder

Refractory metal oxide-metal eutectics are a relatively new class of high-temperature materials that we discovered soon after developing the IZG technique for directional solidification. Recent reports on these materials show that their yield point stress, work-of-fracture, and Charpy impact strength are 2.5 to 10 times those of similar primary-phase materials. These data encourage us to believe that carefully designed refractory eutectics could have important structural applications. Thus, we are exploring the use of eutectic materials for the manufacture of high-strength, tough cutting tools or hard, corrosion-resistant valve trim. This interest has been intensified by the recent shortages of minerals containing cobalt, tantalum, and tungsten, as well as by the recent severe price increases for these critical materials. It is significant that our conventional machine-cutting tool technology is largely based on tungsten and cobalt, both of which are now in increasingly short supply.

In mid-1979 a major supplier of abrasive materials announced its plans for producing a new grinding grit based on a eutectic in the $ZrO_2-Al_2O_3$ system. We had had previous research experience with the eutectic behavior of these oxides in ternary systems containing molybdenum and tungsten. Arrangements have been made with this U.S. manufacturer to evaluate our experimental eutectic materials as grinding grain. Cold-crucible melting and solidification of the pseudobinary eutectic, $ZrO_2(Y_2O_3)-Al_2O_3$ with Mo and Cr_2O_3 additions, were accomplished relatively easily. Soon thereafter, a ternary eutectic in this system was directionally solidified in our IZG equipment. A 63-mm-diam bar about 70 mm long was then fabricated by hot-pressing selected powders of ZrO_2 , Al_2O_3 , Y_2O_3 , and Mo to about 90% of theoretical density before the eutectic growth experiment. The particle size and composition of the powder were tailored such that the aggregate electrical conductivity was in the correct range for the bar to couple directly to a 500-kHz field. The hot-pressed bar was then directionally solidified in our IZG equipment,

resulting in a melt region 55 mm in diameter by 30 mm high. This pseudo-ternary eutectic $\text{ZrO}_2(\text{Y}_2\text{O}_3)\text{-Al}_2\text{O}_3\text{-Mo}$ ingot is now ready for crushing and testing as an abrasive grain. We believe that the 1- μm Mo eutectic fibers may produce a significantly tougher grit for use in metal grinding.

In an effort to produce superior cutting tool and valve trim materials, we have expanded our investigations to include boride, carbide, and nitride phases in complex eutectics with oxides and metals. The first cold-crucible melts of $\text{ZrO}_2\text{-ZrB}_2$ were the most successful. The ZrB_2 formed 1- μm -thick lamella showing strong crystallographic coupling to the ZrO_2 . This is a good example of a material having a hard matrix phase (ZrO_2) and a layered structure of micrometer-sized sheets of the even harder ZrB_2 . The systems $\text{Y}_2\text{O}_3\text{-ZrB}_2$ and $\text{Al}_2\text{O}_3\text{-ZrB}_2$ were also explored. For these, our first impression is that the eutectic composition is less than a few percent ZrB_2 . We shall now work with chemical additives to try to increase the volume concentration of ZrB_2 . As these and similar materials are synthesized, they will be evaluated in our machine-tool, wear test, and abrasive grain programs.

From the chemical point of view we have started with some of the more stable borides and oxides. However, there is much yet to be answered in the chemical thermodynamic area. We also hope that the brittle fracture characteristics of these hard phases can be reduced by finding appropriate solid solution members that can effectively increase the fracture energy.

1.3.3 Growth of Single Crystals -- C. B. Finch

Large single-crystal samples are necessary in determining the intrinsic anisotropic properties of material in relative absence of grain-boundary effects. We continued our work on the improvement of existing crystal-growth techniques and on the growth of additional crystals.

In the realm of Czochralski growth, we completed our experiments to optimize the growth conditions for single crystals of Fe_2SiO_4 (fayalite) and $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (gehlenite). We continued our experiments on the hydrothermal growth of quartz and collaborated to grow several actinide-doped LaPO_4 (monazite) crystals for radioactive waste studies.

The direction of our single-crystal work is shifting to the growth of boride-, nitride-, or carbide-based phases. We expect immediate delivery of a new high-pressure Czochralski crystal growth system, which should facilitate this task.

1.3.3.1 Czochralski Growth of Single-Crystal Fayalite (Fe_2SiO_4) –
C. B. Finch, G. W. Clark, and O. C. Kopp⁴²

We completed our work on the growth and characterization of single-crystal fayalite⁴³ and distributed boules to researchers throughout the United States, including a sample to the Smithsonian Institution mineral collection. The low-temperature specific heat of our crystals was measured by R. A. Robie of the U.S. Geological Survey. In addition, detailed Mössbauer studies by D. Virgo of the Carnegie Institution geophysical laboratory confirmed the original paramagnetic resonance results of M. M. Abraham (ORNL) that our best Czochralski-grown material appears to be essentially Fe^{3+} -free. It would thus seem likely that the dark color of melt-grown fayalite is not associated with the presence of Fe^{3+} .

1.3.3.2 Czochralski Growth of Single-Crystal Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$)⁴⁴ –
C. B. Finch, F. L. Ball,⁴⁵ and J. B. Bates⁴⁶

Single-crystal boules of gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) were grown from even- and off-stoichiometry melts under differing conditions of oxygen fugacity (f_{O_2}). Growth was accomplished by the Czochralski method at about 1600°C and 0.1 MPa (1 atm) total pressure, using inductively heated Ir or Pt-20% Rh crucibles. The *supra* melt gas ambients included air ($f_{\text{O}_2} = 20$ kPa), Ar (10 Pa), Ar-50% CO_2 -2% H_2 (10 mPa), and Ar-4% H_2 -1.5% H_2O (0.1 mPa).

⁴²Department of Geological Sciences, University of Tennessee, Knoxville and Metals and Ceramics Division, ORNL.

⁴³C. B. Finch, G. W. Clark, and O. C. Kopp, *Am. Mineral.* 65: 381-89 (1980).

⁴⁴Abstract of paper submitted to Proceedings of International Conference on Crystal Growth VI, Moscow, September 10-16, 1980.

⁴⁵Analytical Chemistry Division.

⁴⁶Solid State Division.

Colorless, transparent material up to 8 mm in diameter by 15 mm long was obtained from the evenly stoichiometric melt composition under Ar at growth rates of 1.5 mm/h or less. Growth at rates exceeding 2 mm/h or growth at a high f_{O_2} (e.g., air) led to the formation of bubbles and elongated voids or inclusions, predominantly in the core regions of boules. Optical, x-ray diffraction, and electron-induced x-ray fluorescence data are included.

1.3.3.3 Flux Growth of $LaPO_4$ (Monazite) Crystals Containing Pu, Np, Am, and Cm — C. B. Finch and L. A. Boatner⁴⁶

The compound $LaPO_4$ (monoclinic monazite structure) is an attractive host medium for incorporation and immobilization of high-level actinide wastes.⁴⁷ We grew $LaPO_4$ crystals containing up to 10 wt % of the actinides (Ac) ^{237}Np , ^{239}Pu , ^{243}Am , and ^{244}Cm by slow cooling ($1^\circ C/h$) 50-g amounts of $Pb_3(PO_4)_2$ -6 wt % (La,Ac) oxide mixtures from 1360 to $900^\circ C$ in platinum vessels. The crystals were separated from their growth matrix after cooling by leaching in hot concentrated HNO_3 . They have grain sizes of up to 3 by 3 by mm and are being used in physical property and actinide leaching studies.

1.3.3.4 Hydrothermal Growth of Quartz and Other Phases — O. C. Kopp⁴² and G. W. Clark

A programmable temperature control system has been installed and tested. We can now maintain operating conditions of temperature (in both the nutrient and growth regions) of the growth vessel within $\pm 0.3^\circ C$, which is a tenfold improvement over the previously used control system. Pressure control has also improved. Changes in the placement of heaters and insulation have resulted in a sharp thermal gradient across the interior baffle that separates the nutrient and growth regions.

⁴⁷L. A. Boatner, G. W. Beall, M. M. Abraham, C. B. Finch, P. G. Huray, and M. Rappaz, "Monazite and Other Lanthanide Orthophosphates as Alternate Actinide Waste Forms," paper presented at the Materials Research Society Symposium, Boston, Nov. 26-28, 1979; in *Scientific Basis for Nuclear Waste Isolation*, Plenum, New York, in press.

Several crystals of adequate size and perfection will be grown for fabricating oscillators for anelastic loss determinations. We anticipate that this program will be terminated after these crystals have been obtained.

Crystals of Cu_2Se , produced in earlier hydrothermal experiments,⁴⁸ have been analyzed by x-ray diffraction.⁴⁹ The crystals appear to be orthorhombic (or possibly monoclinic with a β -angle near 90°) with cell dimensions: $a = 1.41029$, $b = 2.04024$, and $c = 0.41332$ nm, comparable to material prepared by solid-state equilibration of Cu_2Se with Cu. The compound Cu_2Se is an important material in photovoltaic devices.

1.4 STRUCTURE OF COAL — L. A. Harris and C. S. Yust

Physical attributes of coal such as porosity, mineral content, and microstructure are believed important in the utilization of coal in conversion processes. We are using a variety of optical and electron microscopical techniques to identify the above features as well as to determine their distributions in a given coal. In addition, the acquisition of a specimen heating stage and environmental cell for use in the high-voltage electron microscope (HVEM) has enabled us to perform high-temperature (up to 1000°C) in situ TEM experiments⁵⁰ on coal. Such experiments can aid us in our understanding of the reactions taking place in coal conversion systems.

1.4.1 Techniques Based on Optical Microscopy — L. A. Harris

1.4.1.1 Transmitted Infrared Light Microscopy: An Improved Method for Viewing Coal Thin Sections⁵¹ — L. A. Harris and C. S. Yust

The use of transmitted infrared (700–1200 nm) microscopy for the study of thin sections of coal is discussed. This optical technique is

⁴⁸O. C. Kopp and G. W. Clark, "Hydrothermal Growth of Quartz and Other Phases," *Metals and Ceramics Div. Mater. Sci. Program Annu. Prog. Rep. June 30, 1979*, ORNL-5589, p. 41.

⁴⁹X-ray diffraction measurements by O. B. Cavin.

⁵⁰Experiments performed in which the specimen is observed by transmission electron microscopy while exposed to conditions that could alter the structure.

⁵¹Abstract of paper submitted to the *Journal of Microscopy*.

shown to have the capability of transmitting infrared light through many normally opaque organic constituents of coal in typical thin sections (5–10 μm thick). The relationship between near-infrared transmission, specimen thickness, and maceral type is explored.

1.4.1.2 A Study of Elemental and Maceral Distribution in Coals of Different Paleoenvironments⁵² — H. E. Barrett,⁴² O. C. Kopp,⁴² and L. A. Harris

A comparison of the vertical distribution of major and minor elements and maceral contents in two high-volatile bituminous coals of Eastern Tennessee has been completed. The coals studied are the Pee Wee, deposited in a fresh water environment, and the Upper Grassy Spring, influenced by a late incursion of marine water.

X-ray fluorescent and coal petrographic analyses were performed on a continuous series of specimens obtained from face channel samples representing the entire thickness of each seam. Offcuts from the petrographic samples were analyzed with an EG&G 6110 fluorescent analyzer. Element standards were employed and matrix corrections applied. Correlation coefficients (r) for all element pairs were computed in order to reveal any significant relationships.

The Upper Grassy Spring contained over 3 times the weight of total elements found in the Pee Wee. Comparison of iron and sulfur within these seams shows a near uniform distribution for the Pee Wee, whereas the Upper Grassy Spring shows a continuous increase of both elements from bottom to top. High positive correlations (r) were observed for element pairs normally associated with clay minerals. Equally good correlations were observed for (Si,Ti) and (Al,Ti), suggesting that titanium is associated with clay in both coals. Negative correlation between (Ca,Mg) is consistent with the absence of dolomite in both coals. A major difference in correlation was found for (Sr,P), which showed a high positive r factor in the Upper Grassy Spring but no correlation in the Pee Wee. Other important correlations indicated differences in element accumulations in different paleoenvironments and maceral associations.

⁵²Abstract of talk presented at the meeting of the Geological Society of America, San Diego, California, Nov. 5–8, 1979.

1.4.1.3 A Review of Advanced Coal Petrographic Methods in Characterizing and Assessing Coals for Utilization⁵³ — L. A. Harris and C. S. Yust

The application of coal petrography in the characterization and assessment of coals for conversion to metallurgical coke is well established. These same methods have been used in coal liquefaction studies but with less obvious success. However, recent developments of new petrographic methods, such as ultraviolet fluorescence and near-infrared transmission microscopy, promise to supply additional pertinent data. Specifically, the ultraviolet fluorescence method detects the more hydrogen-rich macerals, whereas the infrared technique appears to identify the less carbonized inert macerals.

1.4.2 Electron Metallography

1.4.2.1 High-Temperature Transmission Electron Microscope Studies of Coal — L. A. Harris, C. S. Yust, and E. A. Kenik

In situ heating experiments have been performed on several samples of a high-volatile bituminous coal (Elkhorn No. 3) using the specimen heating stage in the high-voltage electron microscope (HVEM). Softening of the exinitic constituents in the ultrathin regions of the coal foil resulted in a corrugated appearance for these constituents. In contrast, the exinites in the thicker region of the foil many have actually melted, forcing delamination of the coal. This was especially true in those coal sections that consisted of interbedded exinites and vitrinites. Also observed in these experiments was the profusion of spherical particles (nonmetallic) reminiscent of carbon blacks on both surfaces of the foil. Electron diffraction analysis of these particles revealed some unusual diffraction aspects.

1.4.2.2 TEM Characterization of Coals⁵⁴ — L. A. Harris and C. S. Yust

Transmission electron microscope (TEM) techniques are applied to coals ranging in rank from subbituminous to anthracite, with emphasis on

⁵³Abstract of talk presented at the 109th Annual Meeting of AIME, Feb. 24-28, 1980, Las Vegas.

⁵⁴Abstract of talk given at 1979 Annual Meeting of the Materials Research Society, Boston, November 26-30.

the higher rank coals. The distribution of porosity and mineral content within each coal type as revealed by TEM and AEM and the variations of these features among the several coal types studied are discussed. Selected area diffraction (SAD) experiments and dark field microscopy are also shown to be invaluable in studies of minerals and macerals. Observations of an anthracite by these methods reveal a sharper, more distinct set of diffraction rings with a concomitant improvement in the resolution of domains in the vitrinite, as revealed by dark field techniques. The use of TEM and associated techniques is shown to be important for the complete characterization of coals.

1.4.2.3 A New Improved Standard for Electron Probe Determination of Organic Sulfur in Fossil Fuels⁵⁵ — L. A. Harris, R. Raymond,⁵⁶ and R. Gooley⁵⁶

Electron-probe microanalysis (EPM) has important advantages over conventional methods of analysis for organic sulfur in coal: analysis by EPM is done directly, avoiding problems associated with calculating organic sulfur content by difference; organic sulfur contents of individual macerals can be measured in situ in a sample. A major problem with this technique has been finding a suitable sulfur standard. We recently obtained a petroleum coke and found it to be a suitable standard.

1.5. TRANSFORMATIONS AND SHAPE MEMORY EFFECT IN URANIUM ALLOYS — R. A. Vandermeer

The manufacture and deployment of parts made from uranium alloys demand a high degree of dimensional stability of alloys. Shape change due to small thermal excursions must be minimized. Solid-state phase transformations often are associated with the difficulties encountered in maintaining dimensional stability. Unfortunately, uranium-base alloys exhibit an enormous diversity of phase transformation behavior, and certain transformation states are much less desirable than others. Our main objective

⁵⁵To be published in the proceedings of the EMSA-MAS Joint Meeting, San Francisco, August 3-8, 1980.

⁵⁶Geosciences Division of Los Alamos Scientific Laboratory.

is to unravel the mechanistic details of the complex transformation patterns, especially the metastable states. We explore how composition, temperature, stress, and microstructure influence transformation behavior.

1.5.1 A Phenomenological Study of the Shape Memory Effect (SME) in Polycrystalline Uranium-Niobium Alloys⁵⁷ — R. A. Vanderwerf, J. C. Ogle, and W. G. Northcutt, Jr.⁵⁸

Polycrystalline uranium-niobium alloys spanning the composition range 13.9 to 17.8 at. % Nb were prepared. Decomposition of the elevated-temperature bcc phase to the displacively formed transition phases during continuous cooling to room temperature was studied by dilatometry. With the help of x-ray diffraction, a metastable phase diagram was determined. At room temperature alloys containing less than 15.2 at. % Nb were α'' (monoclinic), while those with more than 16.6 at. % Nb were γ^0 (tetragonal). Reverse transformation behavior during heating was also surveyed.

The stress-strain characteristics of the athermally produced α'' and γ^0 martensitic phases were measured in uniaxial tension at room temperature. Phenomenological parameters (macroscopic) associated with the mechanically reversible deformation modes were defined and their niobium composition and structural state dependencies delineated. The SME reversible strain limit, ϵ_L , was identified with a diffuse maximum in the stress versus strain plots. The ϵ_L varied inversely and continuously with composition from a value of 7.2% in the 13.9 at. % Nb α'' alloy to 4.4% in the 17.8 at. % Nb γ^0 alloy.

All the deformed alloys, whether initially in the α'' or γ^0 state, exhibited SME, but the extent of SME depended on composition and structural state. The α'' alloy showed a much larger effect than did the γ^0 alloy. Heat-activated recovery strains ranged from 5% (α'') down to 1.7% (γ^0) as the niobium content increased from 13.9 to 17.8 at. %. For all the alloys the heat-activated strain recovery occurred in two stages during reversion to the γ phase. Transformation temperatures during shape recovery were higher than expected. This and other peculiarities in shape recovery behavior were attributed to the influence of rapid aging (solute segregation) processes.

⁵⁷Summary of Paper Submitted to *Metallurgical Transactions A*.

⁵⁸Development Division, Y-12 Plant, Oak Ridge.

The plastic yield strength was approximately constant over the composition range studied, with the measured value being 693 MPa.

1.6 X-RAY RESEARCH WITH SYNCHROTRON RADIATION SOURCES — C. J. Sparks, Jr., and H. L. Yakel

Our decision to use the powerful x-ray generator under construction at Brookhaven National Laboratory is involving us in a major way in the design and engineering construction of the necessary instrumentation. We will apply the x radiation from the National Synchrotron Light Source (NSLS) to probe the structure of materials. We have identified several materials science programs at ORNL that will benefit from the unique properties of this radiation source. Among these is the study of local atomic arrangements in iron-base alloys containing Ni, Cr, Co, V, and Ti, where our present x-ray sources are unable to distinguish between these atoms. However, the tunable x-ray energy from synchrotron sources will allow us to determine the atomic arrangement of these alloys and better understand their physical and chemical properties. Another area of research is the study of liquids and amorphous materials. When two or more kinds of atoms are present, two or more measurements with radiations for which the scattering cross sections of the atoms differ are necessary to unravel the pair-wise correlations that characterize their structure. Our use of synchrotron radiation will greatly facilitate these determinations. A host of interesting metal phases are formed in iron-base alloys for which we have insufficient structural information. We are currently conducting research at the Stanford Synchrotron Radiation Laboratory to determine the site occupancies for Fe-Co spinel and an Fe-Cr sigma phase. This promising research will be continued with our equipment at the NSLS. Another area of our research program for which synchrotron radiation will provide major improvements is in the study of defects in materials. Radiation damage, mechanical deformation, and impurity atom defects can now be studied at concentrations levels one-hundredth as much as before. In addition, new structural information on corrosion products and surface films can be obtained.

These research areas involve personnel from the Chemistry, Solid State, Metals and Ceramics, and Analytical Chemistry Divisions. Through organizational meetings held at the Oak Ridge Associated Universities in 1979, we formed a consortium with university and industrial research people with similar research interests in materials science. This collaboration is under the direction of an interim steering committee consisting of R. DeAngelis, Department of Materials Science, University of Kentucky; S. C. Moss, Department of Physics, University of Houston, Texas; C. J. Sparks, ORNL; and R. Young, Engineering Experiment Station, Georgia Institute of Technology. Several consortium members are presently engaged in software development for our recently acquired PDP 11/34 computer, which will be used to control experimental equipment, collect data, and provide for data reduction. DeAngelis' stay at ORNL this summer produced many worthwhile contributions to our software development in association with A. Habenschuss, who is supported by DOE funding through ORAU to manage our computer system and to do research on liquid and amorphous materials.

A schematic drawing of the experimental apparatus to be installed at the NSLS by October 1981 is shown in Fig. 1.12. Both the computer system and the five-axis diffractometer are on hand and are being interfaced. A fast data acquisition system capable of registering and addressing 10^6 photons per second is under development in cooperation with the Los Alamos Scientific Laboratory. (See Sect. 1.2.3.2, this report.) This system has been demonstrated by R. W. Hendricks of ORNL, and little difficulty is expected in reaching fully operational status. This system will ensure that we can take full advantage of the intense synchrotron radiation available to our experiments. As the front end of our beam line (to the left of the concrete shield of Fig. 1.12) is under construction at BNL, our major remaining task is the design and construction of the x-ray optics. We have developed computer tracing programs to examine the many possible x-ray optical configurations. Those with the most desirable properties are being evaluated; one or more will be constructed and tested at ORNL before implementation at the NSLS.

ORNL-DWG 79-14611

Fig. 1.12. Schematic Representation of the ORNL Synchrotron Radiation Beam Line.

1.6.1 X-Ray Optics for Focusing and Monochromatization of Synchrotron Radiation - C. J. Sparks, Jr., G. E. Ice, and B. S. Borie

The large distances between the synchrotron radiation source and the experiment require condensing optics to confine the beam to a reasonable size at the sample and to collect as much of the radiation as possible. The radiation is spread over 2π in the plane of orbit but is confined to small opening angles in a plane perpendicular to the plane of the storage ring. This angle is approximately given by the rest mass energy of the electron divided by the energy of the circulating electron, $m_0 c^2/E$, and is about 0.2 mrad for electron energies of 2.5 GeV. In the plane of orbit, the radiation spread from typical bending magnets is from 20 to 50 mrad. Higher intensities and smaller beam areas are produced at the sample by collecting and focusing this large horizontal divergence.

Two methods for focusing photons are specular reflection from mirror surfaces and diffraction from crystallographic planes. Typical glancing angles for critical reflection of photons from mirror surfaces are about 1/20 of that for diffraction from crystallographic planes. For photon energies exceeding 10 keV the small reflection angles require that mirrors be large if they are to intercept the divergence of the source. In addition, sagittal focusing (perpendicular to the plane of scattering) with mirrors requires very small bending radii and consequently only small divergences may be intercepted.

As crystals are the more desirable optical element, since they both focus and monochromatize the radiation, we have investigated theoretically the possible geometries to determine those that permit the highest x-ray throughput and provide the best energy resolution. To eliminate the complexity of doubly curved shapes required for ideal focusing, we have found that simple cylindrical and conical shapes are satisfactory optical elements for synchrotron radiation.

We have derived geometries that show that the radius of cylindrically and conically curved crystals can be chosen to eliminate the $\Delta\theta$ error introduced by the external shape of the crystals. This provides for both monochromatization and focusing from a single optical element.

1.6.1.1 X-Ray Monochromator Geometry for Focusing Synchrotron Radiation Above 20 keV⁵⁹ — C. J. Sparks, Jr., B. S. Borie, and J. B. Hastings⁶⁰

The relative merits of crystals versus mirrors for focusing synchrotron radiation at energies above 10 keV are explored. As mirrors have critical angles of reflection typically 1/20 of the Bragg scattering angles for crystals, large mirror surface areas are required. Sagittal focusing is weak for mirrors and limits the amount of radiation intercepted. We show that crystals bent to a simple cylindrical curvature will accept large divergences of radiation for sagittal focusing. At a magnification near 1/3, the cylindrically curved crystals are shown to make the proper Bragg angle for energies above 5 keV and for divergences larger than 10 mrad and to produce x-ray beams that are approximately focused.

1.6.1.2 Some Things About X-Ray Optics for Synchrotron Radiation⁶¹ — C. J. Sparks, Jr.

Rating factors for choosing x-ray optics for synchrotron radiation are defined. The ideal doubly curved crystals produce the maximum intensity and best energy resolution but require a bending mechanism that would be difficult to build, if at all possible, to change the radii to select different energies. The DeWolff logarithmic spiral geometry is found not to be useful for focusing synchrotron radiation. Singly curved surfaces are shown to be the best candidates for feasible application to the focusing of synchrotron radiation. Thermal distortions are likely to be as large as the radius required for focusing the vertical divergence. Crystal combinations are listed for achieving maximum intensity and energy resolution. Focusing properties are discussed as a function of the radius of curvature and for curved crystals that are ground flat. It is shown that horizontally focusing mirrors mix the large horizontal divergences of synchrotron radiation into the small vertical divergences. Such mirrors

⁵⁹Abstracted from a paper in press in *Nuclear Instruments and Methods*.

⁶⁰Physics Department, Brookhaven National Laboratory.

⁶¹Summary of a report prepared during an August 1979 Research Collaborator's appointment to the National Synchrotron Light Source at Brookhaven National Laboratory. Report BNL-26740 (August 1979).

placed upstream of the monochromatizing crystals degrade the energy resolution of the optical system. Horizontal focusing of synchrotron radiation should be done by crystal optics for x-ray energies above 10 keV and with mirrors downstream of the crystal optics for x-ray energies less than 10 keV.

1.6.1.3 Conical Section Curved Crystals for Focusing Synchrotron Radiation⁶² — G. E. Ice

Excellent focus of the horizontal divergence from synchrotron radiation sources can be achieved at magnifications near 1 by using crystals bent to conical curvature. The Bragg planes of a conically curved crystal mimic in orientation the Bragg planes of a nearly ideal doubly curved "barrel" monochromator for a fan of horizontally divergent radiation. Furthermore, the crystal acts as a flat crystal to the vertical beam divergence. It is therefore possible to focus simultaneously a horizontal fan of radiation and match the Bragg angles of rays reflected by a flat crystal upstream. This double crystal geometry keeps the diffracted beam fixed in space as energy is changed. The deviation from a cylindrical bend is small, and the horizontal divergence focused by this crystal can be 20 times that focused by a mirror for x-ray energies above 30 keV.

1.6.2 Research Topics

1.6.2.1 Resonant X-Ray Auger Measurements — G. E. Ice

An atom with an electron removed from an inner shell is in an excited state. This is an unstable situation, and the atom relaxes quickly ($\sim 10^{-15}$ s) by filling the hole with an electron from a higher shell. Excess energy is emitted by either a photon (fluorescence decay) or an electron (radiationless decay). The radiationless transition, or Auger effect, is of fundamental importance because it is more sensitive to the detailed nature of atomic wavefunctions than many other observables. Furthermore, very accurate radiationless transition rates and their

⁶²Summary of presentation given at the National Synchrotron Light Source General Users Meeting, Brookhaven National Laboratory, June 9, 1980.

energies and widths are required to interpret a large variety of measurements in nuclear and atomic physics. Auger widths also reflect vacancy lifetimes and, therefore, can be used to determine branching ratios and other de-excitation parameters that are crucial in schemes to obtain stimulated emission. Detailed knowledge of the influence of spectator electrons and holes is also necessary for the design of an x-ray laser.

During the year, a pioneering x-ray photoelectron and Auger electron spectroscopy experiment was begun at the Stanford Synchrotron Radiation Laboratory (SSRL). This experiment represents the first use of synchrotron radiation to excite Auger spectra in the hard x-ray region. The experiment was carried out in collaboration with researchers from the University of Oregon and SSRL. Initial measurements have concentrated on observing the xenon $L_3-M_{45}M_{45}$ Auger line near resonance, where the incident photon has an energy near the absorption edge energy. Preliminary data analysis shows that the Auger line undergoes dramatic changes near resonance. We believe that the interaction with spectator electrons excited to bound states magnifies the edge structure. This may allow for precise determination of absolute binding energies in edges whose absorption structure is difficult to interpret because of core hole broadening. Such absolute binding energies can test energy shifts due to relativistic, quantum electrodynamic, and correlation effects.⁶³

Numerous other experiments that exploit the unique advantages offered by synchrotron radiation and Auger-photoelectron spectroscopy are planned in the near future.

1.6.2.2 Determination of the Cation Site-Occupation Parameter in a Cobalt Ferrite From Synchrotron-Radiation Diffraction Data⁶⁴ — H. L. Yakel

Energy-tuned synchrotron radiation (SR) was used to collect Bragg diffraction intensity data from a single crystal of a cobalt ferrite

⁶³M. Breinig, M. H. Chen, G. E. Ice, F. Parente, B. Crasemann, and G. S. Brown, "Atomic Inner-Shell Level Energies Determined by Absorption Spectrometry with Synchrotron Radiation," to be published in *Physical Review*.

⁶⁴Abstract of paper accepted for publication in the *Journal of the Physics and Chemistry of Solids*.

(nominally CoFe_2O_4). X-ray energies were chosen just below the Fe and Co K absorption edges, where large changes in anomalous dispersion enhance differences in scattering between the two metals. Observations were analyzed by least squares methods to determine the value of the parameter X that describes the distribution of cobalt and iron ions on the octahedral and tetrahedral sites of the cubic spinel structure. Refinements based on over 290 SR data gave $X = 0.83 \pm 0.01$ (83% of the cobalt ions located on octahedral sites); with only 30 specially selected SR data, this value could be fixed at 0.80 ± 0.07 . Estimates of dispersion corrections to the x-ray scattering factors for iron near the Fe K edge were obtained through observations of SR diffraction from a magnetite crystal. Results do not differ appreciably from predicted values in the range 6358 to 7105 eV, though the precision in estimates of the imaginary term is poor at the lower energies.

1.6.2.3 Atomic Distributions in Iron-Chromium Sigma Phases Quenched From Several Temperatures — H. L. Yakel and J. Brynestad⁶⁵

Sparse x-ray and neutron diffraction data, collected over 20 years ago,^{66,67} suggested nonrandom distributions of A and B atoms on the five crystallographically independent lattice sites of many binary sigma phases. The distributions deduced were related to the relative sizes of the atoms and the coordination numbers of the sites. Despite favorable differences in scattering cross sections, results from neutron diffraction powder data⁶⁷ were only precise enough (± 0.5 atoms for a typical site) to indicate trends for such sigma alloys as iron-chromium. There would seem to be little chance of using such data to investigate possible changes in

⁶⁵Chemistry Division.

⁶⁶B. G. Berman and D. P. Shoemaker, "The Determination of the Crystal Structure of the σ Phase in the Iron-Chromium and Iron-Molybdenum Systems," *Acta Crystallogr.* 7: 857-65 (1954).

⁶⁷J. S. Kasper and R. M. Waterstrat, "Ordering of Atoms in the σ Phase," *Acta Crystallogr.* 9: 289-95 (1956).

the distribution parameters from a given sigma phase quenched from various temperatures within the metastable sigma field, though magnetic measurements show that an ordering-type reaction may occur.⁶⁸

Recently developed strain-anneal techniques have allowed iron-chromium sigma-phase crystals with dimensions up to 100 μm to be grown. These crystals are suitable for x-ray diffraction studies, including experiments with synchrotron radiation tuned near Fe K and Cr K edge energies, where dispersion effects magnify the otherwise small scattering factor differences between the two elements. Crystals quenched from 790, 740, and 650°C are currently being characterized via extensive conventional Mo K α diffraction data, preparatory to measurements with 0.175 and 0.207-nm x radiation at the Stanford Synchrotron Radiation Laboratory.

Analyses of Mo K α data from a 740°C-quenched crystal have produced precise position, thermal vibration, and extinction parameters based on the three possible space groups ($P4_2/mmm$, $P4_2nm$, and $\bar{P}4n2$) that are compatible with the observed scattering. Measures of agreement do not clearly demonstrate the superiority of one of these possible groups, but some statistical tests seem to favor the noncentric group $\bar{P}4n2$.

Several sets of synchrotron-radiation diffraction data have been collected from this crystal at 0.175, 0.207, and 0.220 nm. Analyses are now under way to derive estimates of the four occupation parameters that with the average composition describe atom distributions at 740°C. Analogous experiments with crystals quenched from the maximum temperature and the minimum temperature (790 and 650°C) in the metastability region are planned.

1.7 ANALYTICAL AND HIGH-VOLTAGE ELECTRON MICROSCOPY — R. W. Carpenter

The research effort last year was approximately equally divided among analytical microscopy research, applications of analytical microscopy to materials science problems, and in situ experiments⁶⁹ in the high-voltage

⁶⁸P. Bastier and G. Pompy, "Existence of an Order-Disorder Transformation in Iron-Chromium Alloys Near the Equiatomic Composition," *C. R. Hebd. Seances Acad. Sci.* 239: 1636-38 (1954).

⁶⁹"In situ" is used to describe experiments in which a specimen is observed in the electron microscope simultaneously with some thermal, mechanical, or chemical treatment.

electron microscope. The analytical microscopy research emphasized micro-diffraction from crystals containing defects, high-resolution imaging, and electron energy loss spectroscopy. Several applications of analytical electron microscopy to materials science problems began last year. The applications include structural analysis of ceramic as well as metallic materials, and are described below. The first in situ deformation experiments in the high-voltage microscope began this year, and propagating ductile cracks were successfully observed. In situ oxidation experiments on refractory alloys and hydrogenation experiments on lanthanum-base inter-metallic compounds have been continued to include detailed analysis of reaction products first observed last year.

Next year further effort is expected in developing electron energy loss experimental capability. High-resolution imaging will be used in the determination of the structure of interfaces. Several new applications of analytical microscopy that are currently being made to ceramics, geological materials, and wear-resistant materials will continue. Analytical microscopy will be used as an additional experimental method to measure changes in in situ gas-solid and deformation specimens from the high-voltage electron microscope.

Deformation of aluminum alloys containing precipitate-free zones and the oxidation behavior of vanadium alloys will continue as the main emphasis of in situ research.

1.7.1 Diffraction

1.7.1.1 Three-Dimensional Strain-Field Information in Convergent-Beam Electron Diffraction Patterns⁷⁰ — R. W. Carpenter and J.C.H. Spence⁷¹

Convergent-beam electron diffraction (CBED) patterns contain diffracted beams from higher order Laue zones (HOLZ), in addition to the more often observed diffracted beams from the zeroth-order reciprocal lattice zone (ZOLZ) that contains the origin of the reciprocal lattice.

⁷⁰Abstracted from a paper accepted for publication in *Acta Crystallographica*.

⁷¹Department of Physics, Arizona State University, Tempe.

Since HOLZ diffraction vectors have significant nonzero components along the incident electron beam direction, they can detect components of static real lattice displacement fields that lie along the incident electron beam direction, an event not possible for diffracted beams in the zero order Laue zone (i.e., ZOLZ diffracted beams). This effect is used in the present work to determine Burgers vectors of straight dislocations and loops in silicon from observations of splitting of HOLZ lines within the forward scattered beam Bragg disk and from splitting of Kikuchi lines associated with HOLZ Bragg reflections. The method was also applied with limited success to dislocations in aluminum; here splitting was more difficult to observe because of the rather strong diffuse background in the convergent-beam electron diffraction (CBED) patterns. Calculations of HOLZ line splitting due to the presence of a dislocation in the irradiated crystal volume were in good qualitative agreement with the experimental observations. Effects on CBED patterns to be expected from some partial dislocations are discussed. This CBED method can be very useful for the determination of non-ZOLZ fault vector components in an atomic resolution structure imaging microscope. These instruments usually have specimen tilt ranges limited to about 10° ; thus conventional Burgers vector analysis is not generally possible. Finally, the present CBED results show clearly that the projection approximation generally used to interpret structure fringe images is not strictly valid. The changes in fringe images or weak beam images from HOLZ excitations remain to be evaluated.

1.7.1.2 Microdiffraction from Crystals Containing Defects⁷² — R. W. Carpenter

The properties of convergent-beam electron diffraction (CBED) for analysis of various types of lattice defects are discussed. The spatial resolution to be expected in various modes of microscope operation and the related angular resolution are compared with experimental requirements for examination of different types of defects in crystals. The use of convergent-beam shadow images for tilting experiments and placing the electron probe on small areas for microchemical analysis is illustrated.

⁷²Abstracted from an invited paper for the Microbeam Analysis Society, 15th Annual Meeting, San Francisco, August 1980.

1.7.2 Imaging

1.7.2.1 The Observation of "Dumbbell" fine Structure in $\langle 110 \rangle$ Structure Images of Silicon - J. Bentley

Izui and co-workers⁷³ have published structure images (crossed lattice fringe images) of silicon viewed along $\langle 110 \rangle$. Resolution of atomic columns separated by 0.136 nm was claimed. More recently, Yamashita et al.⁷⁴ have produced similar images from CdTe, which has a slightly larger lattice parameter. We have produced $\langle 110 \rangle$ structure images of silicon using a Philips EM400T/FEG analytical electron microscope (AEM), which also show "dumbbell" splitting along $\langle 100 \rangle$. These images are remarkable in a number of ways. First, the specimen normal was $\langle 111 \rangle$ and the specimen was tilted about 35° to a $\langle 110 \rangle$ orientation. Second, this high resolution was obtained in an AEM with 60° tilting capability and equipped with an x-ray energy dispersive detector - not in dedicated high-resolution instruments as used by Izui et al. and Yamashita et al. Finally, the exposure time at a magnification of about 450,000 times was only 0.3 s, because of the high brightness and coherence of the illumination from the field-emission gun (FEG). An example is shown in Fig. 1.13.

The fine structure of these images is an impressive demonstration of the instrument performance, but it can be misleading because the positions of the atomic columns in the crystal are not faithfully reproduced. Careful examination reveals that the images all show a "splitting" along $\langle 100 \rangle$, which is $a_0/3$ rather than $a_0/4$ (the d spacing of $\{400\}$), where a_0 is the crystal lattice parameter. The images of Izui et al. and Yamashita et al. also exhibit this behavior. The "incorrect" spacing can be understood if the splitting is due to $\{311\}$ interferences rather than the $\{400\}$ interference, which is required to reveal the corrugated nature of the $\{311\}$ and $\{111\}$ planes. There are then two possibilities to explain the experimental observations. Images can be formed such that interference between the 000- and 311-type reflections is fulfilled simultaneously with interference between the 000 and both 111- and 220-type

⁷³K. Izui, S. Furuno, and H. Otsu, *J. Electron Microsc.* 26: 129 (1977).

⁷⁴T. Yamashita, F. Ponce, and R. Sinclair, paper presented at 109th AIME Annual Meeting, Las Vegas, Nevada, February 24-28, 1980.

Fig. 1.13. Structure Image of a Silicon Specimen Viewed Along $\langle 110 \rangle$. Foil normal = $\langle 111 \rangle$; exposure time = 0.3 s. Note the "dumbbell" splitting along $\langle 100 \rangle$ with spacing 0.181 nm ($a_0/3$) instead of the "correct" spacing of 0.136 nm ($a_0/4$). (b) Schematic projection along $\langle 110 \rangle$ of silicon unit cell showing dimensions.

reflections. This, in practice, requires operating in aberration-free-focus (AFF) imaging conditions. These are generally fulfilled at a particular defocus of the objective lens of small aberration coefficients. However, in the present case, even with the low energy spread of the beam (<0.5 eV) resulting from the use of the FEG, the chromatic aberration coefficient, C_c is sufficiently large (~ 2.0 mm) that the smallest periodicity for interference involving the axial 000 beam is about 0.19 nm. Thus the formation of $\{311\}$ lattice images ($d_{311} = 0.164$ nm) is not possible if axial 000-311 interference and 0.5 eV energy spread are used. The convergent-beam illumination employed in the present case does, however, enable the formation of $\{311\}$ lattice images by another process — namely, achromatic 311-220 interference. (This process is discussed more fully in Sect. 1.7.2.2.) Since the interference is achromatic, it is independent of focus and thus should be observed over a large range of focus values. Additional constraints may have to be met, such as simultaneous 111-111 achromatic interference to produce $\{220\}$ lattice images. This, in fact, is indicated in the present results by the observation that "dumbbell" images are only seen at foil thicknesses where a dark thickness fringe is formed (i.e., where the 000 intensity is a minimum and 111 intensity is maximized, conditions favoring achromatic 111-111 interference). The above hypotheses will be confirmed through an examination of the detailed behavior of the occurrence of "dumbbell" images.

1.7.2.2 Achromatic Interference Effects in Lattice Images Formed by Using High-Coherence Convergent-Beam Illumination — J. Bentley

Experience gained when the field emission gun (FEG) is used on a Philips EM400T for lattice and structure imaging studies has revealed the necessity for a theoretical consideration of the effects upon image formation of using high-coherence convergent-beam illumination. Typical illumination conditions are shown in Fig. 1.14. Each point on the specimen is illuminated at different angles, and the diffraction disks in the defocused convergent-beam electron diffraction (CBED) pattern are shadow images of the illuminated area of the specimen with a resolution determined by the probe diameter at crossover. The above illumination

Fig. 1.14. Typical Illumination Conditions Employed in the Philips EM400T/FEG for Lattice Imaging Studies.

conditions allow achromatic interference effects, which are not possible with effectively parallel illumination (say $\alpha_i \ll 1\ \text{mrad}$).

The schematic CBED pattern of Fig. 1.15, which represents the $\langle 110 \rangle$ zone axis pattern for a diamond cubic material, will be used to illustrate some of the possible effects. Points within each diffraction disk represent points on the illuminated specimen. For points along the lines labeled in Fig. 1.15, achromatic interference (between beams that are at angles equal to the optic axis) can result, as listed in Table 1.3. For example, for points on the specimen along the line ab achromatic $\bar{1}\bar{1}1-\bar{1}1\bar{1}$ or $\bar{1}\bar{1}\bar{1}-111$ interference can result in the appearance of 220 "lattice fringes"

Fig. 1.15. Schematic $\langle 110 \rangle$ CBED Pattern for a Diamond Cubic Crystal Illustrating Possible Achromatic Interference Effects as Listed in Table 1.3.

Table 1.3. Achromatic Interference Effects Possible in the $\langle 110 \rangle$ CBED Pattern of Fig. 1.15

Line	Achromatically Interfering Beams	Resulting "Lattice Fringe" Image
ab	$\bar{1}\bar{1}1-\bar{1}1\bar{1}$, $\bar{1}\bar{1}\bar{1}-111$	$\bar{2}20$
cd	$1\bar{1}\bar{1}-111$, $\bar{1}\bar{1}1-11\bar{1}$	002
ef	$\bar{1}13-\bar{2}20$	$1\bar{1}\bar{3}$
gh	$\bar{1}\bar{1}\bar{3}-\bar{2}20$	$11\bar{3}$
ij	$1\bar{1}\bar{3}-2\bar{2}0$	$\bar{1}13$
kl	$1\bar{1}\bar{3}-2\bar{2}0$	$\bar{1}\bar{1}\bar{3}$
mn	$\bar{1}\bar{1}\bar{1}-111$	$2\bar{2}2$
op	$\bar{1}11-1\bar{1}\bar{1}$	$\bar{2}22$

in the image. Elsewhere in this report (Sect. 1.7.2.1) achromatic 220-311 interference has been argued as being responsible for the formation of "dumbbell" splitting along $\langle 001 \rangle$ in $\langle 110 \rangle$ structure images of silicon. Another effect is the appearance of "forbidden" 200 lattice fringes as shown in the example of Fig. 1.16.

The above effects were all possible for nonoverlapping beams. When the beam divergence, α_i , is great enough that beams overlap (generally $\alpha_i > \theta_B$, where θ_B is the Bragg angle), additional effects can occur. This is illustrated in Fig. 1.17, which represents the $\langle 001 \rangle$ CBED pattern from a face-centered cubic material. This case has the possibility of forming 200 lattice images from 220-200 achromatic interference for points along the lines ab, cd, ef, gh. Only 200-020 achromatic interferences resulting in 220 lattice images are possible at this orientation for nonoverlapping beams.

Fig. 1.16. Crossed 220 and "Forbidden" 200 Fringes Formed by Achromatic Interference in $\langle 110 \rangle$ Structure Image of Silicon.

ORNL-CWG 80-14259

Fig. 1.17. Schematic $\langle 001 \rangle$ CBED Pattern for a Face-Centered Cubic Crystal Illustrating Possible Achromatic Interference Effects When Beams Overlap.

Finally, if the microscope is misaligned, such that the optic axis does not coincide with the center of the CBED pattern, in general the effect is that the symmetry of the described interference effects is reduced. However, achromatic interference, which normally cannot occur, may be possible in a misaligned microscope, even when the beam divergence is small.

From the above discussion it will be seen that the complex interpretation problems of high-resolution structure and lattice images (which involve a detailed knowledge of the specimen thickness, diffracting conditions, objective lens focus setting, lens aberration coefficients, etc.) are more complex when high-coherence convergent beam illumination is employed. However, the information content of the images is higher than in those obtained by using conventional electron sources with lenses of equal electron-optical quality.

1.7.2.3 Advantages of a Field Emission Gun for a Combined Analytical and High-Resolution Transmission Electron Microscope⁷⁵ — J. Bentley

Various areas of analytical and high-resolution microscopy can be greatly improved by the use of a high-brightness field emission gun (FEG). A quantitative evaluation has been made for the instrumentation at ORNL: a Philips EM400T equipped with an FEG, a 6585 STEM unit, an EDAX EDS detector, and a Kevex 5100 spectrometer.

The brightness β (current density per unit solid angle) normalized to the accelerating voltage, V_0 , is defined by $\beta = 4I/\pi^2 d^2 \alpha_i^2 V_0$, where I is the current in a probe of diameter d and divergence α_i . Results are presented in Table 1.4 for three typical operating conditions. Probe currents exceeding 0.1 μA have been obtained in the TEM mode. Such currents are sufficient for work at medium magnifications (20,000 to 100,000 $\times$). Probe currents were measured from the screen current exposure time system, which had been calibrated with a specially built Faraday cup. Probe diameters in TEM were measured from high-magnification TEM images and in STEM by imaging the STEM raster in the TEM mode. This is possible because of the symmetric objective lens, which can operate at the same excitation in TEM and STEM. An example is shown in Fig. 1.18. The values in Table 1.4 should be compared to conventional tungsten hairpin sources,

⁷⁵Adapted from pp. 72–73 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, Claitor's Publishing Division, Baton Rouge, Louisiana, 1980.

Table 1.4. Measured Values of β for Philips EM400T/FEG

Mode	$I(\text{A})$	$d(\text{nm})$	$\alpha_i (\text{mrad})$	$\beta (\text{A cm}^{-2} \text{ sr}^{-1} \text{ V}^{-1})$
TEM	3×10^{-8}	15	6.9	3.5×10^3
STEM (microanalysis)	7×10^{-9}	4.5	11.5	3.3×10^3
STEM (imaging)	9×10^{-11}	1.0	6.0	3.2×10^3

Fig. 1.18. The TEM image of an STEM Raster. Exposure time 2 s. Frame time 0.02 s. Probe diameter ≈ 1 nm. This imaging mode is useful in focusing and stigmating the probe for high-resolution STEM imaging.

for which $\beta \approx 1$. The important point for microanalysis is that, all other things being equal, a probe of a given size can have greater than 10^3 times as much current as a conventional source. This achieves a greater signal and thus a higher sensitivity.

The minimum detectable mass (MDM) and minimum mass fraction (MMF) define the sensitivity of x-ray microanalysis. The MDM is limited by the probe current density and the availability of a low "systems background" signal. For a given probe current, the systems background with an FEG may be lower than with a conventional gun because of a lower emission current from the FEG. A small specimen of silicon supported on a beryllium grid was used to determine the MDM. The foil thickness was measured from the CBED pattern as 22 nm, the probe diameter was about 15 nm, and the probe current was about 30 nA. The count rate in the Si K peak [Fig. 1.19(a)] was 2800/s and that for the in-hole signal [Fig. 1.19(b)] was 1.1/s. Using the normal criteria the MDM is 9×10^{-22} g. Even for this favorable specimen geometry the MDM is still limited by the systems background count rate. The MMF is limited by the availability of a large number of counts (not usually consistent with the highest spatial resolution) in order for small peaks to be statistically significant above the background. A useful measure of MMF sensitivity is the spatial resolution at which the MMF is limited by the maximum count rate of the EDS spectrometer (MMF $\approx 0.1\%$ at 100 kV and 100 s counting time). This has been determined to be about 15 nm, a spatial resolution that is possible because the high current density of the probe produces high EDS count rates in foils where beam spreading is small.

Fig. 1.19. Silicon EDS Spectra. Acquisition time = 100 s.
 (a) Specimen thickness 22 nm, vertical scale = 33,000 counts per channel.
 (b) In-hole signal, vertical scale = 128 counts per channel.

As regards high-resolution TEM imaging, an FEC provides a number of practical advantages. The high brightness available at high magnifications means better visibility on the screen for astigmatism correction and focusing as well as short exposure times. The crossover size of about 10 nm results in high coherence, which, together with the small energy spread of the beam, results in a less rapid damping of the contrast transfer function and hence a high "information limit" resolution. The "point" or Scherzer resolution limit is determined by spherical aberration and is not improved. Figures 1.13 and 1.16 illustrate performance obtainable.

1.7.3 Electron Energy Loss Spectroscopy – N. J. Zaluzec⁷⁶ and R. W. Carpenter

The first electron energy loss spectrometer completed and interfaced with a JEOL-100CX analytical electron microscope at the end of last year has been used extensively to examine a number of different specimens of materials science interest this year. This instrument operates in the STEM mode, and is a 90° symmetric double-focusing magnetic section spectrometer. A number of results obtained are described below. A new but similar design was created for construction of an electron energy loss spectrometer to be interfaced with the Philips EM400 analytical microscope.

⁷⁶Present address: Materials Science Division, Argonne National Laboratory.

The new spectrometer has a larger radius, 300 mm, and therefore a larger dispersion. The design will permit operation of the microscope in several modes in addition to STEM, which is an advantage for a number of applications. Two spectrometers of the new design were built. One of these was sent to Argonne National Laboratory for installation on the Philips EM400 there.

1.7.3.1 The Influence of Diffracting Conditions on Quantitative Electron Energy Loss Spectroscopy⁷⁷ — N. J. Zaluzec,⁷⁶ J. J. Iren,⁷⁸ and R. W. Carpenter

Since many applications of electron energy loss spectroscopy (EELS) deal with microanalysis of crystalline materials, it is relevant to consider the effects of diffracting conditions on an EELS measurement. It is well known that anomalous effects can be observed during thin-film x-ray microanalysis when crystalline materials are oriented under diffracting conditions near deviation parameter $s = 0$. It is not surprising, therefore, that similar effects will be present in EELS, since this anomalous x-ray generation is a result of variations in the ionization cross section with crystalline orientation. Furthermore, since multiple scattering effects quickly average out these perturbations, one expects the most pronounced effects under conditions appropriate to EELS.

The influence of diffracting conditions on EELS can be observed experimentally by measuring the relative intensity ratio $I_K^A(\beta, \Delta)/I_O(\beta, \Delta)$ as a function of s . The intensity ratio is equal to

$$I_K^A(\beta, \Delta)/I_O(\beta, \Delta) = N_A \sigma_K^A(\beta, \Delta) ,$$

⁷⁷Adapted from pp. 114-15 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, Claitor's Publishing Division, Baton Rouge, Louisiana, 1980.

⁷⁸On leave from Department of Materials Science, University of Florida, Gainesville.

where

$I_K^A(\beta, \Delta)$ is the intensity of electrons that have excited a K th inner shell level,

$I_0(\beta, \Delta)$ is the total transmitted intensity, measured over an energy window Δ and acceptance angle β .

N_A is the number of atoms per unit area in the excited volume, and

$\sigma_K^A(\beta, \Delta)$ is the partial ionization cross section.

If successive measurements are made of the ratio I_K^A/I_0 at constant thickness (hence constant N_A) as a function of g , then all variations are due to the orientation dependence of σ_K^A .

An electropolished single-crystal specimen of vanadium was used to measure the dependence of $\sigma_K^A(\beta, \Delta)$ on diffracting conditions. Measurements of I_{L23}^V/I_0 were made by stepping a 30-nm electron probe ($E_0 = 120$ keV, beam divergence $\alpha \approx 3$ mrad) across a $\langle 112 \rangle$ bend contour from $g < 0$ to $g > 0$ at constant thickness. The local value of g was determined by measuring the separation of the $\pm \langle 112 \rangle$ contours and assuming a linear variation across the analyzed region. Then EELS data were recorded and analyzed by using an integration window for the V_{L23} edge of 150 eV and a spectrometer acceptance angle $\beta \approx 6$ mrad. The specimen thicknesses were determined by using subsidiary bend contour spacings.

Under the experimental conditions used σ_{L23}^V is relatively insensitive to diffracting conditions when $|g| \gg 0$. However as $|g| \rightarrow 0$, σ goes through a shallow minimum, and at $g = 0$ a sharp maximum. The results showed that attempting quantitative EELS near $g = 0$ can lead to substantial errors since most cross-section formulations used do not take into account an orientation dependence of σ .

1.7.4 Microchemical Analysis

- 1.7.4.1 On the Limitations of X-Ray Microanalysis of Heterogeneous Specimens Using Analytical Electron Microscopy⁷⁹ — N. J. Zaluzec,⁷⁶ E. A. Kenik, and P. J. Maziasz

X-ray microanalysis in an analytical electron microscope is becoming a routinely used technique in materials science, and it is important to appreciate its limitations in the quantitative analysis of inhomogeneous elemental distributions. Situations in which the limitations may occur are in the measurement of precipitate compositions or the determination of concentration gradients at defects or interfaces. This usually amounts to extraction of the precipitate from the parent phase, not always a simple task. We developed a procedure by which *semiquantitative* analysis may be obtained in situations where precipitate extraction is difficult or impossible. For example, the analysis of precipitate particles formed in amounts too small to extract under irradiation or metastable precipitates formed during early or intermediate stages of phase transformations.

1.7.5 Applications

- 1.7.5.1 Phase Identification Investigation in Silicon Nitride Ceramic Structural Alloys⁸⁰ — P. S. Sklad, R. W. Carpenter, N. J. Zaluzec,⁷⁶ and J. E. Selle

Ceramic structural alloys based on silicon nitride (Si_3N_4) are of interest for use in high-temperature applications because of their attractive strength, thermal shock resistance, and corrosion resistance. Bodies of Si_3N_4 are fabricated by powder metallurgy methods. Because pure Si_3N_4 does not sinter to high density, sintering aids are ordinarily used to increase densification. Some of these sintering aids can result in glass formation

⁷⁹Adapted from pp. 132-33 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, Claitor's Publishing Division, Baton Rouge, Louisiana, 1980.

⁸⁰Abstracted from paper presented at the 82nd Annual Meeting of the American Ceramic Society, April 27-30, 1980, Chicago.

at grain boundary triple junctions and in grain boundary interfaces. The presence of glass in Si_3N_4 alloys degrades high-temperature strength, corrosion resistance, and resistance to radiation damage. The work described here uses the methods of analytical electron microscopy to identify and characterize glass in grain boundary regions of two commercial hot-pressed and sintered Si_3N_4 alloys, one of which used MgO for a sintering aid and the other Y_2O_3 .

The two materials examined in this study exhibited small grain size, heterogeneous porosity, and a variety of crystalline phases. Glassy (noncrystalline) regions were observed either in thin films along grain boundaries or in pockets at multiple grain junctions. Figure 1.20 shows examples of the microstructures observed in each material.

The analysis of these complex microstructures required the use of all analytical microscopy techniques. Figure 1.21 illustrates the use of convergent-beam electron diffraction to identify the location of glassy regions in a specimen of Si_3N_4 sintered with MgO. The regions that appear white in the upper right are amorphous, as shown in the diffraction pattern in the lower left. Subsequent x-ray microanalysis showed that the glassy region contained magnesium and aluminum as well as silicon (Fig. 1.22).

Fig. 1.20. Complex Microstructures Observed in Sintered Structural Si_3N_4 . (a) With MgO sintering aid. (b) With Y_2O_3 sintering aid.

JRNL-Photo 2416-80

Fig. 1.21. Convergent-Beam Electron Diffraction (CBED) Can be Used to Identify Glassy Regions in Si_3N_4 Sintered With MgO . (a) Greatly under-focused CBED pattern. (b) Slightly underfocused CBED pattern. (c) Focused CBED pattern from glassy region. (d) Bright field image of area examined. Note that the camera length used to obtain the CBED pattern in (c) is much smaller than that used in (a) and (b).

Fig. 1.22. X-Ray Microanalysis Shows That an Amorphous Region in Si_3N_4 Sintered with MgO Contains Silicon, Magnesium, and Aluminum.

Figures 1.23 and 1.24 illustrate a similar analysis for the specimen sintered with Y_2O_3 . This example shows two phases of interest. The first is a glassy region identified as the small white triangle in the under-focused CBED shadow image and shown to be noncrystalline by the diffraction pattern in Fig. 1.23(d). The second phase appears black in the underfocused convergent-beam shadow image and is crystalline, as shown in Fig. 1.23(f). X-ray analysis revealed that the glassy phase in this case contains silicon but not aluminum, magnesium, or yttrium, while the crystalline phase is rich in yttrium (Fig. 1.24). A high-resolution axial fringe image of the yttrium-rich phase is shown in Fig. 1.25. Note that the fringes run in several directions in several small areas. This appearance was found in a number of yttrium-containing regions within the specimen and suggests that microcrystals may have precipitated from an yttrium-containing glass during processing. These small regions of variable fringe appearance were not found in any large yttrium-free grains of this material. It was evident from diffraction patterns of yttrium-containing grains such as this that the "grains" were not single crystals.

Our tentative conclusion from these observations is that the yttrium-containing regions are noncrystalline at the processing temperature but are relatively unstable and devitrify during cooling.

Fig. 1.23. Convergent-Beam Electron Diffraction (CBED) Can be Used to Identify Glassy Regions in Si_3N_4 Sintered with Y_2O_3 . (a) Greatly underfocused CBED pattern. (b) Slightly underfocused CBED pattern. (c) Nearly focused CBED pattern. (d) Focused CBED pattern from glassy region. (e) Bright field image of area examined. (f) Focused CBED pattern from crystalline region. Note that the camera length used to obtain the CBED patterns in (d) and (f) was smaller than the camera length used in (a), (b), and (c).

Fig. 1.24. X-Ray Microanalysis Shows the Presence of an Yttrium-Rich Phase as Well as a Silica Glass in Si_3N_4 Sintered with Y_2O_3 .

This investigation found that CBED is a very useful and fast method for identification of noncrystalline regions in ceramics because of the very strong contrast of these regions in shadow images (note Figs. 1.21 and 1.23). For very small noncrystalline regions, such as the pocket at the triple junction shown in Fig. 1.26, high-resolution imaging must be used, but it is a much slower method. Also CBED is useful for identification of crystalline phases. Figure 1.27 shows a bright field electron micrograph of a large $\beta\text{-Si}_3\text{N}_4$ grain together with its electron energy loss spectrum and two CBED patterns from the grain. Silicon nitride commonly occurs in one of two allotropic forms designated α and β , both of which have hexagonal structures. The a spacings of allotropes differ by about 2%, and differentiating between the two phases is often difficult. They cannot be distinguished by use of selected-area diffraction patterns from the basal plane orientation. However, CBED patterns can be used because they contain three-dimensional information in the form of higher

Fig. 1.25. High-Resolution Phase Contrast Image of Yttrium-Rich Region in Si_3N_4 Sintered with Y_2O_3 . Note areas of differently oriented fringes. Fringe spacings are about 0.35 nm.

Fig. 1.26. Lattice Fringe Images of Neighboring Grains in Si_3N_4 Sintered with MgO . Note the small noncrystalline unfringed regions at triple grain junction.

Fig. 1.27. Convergent-Beam Electron Diffraction (CBED) Can be Used to Obtain Three-Dimensional Information from Materials. (a) Bright-field image of grain examined. (b) Electron energy loss spectrum indicating that the material contains silicon and nitrogen. (c) Low-camera-length CBED pattern containing higher order Laue zone ring. (d) High-camera-length CBED pattern illustrating crystal symmetry information contained in CBED patterns.

order Laue zone (HOLZ) rings or reflections, which are directly related to the size of the unit cell. In Fig. 1.27 the bright ring in the low-camera-length diffraction pattern corresponds to β - Si_3N_4 . The long-camera-length CBED patterns carry symmetry information about the crystal. In this particular case the dark bands across $\{11\bar{2}0\}$ give information about the space group symmetry of the crystal. Electron energy loss spectra are useful for identifying phases containing light elements, but the peak-to-background ratios for such spectra depend on specimen

thickness. Acceptable spectra can be obtained only from specimen regions thinner than a few tens of nanometers. However, CBED patterns containing three-dimensional diffraction information can be obtained from crystals several hundred nanometers thick. It will be useful to correlate EELS spectra with CBED patterns from crystals containing light elements and then use CBED patterns for phase identification because of the low thickness limit for useful EELS spectra.

1.7.5.2 The Intergranular Phase in Hot-Pressed Silicon Nitride Alloys.
I. Elemental Composition⁸¹ — D. R. Clarke,⁸² N. J. Zaluzec,⁷⁶
and R. W. Carpenter

The elemental composition of the noncrystalline intergranular phase in three MgO-fluxed hot-pressed silicon nitride alloys was determined by x-ray microanalysis and electron energy loss spectroscopy in the transmission electron microscope. The composition is similar in all three alloys and lies close to the $\text{SiO}_2\text{-MgSiO}_3$ tie line, with impurities of calcium, aluminum, and chlorine. No nitrogen could be detected in the noncrystalline phase.

1.7.5.3 The Intergranular Phase in Hot-Pressed Silicon Nitride Alloys.
II. Evidence for Phase Separation and Crystallization⁸¹ —
D. R. Clarke,⁸² N. J. Zaluzec,⁷⁶ and R. W. Carpenter

Compositional and morphological evidence obtained by using transmission electron microscopy indicates that the noncrystalline phase in a hot-pressed silicon nitride alloy can undergo phase separation. The compositional range determined for the phase separation is close to the known miscibility gap in the $\text{SiO}_2\text{-MgO}$ pseudobinary system. Crystallization of $\text{Si}_2\text{N}_2\text{O}$ and MgSiO_3 from the noncrystalline phase is also evident, suggesting that it can contain some dissolved nitrogen and that the intergranular phase may be crystallizable.

⁸¹Abstracted from paper submitted to *Journal of American Ceramic Society*.

⁸²Structural Ceramics Group, Rockwell International Science Center, Thousand Oaks, California.

1.7.5.4 Observations of Gas Bubbles in an Austenitic Stainless Steel Charged with ^3H ⁸³ — P. S. Sklad

We are exploring the possibility of using Nitronic 40 as a high-strength substitute for 300 series stainless steels, especially in hydrogen environments. There is also interest in determining the influence of helium on the mechanical properties of this material for use in fusion reactor systems. The alloy is nominally (in weight percent) 21 Cr, 6 Ni, 9 Mn, and 63 Fe and is strengthened by 0.35 wt % N.

Smooth-bar tensile specimens approximately 3.5 mm in diameter with 25 mm gage lengths were machined from high-energy-rate-forged (HERF) stock. These specimens were then gas-phase charged with ^2H at 64 MPa pressure at 197°C or ^3H at 47.5 MPa at 72°C for 1450 h. Following charging, the specimens were stored at about -23°C for 5.5 years. Approximately one-third of the tritium decayed to ^3He during this period, yielding a maximum of 900 ppm of ^3He at the surface of the specimens. Tensile tests at 25°C revealed a significantly greater loss in ductility in the specimens charged with ^3H . Following tensile testing, transmission electron microscope specimens of suitable size were sectioned near the fracture surface, thinned by conventional techniques, and examined in a Philips EM400T equipped with a field emission gun.

The microstructures observed in the two specimens are shown in Fig. 1.28. While both specimens displayed similar dislocation microstructures, the specimen containing ^3He also contained a high concentration ($\sim 2 \times 10^{22}/\text{m}^3$) of small defects. These defects were noticeably absent from grain boundaries. Examination of Fig. 1.28(b) shows that the defects exhibit black-black lobe strain contrast with the line of no contrast approximately perpendicular to the diffraction vector g , typical of Ashby-Brown contrast from small coherent particles having spherically symmetric strain fields. A number of defects measured approximately 5 nm. However, the strain contrast and small size of the defects make it difficult to determine whether they are small precipitate particles or gas bubbles.

⁸³Adapted from pp. 388-89 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, Claitor's Publishing Division, Baton Rouge, Louisiana, 1980.

Fig. 1.28. Bright Field Micrographs of High-Energy-Rate-Forged (HERF) Nitronic 40. (a) Charged with ^2H at 64 MPa pressure at 197°C and aged 5.5 years at -23°C ; $g = 200$. (b) Charged with ^3H at 47.5 MPa at 72°C and aged 5.5 years at -23°C ; $g = 200$.

To differentiate between precipitate particles and gas bubbles a through-focus series of micrographs was made. The results are shown in Fig. 1.29. The objective lens is underfocused at about $8\ \mu\text{m}$ in (a), is close to focus in (b), and is overfocused by about $8\ \mu\text{m}$ in (c). The defects exhibit contrast behavior characteristic of gas bubbles or voids

Fig. 1.29. Bright-Field Through-Focus Series of a Nitronic 40 Specimen Charged with ^3H at 47.5 MPa at 72°C and Aged 5.5 Years at -23°C . (a) Objective underfocused by about $8\ \mu\text{m}$; (b) objective near focus; and (c) objective overfocused by about $8\ \mu\text{m}$. The diffracting conditions are $S_g < 0$ for $g = 200$.

(i.e., a bright center with dark fringes in the underfocused condition and dark center with bright fringes in the overfocused condition). It is also important to note that the best images were obtained with a negative deviation parameter (S_g). This contrast behavior is normally observed most clearly when the specimen is in kinematical diffracting conditions with values of underfocus and overfocus much smaller than those used in the present example.

We used the number density and size of the defects to estimate the amount of gas present, using the gas law expression for the number of gas atoms in an equilibrium gas bubble. The results are consistent with the estimated helium content of the specimen. We conclude that the bubbles were formed in conjunction with vacancies produced during deformation.

G. R. Caskey, du Pont Company, Savannah River, supplied the specimen material.

1.7.5.5 Creep Microstructure of Ferritic 9 Cr-1 Mo Steel — P. S. Sklad, R. W. Carpenter, and V. K. Sikka

The chemical composition of 9 Cr-1 Mo ferritic class steels has often been modified to improve properties such as energy absorption upon fracture and creep strength. We have examined changes in microstructure during creep in two modified alloys of this type. The basic difference in composition between the two alloys is in carbon and in the strong carbide-forming alloying elements silicon, vanadium, and niobium. The alloy with higher energy absorption upon fracture had a higher ratio of strong carbide-forming metals to carbon concentration; however, this alloy also exhibited lower creep strength. Both materials were homogenized followed by air cooling and reheating to temper. The microstructure of each alloy is shown in Fig. 1.30.

Both alloys contain polygonized subgrains, with the dislocation density in the subgrains being significantly lower in the alloy containing the larger concentration of carbide-forming elements. Extraction and x-ray experiments showed higher precipitate concentration (0.92 wt %) in the alloy containing more strong carbide-forming elements relative to the

Fig. 1.30. Microstructure of Modified 9 Cr-1 Mo Steels Before Creep Testing. (a) High carbide-forming element concentration. (b) Low carbide-forming element concentration.

alloy of lower concentration (0.57 wt % precipitate). The precipitate phases in both cases were primarily MC and $M_{23}C_6$. After creep testing at 650°C both alloys exhibited greater subgrain size. Examples are shown in Fig. 1.31.

The lower dislocation density within polygonized subcells observed before creep testing in the alloy having the higher carbide-forming element concentration persisted after creep testing. Precipitation occurred during creep testing in both alloys, with the concentration being higher (1.74 wt %) in the alloy of larger carbide-forming element concentration than in the other alloy (1.03 wt % precipitate). Observations made to date suggest that the reason for the difference in mechanical properties between these alloys is related to precipitate *distribution*, in particular to fine carbide precipitation on dislocations or networks in the alloy of low carbide-forming element concentration. Some higher resolution

Fig. 1.31. Microstructure of Modified 9 Cr-1 Mo Alloys After Creep Deformation at 650°C. (a) High carbide-forming element concentration. (b) Low carbide-forming element concentration.

Investigations of this phenomenon were made, with not entirely satisfactory results. The major barrier to obtaining good-quality high-resolution micrographs is the ferromagnetism of both alloys. The ferromagnetism causes loss of quality in high-resolution images and is the primary reason for the paucity of electron microscopy results on alloys of this type. We expect that a specimen preparation method can be developed that will permit reasonably simple examination of these microstructures under high resolution conditions (weak beam dark field). All other analytical microscopy methods can presently be used. This work is continuing, and the principal effort is directed to detailed examination of deformation substructure and its relation to precipitate distribution.

1.7.6 High-Voltage Electron Microscopy

1.7.6.1 Image Recording System for High-Voltage Electron Microscope Dynamic Studies — E. A. Kenik

In many in situ studies on the HVEM, microstructural changes (i.e., phase transformations, dislocation interactions, etc.) occur too rapidly to be observed at real time or to be recorded with conventional film camera systems. For this purpose, a dynamic image recording system has been designed for the HVEM based on television and videotape recording (VTR) technology. A low-light-level television camera (image isocon) will allow image manipulations and recording at electron densities one-twentieth or less of those of present visual observation or conventional recording. The associated VTR system will allow low-speed or stop-action examination of the recorded microstructural changes. Particular attention has been given to matching the resolution and speed limits of the individual units chosen to provide an optimized system.

1.7.6.2 In Situ Deformation of Aluminum Alloys⁸⁴ — E. A. Kenik and R. W. Carpenter

Deformation processes in a series of aluminum alloys have been investigated by in situ tensile deformation in the high-voltage electron microscope. Both solid-solution-hardened and precipitation-hardened alloys have been studied. Interactions of glissile dislocations with other dislocations, precipitates, grain boundaries, and other defects were investigated, as were the microstructural processes involved in the ductile failure of such specimens. Figure 1.32 illustrates the extensive cross-slip at precipitate particles, which widens the operating slip bands of aluminum alloys. The precipitate strain field produced image forces that promote cross-slip. Companion experiments on stainless steels indicate a lower occurrence of cross-slip, presumably the result of the lower stacking fault energy of austenitic alloys.

⁸⁴Adapted from pp. 28-29 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, Claitor's Publishing Division, Baton Rouge, Louisiana, 1990.

Fig. 1.32. Intense Cross-Slip of Glide Dislocations Near Incoherent Precipitates in Aged 1100 Aluminum.

In quenched Al-4 wt % Cu alloy, the interaction of glissile dislocations with quenched-in loops results in essentially dislocation-free paths through the loop microstructure. This process is similar to "channel slip" observed in irradiated metals. The speed of interaction precluded determining the exact process responsible for the clearing action of the glissile dislocation.

The interaction of glissile dislocations with grain boundaries was investigated in annealed 1100 aluminum. The dislocations initially pile up just short of the grain boundary as a result of image forces. As additional dislocations arrive at the pileup, the leading dislocations are forced into the grain boundary, where they are accommodated. Careful diffraction imaging shows that no dislocations have been generated in the adjacent grain by either the dislocation pileup or absorption at the boundary.

Figure 1.33 illustrates the propagation mode of a shear crack in an annealed 1100 aluminum alloy. Ahead of the advancing crack, intense multiple slip-system deformation results in a localized thinning of the foil and leads to the formation of a hole just ahead of the crack. The

Fig. 1.33. Shear Crack in Aged 1100 Aluminum Exhibiting Ligament Formation During Propagation.

hole enlarges as the result of further slip. The remaining matrix between the hole and crack, the ligament, thins down to a chisel-point fracture.

Further studies will involve the dislocation interactions in precipitation-hardened Al-4 wt % Cu and the fracture mode of such alloys containing precipitate free zones at grain boundaries.

1.7.6.3 Low-Pressure In Situ Oxidation of Vanadium and V-20 % Ti⁸⁵ —
E. A. Kenik, K. R. Lawless,⁸⁶ and R. W. Carpenter

The oxidation of vanadium and V-20 % Ti has been investigated in the environmental cell of the ORNL high-voltage electron microscope at oxygen partial pressures of 1.3 to 4.0 mPa ($1-3 \times 10^{-5}$ torr) from 300 to 800°C. The present studies extend the work previously reported. Detailed structural analysis of the reaction products and additional oxidation studies on high-purity specimens of V-20 % V alloy (residual interstitial impurities ~800 wt ppm) have been completed.

⁸⁵Abstracted from paper presented at 109th AIME Annual Meeting, Las Vegas, Feb. 24-28, 1980.

⁸⁶University of Virginia, Charlottesville.

The interaction of irradiation-induced point defects and the oxidation behavior of vanadium have been reconfirmed both by in situ oxidation under irradiation and by in situ oxidation of an ion-milled specimen. Apparently the oxygen is trapped at the point defects, and the rapid transformation to the ordered suboxide α' (V_9O) is suppressed. The possibility of higher oxides forming at irradiation-produced dislocations is still under investigation.

The phases that form during oxidation of vanadium depend on both temperature and oxygen level. Below about 500°C, the first phase to form is the tetragonal ($c/a \approx 0.97$) α' or V_9O ordered suboxide, which is heavily twinned on (110) planes. As the oxidation proceeds, the α' first nucleates at the thin edge of the specimen, and the transformation zone progressively spreads into thicker regions. Concurrent with the latter process, higher oxides form, again at the thin edge, and grow into the thicker region, dissolving the α' . These higher oxides include the β phase, which is ordered at these temperatures (β'), and possibly γ phase. The change in the position of the superlattice spots of β' in the diffraction pattern as a function of oxygen content has been observed. Over the entire range of oxidation conditions studied to date, the stable surface oxide on pure vanadium is V_2O_3 .

At 500°C and above, the first oxide formed was the tetragonal ($c/a \approx 1.1$) β , in agreement with the published V-O phase diagrams. The oxide is twinned on (110) planes and exhibits some diffuse intensity in diffracting patterns, indicating short-range ordering of the oxygen.

The oxidation behavior of V-20 % Ti differs significantly from that of pure vanadium. The rapid transformation to the ordered α' suboxide was entirely suppressed in the alloy. The first evidences of microstructural change are diffuse streaks of intensity in the diffraction patterns and a "tweed" microstructure, both of which indicate possible clustering of oxygen and titanium atoms. Upon further oxidation, the matrix transforms to an oxide identical in lattice parameter and crystal structure with the β phase observed in pure vanadium. In addition, the stable surface oxide appears to be V_2O_3 , on the basis of lattice parameter and crystal

structure. The only difference in the surface oxide formed on vanadium and on V-20 % Ti is the grain size of the V_2O_3 crystallites, which is significantly larger for the V-20 % Ti.

1.7.6.4 HVEM In Situ Hydriding of Hydrogen Storage Materials⁸⁷ — E. A. Kenik, J. Mullins,⁸⁸ S. Spooner,⁸⁸ and B. R. Livesay⁸⁸

The microstructural changes induced during hydriding have been investigated by high-voltage electron microscopy and in situ hydriding studies. That hydriding generates high dislocation densities has implications for the mechanism involved in the hydride transformation and possible memory effects of prior hydrogen exposures on subsequent hydriding behavior. In situ hydriding of $LaCo_5$ and $LaNi_2Co_3$ has been demonstrated. In addition, an activation barrier to hydriding at low hydrogen pressures was indicated in in situ studies and later confirmed by microbalance weight-gain measurements. This barrier may be significantly reduced or eliminated by heating to about 200°C under a low partial pressure of hydrogen. Internal stresses generated by hydriding and dehydriding result in cracking and ultimately in the fracture of thin foil specimens. The hydriding process either involves a dislocation mechanism such as slip or twinning or generates dislocations by the internal stresses set up during hydriding. Further work will concentrate on producing large-grain evaporated thin films of the alloys, which will allow hydriding to be performed without specimen fracture.

1.7.6.5 The Effect of Stacking Fault Energy on Sliding Wear Behavior of Copper-Aluminum Alloys⁸⁹ — J. J. Wert,⁹⁰ R. W. Carpenter, and S. G. Caldwell⁹⁰

The addition of aluminum to copper results in a well-known reduction of stacking fault energy, which in turn enhances planar slip (i.e., restricts cross slip). We examined in detail the subsurface dislocation

⁸⁷Abstracted from *Trans. Jpn. Inst. Met. Suppl.* 21: 321-24 (1980).

⁸⁸Georgia Institute of Technology, Atlanta.

⁸⁹To be published in the proceedings of the Third International Conference on Wear of Materials, San Francisco, March 1981.

⁹⁰Vanderbilt University, Nashville, Tennessee.

structure under stylus wear tracks and correlated those observations with the alloy stacking fault energy. At the same time, using analytical electron microscopy, we examined the surface topography of the wear track for correlation with the subsurface dislocation structure. In addition, macroscopic unlubricated sliding wear rates were measured for these alloys as a function of aluminum concentration (i.e., stacking fault energy). The magnitude and nature of surface wear damage as a function of sliding distance and normal load were examined by scanning electron microscopy. The relationship among wear-induced dislocation substructure, wear rates, and copper-aluminum alloy stacking fault energy are presented.

1.7.6.6 Metal Surface Deformation and Subsurface Defect Structure: A Microscopy Correlation Study⁹¹ — R. W. Carpenter, J. J. Wert,⁹⁰ and S. G. Caldwell⁹⁰

When a metal surface is deformed by indentation, sliding wear, or similar influences, the crystal volume below the surface deformation trace contains an array of dislocations whose density varies with position relative to the surface deformation trace. It had been shown earlier that the combined imaging modes (TEM-STEM and SEM) of an analytical electron microscope permit convenient and direct correlation between surface deformation markings and subsurface dislocation arrays in aluminum. In this note we report observations of deformation induced at room temperature by single stylus tracks on a Cu-8 wt % Al alloy. The widths of the dense dislocation array at the stylus track determined from TEM and the track itself determined by SEM are in this case nearly equal. The planar slip traces extend large distances from the track. These results differ significantly from those reported earlier for aluminum, in which the subsurface dislocations formed a dense array several times wider than the surface track. They also differed in the absence of planar slip traces extending away from the track. This difference is attributed to the low stacking fault energy of Cu-8 wt % Al, which should inhibit cross-slip and tangling near the track.

⁹¹Adapted from pp. 140-41 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, Claitor's Publishing Division, Baton Rouge, Louisiana, 1980.

1.7.6.7 Catalog of Computer-Simulated TEM Images of Small FCC and BCC Dislocation Loops⁹² — Lawrence J. Sykes,⁹³ Wayne D. Cooper,⁹³ and John J. Hren⁹³

Interest in rapidly quenched materials, radiation damage, and nucleation processes has created the need for a method to identify small point defect clusters observed by transmission electron microscopy. This report is an outgrowth of this general area of interest and concerns itself primarily with the images of small dislocation loops ($r < 0.25$ times the extinction distance). The various parameters important in determining an image are presented and a catalog of computer-simulated images for a large number of loop crystallographies imaged under a large number of beam direction and diffracting vector combinations is assembled. The program that produced the images is also described and included with annotation.

⁹²Abstracted from a manuscript to be published as an ORNL Technical Memorandum as part of the SHARE program.

⁹³The University of Florida, Gainesville.

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2. DEFORMATION AND MECHANICAL PROPERTIES

M. H. Yoo

The research program on deformation and mechanical properties is concerned with the fundamental aspects of mechanical behavior that control the strength and ductility of structural components in energy technology systems. The program encompasses mechanical testing, microstructural analysis, and theoretical modeling. In both experimental and theoretical approaches, emphasis is placed on obtaining quantitative relationships between microstructure and mechanical properties.

The role of interfaces and impurities in deformation and fracture at elevated temperatures has been selected as the central topic on which we focus our major effort. Initially, emphasis is placed on the physical mechanisms of intergranular fracture by experimentally investigating nickel and single-phase nickel binary and ternary alloys as a model system for both nickel-base superalloys and austenitic stainless steels. Effects of trace impurities and inclusions on grain boundary cracking and cavitation are investigated by use of optical metallography, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Auger electron spectroscopy (AES). Trace impurity effects on vacancy clustering and microvoid formation are modeled theoretically by use of an efficient numerical integration method. In order to characterize the intergranular fracture processes, a controlled grain boundary exposure technique by liquid-metal embrittlement is being developed. Anelastic and structural recovery data obtained by stress change experiments during creep testing provide the basis for understanding of both microstructural mechanisms and macroscopic behavior of high-temperature deformation. Current status of the development of experimental facilities for deformation and fracture studies are also summarized.

2.1 INTERGRANULAR FRACTURE

2.1.1 Trace Element Effects in Creep Cavitation — C. L. White and R. A. Padgett

Trace elements and impurities often exert large effects on the ductility and failure mode of alloys in elevated-temperature service. Metalloid impurities such as S, Sn, Sb, and As are known to reduce elevated-temperature ductility and induce intergranular failure in nickel and nickel-base alloys. Aside from the general consensus that such trace impurities probably segregate to internal interfaces, the mechanisms for such effects are not well understood.

Noting that these trace element effects are usually associated with extensive grain boundary cavitation and cracking, a number of possible mechanisms can be suggested. These include trace element segregation to surfaces and grain boundaries to affect their (1) energies, (2) diffusivities, and (3) vacancy source-sink behavior. The sliding characteristics of grain boundaries are also likely to be influenced strongly by trace impurity segregation to them.

2.1.1.1 Studies on Nickel

We initially considered As, Sb, Sn, and P as "model" impurities. These elements were chosen because (1) they are metalloid elements, known to be surface active in other transition metals, and (2) they each have significant solid solubility in nickel at half its absolute melting point (590°C). It is important to have a significant range of solid solubility so that enough impurity can be added to single-phase alloys to permit reliable bulk chemical analyses and so that a range of compositions in the solid solution range can be studied. These considerations led to the rejection of sulfur as an intentionally added impurity in spite of the fact that it is an important impurity in these alloys.

Preliminary studies involved mechanical testing and analysis of Ni-1 wt % Sn, Ni-1 wt % Sb, Ni-0.5 wt % As, and Ni-0.01 wt % P. Low-strain-rate tensile tests ($\dot{\epsilon} = 1.8 \times 10^{-3}/s$) were carried out at 600°C

to determine the effects of these additions on ductility and failure mode. The Ni-1 wt % Sb alloy was most embrittled (see Table 2.1), followed by Ni-1 wt % Sn and Ni-0.5 wt % As. The Ni-0.01 wt % P alloy showed nearly the same ductility as a control alloy having no additions.

Table 2.1. Low-Strain-Rate ($\dot{\epsilon} = 1.8 \times 10^{-3}/s$)
Tensile Properties of Nickel Alloys at 600°C

Alloy	UTS (MPa)	Elongation (%)
Ni-1% Sn	182	18
Ni-1% Sb	115	9
Ni-0.5% As	85	26
Ni-0.01% P	97	34
Ni (undoped)	88	40

Optical metallography and SEM showed the failure mode in the Sb-, Sn-, and As-doped alloys to be primarily intergranular. Extensive internal cavitation and cracking occurred at grain boundaries all along the gage sections (see Fig. 2.1).

Because the antimony- and tin-doped alloys were the most severely embrittled, additional testing and analysis were carried out on them. Ductility in Ni-1 wt % Sb at 600°C increased with increasing strain rate, suggesting that thermally activated phenomena are indeed taking part in the failure mode. Variations in testing temperature indicated a broad minimum in ductility near 600°C for the Ni-1 wt % Sn alloy. Constant-load creep tests at 34 and 103 MPa (5 and 15 ksi) (600°C) also show low elongation accompanied by extensive intergranular cracking.

Specimens prepared from cavitating gage sections of Ni-1 wt % Sb tensile specimens were fractured in the AES vacuum system. Auger spectra of the fresh fracture surfaces showed large concentrations of both antimony and sulfur (Fig. 2.2). The sulfur was present as a residual impurity

Fig. 2.1. Optical Micrograph (Unetched) of Ni-1 wt % Sb, Tensile Tested at 600°C, $\dot{\epsilon} = 1.8 \times 10^{-3}/s$. Note extensive internal cracking and cavitation at grain boundaries.

Fig. 2.2. Auger Analysis of Sample From Cavitated Gage Section of Ni-1% Sb Tensile Specimen. The surface analyzed was a fresh fracture surface of a specimen fractured in vacuum at room temperature.

in the alloy at a level of 30 wt ppm. Sputter profiling showed that these elements were enriched at the surfaces, with the concentration decreasing as material was etched away from the surface.

2.1.1.2 Studies on Type 304 Stainless Steel¹

Extensive characterization of creep cavity growth rates in type 304 stainless steel have been carried out by Chen.² After creep deformation between 600 and 775°C, alloys used in that study were fractured intergranularly at -196°C. This intergranular fracture permitted measurement of grain boundary cavity size and distribution as a function of time, stress, and temperature.

Because grain boundaries and creep cavity surfaces in these alloys can be exposed by low-temperature fracture, AES analysis of these alloys might allow any trace element segregation to grain boundaries or cavity surfaces to be detected. Preliminary AES studies using uncavitated specimens are under way, and specimens cavitated in creep should be available by midsummer.

Auger analysis of the first uncavitated specimen indicates significant segregation of sulfur and phosphorus to grain boundaries. Small cavities (~2 μ m diam) where precipitate particles had apparently pulled out showed large concentrations of sulfur, as indicated in Figs. 2.3 and 2.4. In general, these cavity surfaces are richer in sulfur than the general grain boundaries. Because of the complexity of this alloy, and the presence of second (and possibly third) phases, detailed interpretation of these results may not be possible. There seems to be little doubt however, that trace impurities segregate strongly to grain boundaries and precipitate-matrix interfaces.

¹This work is being carried out in collaboration with I. W. Chen and A. S. Argon, Department of Mechanical Engineering, Massachusetts Institute of Technology.

²I.W. Chen, "Creep Cavitation in Type 304 Stainless Steel," Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, 1980.

Fig. 2.3. Secondary Electron Images of Fracture Surface of Type 304 Stainless Steel Analyzed by Auger Spectroscopy.

ORNL-DWG 80-2060

Fig. 2.4. Auger Spectra of Type 304 Stainless Steel Fracture Surface at Spots Indicated on the lower part of Fig. 2.3

2.1.2 Trace Element Effects on Vacancy Clustering and Heterogeneous Nucleation of Microvoids During Various Thermomechanical Treatments³ — M. H. Yoo

A theoretical investigation of trace element effects has been made by taking the dilute nickel-antimony alloy system as an example. A reaction rate theory model of impurity-induced vacancy clustering was formulated by using a hierarchical grouping method. In characterizing the reaction rate constants, we assumed that only monovacancies are mobile and bind strongly with antimony atoms with the binding energy⁴ of $E_{vt}^b = 0.5$ eV. The specific energy of the microvoid surface is $\gamma_s = 1$ J/m². The model is then applied to predict the kinetics of vacancy clustering during a variety of thermomechanical histories of the system.

Figure 2.5 shows the evolution of microvoid size distribution when the impurity trap atom fraction is $C_t = 10^{-6}$ and the annealing temperature is $T_a = 608$ K. The cluster size increases and the density decreases with increasing annealing time. The evolution of the mean cluster size and density, $\bar{n}$ and N_v , is shown in Fig. 2.6 for various impurity concentrations. The initial vacancy concentration used for this calculation is $C_v = 1 \times 10^{-5}$, which approximates recovery of a heavily cold-worked ($\epsilon = 0.9$) dislocation microstructure. Figure 2.6 shows that when the impurity concentration exceeds the initial vacancy concentration, all the annealing curves essentially merge at $t > 10^3$ s. We find that at $t = 3.6 \times 10^3$ s, $N_v = 5.2 \times 10^{22}$, and $\bar{n} = 11$, which are much lower than the values, $N_v \approx 10^{24}/\text{m}^3$ and $\bar{n} \approx 20$, determined from positron annihilation experiments⁴. The calculated results depend sensitively on the input parameters such as vacancy formation and migration energies ($E_v^f = 1.6$ eV and $E_v^m = 1$ eV), free surface energy, dislocation density ($L = 10^{14}/\text{m}^2$), grain size ($d = 10$ μm), impurity concentration, and vacancy-impurity binding energy. Following numerous calculations based on a set of

³Abstracted from paper to be presented at the Fall Meeting of The Metallurgical Society of AIME, Pittsburgh, October 5-9, 1980.

⁴G. Dlubek et al., "Impurity-Induced Vacancy Clustering in Cold-Worked Nickel," *J. Phys. F* 9: 1961-73 (1979).

Fig. 2.5. Evolution of Microvoids by Impurity-Induced Vacancy Clustering in Nickel at Annealing Temperature 608 K.

Fig. 2.6. Annealing Kinetics of the Total Density and the Mean Size of Microvoids for Various Impurity Concentrations, C_i .

reasonable input parameters for nickel,^{4,5} we find that a high value of microvoid density of the order $N_v = 10^{24}/\text{m}^3$ may occur only at relatively short annealing times ($t < 10^2$ s), but not⁴ at $t = 1$ h.

The calculated results, Figs. 2.5 and 2.6, may also apply to an annealing history starting from a vacancy supersaturation of 4×10^7 following quenching from 1153°C to the annealing temperature. An extended application of this model has been initiated to study grain boundary cavity formation under applied stress.

2.1.3 Creep Cavity Observation in Nickel Alloys⁶ — T. C. Reiley

The objective of these experiments is the understanding of structural and deformation factors leading to the nucleation and growth of creep cavities. In the past there has been severe difficulty in finding a technique that allows convenient observation of these cavities at an early stage ($\sim 0.1 \mu\text{m}$). Thus, the first efforts are directed toward finding such a technique. In the last reporting period the use of liquid metal embrittlement as a technique for exposing grain boundaries was first applied to aluminum, with early promise of success. In this period a new material was chosen for study, Ni-4 wt % W, an fcc alloy with a low stacking fault energy and shown previously to form creep cavities.⁷

The technique used involves first creep testing the material, then at a much lower temperature applying a load in the presence of liquid metal, leading to intergranular failure. The mechanism of liquid metal embrittlement (LME) for polycrystals shows a variety of phenomenology,

⁵M. H. Yoo and J. O. Stiegler, "Growth Kinetics and 'Preference Factor' of Frank Loops in Nickel During Electron Irradiation," *Philos. Mag.* 36: 1305-15 (1977).

⁶Most of this work was performed in the Institut für Festkörperforschung, KFA-Jülich, during the author's year of foreign assignment.

⁷W. R. Johnson, C. R. Barrett, and W. D. Nix, "The High-Temperature Creep Behavior of Nickel-Rich Ni-W Solid Solutions," *Metall. Trans.* 3: 963-69 (1972).

but it is generally pictured as a surface-energy-driven process in which grain boundary decohesion at the crack tip proceeds at a lower stress than would be possible without the liquid metal. The stress and temperature dependent kinetics of liquid metal delivery and, perhaps, adsorption at the crack tip are important to LME. Also, LME is specific to certain metal couples, and the following rules generally apply: (1) the metals should have low mutual solubilities (a factor that aids in the use of LME to observe undisturbed grain boundary features) and (2) the metals should not form intermetallic compounds. Old⁸ has found, perhaps, a better set of criteria based on heats of solution.

Consistent with the above rules, thallium and lead were individually applied to recrystallized Ni-4Z W in two mechanical testing machines built for this purpose. Both liquids were strong embrittling agents at 625 K. Without the presence of liquid the ultimate tensile strength of Ni-4Z W was 275 ± 10 MPa at 625 K, with a strain to failure of $30 \pm 3\%$. With the liquid metals, failure stresses were reduced below 50 MPa for thallium and below 30 MPa for lead, with failure strains below about 1%. Lead was a more effective embrittling agent, given its faster rate of delivery, presumably reflecting a higher grain boundary diffusivity. Figure 2.7 shows a low-magnification fracture surface scanning electron micrograph (SEM) of Ni-4 Z W tested without liquid metal and one tested in thallium. The thallium was chemically removed. The grain boundaries are exposed in rather good detail. Features having diameters at least as small as $0.1 \mu\text{m}$ can be studied with this technique. Figure 2.8 shows SEMs of Ni-4 Z W fractured in the presence of lead, giving similarly detailed grain boundary features. Efforts to examine creep cavities await the preparation of well-cavitated specimens.

⁸C. F. Old, private communication.

Y-172050

Fig. 2.7. Fracture Surface of Ni-4 Z W. (a) Deformed 30% at 625 K at 275 MPa. (b) Deformed less than 1% under 50 MPa at 625 K in the presence of liquid thallium.

Y-172051

Fig. 2.8. Fracture Surfaces of Ni-4 Z W Deformed Less Than 1% at 625 K in the presence of liquid lead.

2.1.4 Microcavities and Their Effects on Elevated-Temperature Mechanical Properties of Austenitic Stainless Steel – R. W. Swindeman and K. Farrell

At high temperatures commercial alloys often exhibit several failure modes. These include plastic instability (P-type) and intergranular separation through wedge cracking (W-type) or microcavity growth and coalescence (R-type). Below 0.6 times the absolute melting point, T_m , the first two mechanisms dominate at the stresses and times convenient for laboratory testing; hence, it is difficult to study microcavity formation. Yet, in structures intended for service times exceeding 100 Ms, failure by microvoid growth and coalescence is expected, and a proper damage accumulation model must account for this fact.

Recently, we discovered a heat of type 304 stainless steel that exhibits the R-type failure in creep at 593°C ($0.5T_m$) in less than 1 Ms. The creep ductility and the creep-fatigue resistance are substantially below the norms for type 304 stainless steel. Optical metallography reveals extensive cavitation [Fig. 2.9(a)], and SEM of the fracture surface shows intergranular voids associated with carbide particles [Fig. 2.9(b)]. Transmission electron microscopy shows considerable precipitation of $M_{23}C_6$ on grain boundaries and dislocation cell walls. Most creep cavities are too large to be encompassed in the TEM foils, but a few small cavities are found on grain boundaries, where they tend to be hidden by the precipitates grown during the test. Precipitation is accelerated by plastic strain and is, therefore, a minimum in the unstrained heads of the specimens. A careful TEM examination of the heads of specimens revealed many microvoids on the grain boundaries. Further investigation showed that these cavities are present in the as-received, untested stock from which the creep specimens were cut. These preexisting cavities are small (5 to 50 nm), and each one is attached to a precipitate or inclusion particle [Fig. 2.9(c)], the cavity often being hidden by a particle. On some boundaries the cavities are spaced only 0.2 to 0.5 μm apart. Before such cavities can grow to a size just visible in an optical microscope, 1 μm or so, they will interconnect and form a narrow, continuous grain

Fig. 2.9. Grain Boundary Cavities in Type 304 Stainless Steel. (a) Optical micrograph of a sample creep tested at 138 MPa and 593°C for 5.3 Ms. Unetched. (b) Scanning electron micrograph of the fracture surface of a sample creep tested at 241 MPa and 593°C for 0.3 Ms. Cavities contain M_{23}C_6 particles. (c) Small grain boundary cavities attached to inclusion particles in unstrained part of creep-fatigue specimen.

boundary crack. We suspect that these cavities are produced during manufacture of the alloy product and are responsible for the degraded creep properties. Such preexisting cavities would eliminate the incubation period for formation of creep cavities.

Cavities of this type might occur commonly during thermomechanical processing of materials, but are unobserved because of their small size. They could be responsible for some of the wide heat-to-heat variations in mechanical properties of alloys of the same nominal composition. If so, appropriate accommodation must be made for them in cumulative damage models based on phenomenological considerations. The causes of these initial cavities require investigation since the answers may lead to control measures that might eliminate substandard mechanical response and may even offer the possibility of raising the general level of mechanical properties. A few cursory tests we have made on this alloy indicate that aging at 815°C can substantially improve creep behavior.

2.1.5 Fracture Initiation at Grain Boundary Inclusions -- Internal Stress Effects -- M. H. Yoo

Fracture strength and ductility of polycrystalline solids are influenced significantly by the presence of inclusions or precipitate particles in grain boundaries. Under creep and high-temperature fatigue conditions, the junction of an inclusion and a grain boundary is usually the principal site of cavity nucleation. We investigated theoretically the effect of internal stresses due to grain boundary inclusions, in the absence of applied load, on crack initiation and cavity nucleation.

Two relevant stress components, the normal σ_n and the shear stress τ , resolved on a grain boundary were calculated with Eshelby theory,⁹ and the results are shown in Fig. 2-10. The stress component normal to the inclusion-matrix interface is $\sigma_n = -2\sigma_n$ at the interface. These internal stresses may be reduced by (1) localized deformation by the dislocation

⁹J. D. Eshelby, "The Determination of the Elastic Field of an Ellipsoidal Inclusion and Related Problems," *Proc. R. Soc. London A241*: 376-96 (1957).

Fig. 2.10. Normal and Shear Stress Components, σ_n and τ , Resolved on a Grain Boundary. These stresses are induced by a spherical inclusion with the misfit transformation strain ϵ ; G is the shear modulus of the matrix.

generation, (2) crack initiation by the boundary decohesion, and (3) diffusional flow of atoms along the boundaries. Four possible modes of crack initiation are depicted in Fig. 2.11, which suggests (a) and (d) as the likely modes of grain boundary cracking and interfacial cracking, respectively. If the origin of the internal stresses is due to a difference in the linear thermal expansion coefficients of matrix and inclusion α and α^* , then the final strain is $\epsilon = (1 + 3K^*/4G)(\alpha^* - \alpha)\Delta T$, where K^* is the bulk modulus of the inclusion and ΔT is the temperature change. In order for σ_n for the case of Fig. 2.11(a) to exceed the threshold stresses of grain boundary decohesion, nominally $10^{-3}G$, it is generally required that $\Delta T > 1000$ K with $(\alpha^* - \alpha) \approx 10^{-6}/K$.

Fig. 2.11. Possible Modes of Crack Initiation by Decohesion of the Grain Boundary and the Inclusion-Matrix Interface.

When the internal stresses are too low for grain boundary cracking but temperature is high ($>0.3 T_m$), the stress relaxation by diffusional flow becomes of relative importance. The characteristic time for this relaxation is approximated as $\tau_c = kT/GD_b\delta$, where kT is the Boltzmann factor, $D_b\delta$ is the product of grain boundary diffusivity and grain boundary width, and the value of τ_c for nickel at 773 K is estimated to be only 2 ns. The influence of the excess chemical potential for atoms created by the transient internal stresses on the formation of grain boundary microcavities is being investigated according to the vacancy clustering model (Sect. 2.1.2).

2.1.6 Low-Temperature Grain Boundary Fracture — C. L. White and R. A. Padgett

Brittle intergranular fracture of metals at low temperatures often results from trace element segregation to the grain boundaries. Less well-known are the beneficial effects of certain elements when they segregate to grain boundaries. Several collaborative efforts have been carried out or are currently under way to characterize and understand the relationship between trace element segregation and intergranular fracture at low temperatures.

2.1.6.1 Fracture Energy Measurements in Fe-3% Si Bicrystals¹⁰

Transformer steel (Fe-3% Si) was doped with varying amounts of phosphorus and given an embrittling step-cool heat treatment. Auger electron spectroscopy was used to determine that large increases in intergranular phosphorus concentration occurred in approximate proportion to the bulk phosphorus level through an equilibrium segregation mechanism. Bicrystals of this material were fractured at 300, 77, and 4.2 K. Grain boundary fracture energy, γ_f^{gb} , was determined as a function of intergranular phosphorus concentration at 4.2 K. An analysis of γ_f^{gb} and fracture mode as a function of temperature was used to evaluate the relative merits of intergranular fracture models based on reduced interatomic separation energy (Gibbs-Griffith model) and reduced interatomic cohesive strength (Seah model). The reduced interatomic separation energy model fitted the experimental findings better.

2.1.6.2 Grain Boundary Segregation and Intergranular Failure¹¹

Trace elements and impurities often segregate strongly to grain boundaries in metals and alloys. Concentrations of these elements at grain boundaries are often 10^3 to 10^5 times as great as their overall concentration in the alloy. Because of such segregation, certain trace elements can exert a disproportionate influence on material properties. One frequently observed consequence of trace element segregation to grain

¹⁰This work was carried out in collaboration with R. G. Thompson (Clemson University), J. J. Wert (Vanderbilt University), and D. S. Easton (ORNL) as part of Thompson's thesis research at Vanderbilt University. A manuscript entitled "On the Mechanism of Intergranular Embrittlement by Phosphorus (in Transformer Steel)" is in preparation for submission to *Metallurgical Transactions*.

¹¹Abstract of a paper presented at the First International Aluminum-Lithium Conference, Stone Mountain, Georgia, May 19-21, 1980. A paper by the same title is to appear in the proceedings of that conference. Work on Al-3% Li alloys is being carried out in collaboration with T. Sanders, Georgia Institute of Technology Fracture and Fatigue Research Laboratory, under auspices of the SHaRE Program.

boundaries is the occurrence of grain boundary failure and low ductility. Less well-known are incidences of improved ductility and inhibition of grain boundary fracture resulting from trace element segregation to grain boundaries in certain systems.

Trace element segregation and intergranular failure in a variety of alloy systems as well as preliminary results from studies on Al-3% Li have been characterized.

2.1.6.3 Boron Segregation to Grain Boundaries and Improved Ductility in Pt-30 wt % Rh-8 wt % W¹²

Boron additions of up to 75 wt ppm have been observed to improve the room-temperature strength and ductility of a Pt-30 wt % Rh-8 wt % W alloy. Alloys without boron fail intergranularly, and those with 75 wt ppm B added fail in a mixed intergranular-transgranular mode. Auger electron spectroscopy on intergranular fracture surfaces indicated that boron segregates strongly to grain boundaries in the boron-doped alloys. Transmission electron microscopy of alloys with and without boron indicated that both were free of internal precipitates. The observed improvements in strength and ductility appear to be related to boron enrichment within a few atomic distances of the grain boundary.

2.1.6.4 A Study of Grain Boundary Embrittlement in Cu-3% Al-1% Si Using AES¹³

Single-phase Al-Si bronze alloys are used in a variety of applications requiring good corrosion resistance, ductility, and strength. These

¹² Abstract of a paper being prepared for submission to *Metallurgical Transactions*. Work on Pt-30 wt % Rh-8 wt % W alloys has been carried out in collaboration with J. R. Keiser and D. N. Braski of ORNL. This work was partially supported by the Division of Advanced Nuclear Systems and Projects.

¹³ Abstract of a paper presented at the 12th Annual Technical Meeting of the International Metallographic Society and to appear in the proceedings of that meeting. Work on Cu-3% Al-1% Si alloys has been carried out in collaboration with T. R. Odom (PGDP) and R. E. Clausen (ORNL). This work was partially supported by Enriching Operations Division of DOE.

fcc alloys normally exhibit tensile elongations between 20 and 60%, depending on annealing conditions, and are not usually prone to intergranular failure. However, material from several different bars of an aluminum-silicon bronze (Cu-3 wt % Al-1 wt % Si) has been found to fail intergranularly, with unusually low tensile elongation. Bulk chemical analysis of these bars indicated higher than normal concentrations of lead in the alloys. Auger electron spectroscopy (AES) of intergranular fracture surfaces has shown the grain boundaries to be highly enriched in lead. There seems to be little doubt that this lead enrichment is responsible for the abnormally low ductility and intergranular failure in this aluminum-silicon bronze.

2.2 DEFORMATION MECHANISMS

2.2.1 Anelastic Creep Recovery in Nickel - T. C. Reiley, M. H. Yoo, and R. H. Shannon

The goal of these experiments is to understand the origin and mechanisms of high-temperature anelastic recovery and, in particular, to prepare a technique to evaluate the amount of grain boundary sliding (GBS) as a function of deformation mode, strain rate, stress, and temperature by monitoring the strain recovery kinetics. Creep failure is thought to involve grain boundary sliding as the primary mechanism for cavity nucleation; however, it is not possible to predict the amount of GBS associated with deformation for a given grain size, strain rate, stress, and temperature. Furthermore, accurate measurements of GBS are difficult and tedious. Therefore, we are looking for a correlation between the amount of grain boundary sliding and kinetics of strain recovery in a manner similar to that of Gibeling;¹⁴ however, for our experiments we have available the accuracy and stability of the Irradiation Creep Facility (ICF) at ORNL.

¹⁴J. C. Gibeling, *The Use of Stress Change Experiments to Study the Mechanisms for Elevated Temperature Deformation*, Ph.D. thesis, Stanford University, 1979.

The first experiments have been exploratory, aimed at determining resolution limits. Data are shown for pure nickel in Fig. 2.12, giving the strain recovery after stress reductions from 30, 20, and 10 MPa to approximately 2 MPa, at an average temperature of 845 K. The total strain recovery depended linearly on stress reduction and at this temperature was essentially complete in about 10 ks, although for these large-grain-sized specimens (approaching the specimen thickness, 125 μm) the slower triple-point-stress-driven recovery processes should have been greatly reduced under that expected for bulk material. Further experiments using ICF on an elastic creep recovery in nickel and its alloys will deal with sheet specimens of fine grain size, and these experiments will be complemented by stress relaxation studies of bulk specimens using a new apparatus described in Sect. 2.4.2.

Fig. 2.12. Creep Strain Responses to Stress Changes in Nickel at 845 K Measured in the Irradiation Creep Facility.

2.2.2 Radius Dependence of the Sink Strength of a Dislocation Loop¹⁵ - W. A. Coghlan and M. H. Yoo

Diffusion of point defects under the influence of a force field is an important physical process involved in phase transformations, radiation damage, and high-temperature deformation of materials. When the force field originates from the interaction of a point defect with another defect or defect cluster, such as a dislocation loop, the role of such interaction in the drift flow of point defects becomes particularly important in the overall diffusion kinetics of microstructure evolution. In this work, a theoretical investigation has been made on the physical sources of the dependence of the capture efficiency, or the sink strength, of a prismatic dislocation loop on its size.

The sink strength of a prismatic loop was calculated by using a numerical method developed earlier.¹⁶ The capture radius of a single loop, r_{∞}^* , is defined as the radius of an equivalent spherical reaction volume based on the analytic solution for an electrostatic analog. The numerical results may be summarized by an empirical equation as

$$r_{\infty}^* = 0.58 r_l^P(r_l, \zeta), \quad \text{for } 10 \leq r_l \leq 500 \\ 0 \leq \zeta \leq 700$$

where

$$P = 0.9852 + 2.779/r_l^{1.25} + 0.05492(\zeta/r_l)^{0.75} - 0.0023(\zeta/r_l)^{1.5},$$

$$\zeta = \mu |\Delta V| / \gamma kT,$$

$$\gamma = 3(1 - \nu)/(1 + \nu),$$

and both r_{∞}^* and the loop radius, r_l , are in units of the Burgers vector, μ is the shear modulus, ν is the Poisson's ratio, and ΔV is the defect

¹⁵ Abstracted from a paper presented at the International Conference on Dislocation Modeling of Physical Systems, June 22-27, 1980, Gainesville, Florida.

¹⁶ W. A. Coghlan, "Transient and Steady State Diffusion Solution for Point Defects in a Stress Field," pp. 166-76 in *Proc. Conf. Computer Simulation for Materials Application*, R. J. Arsenault, J. I. Beeler, and J. A. Simmons, eds., Gaithersburg, Maryland, April 19-21, 1976.

relaxation volume. The sink strength per unit length of edge dislocation line (Fig. 2.13) illustrates that Eq. (1) for a single loop predicts increasing sink strength with decreasing loop size, which is consistent with our previous calculations made for small loops. Figure 2.13 also shows that the sink strength of many coexisting loops with the density of $N_L = 10^{20}/\text{m}^3$ increases with increasing loop size ($r_L > 100$) because of the effect of overlapping diffusion fields. The current result enables us to characterize the reactor rate constants in modeling studies of loop growth and other applications of reaction rate theory, such as the annealing kinetics of a heavily deformed microstructure.

Fig. 2.13. A Summary of the Defect Strength of a Loop Per Unit Length Edge Dislocation.

2.2.3 The Rolling and Recrystallization of (110)[110] Tantalum Single Crystals¹⁷ - R. A. Vandermeer and W. B. Snyder, Jr.¹⁸

A deleterious duplex microstructure and very intense texture sometimes are observed when large-grained, electron-beam-melted tantalum ingots are fabricated to plate and sheet. To understand the origin of the microstructure and preferred orientations, we investigated the rolling and recrystallization behavior of specific tantalum single crystals. Single-crystal studies have been and continue to be useful in providing information concerning grain reorientation during deformation and recrystallization in wrought and annealed products. Little was known about tantalum until this research was carried out.

In this study, which is a companion to one published earlier,¹⁹ (110)[110] oriented single crystals were found to be unstable during rolling and underwent substantial reorientation. The final texture after 80% reduction in thickness consisted of multiple components. Deformation bands were a prominent feature of the microstructure. Several reorientation paths were charted as a function of deformation, these being the cause of considerable fragmentation of the crystal. On a macroscopic scale the deformation was shown to be extremely nonhomogeneous, and through-the-thickness texture variations were common. While most regions exhibited multicomponent textures, occasionally large regions displayed a single-component texture. Accompanying microhardness, lateral widening and microstructural gradients also correlated with the texture gradient. By changing either the geometry of the zone of deformation in rolling or roll friction, the macroscopic inhomogeneities could be diminished, but a deformation-banded microstructure persisted. We noted minor changes in texture and attribute them to changes in the degree of lateral strain.

¹⁷ Summary of paper to be submitted to *Texture*.

¹⁸ Group Leader, Electronics Division of Union Carbide Corporation, Greenville, S.C.

¹⁹ R. A. Vandermeer and W. B. Snyder, Jr., "Recovery and Recrystallization in Rolled Tantalum Single Crystals," *Metall. Trans.* 10A: 1031-44 (1979).

The rolling texture results were interpreted in terms of the Taylor theory of plastic deformation. The reorientation paths and the texture after 80% reduction were consistent with the theoretical predictions of stable orientations in rolling of bcc materials. The changes in texture with increasing lateral widening were greater than the predictions of theory.

Recrystallization took place at temperatures as low as 600°C. Gradients of recrystallization proclivity paralleled the macroscopic rolling texture gradients. Regions with only a single-component texture recrystallized less easily than regions with deformation bands and multi-component textures. The ease of recrystallization correlated directly with the extent of lattice curvature. The recrystallization texture always was the same as the rolling texture.

2.3. HYDROGEN IN METALS — K. Farrell and M. B. Lewis

Most austenitic stainless steels resist hydrogen embrittlement unless they are cathodically hydrogenated in a poisoned electrolyte. Even then, thin specimens (<65 μm) are often required before significant embrittlement is manifest, suggesting a surface-related phenomenon. Under such cathodic hydrogenation the hydrogen concentration in the surface layers of the specimen is expected to be very high, with a steep decline at deeper sites.

The method of nuclear analysis using a probing beam of ions with shallow penetration offers a means of determining the true hydrogen distribution. We have used this technique, together with near-surface transmission electron microscopy (TEM), to gain some revealing insights into the hydrogen distribution near the surface of stainless steel.

The steel was a stable type 310 (Fe-21% Ni-23% Cr-2% Mn) in the annealed condition. It was hydrogenated at room temperature in 1 *N* D₂SO₄ with arsenic poison for periods up to 24 h. Deuterium was used to facilitate detection with a probing beam of ions in a particle accelerator using the nuclear reactions $\text{D}(^3\text{He}, \alpha)\text{H}$ and $\text{D}(d, p)\text{T}$. A near-surface deuterium concentration of about 40 at. % was found immediately after

hydrogenation. Measurements of the decay of this hydrogen-rich region with posthydrogenation time allowed derivation of a room-temperature diffusion coefficient of $1.4 \times 10^{-16} \text{ m}^2/\text{s}$. Diffusion laws indicate that during a 24-h hydrogenation the deuterium front should penetrate to a depth of only 5 μm . We are now measuring such a depth by progressively removing surface layers by electropolishing. In the meantime we have used TEM techniques to observe the damage profile resulting from the hydrogenation treatment. Damage began with the generation of dislocation loops at the specimen surface and at surface inclusions for electrolysis times of less than 30 s. With increasing time dislocations were created at grain boundaries and internal inclusions, and the surface-generated loops evolved into a dense dislocation structure containing heavy twinlike bands. At about 15 min surface cracks formed around inclusions and propagated along grain boundaries and at the dislocation bands. After a 24-h treatment the cracks penetrated no more than 1.5 μm , whereas some dislocation damage had penetrated 5 μm ; there was no damage at a depth of 45 μm , implying that the damage profile was probably following the deuterium profile. Further deuterium profiling will test this hypothesis.

These results show clearly that before hydrogen embrittlement of stainless steel can be addressed and understood it is necessary to carefully examine the conditions of hydrogenation, which may result in considerable surface prestraining and cracking of the test piece.

2.4 FACILITY DEVELOPMENT

2.4.1 High Spatial Resolution AES — C. L. White and R. A. Padgett

Because trace element segregation to interfaces results in solute enriched regions that are only a few atom layers thick, surface analysis techniques are very useful in studying this phenomenon. During the past year we purchased²⁰ a high-spatial-resolution scanning Auger microprobe,

²⁰This instrument was purchased with capital funds from five different ORNL programs, including BES Deformation and Fracture.

which allows us to analyze the top few atom layers on surface areas as small as 200 nm in diameter. This results in an analysis volume containing only a few million atoms, within which a concentration of 0.1 to 1.0 at. % impurity can often be detected. In addition to greatly improved spatial resolution, this system is equipped with a small computer, which performs some of the data acquisition and processing. This new AES facility is proving to be of great value in studying trace element segregation effects in elevated-temperature cavitation.²¹

2.4.2 High-Temperature Mechanical Testing Facility – J. C. Ogle and L. J. Turner

The mechanical testing laboratory is being modified and improved to increase the range of test temperature and the control of test environment. A high-temperature vacuum furnace is being designed for a universal testing machine, which will pump to about 1 μ Pa (10^{-8} torr) at a maximum temperature of 1000°C. This machine will be used first for uniaxial tensile testing and will be modified later to do fatigue testing at elevated temperatures.

A complete system of a dual-purpose stress relaxation and creep tester and a capacitance strain gage system are being purchased. This system enables creep tests or stress relaxation tests up to loads of 44.5 kN (10,000 lb) in either vacuum of 0.1 mPa (10^{-6} torr) or inert atmospheres up to 69 kPa (10 psi) and at temperatures up to 1200°C. Ramp rates are available for strain or load from 0.8 to 190 kN/s (3 to 700 lb/min), and the transducers are accurate to ± 2 μ m or better with a resolution of 1 μ m. These combined systems will be used to conduct the second series of tests for anelastic creep recovery studies.

²¹See, for example, results on type 304 stainless steel (Sect. 2.1.1.2) that would have been impossible to obtain with the lower resolution facilities that were previously available.

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3. PHYSICAL PROPERTIES AND TRANSPORT PHENOMENA

3.1 MECHANISMS OF SURFACE AND SOLID-STATE REACTIONS — J. V. Cathcart

A major scientific objective of the research of this group is to develop a better understanding of the mobility and structure of point defects in solids and to apply this knowledge in investigations of diffusion and oxidation (sulfidation) phenomena of relevance to the DOE mission. Defect mobility is the determining factor in the kinetics of various mass transport processes in solids (e.g., scale growth during corrosion, radiation damage, recovery processes, etc.). Point defects can influence the electrical and thermal properties of materials. Also, mechanical properties, particularly of ceramic materials, are sensitive to defect concentration and character. Clearly, the phenomena we study are basic to a variety of technologically important processes.

The research consists of both theoretical and experimental programs. The conceptual development of *defect* diffusion theory continues to provide the central theme of our theoretical work. Progress has been made in understanding correlation effects related to interstitial defect interactions and in the area of modeling diffusion in crystals containing large defect concentrations. This latter effort is particularly germane to diffusion in highly nonstoichiometric compounds such as Fe_{1-x}S . In a parallel series of experimental studies we are investigating the pressure dependence of the sulfidation kinetics and sulfide scale microstructure of iron. Tracer and intrinsic diffusivity measurements in Fe_{1-x}S , specifically designed to elucidate transport processes in FeS and to test our theoretical model, are in the planning stage. The single crystals of FeS needed to initiate this effort have been grown.

A significant fraction of the previous research of this group is being phased out this year in order that we might concentrate more fully on sulfidation studies. Included in this category is an investigation of the high-temperature oxidation characteristics of the important class of refractory metals and alloys typified by zirconium, niobium, and hafnium. This work has special relevance to reactor safety concerns, and projects completed this year included determinations of the influence of oxide

phase transformations, specimen geometry, and gaseous impurities on the steam oxidation kinetics of zirconium and zirconium-base alloys. The effect of alloying on oxidation kinetics and on oxygen diffusivities in the oxide scale and oxygen-stabilized α -zirconium layer was also determined. An investigation of tritium diffusion in alumina in the temperature range 800 to 1000°C emphasized the importance of mechanical damage (e.g., dislocation arrays) to the permeability of Al_2O_3 to hydrogen. This study, now complete, is relevant to the tritium containment problem in fusion reactors and to the hydrogen embrittlement of metals.

3.1.1 Sulfidation Studies

Our sulfidation studies deal with transport phenomena in Fe_{1-x}S and with the influence of pressure on the kinetics and microstructural evolution of sulfide scales formed on iron. These and planned future studies are designed to parallel applied investigations of sulfidation in fluidized bed combustors for coal currently being carried out in the Materials Compatibility Group of the Metals and Ceramics Division.

3.1.1.1 Evolution of Scale Microstructure and the Pressure Dependence of the Sulfidation Rate of Iron — R. A. McKee and R. E. Druschei

The rate of sulfidation of iron in sulfur vapor was measured at 700°C at sulfur pressures ranging from 1 to 100 Pa. The parabolic sulfidation rate constant at 1 Pa differed by a factor of 2 from that determined by Fryt¹ et al., who made their measurements in H_2 - H_2S mixtures. The cause of this difference, which may have important implications for the point defect structure of Fe_{1-x}S , has not been completely determined. One possible explanation lies in the difference between the microstructures of the sulfide scales formed in our experiments and those observed by Fryt et al. Both sets of results agree in that low-pressure sulfidation

¹E. M. Fryt, V. S. Bhide, and W. W. Smeltzer, "Growth of Iron Sulfide Scale (Fe_{1-x}S) on Iron at Temperatures 600-1000°C," *J. Electrochem. Soc.* 126: 684-88 (1979).

(i.e., 1 Pa) favors the development of a columnar FeS scale with the α -direction of the FeS oriented perpendicular to the sample surfaces. However, at higher pressures in our experiments the columnar structure of the scale disappears, and no evidence exists for the transition to preferred growth in the β -direction, as was suggested by Fryt et al. This behavior is illustrated in Fig. 3.1.

It should also be noted that the enhanced grain growth in the FeS at the higher pressures is the opposite of what is normally expected; that is, the higher the pressure of an oxidant gas, in general, the smaller will be the grain size of the reaction product. Understanding the cause of this behavior may be important to the question of the mechanical stability of sulfide scales, and, if short-circuit diffusion is at all important in the sulfidation of iron, this property of growing sulfide scales must have a controlling effect on sulfidation kinetics under conditions of transient-pressure sulfidation.

3.1.1.2 Iron and Vacancy Diffusion in Fe_{1-x}S (Ref. 2) — R. A. McKee

A theoretical analysis of diffusion in the cation-deficient compound Fe_{1-x}S is undertaken to account for the effects of site exclusion and vacancy correlation on diffusion in highly nonstoichiometric compounds. The dependence of the defect structure on temperature and sulfur pressure is used to develop an understanding of defect diffusion kinetics in this material. We show that the strong repulsive interaction (~ 0.3 eV) of the cation vacancies causes them to diffuse in a highly nonrandom manner. Using a recently developed theoretical treatment (see Sect. 3.1.2.1 below) to account for this phenomenon, we explain the concentration dependence of both tracer and intrinsic diffusion in compounds of this type.

²Abstract of paper prepared for submission to the *Journal of the American Ceramic Society*.

Fig. 3.1. Cross Sections Through Iron Specimens After Reaction in Sulfur Vapor at 700°C Viewed in Polarized Light. Note difference in grain structure in the sulfide scales on the two specimens. (a) Sulfidized 14 min at 1 Pa sulfur. (b) Sulfidized 2.5 min at 100 Pa sulfur.

3.1.2 Diffusion Theory — R. A. McKee

We utilize the modeling of diffusion processes as a guide in much of our experimental work. Recent developments are summarized in the abstracts listed below.

3.1.2.1 Diffusion in a Pure, High-Vacancy-Content Crystal³ — R. A. McKee

The idea that vacancies can follow a nonrandom walk in a solid has been developed and put into a quantitative form for diffusion in a pure, high-vacancy-content crystal. Intrinsic and tracer diffusion in a metal have been analyzed, and the electrical mobility in an ionic solid has been expressed in terms of the tracer diffusion coefficient and the separate correlation factors for atoms and vacancies. The description uses classical methods of diffusion theory, and generalized results that account for nonrandom vacancy walk have been shown to reduce to those obtained by Howard and Lidiard in a system where the vacancy moves randomly as a isolated point defect. Experimental data for carbon diffusion in fcc iron have been examined to illustrate the interstitial-vacancy analog that was used in this analysis, and the general result has been applied specifically to discuss vacancy diffusion in Fe_{1-x}S .

3.1.2.2 Thermodynamics and Kinetics of Interstitial Diffusion in a Two-Component System⁴ — R. A. McKee

Diffusion theory is developed for a two-component system in which only the interstitial element is mobile. A thermodynamic formalism is used in direct parallel with a kinetic theory to construct a mechanism-independent relationship between tracer and chemical diffusion coefficients.

³Abstract of paper submitted to *Physical Review*.

⁴Abstract of paper accepted for publication in *Physical Review*.

A result is that

$$D^I = \frac{D^*}{f} \left(1 + \frac{\partial \ln \gamma}{\partial \ln C} \right).$$

Here, D^I is the intrinsic or chemical diffusion coefficient for the interstitial, D^* is the tracer diffusion coefficient, f is the correlation factor, and γ is the activity coefficient. This expression accounts for site exclusion, correlation, and drift effects that occur as the interstitial content changes. Generalized phenomenological coefficients that are determined in this analysis can be used for standard representations of diffusion in electric fields and temperature gradients. Moreover, the forms that the phenomenological coefficients take for the interstitial system are the same as those previously derived for vacancy diffusion. A test of this predicted relationship between tracer and chemical diffusion coefficients is developed and uses a comparison between theory and experiment for carbon diffusion in fcc iron.

3.1.2.3 Site Blocking and Correlated Defect Motion in Tracer and Chemical Diffusion⁵ - R. A. McKee

A method is developed for analyzing defect diffusion coefficients. Defect diffusion is an integral part of considerations in diffusion theory for atom motion in crystals, but it has not been developed as a distinct concern in diffusion kinetics. An "alloy" of tracer and nontracer atoms occupying octahedral interstices of the fcc lattice has been used as a model to develop quantitative descriptions of site blocking, correlation, and flow effects that are all characteristic elements of defect diffusion kinetics. Correlated walk of vacancies in and near a divacancy can be discussed by using these results, and this analysis suggests a method for generalizing theoretical treatments of atom-defect and defect-defect interactions in diffusion related phenomena.

⁵Abstract of paper accepted for publication in *Physical Review*. This work was initiated while the author was assigned to the Theoretical Physics Division, AERE, Harwell.

3.1.3 Alloy Oxidation at Elevated Temperatures — R. E. Pawel

We have now completed a comprehensive series of interrelated studies of the steam-oxidation characteristics of crystal-bar zirconium and the zirconium-base alloy Zircaloy-4 (Zr-1.6 wt % Sn-0.25 wt % Fe-0.12 wt % Cr) over the temperature range 1000 to 1400°C. Previous precision kinetic measurements were augmented by investigations of the influence of oxide phase transformation, specimen geometry, and gaseous impurities on oxidation kinetics. Other studies have detailed the effect of alloying elements on oxide microstructure and on the diffusivity of oxygen in the oxide and in oxygen-stabilized α -zirconium. This body of results provides the basis for a much improved mechanistic understanding of the oxidation behavior of zirconium and its alloys and has enabled the computer modeling of the high-temperature oxidation of these materials under a variety of conditions.

We also describe in this section a further analysis of previously measured oxidation-induced stresses in tantalum-base alloys. These results explain the catastrophic oxidation sometimes observed in these alloys and delineate the role of alloying additives such as hafnium as saturable oxygen traps.

3.1.3.1 The Oxidation of Zirconium from 1098 to 1416°C — R. E. Pawel and J. J. Campbell

The rates of thickening of the oxide and oxygen-stabilized alpha layers during oxidation of pure crystal-bar zirconium in steam were measured at 1098, 1200, and 1416°C. In the early stages of oxidation parabolic growth rates were observed for both phases. The experimentally determined parabolic rate constants plus that calculated for total oxygen consumption are given by:

$$\delta_{\phi}^2/2 = 4.361 \exp(-176500/RT) \text{ mm}^2/\text{s}$$

$$\delta_{\alpha}^2/2 = 26.91 \exp(-185400/RT) \text{ mm}^2/\text{s}$$

$$\delta_T^2/2 = 49.48 \exp(-187300/RT) \text{ kg}^2/\text{m}^4 \text{ s}$$

where left-hand members are the parabolic rate constants and the subscripts, ϕ , α , τ refer to oxide and alpha growth and oxygen consumption, respectively. Activation energies are expressed in joules.

These rate constants differ significantly from those for Zircaloy-4. At 1098°C $\delta_{\phi}^2/2$, $\delta_{\alpha}^2/2$, and $\delta_{\tau}^2/2$ for Zircaloy are 259, 64, and 197% of the corresponding values for pure zirconium. These differences are smaller at 1400°C, but the same trend continues.

3.1.3.2 Oxygen Diffusion and Diffusion Modeling in the Zirconium-Oxygen System — R. E. Pavel and J. J. Campbell

On the basis of on a multiphase, moving boundary diffusion model, we previously derived equations that relate the effective chemical diffusion coefficients for oxygen in the growing oxide and alpha phases to the measured parabolic rate constants for phase growth.⁶ Applying these equations to the oxidation data for pure zirconium, we found that the oxygen diffusion coefficient in the oxide on pure zirconium varied from 0.5 to 0.7 times that in the oxide on Zircaloy-4, although the difference in the oxygen diffusion coefficients for the alpha layers was statistically negligible. Thus, in spite of the existence of marked differences in the growth kinetics of both product layers on zirconium and Zircaloy-4, only diffusion in the oxide phase is influenced to a measurable extent by the alloying additions in Zircaloy-4. For oxidation of zirconium in steam from 1098 to 1416°C, the effective oxygen diffusion coefficient in the growing oxide phase is given by

$$D_{\phi} = 46.84 \exp(-168,500/RT) \text{ cm}^2/\text{s} ,$$

where the activation energy is expressed in joules.

Having established the oxygen diffusivities in the growing product phases for the zirconium, we then used these values as input to a finite-difference-based computer code, MULTRAN, which permitted diffusion to be

⁶R. E. Pavel, "Oxygen Diffusion in the Oxide and Alpha Phases During Reaction of Zircaloy-4 with Steam from 1000 to 1500°C," *J. Electrochem. Soc.* 126: 1111-18 (1979).

modeled for a variety of experimental conditions. For example, this modeling accurately predicted the changes in the growth of the alpha layer as a function of specimen thickness for extended oxidation, where the beta phase tends to become saturated with oxygen during the experiment. Additionally, these techniques have proved useful in providing insight into a mechanism that can explain anomalies in the oxidation behavior apparently caused by phase changes in the oxide.

3.1.3.3 Effects of Finite Specimen Geometry on the Oxidation Kinetics of Zircaloy-4⁷ — R. E. Pawel and J. J. Campbell

The oxidation of zirconium and zirconium-base alloys at temperatures above the alpha-beta transition involves the growth of layers of oxide and oxygen-stabilized alpha into the host beta phase. If the growth is governed by diffusion processes, the kinetics of layer growth on thin specimens will vary significantly if the reaction continues long enough to promote large changes in the degree of saturation of the underlying metal with oxygen. We have examined this effect for the oxidation of Zircaloy-4 in steam by modeling analyses and by a series of extended-time oxidation experiments at 1300°C. These experiments confirmed the predicted increase in the rate of alpha layer growth as the beta phase became saturated. For example, at 1300°C the rate constant more than doubles. While the appearance of "alpha incursions" leading to an irregular alpha-beta interface also seems to be initiated at this time, the experimental observations generally agreed well with those predicted on the basis of the modeling analysis. This behavior clearly needs consideration in the interpretation and comparison of oxidation data, particularly where large differences in the specimen geometry or dimensions are involved.

⁷Abstract of paper accepted for publication in the *Journal of the Electrochemical Society*.

3.1.3.4 Some Experiments and Calculations Regarding the Effect of Specimen Dimensions and Oxygen Solubility on Oxidation Kinetics⁸ — R. E. Pawel and J. J. Campbell

For the oxidation of pure zirconium and Zircaloy-4 (Zr-1.6% Sn-0.25% Fe-0.12% Cr) at temperatures above the alpha-beta transition, the products of the reaction, oxide and oxygen-stabilized alpha, form as uniform layers growing into the host beta phase. In the early stages these layers exhibit parabolic kinetics consistent with growth by diffusion control. We have analyzed this kinetic system as a multiphase moving boundary diffusion problem. Using a finite difference computer program, MULTRAN, we examined the effect of specimen thickness and the degree of oxygen saturation in the beta phase on the oxidation kinetics for a model system. Experimental results for both zirconium and Zircaloy-4 agree well with the predictions of this aspect of diffusion modeling. Furthermore, because prolonged oxidation of pure zirconium is not accompanied by alpha "incursion" formation as in the case of Zircaloy-4, the observed layer growth remains in accord with the idealized diffusion model for longer times.

3.1.3.5 The Oxidation Kinetics of Zirconium at 1000°C — R. E. Pawel and J. J. Campbell

The growth of the oxide and oxygen-stabilized alpha layers during oxidation of crystal-bar zirconium in steam at 1000°C is characterized by complicated kinetics. At one stage, for example, it appears that the oxide layer actually decreases in thickness as the reaction proceeds. Figure 3.2 illustrates this behavior, showing departures from parabolic growth for both the oxide and alpha layers. We interpret these features as being due primarily to changes in the structure of the oxide phase during oxidation. The structural changes reduce the effective diffusivity

⁸Abstract of a paper presented at the Spring Meeting of the Electrochemical Society, St. Louis, May 11-16, 1980.

Fig. 3.2. Growth of Oxide and Alpha During Oxidation of Crystal-Bar Zirconium in Steam at 1000°C. The dashed lines indicate the corresponding parabolic kinetics exhibited by Zircaloy-4 under the same conditions.

of oxygen in the oxide, and this perturbation, influences the rates of growth of both product layers. Modeling analyses predict that for an abrupt change in diffusivity the transition to the new steady-state condition can involve a temporary thinning of the oxide layer.

3.1.3.6 Effects of the Monoclinic-Tetragonal Transformation on Oxidation Kinetics of Zirconium — R. E. Pawel and J. J. Campbell

In order to test our hypothesis that the monoclinic-tetragonal transformation for ZrO_2 influences the oxidation kinetics of zirconium (and Zircaloy-4) under certain conditions, we performed several experiments in which specimens were oxidized at 1100°C for varying times. At a specified time during these exposures, each specimen was quenched to 600°C and then quickly reheated to the reaction temperature. This cycle causes the existing tetragonal oxide to transform to the monoclinic form. Then, because of the hysteresis thought to exist for the reverse transformation, subsequent oxidation at 1100°C results in the persistence of the monoclinic oxide rather than the continued growth of the tetragonal modification

that would normally occur for isothermal reaction at this temperature. The suddenly different diffusional characteristics of the oxide result in spectacular changes in the growth kinetics for both product layers. Diffusion modeling is being utilized to interpret the kinetic data.

3.1.3.7 Oxidation of Zirconium in Oxygen and Oxygen-Steam Mixtures - R. E. Pawel and J. J. Campbell

Zirconium, like Zircaloy-4, exhibits small but reproducible differences in the reaction kinetics at high temperatures, depending upon whether the oxidant is steam or oxygen. Such a result is unanticipated on the basis of a difference in oxygen partial pressure alone if the oxidation mechanism is entirely one of diffusion via anion vacancies in the oxide lattice.

We oxidized crystal-bar zirconium in dry oxygen at 1210°C and found that the parabolic rate constant for oxide growth was about 40% higher than that for oxidation in steam. (For Zircaloy-4 at 1253°C, the corresponding difference was about half as much.) Small additions of steam to the oxygen had little effect on the kinetics, although the surface luster of the oxide was altered noticeably. On the other hand, small additions of oxygen (~5 mol %) to steam produced measurable increases in oxide growth without a change in the appearance of the oxide surface.

3.1.3.8 A Comparison of the High-Temperature Oxidation Behavior Zircaloy-4 and Pure Zirconium⁹ - R. E. Pawel and J. J. Campbell

Oxidation rate data for Zircaloy-4 in steam under isothermal conditions in the temperature range 1000 to 1500°C indicate that the kinetics of layer growth and oxygen consumption can be described by virtually ideal

⁹Abstract of paper for presentation at the ASTM-ANS Fifth International Conference on Zirconium in the Nuclear Industry, Boston, Aug. 4-7, 1980. The paper will be published as part of an ASTM Special Technical Publication in August 1981.

parabolic behavior. Thus, the growth of the two product phases, oxide and oxygen-stabilized alpha, is presumed to be controlled by diffusion processes leading to uniform thickening. We have measured the oxidation rate of pure arc-melted crystal-bar zirconium under similar conditions and have found differences in the reaction characteristics compared with Zircaloy-4. At temperatures from 1098 to 1416°C, while parabolic kinetics is still observed, the growth rates for both phases are measurably different. Our analysis of these data in terms of a multilayer diffusion model suggests that the effective chemical diffusion coefficient for oxygen in the oxide phase has been altered. However, despite the kinetic differences, the analysis also concludes that the diffusion coefficient of oxygen in the alpha layers is identical, a finding consistent with the results of independent measurements. Such responses are important in defining the various effects of alloying on oxidation and diffusion processes in this and similar systems.

In addition to the smaller oxygen diffusivity in the oxide phase on pure zirconium than in that on Zircaloy-4, a higher activation energy was also observed, suggesting the possibility that some mechanistic differences exist. Without additional information, it is not possible to attribute these differences to changes in oxide defect structure as a result of alloying. However, metallographic observations reveal significant morphological and grain size differences in the columnar oxide growing on the two materials. Thus, such complications, perhaps associated with the relative contributions to oxide growth from short-circuit diffusion, could be responsible for this behavior.

3.1.3.9 The Interaction of Stress and Mechanical Property Effects During Oxidation of Tantalum-Base Alloys⁷ — R. E. Pawel and J. J. Campbell

Specimens of the tantalum-base alloys Ta-10% W and Ta-10% W-2.5% Hf (T-222) ignited after prolonged isothermal oxidation at elevated temperatures. The characteristics of this behavior were examined, and the time-temperature regime in which one might expect this catastrophic response to oxidation of thin specimens was defined. Ignition of specimens was the final step in a sequence that involved oxygen penetration

into the alloy in advance of the oxide-metal interface, a resulting embrittlement and stress buildup, and finally a release of the strain energy of the system through a sudden disintegration of the specimen along grain boundaries. This sudden increase in metal surface area led to a violent ignition.

3.1.3.10 The Influence of Alloying Elements on Oxygen Diffusion in Tantalum-Base Alloys — R. E. Pawel and J. J. Campbell

Experimental data dealing with the flexure of specimens of tantalum and tantalum-base alloys exposed on one side to oxygen at low pressures were reexamined with regard to oxygen diffusion and oxygen solution effects. Diffusion coefficients for oxygen in Ta, Ta-10% W, and Ta-10% W-2.5% Hf (T-222) were calculated from the flexure measurements on the basis of a simple strain-diffusion relationship. The results indicated that both tungsten and hafnium influence oxygen diffusion in tantalum and that a model with hafnium serving as a saturable trap for oxygen is consistent with the observations.

3.1.4 Diffusion in Oxides — J. V. Cathcart and L. C. Manley, Jr.

The completion of our studies of tritium diffusion in Al_2O_3 marks the end of our current investigations of interstitial diffusion in oxides. Using the constant-source solution for the diffusion equation, we obtained apparent tritium diffusivities along the c -direction of α - Al_2O_3 single crystals ranging from 10^{-15} to 10^{-12} m^2/s as the temperature was increased from 800 to 1000°C. The corresponding diffusivity measured in the a -direction at 1000°C was a order of magnitude larger. We observed, however, that tritium diffusivity values were highly sensitive to the surface treatment given a specimen. For example, the value cited above for diffusion parallel to the a -direction of an Al_2O_3 crystal was obtained with specimens that were mechanically polished through 1- μm diamond paste and preannealed for 4 d at 1000°C in hydrogen at about 500 Pa before being annealed in tritium at the same pressure and temperature for 8 h. When a similar specimen was subjected to a 24-h preanneal at 1300°C before being

given the same treatment described above, the tritium activity in the first 10 μm below the specimen surface had been reduced by an order of magnitude, and the penetration distance into the sample at which background activity levels were approached was also reduced by an order of magnitude or more. This result suggests a 100-fold reduction in the tritium diffusion coefficient. It appears clear that both the effective solubility (and hence the permeability) and the diffusivity of tritium in Al_2O_3 depend on the extent of mechanical damage of the sample.

3.2 PHYSICAL PROPERTIES RESEARCH — D. L. McElroy

We develop and apply accurate measurement techniques to obtain thermal conductivity, electrical resistivity, Seebeck coefficient, thermal expansion, and specific heat data for metals and nonmetals in the range from 4.2 to 2600 K. Analysis of these data provides useful descriptions and improved understanding of particular relations between these properties for specific solids. This measurement and analysis approach yields several benefits, including property estimates for systems where data are missing, ways to improve and control properties, improvement in measurement techniques and standards, and experimental tests of theoretical models for energy transport phenomena, such as for scattering mechanisms involving electrons and phonons. A by-product of this research is the capacity to measure thermal conductivity and electrical resistivity at high temperatures to evaluate innovative materials of construction for use in power generating systems.

3.2.1 Transport in Metals

3.2.1.1 Experimental Determination of the Phonon and Electron Components of the Thermal Conductivity of bcc Iron¹⁰ — R. K. Williams, D. W. Yarbrough, J. W. Masey,¹¹ T. K. Holder,¹¹ and R. S. Graves

A study of the factors that affect the thermal conductivity of α -iron and its solid solutions is described. The results of these experiments

¹⁰Abstract of paper submitted to *Journal of Applied Physics*.

¹¹ORAU Graduate Fellow from Tennessee Technological University.

define the phonon and electronic components of the thermal conductivity of pure α -iron between 90 and 450 K. The phonon conductivity can be analyzed to identify the strengths of electron-phonon and phonon-phonon scattering, and the latter resistance agrees well with theoretical estimates. The scattering of phonons by electrons is intermediate between the small values of the noble metals and the strong scattering found in niobium and tantalum. An experimental estimate of the electron-phonon mass enhancement factor, 0.4, is derived from the results. Finally, reexamination of the data for ten solid-solution alloys suggests that both phonon scattering mechanisms are influenced by the alloying elements.

3.2.1.2 Thermal Transport Properties of Niobium and Some Niobium-Base Alloys from 80 to 1600 K (Ref. 12) — J. P. Moore, R. S. Graves, and R. K. Williams

The electrical resistivities and absolute Seebeck coefficients of 99.8 at. % Nb with a resistivity ratio of 36, Nb-4.8 at. % W, Nb-5 at. % Mo, Nb-10 at. % Mo, and Nb-2.4 at. % Mo-2.4 at. % Zr were measured from 80 to 1600 K, and the thermal conductivities of the niobium and Nb-5 at. % W were measured from 80 to 1300 K. A technique is described for measuring the electrical resistivity and Seebeck coefficient of a specimen during radial heat flow measurements of the thermal conductivity. The transport property results, which had uncertainties of $\pm 0.4\%$ for electrical resistivity and $\pm 1.4\%$ for thermal conductivity, showed the influence of tungsten and molybdenum solutes on the transport properties of niobium and were used to obtain the electronic Lorenz function of pure niobium, which was found to approach the Sommerfeld value at high temperatures.

3.2.1.3 Phonon Conductivity of Niobium — J. P. Moore, R. K. Williams, R. S. Graves, F. J. Weaver, F. J. Pinski,¹³ and W. H. Butler

Thermal and electrical conductivity data for a zone-refined niobium (resistivity ratio = 325) specimen and three niobium-base alloys (5 at. %

¹²Abstract from a paper submitted to *High Temperatures — High Pressures*.

¹³Guest scientist from State University of New York, Stony Brook.

Mo, 10 at. % Mo, 2.4 at. % Mo-2.4 at. % Zr) were analyzed to obtain phonon conductivity, λ_p , estimates for pure niobium over the 80 to 300 K range. These results show that electron-phonon scattering, W_{ep} , is very strong and much more effective than phonon-phonon scattering in limiting λ_p . An experimentally derived numerical constant used to describe W_{ep} appears to be about 30% larger than the theoretical estimate,¹⁴ and about 3 times as large as a similar estimate obtained from very low-temperature data.¹⁵ The 30% difference between theoretical and experimental values is about equal to the experimental uncertainty, and similar differences in W_{ep} values derived from low- and intermediate-temperature data have previously been noted for tungsten and tantalum. The results also suggest that the λ_p values for the molybdenum alloys are higher than the λ_p of pure niobium. This can be explained by the change in the density of states on alloying, and low-temperature experimental data¹⁵ have also been interpreted in this fashion.

As shown by Fig. 3.3., the electronic thermal conductivity values obtained in this study agree well with first-principles theoretical calculations. These calculations include the full complexities of the electronic band structure and phonon dispersion; however, they employ the "rigid-muffin-tin" approximation for the electron-phonon matrix elements. The good agreement between theory and experiment gives confidence in the validity of this approximation for transition metals. The differences between our experimental results for the electronic thermal conductivity and previously accepted values are due to improved experimental accuracy, a purer sample, and the inclusion of a correction for phonon conduction.

¹⁴W. H. Butler and R. K. Williams, "Electron-Phonon Interaction and Lattice Thermal Conductivity," *Phys. Rev. B* 18: 6483-94 (1978).

¹⁵J. B. Sousa, "Lattice Thermal Conductivity of Ta-Nb and Nb-Mo Solid Solution Alloys in Normal and Superconducting States," *J. Phys. C* 2: 629-39 (1969).

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Fig. 3.3. An Improved Theoretical Calculation of the Electronic Thermal Conductivity Is in Relatively Good Agreement with New Experimental Data for Niobium. The literature values [C. Y. Ho, R. W. Rowell, and P. E. Liley, *J. Phys. Chem. Ref. Data* 3: Suppl. 1 (1974)] were not corrected for phonon transport, and the improvement is due to both this correction and the improved accuracy of the new experimental data.

3.2.1.4 The Thermal Conductivity, Electrical Resistivity, and Seebeck Coefficient of SRM-735¹⁶ — R. S. Graves, R. K. Williams, and J. P. Moore

The scarcity of recognized thermal conductivity standards has been a problem in the development of thermal conductivity techniques for many years. The National Bureau of Standards now supplies an austenitic stainless steel to fill one thermal conductivity range, but the standard values are based on few data. We have recently tested two apparatuses using this standard. One apparatus measured the thermal conductivity, electrical resistivity, and Seebeck coefficient from 300 to 1000 K with total determinate measurement errors of $\pm 2.2\%$, $\pm 0.4\%$ and $\pm 0.3 \mu\text{V/K}$, respectively. The other apparatus was installed in a helium-cooled cryostat at the Kernsforschungszentrum, Karlsruhe, West Germany. The limited sensitivity of Chromel-vs-constantan thermocouples limited the lowest temperature of the thermal conductivity measurements to 20 K, and the combination of temperature measurement and geometry errors limited the accuracy to $\pm 3.5\%$ at 300 K and $\pm 6\%$ at 20 K.

All electrical resistivity (ρ) results were within the $\pm 2\%$ uncertainty claimed for the standard. The maximum deviation between any thermal conductivity datum from the high-temperature apparatus and the calibration value was -3.2% at 470 K, which is within the uncertainty of the standard. Thermal conductivity data from the low-temperature apparatus for temperatures above 60 K were within the 2% uncertainty of the standard, but results between 20 and 60 K were as much as 4% higher than the standard values. This is still well within the combined uncertainties of the standard and experimental values. Thus these present results support the calibration values of the stainless steel. Analysis of the data indicates that the phonon component, λ_p is dominant in this stainless steel below 150 K and that λ_p has a broad maximum near 100 K.

¹⁶Abstract from a paper to be published in *Thermal Conductivity 18*, Plenum Press, New York.

3.2.1.5 The Electrical Resistivity and Thermal Conductivity of Niobium-Titanium Alloys at Low Temperatures¹⁷ — J. P. Moore

The electrical resistivities (ρ) of several superconducting niobium-titanium alloys were measured from their critical temperatures (T_c) to 300 K, and the thermal conductivity (λ) of one of them (Nb-78 at. % Ti) was measured at temperatures above 5 K. The Nb-78 at. % Ti was fabricated from an electron-beam-melted rod, and measurements were made on this rod first after a diameter reduction from 12 to 5 mm and then after an anneal at 1120 K for 2 h followed by a slow cool to room temperature. In both states, λ showed a slope change at T_c , and λ decreased rapidly on cooling below T_c . Although ρ and λ both changed on annealing, the most drastic change occurred in the lattice component of the thermal conductivity. The temperature dependences of the lattice component indicate that this large shift may be due to a reduced dislocation density in the annealed specimen.

3.2.1.6 Tantalum — R. K. Williams, J. P. Moore, R. S. Graves, and F. J. Weaver

Electrical and thermal conductivity data for an isoelectronic tantalum-base alloy containing 2.5% W and 2.5% Hf were obtained. These results indicate that the electron-phonon scattering (W_{ep}) for this element is surprisingly close to the value for niobium. A zone refined tantalum specimen has been obtained as a further experimental test of the result because we had anticipated¹⁴ that the W_{ep} values for the two elements would differ by about a factor of 2.

3.2.1.7 Measurements on Al5 Compounds — R. K. Williams and F. J. Weaver

The electron-phonon interaction is especially strong in high- T_c Al5 compounds, such as Nb₃Sn, and we are attempting to produce bulk samples

¹⁷Work completed during assignment to Institut für Kernphysik, Kernforschungszentrum, Karlsruhe, FRG.

of Nb_3Sn alloyed with zirconium and molybdenum to determine the phonon conductivity at intermediate temperatures. This would extend our studies of the interelement variation of $\bar{W}_{ep}$ and the high normal state electrical resistivities of the compound. Preliminary work on bronze-process samples made with Nb alloyed with Mo, Zr, and Ti indicates that the T_c values follow the trend predicted by application of the rigid band theory to the detailed band structure calculations.¹⁸ Substitution of small amounts of zirconium and titanium in Nb_3Sn enhance T_c , while molybdenum additions depress T_c . We have noted that zirconium and titanium additions enhance the growth rate of the Nb_3Sn layer by a factor of about 30.

3.2.1.8 Deviations from Matthiessen's Rule — R. K. Williams and F. J. Weaver

Deviations from Matthiessen's Rule (DMR) in transition metal alloys are currently of interest because of recent theoretical progress. The electrical resistivity of palladium (resistivity ratio 1460) and Pd-0.1 and 0.5 at. % Ti alloys were measured between 4.2 and 300 K because published results¹⁹ indicate that the DMR do not reach a constant positive value at high temperatures. The new data confirm this behavior but do not contain the anomalous concentration dependence of the original data set. The low-temperature ρ values for the pure palladium follow the data of Schindler and Rice²⁰ and appear to vary as T^2 up to about 8 K. Data for the 0.1 at. % Ti specimen show 40% larger T^2 coefficient and no unusual behavior. An anomaly was detected for the 0.5 at. % Ti specimen. In this case the ρ varies more strongly at the lowest temperatures and then becomes only weakly temperature dependent in the 10 to 15 K range.

¹⁸B. M. Klein, L. L. Boyer, D. A. Papaconstantopoulos, and L. F. Mattheissen, "Self-Consistent APW Electronic Structure Calculations for the A15 Compounds V_3X and Nb_3X , X = Al, Ga, Si, Ge and Sn," *Phys. Rev. B.* 18: 6411 (1978).

¹⁹E. K. Azarbar and G. Williams, "Matthiessen's Rule Breakdown in Some Pt- and Pd-Based Alloys," *Phys. Rev.* 14: 3301-09 (1976).

²⁰A. J. Schindler and M. J. Rice, "s-Electron-Paramagnon Scattering in Dilute Pd-Ni Alloys: Theory and Experiment," *Phys. Rev. B.* 164: 759-64 (1967).

3.2.2 Equipment Development

3.2.2.1 Analysis of Apparatus with Radial Symmetry for Steady-State Measurements of Thermal Conductivity²¹ — J. P. Moore

Steady-state radial heat flow apparatuses, which use specimens in the shape of right circular cylinders for measuring the thermal conductivity of solids and powders, were analyzed in detail. A finite-difference heat conduction code was used to determine the temperature distributions in radial heat flow apparatuses. The distributions demonstrated the failure of most systems to conform to normally assumed boundary conditions and were used to calculate apparatus errors due to nonideal heat flow. Analyses of a simple apparatus and selected experimental apparatuses showed clearly the importance of system symmetry, end guards, and specimen length-to-diameter ratio to measurement errors. The temperature profile along the main heater was found to be extremely influential. The application of an "isothermal correction" will reduce errors due to nonideal heat flow. This correction reduces errors from as high as 61% down to 2%. This study has provided the background for accurate experimental measurements on powder systems consisting of gas plus spherical oxide particles, which should have reproducible and predictable thermal conductivities.

3.2.2.2 Multiproperty Apparatus — J. P. Moore

The primary components for an apparatus designed for measuring several thermophysical properties of electrically conducting solids to temperatures of 2600 K have been assembled. The vacuum system is ready for test and evaluation, and other components, which will be required for property measurements, are being acquired. We have decided to use a tungsten specimen for initial tests of the apparatus since the high-temperature properties of tungsten have been studied and since our group

²¹Summary of a chapter prepared for the *The Compendium on Thermophysical Property Measurement Methods*, K. O. Maglic, ed., publisher not decided.

has measured its electrical resistivity to high temperatures. The latter is important since a knowledge of ρ vs T is essential for measuring the thermal conductivity with this apparatus.

3.2.2.3 The Thermal Conductivity of Powders of Microspheres —

R. O. A. Hall,²² J. P. Moore, R. S. Graves, and D. L. McElroy

A radial heat flow technique was used to measure the thermal conductivity (λ) of four UO_2 microsphere beds and an Al_2O_3 microsphere bed at conditions given in Table 2.1. The λ results show the influence of temperature, gas type and pressure, sphere size, and bed density. For example, λ of the denser beds 3 and 4 decrease with increasing temperature, increase with gas pressure, and increase with decreasing gas molecular weight, $\lambda(\text{He}) > \lambda(\text{N}_2) > \lambda(\text{Kr})$. Bed 4 has a λ 50% greater than bed 3 because of its greater density (87% vs 80%). The temperature dependence of λ is positive for the large-sphere beds, 2 and 5, but negative for the fine-sphere bed 1. Since powders of known λ do not exist, the results on bed 5 support it as a candidate reference material, and further testing is planned.

²²Visiting scientist from A.E.R.E., Harwell, U.K., until April 1980.

Table 3.1. Microsphere Bed Characteristics, Measurement Conditions, and Thermal Conductivity Results at 400 K

Bed	Material	Size (μm)	Density (% of Theoretical)	Measurement Temperature Range (K)	Gas	Gas Pressure		λ (W/m K)
						(MPa)	(atm)	
1	UO_2	Fine, 50	58.5	400-800	He	0.1	1	0.6
2	UO_2	Coarse, 1200	61.6	400-900	He	0.1	1	1.2
3	UO_2	50, 1200	79.9	400-1100	He	0.1	1	1.4
						0.3	3	1.8
						0.6	6	2.1
					N_2	0.1	1	0.9
						0.3	3	1.1
						0.6	6	1.2
4	UO_2	50, 300, 1200 ^a	86.7	400-1100	He	0.1	1	2.1
						0.3	3	2.7
						0.6	6	3.1
					N_2	0.1	1	1.8
						0.3	3	1.9
						0.6	6	2.0
5	Al_2O_3	Medium, 500	60.7	400-900	Kr	0.1	1	1.1
					N_2	0.1	1	0.3

^aVibratorily compacted bed; others were poured.

3.3. METASTABLE MATERIALS — C. C. Koch

This year completed the transition period in which research on superconducting materials was redirected to studies of metastable materials. Metastable materials, a prime example of which is metallic glasses, open numerous possibilities for the formation of new materials not obtainable under equilibrium conditions. The properties of metastable materials can differ markedly from their crystalline counterparts. Notable are the unique properties of metallic glasses in terms of mechanical strength combined with ductility, corrosion resistance, and favorable ferromagnetic properties. The research in this field is advancing rapidly, and applications are beginning to be realized. The initial research efforts in metastable materials in our program involve development of facilities to produce amorphous alloys, studies of the formation and stability of amorphous phases, and the measurement of selected properties. The first property of metallic glasses that we are emphasizing is superconductivity. Our interest will probably shift to mechanical behavior in the next few years. This report will first summarize the superconducting experiments that were completed during the reporting period and culminated in two invited papers at the International Cryogenic Materials Conference, Brookhaven National Laboratory, May 27-29, 1980.

3.3.1 Summary of Completed Superconductivity Experiments

3.3.1.1 Evidence for Microstructural Effects Under Strain in Bronze Process Nb₃Sn²³ — D. M. Kroeger, D. S. Easton, C. C. Koch, A. DasGupta, and J. O. Scarbrough

In both mono- and multifilament conductors, we have found that the maxima in the critical current density, J_c , and the upper critical field,

²³Abstracted from an invited paper given at International Cryogenic Materials Conference on Filamentary Al₅ Superconductors, Upton, N.Y., May 28-29, 1980.

B_{c2} , as functions of strain do not coincide. This indicates that variation of the equilibrium property, B_{c2} , does not account for all the variation of J_c with strain and suggests that microstructural effects associated with the pinning centers are involved. Comparison of the strain dependences of the transition temperature, T_c , and the slope, $(dB_{c2}/dT)T_c$, near T_c indicates that the relationship between them is not unique. The relationship changes when strain is increased beyond that required to produce maxima in T_c and $(dB_{c2}/dT)T_c$. Since $(dB_{c2}/dT)T_c$ is proportional to $\gamma\rho_n$ (γ = electronic specific heat coefficient, ρ_n = normal state resistivity) and T_c is determined by the density of states near the Fermi energy, or γ , the relationship between T_c and $(dB_{c2}/dT)T_c$ is expected to be determined uniquely by crystal structure and resistivity.

From measurements of J_c and B_{c2} as functions of strain and temperature, the forefactor A in the semiempirical expression for F_p , the bulk pinning force density,

$$F_p = AB_{c2}^n b^l(1-b)^m,$$

was found to depend strongly on strain. In this equation A is determined by pin strength, pin density, and the Ginzburg-Landau parameter, κ . Measurements of $(dB_{c2}/dT)T_c$ and T_c as functions of strain indicate that variation of κ with strain does not account for the change in A . Therefore, a microstructural effect, associated with the pins, is implied.

Microstructural effects that could account for these results include a stress-induced martensitic transformation, twinning, microcracks, and changes in the stress distribution about pinning sites. If pinning involves a second superconducting phase, a change in the superconducting properties of the second phase with strain could alter the pin strength.

3.3.1.2 Superconducting and Mechanical Properties of Nb₃Sn Conductors Under Tensile Stress²³ — D. S. Easton, D. M. Kroeger, and C. C. Koch

Studies at ORNL on stress effects in commercial multifilamentary Nb₃Sn superconductors have resulted in the following major findings: (1) Degradation of the critical current density, J_c , and critical temperature, T_c , occurs with either compressive residual strain or applied tensile strain. Maximum values of J_c are found when the Nb₃Sn is in a near zero strain condition. (2) Calorimetric measurements show that significant amounts of heat are generated both when a tensile strain is applied to a conductor in which the Nb₃Sn is under compressive residual strain and when stress cycles on the conductor produce hysteresis loops in the stress-strain curve. (3) Kirkendall voids at the filament-matrix interface can lead to reduced mechanical properties, thermal instabilities, and crack initiation in the filaments. (4) The residual stress state in Nb₃Sn composites can be estimated by a relatively simple analytic model.

3.3.1.3 Flux Pinning by Small Perturbations in the Superconducting Order Parameter in Type II Superconductors²⁴ — A. DasGupta, D. M. Kroeger, C. C. Koch, and Y. T. Chou²⁵

The calculations reported last year were extended to enable interpretation of the flux pinning results by grain boundaries in niobium bicrystals.

From the first-order perturbation of Ginzburg-Landau free energy, the effects of local variation of the upper critical field H_{c2} , and Ginzburg-Landau parameter, κ , are combined. The interaction energy

$$[|\chi|^2(1 - |\chi|^2)]$$

²⁴Abstracted in part from a paper accepted for publication in the *Philosophical Magazine*.

²⁵Department of Metallurgical and Materials Engineering, Lehigh University, Bethlehem, Pennsylvania.

thus obtained, varies locally, where $|\chi|$ is the superconducting order parameter. The elementary pinning force, f_p , is calculated from the interaction energy as a function of the magnetic induction, B , and agrees well with the results in several flux pinning systems, including grain boundary pinning in niobium bicrystals.

3.3.2 Equipment Development

3.3.2.1 Arc-Hammer — Quenching From the Liquid State — D. M. Kroeger, D. S. Easton, J. O. Scarbrough, and C. C. Koch

Our model of the spreading and cooling of the sample in the arc-hammer process indicates, and measurements confirm, that the final thickness, and thus the cooling rate of the specimen, is very weakly dependent upon hammer mass. Increasing hammer speed, however, does appreciably increase the cooling rate. Accordingly, we have modified the arc-hammer apparatus by lightening the hammer and propelling it toward the hearth by means of springs. By so doing, we have increased the maximum available hammer speed from 5.5 to about 10 m/s.

3.3.2.2 Melt Spinning Apparatus — Quenching From the Liquid State — D. S. Easton, C. C. Koch, and C. E. Zachary

A melt spinning apparatus has been constructed, and ribbons (1–2 mm wide, 10–20 μ m thick) of several alloys have been formed. The ribbon is produced by forcing a jet of molten metal through a small orifice in a quartz crucible onto the surface of a copper wheel rotating at speeds up to 10,000 rpm. The surface velocity of the wheel, and thus the rate of ribbon produced, can be controlled to rates up to 80 m/s.

A ribbon of Pd-6% Cu-16% Si is shown in Fig. 3.4 as it is being formed at a rate of 60 m/s. Some small droplets of molten material can be seen in addition to the ribbon.

Y-172913

Fig. 3.4 Molten Pd-6% Cu-16% Si Alloy being Spun from Rotating Copper Wheel at Tangential Velocity of 60 m/s.

The method allows quenching rates comparable to those achieved in the arc hammer ($\sim 10^6$ °C/s) as well as the production of a large volume of material in a very short time. In addition to the formation of metallic glasses and metastable alloys, the method is very useful to produce material directly from the melt without the necessity of intermediate deformation operations. A typical ribbon of an Fe-20% B alloy is shown in Fig. 3.5.

Fig. 3.5. Ribbon of Amorphous Fe-20% B Alloy Made by Melt Spinning.

3.3.2.3 Vapor Deposition Apparatus: Quenching From the Vapor State —
D. S. Easton, C. C. Koch, and C. E. Zachary

An electron-beam deposition system, employing an Airco Trigon electron-beam source, has been installed, and preliminary testing and

calibration are under way. This apparatus, shown in Fig. 3.6, can simultaneously or sequentially evaporate three different materials. This permits the production of an almost unlimited range of alloy compositions. Substrate temperatures can be controlled from 4.2 to 300 K by the use of a liquid helium refrigerator shown entering the system by a central feedthrough on the chamber dome.

A Dektak thickness measuring instrument is used to measure films deposited on the surface of the substrate. Initial deposition rate as a function of power has been tested on several elements. The deposition rates of selected elements at about 40% power are as follows:

<u>Element</u>	<u>Deposition Rate (nm/s)</u>
Cu	2.5
Nb	0.50
Mo	2.7
Zr	1.4

Copper-zirconium alloys can be easily produced in the amorphous state by rapid quenching from the liquid state; however, we have found no reference in the literature whereby amorphous copper-zirconium has been made by evaporation. We have deposited an 11.4- μ m-thick Cu-50% Zr alloy (deposition time 70 min) that appears to be amorphous when examined by routine x-ray diffraction, although examination of this material by a high-resolution, long-exposure diffraction technique detects a small fraction of crystalline phase in the material.

Extensive calibration tests of the rate and thickness controllers are continuing. A residual gas analyzer to monitor the environment during deposition will soon be installed.

3.3.3 Quenching Rate Studies in the Arc-Hammer Apparatus — D. M. Kroeger, W. A. Coghlan, D. S. Easton, C. C. Koch, and J. O. Scarbrough

The most widely used apparatus for rapidly quenching small amorphous alloy samples is known as the arc-hammer or piston and anvil. A small button of the alloy is arc-melted on a flat copper hearth and then quenched by dropping or propelling a flat copper hammer onto the molten sample, squeezing it to a thin (20–40 μ m thick) sheet from which the heat

Y-172217

Fig. 3.6. Electron-Beam Vapor Deposition System.

is rapidly extracted by the copper hearth and hammer. The method has the advantages that samples are uniform in thickness, that their properties are reproducible, and that no crucible is required, so that high-melting alloys can be prepared. The glass-forming tendency of an alloy has been rather loosely defined in terms of the ease with which it can be made glassy by such a process. Knowledge of the cooling rates obtained by this process is essential to studies of the kinetics of alloy glass formation. A number of studies have been made of cooling rates in the arc-hammer and splat quenching processes, but until recently no attempt had been made to model mathematically the spreading and cooling of the drop. Miyazawa and Szekely²⁶ have presented such a model in which they assume that the sample crystallizes at the melting point. Solidification fronts propagate from the surfaces, and spreading of the sample is arrested by meeting of the fronts at the center of the sample. A two-dimensional calculation of heat flow during the spreading of the drop was also carried out. We have modified their model to describe the formation of a glassy rather than a crystalline specimen.

We assume that during cooling the sample remains liquid at all times, but with an ever-increasing viscosity, the temperature dependence of which we describe by either the Vogel-Fulcher expression or one derived more recently by Ramachandrarao, Cantor, and Cahn.²⁷ We assume that, since the sample does not crystallize, most of the latent heat of fusion is retained in the solid. Sample deformation is arrested by the increase in viscosity of the specimen as it cools below its melting point. The increased complexity resulting from assuming a temperature-dependent viscosity made it desirable to assume Newtonian or interface controlled cooling. That is, we assume that there are no temperature gradients within the sample, and that all the temperature difference between sample and copper lies in

²⁶K. Miyazawa and J. Szekely, "A Mathematical Model of the Splat Cooling Process Using the Piston and Anvil Technique," *Metall. Trans. B* 10: 349-58 (1979).

²⁷R. Ramachandrarao, B. Cantor, and R. W. Cahn, "Free Volume Theories of the Glass Transition and the Special Case of Metallic Glasses," *J. Mater. Sci.* 2: 2488-2502 (1977).

the interface between them. Although this approximation is reasonably good after the sample has been squeezed to its final thickness, heat flow calculations performed by Ruhl²⁸ for thin samples of static dimension indicate that Newtonian cooling is not a good approximation during the early stages of spreading. However, Ruhl's calculations do not take account of the mechanical mixing that accompanies spreading of the drop. We believe this mixing acts strongly to suppress temperature gradients. We have included the work done on the sample by the hammer during deformation and found that, under some conditions, it can represent an important heat input to the sample. Finally, we found that the mechanical response of the structure supporting the hearth to the striking of the hammer must be included so that the model would predict the correct dependence of final sample thickness on hammer speed.

Using the mechanical model shown in Fig. 3.7 and the heat flow assumptions outlined above, we reduced the problem to a series of coupled first-order differential equations. These equations were solved by using the standard Runge-Kutta technique. The resulting calculations predict not only the sample temperature as a function of time during the quench, but also the effect on foil thickness, d , of such variables as hammer speed, hammer mass, sample mass, sample superheat, and the interface heat transfer coefficient, h , between the sample and the copper surfaces. We have measured d as a function of hammer speed, sample mass, and hammer mass in three alloys, Co-34% Zr, Ta-45% Ir, and Nb-45% Rh and compared the results with the calculation. The heat transfer coefficient, h , was used as an adjustable parameter to fit the data for one hammer speed, 3 m/s. Not only does the model accurately predict the foil thickness at other hammer speeds, as shown in Fig. 3.8. for Nb-45% Rh alloy, but the best fit to the data for all three alloys was provided by the same value of h ($2.0 \times 10^5 \text{ W/m}^2 \text{ K}$). These results not only indicate the essential correctness of the model but suggest that the rate of heat transfer across the interface between samples and copper is determined primarily by properties of the

²⁸R. C. Ruhl, "Cooling Rates in Splat Cooling," *Mater. Sci. Eng.* 1: 313-20 (1967).

ORNL-DWG 80-12057

Fig. 3.7. Mechanical Elements in the Model for Quenching Rate Studies in the Arc-Hammer.

ORNL-DWG 80-12058

Fig. 3.8. Sample Thickness vs Hammer Speed for Nb-45% Rh Samples. Solid line is the model calculation; squares are experimental values.

copper surfaces, perhaps by an oxide layer. Additionally, the calculated cooling curves indicate that the sample is well above the glass transition temperature when deformation stops. This is confirmed by high-speed photography in which the sample remains incandescent to small dimensions. The model also predicts the experimental observation that d is nearly independent of hammer mass.

These results suggest that the model is realistic and give us some confidence in the cooling curves that can be calculated from it. We intend to use the model as a tool in studies of the kinetics of glass formation and glass forming tendency.

3.3.4 Stability and Physical Properties of T_5 - T_9 Amorphous Alloys -

A. DasGupta, C. C. Koch, and J. O. Scarbrough

The physical basis and systematics of the thermal stability of metal-metal glasses are uncertain at the present time. To understand this phenomenon, differential thermal analysis (DTA), electrical resistivity, microhardness, and x-ray diffraction studies of both binary and ternary T_5 - T_9 metallic glasses (where $T_5 = \text{Nb}$ or Ta , and $T_9 = \text{Ir}$ or Rh) have been performed. In $\text{Ta}_{55-x}\text{Nb}_x\text{Ir}_{45}$ glasses, where the subscripts denote atomic percentages, the crystallization temperature T_x decreases monotonically with increase of x . In the above series of alloys, the ternary compositions show a double peak in DTA upon crystallization, whereas a single peak is found for the two binary end members, namely $\text{Ta}_{55}\text{Ir}_{45}$ and $\text{Nb}_{55}\text{Ir}_{45}$. In the binary alloy system $\text{Ta}_x\text{Ir}_{100-x}$, the glass formation range has been extended to compositions such as $\text{Ta}_{65}\text{Ir}_{35}$, which have not been previously attainable.

Presently the physical properties are being measured in an extensive series of alloys to establish the systematics of thermal stability.

3.3.5 Amorphous Superconductors

The best amorphous superconductors exhibit fundamental superconducting properties comparable to the crystalline alloy superconductors

such as niobium-titanium. While the superconducting compounds, such as Nb_3Sn , have superior superconducting properties, they have problems such as brittleness and sensitivity to radiation damage, which can be avoided in amorphous superconductors; thus, amorphous alloys with superconducting properties only somewhat better than exist at present (e.g. $T_c > 10$ K, $H_{c2}^{(4.2\text{ K})} > 12$ T) would be of practical interest. The initial studies of properties of amorphous alloys in this program are concentrating on the systematics of superconductivity and certain structure-property relationships.

3.3.5.1 Superconductivity in Amorphous "T₅-T₉" Transition Metal Alloys²⁹ —
C. C. Koch, D. M. Kroeger, J. O. Scarbrough, and B. C. Giessen³⁰

The superconducting transition temperature, T_c , has been measured for amorphous T₅-T₉ alloys (where T₅ = Nb or Ta, T₉ = Rh or Ir) as a function of composition. Niobium and tantalum dominate the T_c behavior, with T_c for niobium alloys ≈ 4.8 – 5.1 K and T_c for tantalum alloys ≈ 3.1 – 3.3 K. Changing the average group number by varying the T₅/T₉ ratio had little effect on T_c within the ~ 10 at. % range of composition in which the amorphous alloys form. Also, T_c decreased approximately linearly with x for $(\text{Nb}_{1-x}\text{Ta}_x)_{55}\text{Rh}_{45}$ and $(\text{Nb}_{1-x}\text{Ta}_x)_{55}\text{Ir}_{45}$. The electrical resistivity, ρ_n , and the upper critical field, B_{c2} , were measured as functions of temperature. The Sommerfeld constant, γ , was calculated from ρ_n and $(dB_{c2}/dT)T_c$ by using the Ginzburg-Landau-Abrikosov-Gor'kov theory. The Debye temperature, θ_D , was calculated from measurements of Young's modulus. The above parameters allowed calculations to be made of $N(E_F)$, the density of electronic states at the Fermi level, and λ , the electron-phonon coupling constant. We found that λ more accurately reflected the T_c behavior than did $N(E_F)$ and that both electronic and phonon contributions had to be considered in the determination of λ .

²⁹Abstracted from a paper submitted to *Physical Review B*.

³⁰Materials Science Division, Institute of Chemical Analysis, Northeastern University, Boston, Massachusetts.

3.3.5.2 The Effects of Cold Rolling on Fluxoid Pinning in a Superconducting Metallic Glass³¹ — C. C. Koch, J. O. Scarbrough, D. M. Kroeger, and A. DasGupta

The influence of cold rolling on fluxoid pinning in a metallic glass superconductor, $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{82}\text{B}_{18}$, was determined. Inhomogeneous deformation up to 20% reduction in thickness does not change either the superconducting transition temperature, T_c , or upper critical field, H_{c2} , but it does degrade the critical current density, J_c , by as much as 34% from the value in the as-cast condition. Possible mechanisms for this degradation of J_c involve surface pinning, pinning by unresolved crystalline precipitates, and inhomogeneities in bulk composition or structure. The experimental evidence appears to favor the last mechanism. Work is in progress to better define the mechanism responsible for the degradation of J_c . Fluxoid pinning measurements may be good probes of the structure of metallic glasses.

³¹Abstracted from a paper submitted to *Applied Physics Letters*.

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4. RADIATION EFFECTS

L. K. Mansur

The Radiation Effects task is developing an understanding of the mechanisms by which irradiation changes physical and mechanical properties of metals and alloys. The program is focused on the phenomena and conditions typically encountered or anticipated in fission and fusion reactors. The scope includes void and bubble swelling, irradiation creep, and embrittlement. An integrated theoretical and experimental approach is brought to bear on major problem areas. The chief observational techniques used are electron microscopy and analytical electron microscopy for the direct observation of microstructural and microcompositional changes. For producing radiation effects, the reactors EBR-II, HFIR, and ORR are used, and, to supplement these, accelerated charged particle bombardments are carried out with the 5-MV Van de Graaff - 0.4 MV Van de Graaff facility, the 1-MV high-voltage electron microscope (HVEM), and the Oak Ridge Isochronous Cyclotron. A sophisticated irradiation creep apparatus has been constructed and is in operation at the cyclotron. It is presently being used to study the characteristics of and to understand the mechanisms leading to irradiation creep. The Van de Graaff is a dual- and triple-beam system, where nickel ions typically are used to produce the displacement damage, and helium and/or deuterium ions are injected simultaneously to simulate neutron-induced transmuted gases. Nuclear microanalysis techniques that use the accelerated particles to probe the chemical composition as a function of depth in the target are being exploited.

Developing the theory of radiation effects continues to receive a major emphasis. In the recent past this effort has focused on two areas. One is modeling the effects of the large increases in damage rate and the marked spatial variation in swelling during charged particle bombardment. The other is the generalization of the theory to include the effects of impurities and alloying elements. The often-observed large reductions in void nucleation and the milder reductions in void growth and creep can be explained by our theory of point defect trapping. The effects of helium,

a most potent impurity, are presently being elucidated. The development of the theory of basic processes is also continuing, including the calculation of the efficiencies of sinks for the absorption of point defects and the analysis of mechanisms of irradiation creep. In this general area, we have also developed a cascade diffusion theory to more realistically describe the fluctuating nature of the local point defect concentrations.

This task is performed in the Radiation Effects and Microstructural Analysis Group of the Metals and Ceramics Division, which includes investigators pursuing related problems in programs for breeder reactors and magnetic fusion energy. These applied programs are part of national alloy development programs coordinated by HEDL and ORNL, respectively. Work on this program also complements the radiation effects activities of the ORNL Solid State Division,, which are directed at understanding the primary production of defects by particle irradiation. Our facilities have been used by General Electric and Westinghouse in connection with the applied programs and by a number of universities in the Basic Energy Sciences program. International cooperation is maintained through exchanges of personnel with the U.K., FRG, French, and Japanese nuclear energy establishments.

4.1 NEUTRON RADIATION EFFECTS

4.1.1 Defect Structures in Neutron-Irradiation Iron - J. Bentley, L. L. Horton, and K. Farrell

The secondary defect structures formed in iron by neutron irradiation have received little attention relative to both the bcc refractory and fcc metals. This is surprising in view of the importance of ferritic steels but may be partly due to the difficulty of transmission electron microscope (TEM) examination of ferromagnetic materials. We have performed a TEM study of iron neutron-irradiated in the Oak Ridge Research Reactor at temperatures from 182 to 500°C to about 1 dpa and at 650 and 740°C to about 0.5 dpa. The specimens were fabricated from two-pass zone-refined Ferrovac E iron (0.003 wt. % C), and disks were irradiated in

sealed capsules. We performed TEM examination at 120 kV in a JEM 120C equipped with a special objective lens pole-piece (AMG) for the observation of magnetic materials to enable high-angle tilting experiments.

The dislocation component of the various microstructures observed is illustrated in Fig. 4.1. At 182°C "black-spot" defects smaller than 6 nm in diameter are present at a concentration of about $1 \times 10^{22}/\text{m}^3$. At 275°C the small loops cluster to form localized groups of about 30 loops. The concentration of these ~200-nm-diam clusters is about $2 \times 10^{19}/\text{m}^3$. The reason for cluster formation is not clear but may be related to the formation of rafts of $(a/2)\langle 111 \rangle$ loops observed in neutron-irradiated bcc refractory metals. At irradiation temperatures from 350 to 450°C a fairly homogeneous distribution of loops with some network segments is present. Loop size increases and loop concentration decreases with increasing temperature. Eventually only a coarse network is evident, and at 650 and 740°C the dislocation density is very small. The geometry and nature of the loops have been analyzed. The dislocation loops were found to be

Fig. 4.1. Development of Dislocation Structures in Neutron-Irradiated Iron. Irradiation temperatures indicated. Diffraction vector $g = 011$. Deviation parameter $w_g \approx 1$, Beam direction $z \approx 111$. Scale markers = 0.2 μm .

interstitial, near edge with $\vec{b} = \alpha\langle 100 \rangle$, in agreement with previous observations by various investigators. As is evident in Fig. 4.1, some loops intersect the foil surfaces without gliding out — an indication that they are pinned. Cottrell atmospheres may be responsible since no precipitates were observed. At some irradiation temperatures cavities are also present, as shown in Fig. 4.2. At 275°C the cavities tend to form only near the clusters of dislocation loops, illustrating the cooperative growth of dislocation loops and cavities. At 350° the distribution of ~18-nm-diam cavities at a concentration of about $1 \times 10^{21}/\text{m}^3$ is much more homogeneous, but at 450°C the distribution is again inhomogeneous, with some cavities associated with precipitates. At 650 and 740°C, in addition to isolated cavities on grain boundaries, high local concentrations of cavities were observed in damage halos, which are suspected of being centered on particles containing ^{10}B . These observations illustrate the stabilizing effect that insoluble gases have on cavities formed at high temperatures. Damage halos were also observed at low temperatures, but only high concentrations of small loops without any cavities were visible.

In general the results have revealed a lower point defect retention in clusters than in other bcc and fcc metals of similar purity. This may be due in part to the dominant role that carbon plays in the behavior of α -iron, both through segregation at defect clusters and through trapping of point defects.

Fig. 4.2. Cavity Distributions in Neutron-Irradiated Iron. Irradiation temperatures indicated. The structure in (c) is in a damage halo. $g = 03\bar{3}$, $w_g > 0$, $z \approx 111$. Scale markers = 0.1 μm .

4.1.2 Microstructure and Tensile Properties of Heavily Irradiated 5052-0 Aluminum Alloy¹ — K. Farrell

Many aluminum alloys depend on precipitates to provide strength for industrial applications. The 6000 series alloys, for example, contain magnesium and silicon in proportions required to produce precipitates of stoichiometric Mg_2Si . The 5000 series alloys, however, are not precipitation hardened; they derive their strength from solid solution hardening by magnesium additions. The 5052 alloy contains 2.5 wt % Mg and is used for the poolside tank face of the Oak Ridge Research Reactor and for the calandria of the British SGHW Reactor. This alloy in the "0" temper (i.e., fully annealed condition) was examined for its response to high-level neutron irradiation.

Tensile specimens of 3-mm gage diameter were irradiated in the High Flux Isotope Reactor at 328 K (0.357_m) for periods up to 3.5 years. The maximum fast fluence reached was $1.8 \times 10^{27} \text{ n/m}^2$ ($>0.1 \text{ MeV}$), corresponding to 260 dpa. Thermal fluences were 1.7 times the fast fluences and were responsible for the creation of up to 6.9 at. % (7.15 wt %) Si from the reactions $^{27}Al(n, \gamma)^{28}Al$; $^{28}Al + ^{28}Si + \beta$. Neutronically generated gases ranged up to 85 at. ppm He and 500 at. ppm H.

Before irradiation the microstructure of the alloy consisted of a solid solution matrix containing a few inclusion particles. The first signs of radiation damage appeared at a fast fluence of $1 \times 10^{25} \text{ n/m}^2$ (1.5 dpa) in the form of dislocation loops at grain boundaries and residual inclusions. With increasing fluence a general dislocation structure and a finely divided precipitate of Mg_2Si appeared. The precipitate is the product of interaction of the transmutation-produced silicon with the dissolved magnesium. At the higher fluences the silicon levels greatly exceeded that needed to satisfy the Mg_2Si reaction, and the excess silicon, which is insoluble, was incorporated as a precipitate. Only a few irregularly dispersed cavities were created.

¹Presented at the ASTM Tenth International Symposium on Effects of Radiation on Materials, Savannah, Georgia, June 3-5, 1980; to be published.

Tensile tests were made at a strain rate of $7.4 \times 10^{-5}/s$ in air. In tests at 323 K the unirradiated alloy displayed a well-defined yield point and continuous serrated flow throughout the test. Progressive irradiation eliminated both the yield point and the serrated flow. Considerable radiation strengthening occurred, as shown in Fig. 4.3. The ultimate tensile strength was raised continuously from 220 to 600 MPa, and the 0.2% flow stress was increased by a factor of 6.5. Correspondingly, the ductility fell from 26% elongation for the unirradiated material to about 8%

Fig. 4.3. Fluence Dependence of Tensile Properties of Aluminum Alloy 5052-0 at 323 K.

at a fast fluence of about 2×10^{26} n/m². At higher fluences the ductility was seemingly independent of fluence. The loss in ductility was caused entirely by loss of uniform strain associated with the increased strength. The fracture mode was transgranular and invariant.

At higher test temperatures of 373 and 423 K similar patterns of fluence dependence of tensile properties prevailed, but the strengths and ductilities were lower, with only about 3% total elongation at 423 K and no measurable uniform elongation. At the highest fluence at 423 K the fracture mode changed to a faceted, seemingly intercrystalline type. Increasing the thermal-to-fast ratio to 2 caused more hardening and ductility loss than anticipated from a simple increase in silicon level.

In summary, when the solid-solution 5052 aluminum alloy is irradiated to very high exposures in a mixed neutron spectrum it is converted to a precipitation-hardened 6000-type alloy containing excess silicon. It displays good resistance to swelling and suffers severe hardening and associated loss in ductility. It does not undergo sudden brittle failure.

4.1.3 Grain Boundary Segregation and Radiation Effects – C. L. White and G. R. Gessel

The effects of neutron irradiation on the properties of structural materials frequently involve internal interfaces such as grain boundaries, precipitate-matrix interfaces, and internal free surfaces (e.g., of voids and bubbles). The properties of these interfaces are likely to be strongly influenced by trace element segregation. Reductions in both fracture stress and total elongation for tensile tests have been observed to coincide with equilibrium segregation of metalloid elements to internal interfaces. Thermodynamic arguments, as well as experimental observations, show that equilibrium segregation to interfaces decreases interfacial energy. Modest changes in interfacial energy associated with segregation can, in turn, profoundly affect other material behavior.

While much of the literature connecting impurity segregation with embrittlement addresses only equilibrium segregation, irradiated materials may also experience nonequilibrium segregation. Nonequilibrium segregation

results from the flux of irradiation-induced point defects to internal sinks. Impurities or alloy constituents can be enriched or depleted at grain boundaries depending upon how these elements and the point defects interact. In addition, significant quantities of helium can be produced via (n, α) reactions in many alloys. Segregation of helium to internal interfaces could significantly affect alloy behavior.

When segregation occurs in a very thin region at an interface, it can be very difficult to detect with conventional analytical techniques. Auger electron spectroscopy (AES) is a well-established tool for examining thin interfacial regions *when they can be exposed as external surfaces*. Subsurface regions can be exposed for analysis by sputtering with inert gas ions. Alternate AES and sputtering permit information about the depth distribution of segregated species to be obtained. An important requirement for the use of AES to study interfacial segregation is that the interface in question must be exposed as a free surface. In the case of internal interfaces, this is normally achieved by fracturing the specimen along those interfaces.

In order to study the effects of neutron irradiation on grain boundary composition in simple alloys, a series of 14 binary alloys based on Fe, Ni, and V and one ternary (Fe-5% Ni-5% Cr) alloy (Table 4.1) was

Table 4.1. Compositions of Binary and Ternary Alloys in the Row 7 Experiment^a

Fe Base	Ni Base	V Base
Fe-5% Ni	Ni-5% Fe	V-5% Mo
Fe-5% Cr	Ni-5% Cr	V-5% Ni
Fe-5% V	Ni-5% V	V-5% 0.5 Ti
Fe-0.3% Nb		
Fe-5% Mo		
Fe-4% W		
Fe-3% Mn		
Fe-2% Ti		
Fe-5% Ni-5% Cr		

^aAll specimens received 0.5-h 1000°C vacuum anneal before loading into capsules.

irradiated in the EBR II-Row 7 (AAX) experiments. Tensile AES specimens of each alloy were exposed at 400, 525, 575, 625, and 700°C. Neutron fluences at 525°C were about 4×10^{26} n/m²; fluences at all other temperatures were about 3×10^{26} n/m².

Unirradiated specimens of the same Fe-5% Ni, Fe-5% Cr, and Fe-2% Ti alloys as were in the EBR-II, row 7 experiment have been heat-treated and then fractured at -196°C, -76°C, and 26°C. Scanning electron microscopy of the resulting fracture surfaces indicates that the Fe-2% Ti fractured at -196°C is likely to fail at least partially along its grain boundaries and hence be amenable to Auger electron spectroscopy (AES) studies. The next step will be to fracture a similar specimen inside the AES system to provide baseline information on grain boundary composition in the unirradiated alloy, followed by analysis of irradiated specimens. Hydrogen charging of both irradiated and unirradiated alloy 706 has been carried out to produce partially intergranular failures at room temperature. A similar charging procedure may be useful in inducing intergranular fracture in the nickel-base binaries in the row 7 experiment.

4.2 CHARGED PARTICLE RADIATION EFFECTS

4.2.1 Depth Profiles of Swelling in Ion-Bombarded Nickel - N. H. Packan, K. Farrell, and J. T. Houston

Simulation of neutron damage structure by heavy-ion bombardments has some complications involving depth dependence of the damage. These are the strong depth damage gradients resulting from nonuniform dissipation of energy along the path of the ions, the implantation of the bombarding ions, the diffusional spreading of the point defects from their region of generation, and point defect losses to the specimen surface. The implanted ions interfere with development of damage microstructure. Diffusional spreading broadens and lowers the point defect concentration profiles with respect to the peak displacement damage profile.² Helium

²The theoretical methods for calculating these effects and the resulting spatial dependence of swelling are described by L. K. Mansur and M. H. Yoo, "Advances in the Theory of Swelling in Irradiated Metals and Alloys," *J. Nucl. Mater.* 85 and 86: 523-32 (1979) and were reported in *Metals and Ceramics Division Materials Science Program Annu. Prog. Rep. June 30, 1979, ORNL-5589, pp. 168-71.*

implantation introduces further depth complexities since the helium concentration profile is usually not symmetric with the heavy-ion damage profile, causing a variation in He/dpa ratio along the superimposed profiles. Consequently, with implanted helium there is more cause for concern over both the choice of the depth at which the damage microstructure is measured and the accuracy with which this depth is attained.

In studying the microstructural details, the usual method is to excise TEM samples parallel to the target surface at a depth calculated to include the peak damage region or at a depth corresponding to some particular estimated He/dpa ratio. The full microstructure-depth profile is rarely assessed. In principle, such an assessment can be done by covering the narrow damaged region with an electrodeposited overlay, then sectioning TEM samples normal to the bombarded surface and thinning them at the electroplate-target interface. In practice, it is very difficult. With perseverance, we were successful with several specimens of pure nickel bombarded with nickel ions at 600°C to damage levels of 1 and 50 dpa. In these experiments, the effects of cold-preimplanted and simultaneously implanted helium on the damage microstructure at a nominal peak He/dpa of 20 are measured. Figure 4.4 shows an example for the full-depth microstructure observed for nominally 50 dpa and 1000 at. ppm cold-preimplanted helium.

Some salient features of the experimental data in Fig. 4.4 are:

- (1) Point defect losses to the surface affect a layer about 0.1 μm deep.
- (2) The maximum concentration of cavities occurs at a depth of about 0.7 μm , which is the predicted depth for maximum atomic displacements and is at the center of the implanted helium distribution.
- (3) Cavity parameters change notably with depth. This demonstrates the need for accurate control of depth sectioning in preparing conventional TEM specimens.
- (4) Cavities are seen at depths significantly beyond the estimated depth for damage production and helium implantation. This is an expected result of diffusional spreading.
- (5) The sizes and concentrations of cavities, and hence the degree of swelling, are sensitive to the local dpa and helium levels; that is, to the varying He/dpa ratio along the heavy ion range. Generally, with increasing He/dpa the cavity

Fig. 4.4. Variation of Swelling, Cavity Size, and Cavity Concentration with Depth in Pure Nickel Bombarded with 4-MeV Nickel Ions. The upper curves show the predicted distribution of damage and helium based on theory.

concentration is increased and the cavity size and swelling are decreased, but there are deviations from this pattern in the deepest regions of the cavity profile.

4.2.2 Experimental Observations of Effects of Inert Gas on Cavity Formation During Irradiation³ - K. Farrell

Experimental results on the effects of gases on formation of radiation damage microstructure were reviewed and assessed. Gas appears to be essential for establishing the structure and especially the formation of cavities. Degassing renders a metal immune to visible damage formation, whereas gas implantation markedly promotes damage structure. Inert gases are more effective than chemically active gases. Helium has received the most attention because it is always created during neutron irradiations.

The primary role of helium is to promote cavity nucleation. In neutron irradiations the concentrations of cavities increase linearly with the generation rate of helium at low fluences, tending to a slower increase at higher fluences. This behavior is consistent with the supposition that the helium forms tiny gas bubbles, of which only those that reach a critical size can survive as viable cavities. As these cavities develop, the point defect sink strength is increased, reducing the population of excess vacancies and thereby requiring a larger critical bubble size, that is, more helium per cavity, for continued nucleation of cavities. Higher temperatures also require a larger critical size. Calculations based on experimentally observed cavity concentrations and helium levels in pure aluminum and nickel neutron irradiated at $0.35T_m$ indicate a critical bubble diameter of 1 to 2 nm; in stainless steel and Nimonic PB16 alloy ion irradiated at about $0.5T_m$ preexisting helium bubbles longer than about 3 nm grow into cavities. In tying up vacancies in bubbles and cavities the helium allows the corresponding interstitial atoms to increase the nucleation and growth of dislocations. Since the fluxes of point defects to these sinks induce a coupled flow of dissolved impurities and alloying elements, constituent elements redistribute to or

³Presented at Consultant Symposium on Rare Gases in Metals and Ionic Solids, Harwell, England, September 10-14, 1979. To be published in Proceedings. Also available as ORNL/TM-7193 (April 1980).

from the sinks, resulting in phase instability. Helium, therefore, increases the concentrations of all point defect sinks and thereby affects phase decompositions.

The influence of helium on microstructural evolution is sensitive to the method of implanting the helium. If the helium is coimplanted slowly with the damaging particles, as it is in neutron irradiations, the helium usually accelerates the formation of damage structure. If it is implanted before the damage process, as is often the case in damage simulation experiments using charged particle bombardments, it can either enhance or depress the damage structure. When helium is preimplanted to high levels or at temperatures significantly lower than the damage temperature, cavity nucleation is so pronounced that the cavities become the dominant point defect sinks and recombination sites; damage evolution is retarded and swelling is diminished. This is particularly evident at irradiation temperatures in the lower end of the swelling range. At higher temperatures, high helium levels promote cavity nuclei by reducing thermal emission from cavities. The swelling range is therefore extended to higher temperatures. The implantation technique is thus a critical factor in assessing damage simulation experiments for relevance and reactor applications. Advanced simulation techniques using coimplantation of helium are now overcoming some of these difficulties.

4.2.3 Comparing Simultaneous vs Preimplantation of Helium in Radiation Damage Simulation⁴ - N. H. Packan and K. Farrell

In the simulation of neutron damage microstructures using energetic electrons or ions, a serious question is how an important transmutation product, helium, should be introduced. (See Section 4.3.2 for theoretical discussion of this process.) Since helium is known to promote the nucleation of cavities, injection of the helium before bombardment, which is the usual practice, may overstimulate void formation and give a microstructure that is not representative of the required neutron damage structure. A

⁴Part of this work is described by N. H. Packan and K. Farrell, "Simulation of First Wall Damage: Effects of the Method of Gas Implantation," *J. Nucl. Mater.* 85 and 86: 677-81 (1979).

more appropriate simulation of neutron irradiation is to begin with no helium and to build it up continuously thereafter (i.e., simultaneous implantation).

This question was addressed by directly comparing the effects of pre-injected helium and simultaneously injected helium on swelling in an ion-bombarded austenitic alloy of composition Fe-17% Cr-16.7% Ni-2.5% Mo-0.005% C (by weight). This single-phase alloy swells readily and is free of radiation-induced phase instabilities. Ion bombardments were carried out by using the ORNL dual-accelerator irradiation facility,⁵ whose main accelerator provides a beam of damage-creating 4-MeV ⁵⁸Ni ions, while the secondary accelerator injects helium at cyclically varying energies (0.2-0.4 MeV) in order to distribute the implanted atoms throughout the heavy-ion damage region. The bombardment temperatures were 570, 630, 680, 750, and 825°C; the displacement rate in the peak damage region was about 6×10^{-3} dpa/s; and the nominal doses achieved were 1, 10, and 70 dpa. For simultaneous injection of helium the rate was set at 20 at. ppm He/dpa to simulate fusion reactor first-wall conditions; for preinjection the equivalent quantities of helium corresponding to the final dpa level were implanted at room temperature. Specimens bombarded without any helium ("Ni ions" only) constituted the reference condition.

The temperature dependence of swelling is shown in Fig. 4.5 for doses of 1 dpa (lower part) and 70 dpa (upper part). Together with the results for 10 dpa (not shown), there is a consistent increase in the peak swelling temperature of about 50°C for either gas implantation method above that for no gas. At all three doses simultaneous helium implantation causes swelling to persist to the highest temperatures. The representative void characteristics for the 70 dpa dose are shown in Fig. 4.6. Cavities in the preimplanted material are the smallest and most numerous at every temperature; furthermore, they exhibit a bimodal size distribution (not observed for simultaneous implantation or for no helium) at all temperatures. These features can be seen in Fig. 4.7, which presents example microstructures for each technique at temperatures on each side of the peak swelling temperature. The population of small cavities in preinjected material is more discernable in the enlarged inset pictures.

⁵M. B. Lewis, N. H. Packan, G. F. Wells, and R. A. Buhl, "Improved Techniques for Heavy-Ion Simulation of Neutron Radiation Damage," *Nucl. Instrum. Methods* 167: 233-47 (1979).

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Fig. 4.5. Dependence of Swelling upon Bombardment Temperature at Doses of 70 and 1 dpa.

Fig. 4.6. Variation of Cavity Concentration (Upper) and Mean Diameter (Lower) with Temperature.

Fig. 4.7. Representative Microstructure of Materials Bombarded to 70 dpa at 1025 and 900 K.

Helium implantation at this high gas/dpa ratio induced small cavities (presumably gas bubbles) on the grain boundaries of preimplanted and also (not shown) coimplanted material. However, in contrast to these major changes in cavity statistics for the different implantation techniques, the dislocation densities were essentially insensitive to the introduction method or even the presence of helium.

The behavior of the alloy without injected gases is noteworthy for its high swelling — a result of relatively few but very large cavities. These voids were also frequently found in patches or strings. This implies nucleation on gases (this material contained about 0.1 at. % O, by analysis) or other heterogeneously distributed indigenous impurities. The high void growth rate is thought to be the result of early nucleation on relatively few preexisting sites such that subsequent void growth took place in a microstructure where the dislocations were the dominant sink.

The addition of 20 at. ppm He/dpa had the general effects of increasing the peak swelling temperature about 50 K and producing essentially uniform spatial distributions of cavities. The *method of introducing* helium proved to be a strong variable. Room-temperature preinjection generated profuse cavity nucleation and a bimodal cavity size distribution, the smaller population of which stayed about the same size (<10 nm) regardless of dose or temperature. This behavior evokes a picture of rapid nucleation at the beginning of bombardment, with the cavities the dominant sink, resulting in reduced cavity growth rate. The use of dual-beam simultaneous helium implantation, which did not produce such behavior, is clearly to be preferred for experiments to simulate neutron radiation damage, where helium is generated simultaneously by (n, α) transmutation reactions.

4.2.4 Growth of Interstitial Loops in Electron-Irradiated Nickel — J. E. Spruiell,⁶ W. A. Coghlan, and E. A. Kenik

During the past year, research has been performed to measure and model the growth rates of Frank interstitial loops in pure nickel under HVEM irradiation. The objectives are to test quantitatively the present

⁶Part time employee from University of Tennessee.

understanding of loop growth and to extract the basic defect parameters required for accurate modeling of radiation effects. This work extends the work reported by Yoo and Stiegler^{7,8}

Foils were cut from a zone-melted single-crystal rod of 99.99%-pure nickel so that a [100] zone axis was approximately perpendicular to the surface. After thinning, the irradiations were carried out in the hot stage of the Hitachi HVEM at 400, 450, and 500°C with 1-MeV electrons. The point defect generation rate under these conditions is estimated at 9.6×10^{-5} dpa/s. The diameters of 30 to 60 loops in each irradiated area were determined from the largest dimension of the projected image. Attempts were made to obtain foil thickness, loop number density, and loop position in the foil by stereomicroscopy. Each specimen was given a 5-min irradiation at room temperature to nucleate loops of satisfactory density and uniformity for the elevated-temperature loop growth experiments. The loop density remained approximately constant until unfaulting began.

The experimental measurements of average loop radius as a function of time are presented in Fig. 4.8. The radius is given as r/b where b is the magnitude of the Burgers vector. In the temperature range studied, the average loop size varies linearly with time. This agrees with the work of other investigators⁹ who have studied loop growth in nickel. The lines shown in Fig. 4.8 do not pass through the origin of coordinates because of the preirradiation at room temperature. The slope of each line gives the measured average growth rate. The growth rate of loops in each specimen is given in Table 4.2.

It is clear from both Fig. 4.8 and Table 4.2 that the average growth rate tends to increase with increasing irradiation temperature, but it also varies significantly from specimen to specimen at a given temperature. The differences at a given temperature are related to differences in foil thickness, loop number density, and perhaps other factors

⁷M. H. Yoo and J. O. Stiegler, "Growth Kinetics and 'Preference Factor' of Frank Loops in Nickel During Electron Irradiation," *Philos. Mag.* 36: 1305-15 (1977).

⁸M. H. Yoo, "Growth Kinetics of Dislocation Loops and Voids - The Role of Divacancies," *Philos. Mag. A* 40: 193-211 (1979).

⁹K. Urban, "Growth of Defect Clusters in Thin Nickel Foils During Electron Irradiation," *Phys. Status Solidi a* 4: 761-72 (1971).

Fig. 4.8. Radius of Interstitial Loops as a Function of Irradiation Time.

Table 4.2. Measured Interstitial Loop Growth Rates

Specimen	Temperature (°C)	Growth Rate ^a		
		$\frac{d(R/b)}{dt}$ (s ⁻¹)	dD/dt , nm/s	
			Specimen	Average
A	400	0.119	0.0484	0.032
B		0.073	0.0299	
C		0.044	0.0180	
D	450	0.097	0.0396	0.048
E		0.169	0.0688	
F		0.091	0.0373	
G		0.091	0.0449	
H	500	0.375	0.1530	0.139
I		0.305	0.1244	

^a d is loop diameter in nanometers.

such as surface condition of the foil. Preliminary evaluation indicates that number density may vary significantly. For example, the foils irradiated at 400°C all appear to have thicknesses in the range 300 to 500 nm, but their number densities vary from 2.0×10^{19} loops/m³ for specimen A to 7.0×10^{20} loops/m³ for C. The higher number density results in lower growth rate, as would be intuitively expected. This trend also agrees with the lower growth rates measured in the present experiments compared with those reported by Urban.⁹ The growth rate reported⁷ by Yoo and Stiegler at 450°C lies below the present results, but their number density was well above the number densities observed in the present measurements.

In the original experiments⁷ the growth of faulted loops in nickel was measured at 450°C, and the model was able to predict this growth as a function of time with reasonable accuracy. In the subsequent report⁸ the inclusion of divacancies in the analysis complicated the picture, since more parameters are involved and divacancy parameters are not well known.

The computer model was modified to explore several different physical effects to reproduce our observed strong temperature dependence. The effects explored included (1) utilizing loop capture radii recently calculated from elasticity and diffusion theory, (2) the effect of divacancies, (3) reaction control of the vacancy at the foil surface, and (4) modeling the dislocation loop sink strength as proportional to the length of dislocation line contained in the loop, a form used previously by Heald and Speight.¹⁰ Only (3) and (4) show a reasonable possibility for explaining the strong temperature dependence. In addition, foil thickness, loop density distributions, and loop growth rate as functions of depth will be explored.

4.2.5 Precipitation of Mo₂C in Nickel-Molybdenum Alloys During High-Temperature Ion Irradiation Experiments — W. Kesternich,¹¹ E. A. Kenik, R. W. Carpenter, and M. B. Lewis

Nickel-ion and high-voltage electron microscope irradiation experiments have shown nickel-molybdenum alloys and the ordered composition

¹⁰P. T. Heald and M. V. Speight, "The Influence of Cascade Damage on Irradiation Creep and Swelling," *J. Nucl. Mater.* 64: 139-44 (1977).

¹¹Kernforschungsanlage Jülich, FRG.

Ni_4Mo in particular to be highly resistant to void swelling. However, unpredicted precipitates were observed by transmission electron microscopy in specimens that had been ion irradiated. These alloys are normally single-phase, ordered Ni_4Mo (with structure $D1a$) or are a face-centered-cubic solid solution containing $D1a$ Ni_4Mo precipitate. The precipitate that formed under ion irradiation was not of the $D1a$ structure, although analytical electron microscopy showed it to have a high molybdenum concentration. The volume fraction of this precipitate increased with ion dose.

The nickel-molybdenum specimen alloys used were prepared from high-purity materials. For example, the carbon concentration was 46 at. ppm. Thus the appearance of the precipitate was not attributable to simple impurity effects. A detailed analysis of the precipitate structure was undertaken by using microdiffraction. Composition variation in the near-surface regions of the specimens was examined by nuclear microanalysis. The precipitate was found to have hexagonal structure corresponding to Mo_2C . The crystallographic habit was

$$(0001)_{\text{ppt}} \parallel (111)_{\text{matrix}}$$

$$(10\bar{1}0)_{\text{ppt}} \parallel (11\bar{2})_{\text{matrix}}.$$

Using measurements of precipitate volume fraction in the damage layer of nickel-ion irradiated specimens and alloy composition, we showed that the specimens had insufficient carbon near the irradiated volume to account for the precipitation observed. Nuclear microanalysis showed that the carbon concentration in irradiated specimens was high on the incident ion surface and decreased monotonically with depth into the specimen, and that the carbon concentration depended on ion dose. The source of the additional carbon responsible for the precipitation observed appears to be contamination during the irradiation experiments, probably by surface diffusion from the surrounding area. However, the magnitude of carbon contamination *does* depend on total dose, so a simple time-at-temperature diffusion model is not sufficient to explain the observations. These

results emphasize that stringent precautions are necessary in specimen preparation and irradiation procedures to control and identify chemical contamination.

4.2.6 Heavy-Ion Damage Structure in Ordered $(\text{Co}_{0.78}\text{Fe}_{0.22})_3\text{V}$ Alloy — D. N. Braski and K. Farrell

The alloy $(\text{Co}_{0.78}\text{Fe}_{0.22})_3\text{V}$ is one in a class of Li_2 long-range-ordered (LRO) alloys developed at ORNL for elevated-temperature applications. To assess its potential for reactor use, we are studying the microstructural changes induced by heavy-ion irradiation.

The alloy was quenched from 1080°C and aged for 8 h at 800°C (i.e., $\sim 150^\circ\text{C}$ above the critical ordering temperature). Irradiations with 4-MeV nickel ions were done at 570, 625, 680, and 750°C to a damage level of 70 dpa. The unirradiated microstructure of $(\text{Co}_{0.78}\text{Fe}_{0.22})_3\text{V}$ consisted of grains containing approximately equal numbers of extrinsic or interstitial-type faulted loops. These loops were decorated with VC particles and intrinsic or vacancy-type stacking faults, which were always free of precipitate. Aging the heat-treated alloy at the irradiation temperature for 3 h to simulate the thermal exposures during irradiation produced no discernable change in microstructure, as shown in Fig. 4.9(a). The microstructure also contained thermal antiphase boundaries (APBs), and these have been imaged for the same area [Fig. 4.9(b)] by using a (100) superlattice reflection in dark field. The fact that most of the faults terminate on APBs suggests that cooperative growth between these two features occurred during the preirradiation heat treatment. The APBs were wavy, with no preference for any particular crystallographic orientation. Transmission electron microscope contrast experiments using superlattice reflections showed that the displacement vector for these APBs was of the $(1/2)\langle 110 \rangle$ type and, consequently, only two-thirds of the APBs are visible by use of the (100) diffraction vector, as shown in Fig. 4.9(b). Besides being structural defects, the stacking faults also serve as APBs because a "chemical" discontinuity in

Fig. 4.9. Microstructure of $(\text{Co}_{0.78}\text{Fe}_{0.22})_3\text{V}$ Quenched in Water from 1100°C , Annealed at 800°C for 8 h, and Annealed at 570°C for 3 h. (a) Bright field showing extrinsic faulted loops (e), intrinsic stacking faults (i), and VC precipitate. (b) Superlattice dark field of same area obtained by using (100) reflection, showing faults and antiphase boundaries.

ordering exists across them. However, these latter APBs possess displacement vectors of the $(1/6)\langle 112 \rangle$ type and lie on $\{111\}$ planes. Therefore, the ordered domains were bounded by two types of APBs — wavy or thermal APBs and stacking faults.

Irradiation of $(\text{Co}_{0.78}\text{Fe}_{0.22})_3\text{V}$ with 4-MeV nickel ions to 70 dpa did not disorder the material, but it did reduce the domain size and introduce other microstructural features. The most obvious addition was a high density of stacking faults on $\{111\}$ planes and dislocations, as shown in Fig. 4.10(a) for a specimen irradiated at 570°C. Again, roughly half the faults were extrinsic, while the remaining were intrinsic. The introduction of additional faults into the microstructure effectively reduced the domain size as shown in Fig. 4.10(b) [compare with Fig. 4.9(b)]. The radiation-induced faults actually subdivided the original domains, producing the much finer size. Small cavities less than 7 nm in diameter were also created and are shown in Fig. 4.10(c). The cavities were usually located on matrix dislocations or on dislocations bounding grown-in faults and radiation-induced faulted loops.

With increasing irradiation temperature, lower number densities but larger sizes of faulted loops and cavities were produced. Higher irradiation temperatures also increased the domain size toward that before irradiation, while the amount of VC precipitation was decreased. Swelling from the cavities was less than 0.05% at all temperatures. Simultaneous injections of 3 ppm/dpa of helium and 12 ppm/dpa of deuterium to simulate a first-wall fusion reactor condition increased the swelling to values as high as 0.2%. However, these values were still substantially lower than the 2% maximum swelling measured for a 20%-cold-worked type 316 stainless steel bombarded under similar conditions. The potential for LRO alloys as nuclear reactor materials appears good.

Fig. 4.10. Microstructure of $(\text{Co}_{0.78}\text{Fe}_{0.22})_3\text{V}$ Quenched, Aged at 800°C for 8 h, and Irradiated with 4-MeV Nickel Ions to 70 dpa at 570°C (3 h). (a) Bright field, showing high density of faulted loops and tiny cavities. (b) Dark field of same area imaged by using (100) superlattice reflection to show ordered domains. (c) Bright field at higher magnification to show cavities.

4.2.7 Irradiation Creep Using Light Ions — T. C. Reiley, P. Jung,¹² and W. A. Coghlan

Most of the work described below is a collaborative effort of Reiley and Jung performed at KFA-Jülich on the cyclotron there. These experiments sought to prepare specimens with a well-characterized and homogeneous microstructure. This was accomplished for type 316 stainless steel through a treatment of solution annealing plus deformation at 600°C and 275 MPa for 24 h. Although this steel (as well as most other materials) normally forms dislocation cells or subgrains during deformation, the above treatment leads to a homogeneous distribution of dislocations¹³ at a density measured to be $1-2 \times 10^{14}/\text{m}^2$. The origin of this unusual structure is very likely associated with the carbon-dislocation interaction, as indicated by the strain aging occurring at this temperature. Furthermore, Class I solid solutions, in which solute atmospheres affect dislocation motion, also do not form subgrains.

Two kinds of type 316 stainless steel specimens were prepared: PC, pre-crept as described above, and A-PC, aged (200 h at 552°C) and pre-crept. The aging treatment was designed to cause precipitation of M_{23}C_6 . Also prepared were specimens of Ni-4 wt % W, Class II solid solution with a fairly low stacking fault energy, chosen as a model system for stainless steels. Specimens of these materials were tested in a 5.5-MeV proton beam in the cyclotron at several stresses and temperatures. The creep rates, dislocation densities, and loop densities were measured. The structural results are shown in Table 4.3. The creep behavior of the PC type 316 specimens is given in Fig. 4.11 along with earlier work of C. Schwaiger, P. Jung, and H. Ullmaier¹⁴ on 20% cold-worked type 316 stainless steel. The creep of the Ni-4 % W is shown in Fig. 4.12.

¹²KFA-Jülich, FRG.

¹³D. Challenger and J. Moteff, "Quantitative Characterization of the Substructure of AISI 316 Stainless Steel Resulting from Creep," *Metall. Trans. A*, 4: 749-55 (1973).

¹⁴C. Schwaiger, P. Jung and H. Ullmaier, International Conference on Fundamental Mechanisms of Radiation-Induced Creep and Growth, Chalk River Nuclear Laboratories, Chalk River, Canada, May 1979.

Table 4.3. Structural Features After Light-Ion Irradiation

Alloy Condition ^a	Irradiation Temperature (°C)	Displacement Damage (dpa)	Dislocation Density, 10 ¹⁴ /m ²		n _L , Loop Density (10 ²⁰ /m ³)	Maximum Loop Diameter (nm)
			ρ _n , network	ρ _t , total		
<u>Type 316 Stainless Steel</u>						
Solution annealed		0	~0.01			
20% cold worked		0	>10 ^b			
Neutron irradiated	450	20	1-3	1-3	~1	150 ^c
PC		0	1.3			
A-PC		0	1.4			
PC	300	0.1	1.8	2.2	13	30
A-PC	300	0.1	1.7	2.1	6	60
PC	375	0.2	1.3	1.7	2	160
PC	420	0.2	1.6	1.6	<1	
<u>Ni-4% W</u>						
20% cold worked			>10 ^b			
20% cold worked	300		3.0	3.6	11	50

^aPC = precrept 24 h at 600°C and 275 MPa; A-PC = aged 200 h at 550°C, then precrept; irradiation is with 5.5-MeV protons unless otherwise indicated.

^b ρ_n may vary more than a factor of 10 between cell wall and cell interior.

^cAverage loop size, not maximum.

Fig. 4.11. Normalized Irradiation Creep Rate of Precept Type 316 Stainless Steel Under 5.5-MeV Protons. Also shown are data for cold-worked material under 7-MeV deuterons.

Fig. 4.12. Normalized Irradiation Creep Rate of Cold-Worked Ni-4% W Under 5.5-MeV Protons.

The structural results¹⁵ for type 316 stainless steel neutron irradiated to 20 dpa at 450°C is given in Table 4.3 as an indicator of the desired magnitude of loop and dislocation densities in stabilized irradiated material. Both PC type 316 and A-PC type 316 have similar values of ρ_n , the network dislocation density, and remain essentially unchanged after irradiation. The loop density, n_L , of these materials after light-ion irradiation is comparable to that of the stabilized material, although loop sizes are much different, reflecting the short period for loop growth during the light-ion experiments. There is a slight difference in loop size between the PC and A-PC materials, indicating an effect of carbon in solution on loop growth rates, perhaps through trapping. The loop growth rate increases and the number density decreases with an increase in temperature.

The normalized creep rates (strain rate/displacement rate) for type 316 stainless steel under light ions show (1) a low stress exponent, ~ 1 , at low to moderate stresses; (2) a small temperature dependence; (3) a very small, if any, dependence on dislocation density or morphology for $\rho_n > 10^{14}/\text{m}^2$. These features are all consistent with predictions of preferred absorption climb models; however, climb-glide models can not be ruled out.

The data for Ni-4% W, given in Fig. 4.12, show a higher average stress exponent, which probably indicates a transition from a low (irradiation creep) to high (thermal creep) exponent. For this material as the degree of thermal creep increases, the stress exponent clearly increases.

A comparison among commercial cold-worked type 316 stainless steel, cold-worked "pure" type 316 (with low impurity levels, especially carbon), Ni-4% W, and nickel shows a significant difference in irradiation creep rates, even though elastic moduli and diffusion activation energies are quite similar. A factor that correlates well with the observed differences is stacking fault energy (low stacking fault energy, low creep rate). Given the influence of this factor on dislocation climb and cross-slip processes, it is reasonable to expect that creep processes involving the motion of network dislocations, at least, should be influenced by stacking fault energy. The theories do not include stacking fault energy effects, even though dislocation climb and climb and glide are the deformation mechanisms. This may indicate a major deficiency in the theory.

¹⁵R. J. Barton, B. L. Eyre, and D. A. Stow, *J. Nucl. Mater.* 67: 181 (1977).

The work performed at ORNL included several instrument improvements and two irradiation creep experiments on cold-worked type 316 stainless steel at the end of the reporting period. Results from these experiments are similar to earlier experimental results.

4.3 THEORY AND MODELING

4.3.1 Effective Diffusion Coefficients of Point Defects in Impure Materials¹⁶ - L. K. Mansur

When vacancies or interstitials diffuse in a material containing impurities, the point defect diffusion coefficients characteristic of the pure material are altered. An effective diffusion coefficient may be calculated from the diffusion coefficient in the pure material and detailed knowledge of the point defect-impurity reactions. The effective coefficient may be used for some purposes as if it were a simple coefficient characteristic of the material.

Where impurity-point defect complexes are immobile and there is no irradiation, the impurities are characterized as traps and the effective point defect diffusion coefficient, or as it is sometimes called, delayed diffusion coefficient, is the free point diffusion coefficient reduced by a factor calculable from the trap characteristics. The result has been shown to be given by

$$D_v^{ef} = D_v / (1 + \kappa_v \tau_v C^t) \quad (1)$$

where D_v^{ef} is the effective vacancy diffusion coefficient. Here D_v is the vacancy diffusion coefficient in the pure material, κ_v is the capture coefficient of the trap for free vacancies, C^t is the trap concentration and τ_v is the mean time a vacancy is trapped before thermal release. The result for self-interstitial diffusion is simply obtained here and in what follows by substituting the subscript i for v .

Where vacancy-impurity complexes are mobile, a generalized form of Eq. (1), again for the case of no irradiation, has been given as

¹⁶Paper to appear in *Acta Metallurgica*. Also available as ORNL/TM-7247.

$$D_v^{ef} = \frac{D_v + D_v^* \kappa_v \tau_v C^t}{1 + \kappa_v \tau_v C^t} \quad (2)$$

where D_v^* describes the transport of vacancies associated with both formation and migration of mobile vacancy-impurity complexes.

Under irradiation, however, the effective diffusion coefficients contain additional terms. For the case where the complexes are mobile, where vacancy-interstitial recombination and loss of vacancy-impurity complexes to sinks are accounted for we have derived the following expression

$$D_v^{ef} = \frac{D_v + D_v^* \left[\frac{\kappa_v \tau_v C^t}{1 + C_v \kappa_v \tau_v + R_v \tau_v C_i + \tau_v K_v^*} \right]}{\left[1 + \frac{\kappa_v \tau_v C^t}{1 + C_v \kappa_v \tau_v + R_v \tau_v C_i + \tau_v K_v^*} \right]} \quad (3)$$

Here C_v and C_i are the free vacancy and interstitial concentrations, R_v is the recombination coefficient for free interstitials with bound vacancies, and K_v^* is the loss rate to internal sinks of vacancy-impurity complexes per unit complex concentration.

The effective diffusion coefficients, which have been set forth in the literature from time to time by ourselves and others, including Eqs. (1) and (2), are limiting or approximate forms of Eq. (3) that are obtained for special conditions, namely, no irradiation, low vacancy-impurity binding energies, or low internal sink strength.

The effective diffusion coefficient of point defects in a material containing impurities is a convenient and useful concept. It is convenient because in terms of overall transport of point defects what is obtained is a composite measure of the effects of several point defect-impurity processes. Knowing that the measured diffusion coefficient is actually a composite entity allows interpretation and testing in terms of more fundamental parameters. It is shown in Ref. 16 that the equations describing the fates of free and bound vacancies under irradiation (and thermally) in terms of free and impurity-associated diffusivities, trapping rate, thermal release rate, and bound recombination rates are indistinguishable from a set of two equations characteristic of a system with no impurities, provided the diffusion coefficients in the new

equations are effective diffusion coefficients. As one application of these ideas, consider that the irradiation-induced swelling observed at one temperature has often been quantitatively fit with numerical values for vacancy migration energies characteristic of simple diffusion coefficients by using simple rate equations (i.e., not accounting for impurities) and using the point defect concentrations computed from these in the expressions for void swelling. The theoretical forms for the effective diffusion coefficients given here show how the effective diffusion coefficients are actually expected to vary with temperature.

The effective diffusion coefficient is a useful concept because it is a composite of terms, each describing a physical process, constructed in precisely the correct way to permit evaluation of the relative importance of the processes for a given material. In Eq. (3) the terms in the denominator of the term multiplying D_p^* and also appearing in the lower denominator describe the processes controlling the concentration of bound vacancies. These terms determine the contribution of the bound vacancies to the effective diffusivity.

Thus four processes are now accounted for in determining the concentration of bound vacancies. The terms above, which are normalized to τ_p^{-1} in the form shown, can be identified with vacancy thermal release, trapping, recombination of bound vacancies with free interstitials, and impurity-associated transport to sinks. We have examined the conditions under which the trapping, bound recombination, and impurity-associated transport terms may be important with respect to the thermal release term in determining the concentration of bound vacancies. Expressions are given for the requirements on the parameter values of the system to enter these various regimes.

4.3.2 Applications of the Theory of Cavity Growth to Dual-Ion Swelling Experiments¹⁷ — M. R. Hayns¹⁸ and L. K. Mansur

Helium may be injected into a metal or alloy during irradiation as the result of reactor neutron-induced transmutation reactions, or during accelerator bombardment with the use of dual beams of helium and a more

¹⁷Abstracted from paper presented at the ASTM Tenth International Symposium on Effects of Radiation on Materials, June 3-5, 1980, Savannah, Georgia; to be published in the proceedings.

¹⁸On assignment to ORNL from Theoretical Physics Division, AERE, Harwell, England.

highly damaging heavy ion (e.g., Ni). In this work we are concerned with the effect of helium on cavity swelling. In particular, the effect on the temperature dependence of swelling is emphasized. The results can be separated into three parts. (1) Expressions are derived showing that the primary effect of the helium is in pressurizing cavities and that a secondary effect is in altering the microstructural sink strengths. (2) Recent experimental data of Packan and Farrell (Sect. 4.2.3, this report) on swelling of a pure stainless steel type alloy under dual nickel and helium-ion bombardment is interpreted and can be explained satisfactorily by the theory. (3) Model studies for physically reasonable parameters reveal the importance of the He/dpa ratio.

The method employed to find the temperature shift due to helium is similar to that developed previously¹⁹ to derive the temperature shift of cavity growth with changes in dose rate, changes in the primary point defect loss processes, and changes in microstructural sink strengths. It is based on the fact that the cavity growth rate can be approximately expressed as the difference between a radiation-driven term and a thermal shrinkage term. We may select the ratio of the second term to the first term to be any constant A , and this value would define a specific temperature T_A . If the gas pressure or sink strength (or dose rate) were changed, then a new temperature could be found where this ratio would again be A . These new conditions would define a temperature shift in the temperature T_A . The value of A varies from zero at temperatures near the peak swelling temperature to unity at the swelling cutoff temperature. Thus the analysis here applies to temperatures above the peak swelling temperature up to the upper swelling cutoff temperature. Requiring that the ratio A be retained at two different gas pressures or sink strengths, we obtain an expression giving the temperature shift, ΔT , in terms of changes in the gas pressure within the cavities and in terms of the changes in microstructural sink strengths. For typical parameter values applicable to stainless steels we obtain a predicted ΔT of about 50°C.

Figure 4.13 shows swelling versus temperature for helium-free and helium-coimplantation bombardment experiments where the ratio of the gas

¹⁹L. K. Mansur. "Correlation of Neutron and Heavy-Ion Damage II. The Predicted Temperature Shift of Swelling with Changes in Radiation Dose Rate," *J. Nucl. Mater.* 78: 156-60 (1970).

Fig. 4.13. Measured and Calculated Swelling at 70 dpa. Circles represent measurements for no gas. Triangles represent simultaneous bombardment. The lower curve represents the calculated curve fitted to no-gas points. The two upper curves use the parameters obtained by this fit to predict the effect of gas. Calculations for 3×10^{-11} and 5×10^{-10} atoms He per atom metal per second bracket the data.

to displacement production rate is 20 at. ppm He/dpa. The points represent the experimental measurements, while the curves represent the calculations. The main effects of the gas are to increase the swelling temperature range by 50 to 100°C and to raise the peak swelling value. The calculational procedure consists of fitting the helium-free points by varying the rate theory parameters within a physically reasonable range and then attempting to predict the swelling behavior with continuous

helium coimplantation using this fixed set of parameters. Placing all the generated gas into the cavities, 20 at. ppm He/dpa (or about 10^{-7} apa He/s) (apa the means atoms helium per atom of metal), results in much too high a swelling at high temperature. In order to explain the experimental results it is necessary to reduce the rate of gas introduction into cavities to about 0.1 at. ppm He/dpa for doses where the cavities are below their critical radius. A reasonable basis for this large reduction from the injection rate is the partitioning of gas among the various sinks in the microstructure.²⁰

The results of gas preinjection experiments were also analyzed. If the cavity number density measured was used in the rate theory cavity growth calculations, results could also be explained satisfactorily.

After the values of the parameters appearing in the theory had been fixed with the help of the experimental data, the relative effects of varying the amount of helium implanted simultaneously with displacement damage were investigated. Figure 4.14 gives the calculated swelling with temperature for the range 0 to 2 at. ppm He/dpa injected into cavities. The injection rate of helium into the specimen is simply related to this injection rate into cavities by multiplying the cavity injection rate by the ratio of the cavity plus dislocation sink strength to the cavity sink strength. Below about 2×10^{-3} at. ppm He/dpa, the helium has little effect on void growth. When the ratio is 0.02, however, the swelling increases substantially at high temperatures. When the ratio is further increased by a factor of 100 a further substantial increase in swelling is seen at high temperature, although the increase per helium atom is not as large as for the initial dose increase.

²⁰M. H. Yoo and L. K. Mansur, "The Inclusion of Mobile Helium in a Rate Theory Model of Void Swelling," *J. Nucl. Mater.* 85 and 86: 571-75 (1979).

Fig. 4.14. Calculated Swelling at 70 dpa for a Range of Helium Injection Rates into Cavities. Parameters obtained by fitting the no-gas case are used. Since sink strengths at all injection rates have not been measured, the values measured at this injection rate of 10^{-7} at. ppm He/dpa into the specimen were used.

4.3.3 The Dependence on Cascade Size of Point Defect Fluctuations Calculated by Using the Cascade Diffusion Theory — L. K. Mansur

The time-dependent point defect concentrations at a point in an irradiated material have been calculated as a function of cascade size. These calculations account for the spatially and temporally discrete nature of point defect production in cascades. The diffusion of defects from each cascade occurring in the material is followed until all the defects are

absorbed.²¹ In principle, the point defect concentration at a point is obtained by the superposition of the contributions from all cascades that have occurred at earlier times at discrete positions in the material. In calculations using realistic interstitial and vacancy diffusion coefficients, only the vacancy concentration is composed of the integrated contributions of many decaying cascades. Since interstitial diffusion is so rapid, the interstitial concentration is nearly always the concentration resulting from the most recent cascade within the region of material that can contribute to the concentration.

In the present work the size of cascades, that is, the number of defects in a cascade, was varied from sizes typical of fast reactor irradiations to that typical of fusion reactor irradiations. The spatially averaged displacement rate was kept constant at 10^{-6} dpa/s since dose rates in both types of reactors are expected to be near this value. Thus the fission reactor case corresponds to more cascades of smaller size while the fusion reactor case corresponds to fewer cascades of larger size (although these may be composed of subcascades).

Figure 4.15 shows the vacancy concentrations corresponding to cascades induced by primary knock-on atoms of damage energies 10, 50, and 250 keV. The number of defects per cascade was computed by the IAEA recommended relation, $N = \beta E_{\text{dam}}/2E_d$, with $\beta = 0.8$ and $E_d = 40$ eV. To account in a rough way for in-cascade recombination the number of defects produced was reduced to 20% of the value given by the equation above and used as the cascade strength in the source term for the present calculations. The material and defect parameters are given in Ref. (21).

As seen from Fig. 4.15, the larger and less frequent the cascades, the lower is the "background" level of vacancy concentration and the more jagged is the concentration versus time profile. The background is contributed mainly by the more numerous cascades at large distances, and the spikes are contributed mainly by the fewer nearby cascades. The interstitial concentration is nearly always zero, punctuated by very large

²¹L. K. Mansur, W. A. Coghlan, and A. D. Brailsford, "Swelling with Inhomogeneous Point Defect Production - A Cascade Diffusion Theory," *J. Nucl. Mater.* 85 and 86: 591-95 (1979).

Fig. 4.15. The Variation of Vacancy Concentration with Time for Cascades Produced by Primary Knock-On Atoms with Damage Energy (a) 10, (b) 50, and (c) 250 keV at a fixed dose rate of 10^{-6} dpa/s.

spikes with instantaneous concentrations exceeding $10^{19}/\text{m}^3$, which decay in less than 0.5 μs . On the average these spikes are separated in time by 22, 110, and 550 ms, respectively, for cascades of 10, 50, and 250 keV and a sink strength of $1 \times 10^{15}/\text{m}^2$.

The significance of the present work is that

1. quantitative descriptions of fluctuations in point defect concentrations have now been extended to explore the important parameter cascade strength;
2. subsequent efforts to characterize irradiation creep and cavity nucleation in the presence of point defect concentration fluctuations should stress fusion reactor conditions since the fluctuations are more pronounced in that case.

4.4 FACILITY DEVELOPMENT AND NUCLEAR MICROANALYSIS

4.4.1 Nuclear Microanalysis as a Probe of Impurity-Defect Interactions²² — M. B. Lewis and K. Farrell

The technique of nuclear microanalysis using an ion beam probe is a nondestructive method of measuring the quantity and depth distribution of impurity atoms in the near-surface regions of the target material. It can measure changes in the original position and shape of the impurity profile with respect to time, temperature, displacive irradiation, and other impurities. It, therefore, yields information on kinetics of migration of the impurity on a small scale. It is especially useful for the lighter elements such as C, H, He, O, and N, which are often difficult to follow on a microscopic scale by other analytical techniques. These elements are known to be intimately involved in nucleation of the radiation damage microstructure.

With nuclear microanalysis, vacancies and interstitial atoms are created by atomic displacements by the probing beam and by any ion beam used to implant a selected impurity. This may be a drawback for some

²²Abstracted from paper presented at Symposium on Advanced Techniques for the Characterization of Microstructures, 109th AIME Annual Meeting, Las Vegas, Nevada, February 24–28, 1980; to be published in proceedings.

applications, but for radiation damage studies it can be used to advantage to determine important fundamental parameters. Procedures are outlined for extracting impurity diffusion coefficients, impurity-point-defect binding energies, and trap generation coefficients of heavy ions used to create displacement damage. Examples involving the impurities deuterium and helium in austenitic stainless steels and nickel are described. Preliminary values are given for the bulk diffusion coefficient of deuterium in austenite at 25°C ($1.4 \times 10^{-16} \text{ m}^2/\text{s}$), the binding energies of deuterium with point defects in austenite and of ^3He in nickel (0.33 and 2.1 eV, respectively), and a room-temperature trap generation coefficient for deuterium in nickel-ion-bombarded austenite of about 15 per incident nickel ion.

4.4.2 An Ion-Beam Technique for the Measurement of Deuterium Diffusion Coefficients²³ — M. B. Lewis and K. Farrell

The method of nuclear microanalysis using the reaction $\text{D}(d,p)\text{T}$ has been used to measure profiles of deuterium in austenitic steels. Targets were prepared by electrocharging (in deuterated solutions), electropolishing, and ion implantation. The electrocharged specimens absorbed deuterium up to concentrations of 40 at. %. By measuring the time release of deuterium from these specimens, diffusion behavior of deuterium in type 310 stainless steel was deduced. The specimens that were electropolished in deuterated solutions were subsequently measured to have less than 100 at. ppm bulk deuterium and less than one monolayer of surface deuterium. When the electropolishing was carried out at 223 K the values were even less: <0.1 monolayer and <10 at. ppm.

When the deuterium was introduced by ion implantation, the normal bulk diffusion of the implanted gas was not observed. Instead the gas appeared to be trapped near the site of implantation. Subsequent thermal aging and remeasuring the deuterium concentration profiles found that most of the gas detrapped near 400 K. A computer program utilizing the differential equation solver GEAR was written and applied to diffusion and

²³Abstract of paper accepted for publication in *Applied Physics Letters*.

trapping in the above type of experiments. In this way a deuterium-defect binding energy in type 316 stainless steel has been deduced.

4.4.3 Carbon Migration and Contamination Studies — M. B. Lewis,
K. Farrell, N. H. Packin, and E. Kenik

The examination of type 316 stainless steel samples that had been implanted with titanium and subsequently ion bombarded at 600°C showed the formation of titanium carbide in the peak damage region. This suggests the presence of excessive carbon in the bulk of the specimen. For this reason, ^{12}C concentration profiles were measured by the $^{12}\text{C}(d,p)^{13}\text{C}$ reaction technique. Even carefully polished specimens contained about 10 monolayers equivalent of carbon on their surfaces. Measurements of samples that had been ion bombarded to levels of 1 and 70 or 100 dpa were also made. All measurements indicate a carbon concentration gradient that peaks at the specimen surface and decreases with increasing depth. All measurements indicate that the longer or higher dpa runs show greatly enhanced carbon concentration to depths of at least 1 μm below the specimen surface. Table 4.4 summarizes some of the concentrations at the peak damage depth, 0.7 μm .

In future experiments we plan to examine to what extent the level of carbon after bombardment is determined by (1) the presence of surface carbon, (2) the value of the initial bulk carbon, or (3) the finite pressure of carbon-containing gases in the target chamber. Although the present data are consistent with (1) and (2), the significance of (3) has not yet been determined.

Table 4.4. Carbon Concentrations Found at a 0.7- μm Depth
in Ion-Bombarded Alloys

Alloy	Carbon Concentration, at. ppm, at Each Dose Level			
	Unbombarded	1 dpa	70 dpa	100 dpa
316 stainless	500 $\pm$ 100	1100 $\pm$ 200	2600 $\pm$ 500	
Ni-25% Mo	60 $\pm$ 20	70 $\pm$ 20		600 $\pm$ 100

4.4.4 Beam Shutters and Computer Automation of Target Chamber Measurements — M. B. Lewis and R. A. Buhl

Shutter systems have been developed to interrupt both the nickel and helium ion beams synchronously during dual-ion bombardments, so as to provide an intermittent irradiation environment for planned swelling experiments. Presently available cycle times range from tenths of seconds up to arbitrarily long times.

Computer control has been implemented for periodically inserting a nine-hole Faraday cup array to intercept the ion beams and to record the signals so as to provide information on beam uniformity during interrupted or steady bombardments. The system uses a Tennecomp TP-50 minicomputer interfaced to an external current integrator and servodevice. The ion beam profile is measured in a 3×3 matrix. The computer also determines the correct fluence for the three possible fluences in a single bombardment. Work is in progress to interface specimen temperature and target chamber vacuum measurement to the computer.

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5. ENGINEERING MATERIALS

5.1 EROSION AND WEAR OF CERAMICS — C. S. Yust

The characteristic process in erosion is impact of a solid surface by a stream of particulate matter, either liquid or solid. At each point of impact localized damage may be introduced into the solid surface. The erosion process itself is the cumulative effect of many collisions of particles with the surface. This study has been concerned with local damage in ceramics as a result of particle impact. We have demonstrated by single-particle impact tests on alumina that very high-strain-rate shear processes may occur at the specimen surface and that extensive plastic deformation may occur beneath the impact site. We have devoted some effort to analysis of another very high-strain-rate deformation process in alumina, explosive compaction, to extend our knowledge of high-strain-rate effects in this material. The similarity in appearance between dislocation arrays at some single particle impact sites and in the explosively compacted alumina suggested that this comparison could be useful. The analysis of the explosively compacted alumina is now complete and has resulted in publications describing various aspects of the damage introduced under such conditions.

In general, the explosive compaction of alumina yields a lattice filled with slightly misoriented layers of material. The regions of misorientation are bounded by dislocation arrays lying on the basal plane of the hexagonal alumina lattice, spaced irregularly at distances in the range from 0.2 to 0.4 μm . In many cases the dislocations are present as a network. Basal plane twinning is also common, and most of the twin boundaries contain dislocations. The mechanism of dislocation generation under the shock conditions experienced in explosive compaction are not well understood, but theories of dislocation generation under such conditions have been proposed. The dislocation arrays observed in this work have some features suggestive of the operation of the shock generation theories and some indicative of dislocation generation by more conventional means.

Some of the dislocation damage at particle impact sites in alumina is in the form of networks similar in appearance to those introduced into alumina during explosive compaction. In both instances, the dislocations have Burgers vectors of the type $(1/3) 11\bar{2}0$, the common Burgers vector for basal plane glide. Further details are presented in the papers abstracted below.

5.1.1 High-Strain-Rate Deformation

5.1.1.1 Explosive Compaction and Microstructural Analysis of AlN, Amorphous Si₃N₄, Boron, and Al₂O₃ Ceramics¹ — C. L. Hoenig² and C. S. Yust

Ceramic powders were explosively compacted to high density at pressures up to 7 GPa. Microstructures of the compacted and annealed ceramics were examined by transmission and scanning electron microscopy and microhardness techniques. Lattice damage is evident in the form of dislocations and planar faults. Interparticle bonding and melting are also apparent.

5.1.1.2 Observation of Dislocations and Twins in Explosively Compacted Alumina³ — C. S. Yust and L. A. Harris

The microstructure at the half-radius position of a polycrystalline alumina rod formed by explosive compaction has been studied by transmission electron microscopy. The as-compacted lattice is composed of misoriented bands aligned predominantly in one direction. Such bands may correspond to frequently observed shock lamellae. The band edges are defined by dislocation arrays lying on the basal planes of the hexagonal

¹Submitted to *Journal of the American Ceramic Society*.

²Lawrence Livermore Laboratory.

³Submitted for inclusion in the International Conference on the Metallurgical Effects of High Strain-Rate Deformation and Fabrication, Albuquerque, New Mexico, June 22-26, 1980.

alumina lattice. The dislocations have Burgers vectors of the types $\langle 11\bar{2}0 \rangle$ and $\langle 10\bar{1}0 \rangle$, which are the Burgers vectors of slip dislocations in the basal plane. Basal plane twinning is also observed, and the twin boundaries contain interfacial dislocations. While dislocation generation occurs primarily on basal planes, some dislocation activity is also noted on prism, $\{11\bar{0}0\}$, and on rhombohedral, $\{11\bar{0}1\}$, planes. Nonbasal twinning, however, has not been detected. The lattice damage is discussed in terms of possible dislocation and twinning mechanisms.

5.1.2 Erosion of Alumina — C. S. Yust

Investigation of single-particle impact damage in single-crystal alumina is continuing. In these experiments, limited numbers of particles of SiC are accelerated in an air pressure gun onto small alumina single-crystal samples. The alumina sample is then thinned for transmission electron microscopy (TEM) by removal of material from the back surface. The TEM investigation permits the study of subsurface damage associated with the individual impact sites. In alumina the damage has been found to include both plastic deformation and fracture. The plastic deformation occurs principally on basal planes and involves dislocations having a Burgers vector of $(1/3)\langle 11\bar{2}0 \rangle$. A series of experiments is currently in progress to assess the variation of the damage with erosion conditions. The test matrix is outlined in Table 5.1. To date, tests have been performed at room temperature at a 20° angle of impingement and 90 m/s particle velocity, with particles 100 and 240 μm in diameter. The damage introduced by these tests is under study.

5.2 FUNDAMENTALS OF WELDING AND JOINING — S. A. David and J. M. Vitek

The purpose of this program is to understand the development of the structure, stability, and properties of austenitic stainless steel weld metal. The program has two major parts relating to the study of (1) weld pool solidification and (2) phase stability.

The weld pool solidification study is directed toward an understanding and modeling of the basic solidification characteristics

Table 5.1 Test Matrix for Alumina Single-Particle Impact Tests

Particle Diameter (μm)	Particle Velocity (r./s)	Tests for Each Temperature and Impingement Angle ^a					
		Room Temp		500°C		1000°C	
		20°	90°	20°	90°	20°	90°
240	65			x		x	
	90	ER-113 ER-116	x	ER-114	x	x	x
100	65			x		x	
	90	ER-115	x	x		x	x
35	65			x			
	90			x			

^aER-number indicates test performed. x indicates test condition presently planned as an experiment.

of austenitic stainless steel weld metal over the normal range of welding conditions for a reasonable variation in alloy content and toward forming a base for developing weld metal structure with desirable properties.

The phase stability study is directed toward an understanding of the stability of ferrite, austenite, and second phases and to characterize and model the sequences of precipitation in the weld metal. Significant changes occur on aging at elevated temperatures. Ferrite transforms to sigma, carbides, nitrides, and other intermetallic phases.

The program described as above should lead to the following: better insight into the fundamentals of ferrite formation and its stability and control, better understanding of the role of ferrite in preventing hot cracking during welding, and finally a better correlation between weld metal structure and properties.

5.2.1 A Study of Ferrite Morphology in Austenitic Stainless Steel Welds — S. A. David

A certain amount of ferrite (δ) is present in austenitic stainless steel welds to prevent hot cracking. This ferrite has been found to influence in various ways the strength and corrosion behavior of welds. In particular, the γ - δ interfacial area and, hence, the morphology of ferrite has been found to be a critical factor in the sensitization behavior of austenitic stainless steel welds containing duplex structures. Ferrite may be present in various amounts and in different morphologies within the weld metal depending on the welding process and welding parameters.

An investigation to identify and classify distinct ferrite morphologies into various types has enabled us to identify four distinct types of ferrite morphology in type 308 stainless steel weld metal. They are: (1) vermicular, (2) lacy, (3) acicular, and (4) globular and are shown in Fig. 5.1. For the various observed morphologies, the ferrite number varied from 5 to 15. Factors such as composition, solute segregation, and thermal history have been found to influence the ferrite morphology. An earlier study showed that most of the ferrite observed in duplex stainless steel welds may be identified as the following:

1. residual primary ferrite resulting from incomplete $\delta \rightarrow \gamma$ transformation during solidification or
2. residual ferrite after Widmanstätten austenite precipitation in primary ferrite.

These modes of ferrite formation can be used to explain the above-described ferrite morphologies in austenitic stainless steel welds.

5.2.2 Ferrite Content Variations in Austenitic Stainless Steel Multipass Welds — S. A. David

Variations in ferrite content within a multipass weld are commonly observed in austenitic stainless steel welds. Such variations are bound

Fig. 5.1. Three-Dimensional Composite Photomicrographs of Various Ferrite Morphologies in a Type 308 Stainless Steel Multipass Weld. (a) Type I, vermicular. (b) Type II, lacy. (c) Type III, acicular. (d) Type IV, globular.

to influence the mechanical and corrosion behavior of weld metal. The variation in ferrite content has often been attributed to the inadequacies of the present ferrite measuring devices. In addition to the problems associated with the accuracy of ferrite measurement techniques, a number of other factors that contribute to the observed variations in ferrite content within the weld metal have been identified. They are (1) composition, (2) ferrite morphology, (3) dissolution and transformation of ferrite due to thermal cycles, and (4) cooling rates. The extent of their influence on ferrite content within the weld metal is being investigated in great detail.

5.2.3 Structure of Austenitic Stainless Steel Laser Welds — S. A. David and J. M. Vitek

During a recent investigation on austenitic stainless steel weld metal conducted at ORNL, various factors were found to influence the amount of ferrite in duplex austenitic stainless steel weld metal. They are (1) composition, (2) ferrite morphology, (3) dissolution and transformation of ferrite due to thermal cycles, and (4) cooling rates.

The influence of one of the above factors, namely weld metal cooling rates, on the ferrite content and weldability was investigated by making autogenous bead-on-plate welds at 13, 25, and 63 mm/s on a type 308 stainless steel weld metal pad with approximately 10 vol % ferrite. The welds were made by using a multikilowatt high-power laser system. Microstructural analyses of these welds showed a wide variety of features. The weld made at 13 mm/s contained microstructures ranging from nearly 100% austenitic at the root of the weld to ferrite plus austenite duplex structure at the crown of the weld. However, nearly 100% austenitic weld metal structures were obtained in the welds made at 25 and 63 mm/s. In spite of the very low level of ferrite in the weld metal, no weld metal cracking was observed in any of these welds. The fully austenitic welds contained an excessive number of microtwins.

Further microstructural analyses by transmission and scanning transmission electron microscopy are under way to characterize and understand the origin of the above microstructures and their stability.

5.3 STUDIES IN NONDESTRUCTIVE EVALUATION — W. A. Simpson and C. V. Dodd

Elastic waves have often been used to investigate nondestructively the internal structure of materials. Because of the lack of understanding of the basic phenomena involved, however, the results of such studies have often been qualitative and highly subjective. This is particularly true of the case in which the material under investigation is composed of two dissimilar, possibly anisotropic components having a well-defined interface across which the interrogating energy must propagate. Therefore, we are studying such a system to determine what effect the interface has on the characterization of flaws in either component.

We previously obtained the solution for propagation between two dissimilar isotropic media in contact. A computer program was written to allow several binary systems of interest to be studied. The solution was then extended to the case of an isotropic material in contact with an arbitrary anisotropic one. The anisotropic component principal axis may have an arbitrary orientation with respect to the interface. A computer program is being written to provide quantitative results for several systems of interest.

A diffusion-bonded sample containing two dissimilar metals has been obtained for concurrent experimental studies. Unfortunately, for such samples the choice of possible components is extremely limited; the present sample is composed of titanium bonded to a carbon steel, neither of which is macroscopically anisotropic. Although the sample will be very useful for studying the effects of propagation across an interface on flaw characterization, efforts are continuing to obtain a sample containing an anisotropic component.

Analytical studies were begun on scattering of elastic waves from selected flaw shapes. Of principal interest is the crack or cracklike scatterer, since such shapes are most likely to prejudice the use of the

host material. A computer program is being developed for the analytical solution obtained by Maue⁴ for diffraction of elastic waves by a half plane. An attempt will be made to extend the solution to anisotropic media.

In many materials electrical conductivity measurements can be used to determine other material properties such as thermal conductivity, alloy content, state of heat treatments, and hardness. This electrical conductivity can be easily measured by eddy-current techniques but until now had to be referred back to dc conductivity standards to obtain an absolute measurement.

By using our eddy-current theory⁵ and computer programs,⁶ we have analyzed the errors present in the ac measurement to reduce them to a minimum. The eddy-current system used consisted of a driving coil that transmitted an alternating signal through a flat conducting plate to a detector coil. The magnitude and phase of the signal is a function of the dimensions of the coil and conductor, the driving frequency, and the conductivity of the plate. By accurately controlling these dimensions we have been able to make an accurate absolute ac conductivity measurement. Measurements have been made from a set of plates whose resistivities were compared with secondary standards, as shown in Table 5.2.

The secondary dc standards were only specified to within 1% accuracy, and all ac measurements were within this limit, with an average absolute error of 0.46%.

The error is being reduced further by small improvements in the experimental setup, and a set of secondary dc standards that can be measured directly has been ordered.

⁴A. W. Maue, "The Diffraction of Elastic Waves at the Half Plane," *Z. angew. Math. Mech.* 33: 1-10 (1953).

⁵C. V. Dodd, W. E. Deeds, J. W. Luquire, and W. G. Spoeri, *Some Eddy-Current Problems and Their Integral Solutions*, ORNL-4384 (April 1969).

⁶W. E. Deeds, C. V. Dodd, and G. W. Scott, *Computer-Aided Design of Layered Conductors with Multiple Property Variations*, ORNL/TM-6856 (October 1979)

Table 5.2 Preliminary Measurements of AC
Electrical Resistivity of Samples
Compared with Secondary
DC Standards

Sample Thickness (mm)	Absolute AC Resistivity (mΩ m)	Error Relative to DC Standards (%)
3.063	60.24	-0.10
3.173	39.11	0.78
3.414	50.25	-0.09
3.115	50.35	-0.52
3.139	60.67	-0.85
4.205	38.15	-0.14
4.334	37.84	0.38
3.051	39.13	0.81

6. THE HIGH TEMPERATURE MATERIALS LABORATORY

J. V. Cathcart

We have continued our efforts to establish a High Temperature Materials Laboratory (HTML). This action is motivated by the recognition that high-temperature materials problems seriously limit the efficiency, reliability, and, in some instances, the feasibility of advanced energy generating systems. The severe corrosion problems being encountered in certain coal-conversion systems and the need for better hard and corrosion-resistant valve-liner materials in these systems are examples of some of the sorts of problems that must be solved.

High-temperature phenomena of this kind are inherently complex and are most efficiently resolved by a multidisciplinary staff working cooperatively in a centralized facility. Consequently, we have proposed that the Office of Basic Energy Sciences of DOE fund the construction of an HTML at Oak Ridge. Because of budgetary constraints we plan a reduction in size of the HTML from about 7000 to about 4700 m² (80,000 to 50,000 ft²). The total staff size (~75 professionals) will remain unchanged, although some research efforts will have to be housed in an adjacent building. As before, the staff expertise will encompass six functional research areas: Environmental Interactions, High-Temperature Chemistry, Physical Properties, Mechanical Behavior, Structural Characterization, and Materials Synthesis and Preparation. Assuming funding in FY 1982, the HTML should be ready for occupancy in late 1985.

In anticipation of the construction of the HTML, we have established a High Temperature Materials Program, and the selection of a director for the HTML is in progress. The initial staff, which was recruited from existing groups in the Metals and Ceramics, Solid State, Chemistry, and Chemical Technology Divisions, consists of about 55 full-time employees, the large majority of whom are professionals. The initial program consists of both applied and basic research projects, reflecting our belief that interaction between basic and applied workers is essential in the HTML. Applied projects include an investigation of corrosion in a fluidized bed combustor for coal and studies dealing with the evaluation

and development of structural ceramics (principally silicon carbide and Al_2O_3) for use in heat exchangers. Basic studies are performed in all six of the functional research areas mentioned above, and some of these investigations (e.g., studies of sulfidation kinetics of iron and transport processes in FeS) are specifically designed to parallel the applied efforts.

We consider interaction with the university and industrial research community to be an essential feature of the effective operation of the HTML; when fully staffed, we anticipate an active users' program with 10 to 15 full-time equivalent participants per year. We have now initiated such a program, with personnel from the University of Virginia and Vanderbilt University spending time at ORNL to perform research utilizing the HTML's 1-MV electron microscope and our electron microscopy facilities as a part of the SHaRE program.

7. USERS GROUPS

C. J. McHargue

Interactions with the scientific community in the United States and abroad have always been an essential part of our program. In recent years users groups have been formed to ensure that the unique facilities of the Materials Science Program are freely available to scientists from universities and other research laboratories.

7.1 SHARED RESEARCH EQUIPMENT PROGRAM (SHaRE) — R. W. Carpenter

The last year was a productive period for the SHaRE program. It began in December 1978 as a collaborative research venture between the research staff of the Materials Science Section of the Metals and Ceramics Division and staff members of several southeastern universities and their students. The program facilitates research in areas pertinent to the DOE mission and gives SHaRE members external to ORNL access to research equipment, especially electron microscope equipment, much more sophisticated than that available at their home laboratories. Research involving Auger surface analysis, ion implantation, and nuclear micro-analysis is also part of the SHaRE program.

The initial expenses of the SHaRE program were borne by the Materials Science Section, and the assistance required for familiarization of SHaRE visitors with ORNL equipment was furnished by ORNL research staff members. During FY 1980 the Division of Materials Sciences, Office of Basic Energy Sciences, provided funds through the Oak Ridge Associated Universities (ORAU) to support the SHaRE activity directly. Program funds are used for travel grants and local living expenses of SHaRE program members while at ORNL. SHaRE program policy is defined by a steering committee, whose current membership is:

William Feiling, Assistant Director, ORAU

R. W. Carpenter, ORNL

C. L. White, ORNL

J. J. Wert, Professor and Chairman, Department of Mechanical and Materials Engineering, Vanderbilt University, Nashville, Tennessee

E. A. Starke, Professor and Director, School of Chemistry and Metallurgy, Georgia Institute of Technology, Atlanta, Georgia

An electron microscope engineer, G. L. Lehman, became a member of the SHaRE program staff this year. His responsibility is to familiarize SHaRE members with the electron microscope and computer equipment available to the SHaRE program and to participate in SHaRE research when the required microscope or computer operations make this appropriate.

Eight research projects were active during the first year of the program. The 13 research programs active at present are listed below:

B. R. Livesay, Georgia Institute of Technology, with E. A. Kenik: Hydrogen Storage Alloy Investigations.

K. R. Lawless, University of Virginia, with E. A. Kenik and R. W. Carpenter: HVEM Imaging: In Situ Oxidation of Vanadium, Vanadium-Titanium.

R. B. Benson, Jr., North Carolina State, with J. Bentley and R. W. Carpenter: Defect Analysis in Ion Implanted GaAs.

P. J. Reucroft, University of Kentucky, with J. Bentley and E. A. Kenik: Chemical and Physical Characterization of Dispersed Metal Particles in Porous Media.

J. J. Wert, Vanderbilt University, with R. W. Carpenter: The Role of Structure in the Wear Process.

R. Sisson, VPI and State University, with M. B. Lewis: Nuclear Microanalysis of Hydrogen in Oxides Formed by Steam Oxidation.

E. Schulson, Dartmouth University, with C. T. Liu and C. L. White: Collaborative Experiments on the Brittle to Ductile Transition in Polycrystalline Ni_3Al .

T. H. Sanders, Jr., Georgia Institute of Technology with C. L. White: Scanning Auger Analysis of Al-Li Alloys.

D. R. Clarke, Rockwell International, Thousand Oaks, California, with R. W. Carpenter: Elemental Microanalysis of the Intergranular Phase in Silicon Nitride Alloys.

H. Anderson, University of Missouri-Rolla, with R. W. Carpenter and J. Bentley: Lattice Imaging Studies of Donor Doped Transition Metal Oxides.

D. Northwood, University of Windsor, Canada, with E. A. Kenik: HVEM Studies of Hydrogen and Hydrides in Zirconium and Its Alloys.

A. Krawitz, University of Missouri-Columbia, with E. A. Kenik: Deformation Substructures in Cemented Carbide Drill Bits.

J. J. Hren, University of Florida, with J. Bentley, K. Farrel, and R. W. Carpenter: High-Resolution Studies in Radiation Effects, Image Simulation Calculations.

During the last year the SHaRE program was extended to include industrial participation and participation of universities and laboratories beyond the Southeast.

Current results from research on some of the programs listed above are described in Sect. 1.7 of this report.

Guests outside the SHaRE program who have conducted research on this equipment during 1979-1980 include:

J. B. Clark, University of Missouri-Rolla

R. J. Bayuzick, Vanderbilt University

D. J. Bradley, Montana College of Mineral Science and Technology

H. C. Eaton, Tennessee Technological University

S. Mehta, Iowa State University

M. J. Goringe, Oxford University

L. L. Horton, University of Virginia

7.2 SMALL-ANGLE SCATTERING RESEARCH — R. W. Hendricks

In January 1978 a program devoted to users was initiated under an interagency agreement between DOE and NSF. A National Small-Angle Scattering Research Center was established, and construction of a new small-angle neutron scattering facility at HFIR was started. As a part of this effort 30% of the beam time of the Small-Angle X-Ray Scattering Facility was reserved for users in this program. Other users or collaborators come from the Materials Science Program at ORNL or other installations.

Users during 1979-1980 who were not NSF Center guests were:

S. Suehiro, University of Massachusetts and Kyoto University

P. Young, University of Massachusetts

J. M. Schultz, University of Delaware

K. M. Gupta, University of Delaware

G. L. Lehman, University of Florida

P. D. LaBarbe, University of Montpellier (France)

J. Petermann, University of Saarlandes, Saarbrücken, FRG

7.3 ORNL-ORAU SYNCHROTRON LIGHT SOURCE USERS GROUP - C. J. Sparks, Jr.

The x-ray studies contained in the Materials Science Program as well as other programs at ORNL have made a major commitment to the use of synchrotron x-ray sources. Our current research, which uses the Stanford Synchrotron, is described in Sect. 1.6 of this report.

Oak Ridge National Laboratory has continued work toward the design and construction of the equipment needed to instrument one of the beam lines that will be available once the National Synchrotron Light Source (NSLS) is completed at Brookhaven National Laboratory. In connection with this activity, G. E. Ice was added to our staff.

To involve the university community in planning the facility as well as its use, a users group has been formed. It consists of

C. J. Sparks, Metals and Ceramics Division, ORNL, Chairman;

B. C. Larson, Solid State Division, ORNL;

A. H. Narten, Chemistry Division, ORNL;

S. C. Moss, University of Houston;

R. A. Young, Georgia Institute of Technology; and

R. J. DeAngelis, University of Kentucky.

Thirteen university scientists and six ORNL staff members (from three divisions) met in November 1979 to develop research plans for using the NSLS. Another working-planning meeting will be held in the summer of 1980.

During FY 1980, the Division of Materials Sciences, Office of Basic Energy Sciences, provided funds through Oak Ridge Associated

Universities (ORAU) to support the users' participation. With this support, A. Habenschuss was added to the staff to act as an interface between the university community and ORNL.

The current members of the ORNL Synchrotron X-Ray Source Users Group and their fields of interest are listed below.

R. A. Young, Georgia Institute of Technology, School of Physics and Engineering — Phase Transformations, Structures of Small Crystals, X-Ray Topography.

R. Kaplow, Massachusetts Institute of Technology, Department of Materials Science and Engineering — Glass to Crystalline Transformations, Amorphous Materials, Physics of Surfaces.

B. S. Borie, ORNL, Metals and Ceramics Division — Diffuse Scattering from Defect Structures, Extinction.

A. Habenschuss, ORNL, Metals and Ceramics Division — Structure of Liquid and Noncrystalline Materials.

G. E. Ice, ORNL, Metals and Ceramics Division — X-Ray Scattering, X-Ray Spectroscopy, X-Ray Optics.

C. J. Sparks, Jr., ORNL, Metals and Ceramics Division — Scattering from Imperfect Structure, Anomalous Scattering, Order-Disorder.

H. L. Yakel, ORNL, Metals and Ceramics Division — Structure of Intermetallic Compounds.

A. H. Narten, ORNL, Chemistry Division — Structure of Amorphous Solids and Liquids.

B. C. Larson, ORNL, Solid State Division — Crystal Defects, Strain Fields, Alloying Effects.

E. K. Ryba, Pennsylvania State University, Department of Materials Science — Structure of Clustering, Precipitation, and Imperfections in Materials.

A. Angell, Purdue University, Department of Chemistry — Structure of Amorphous Materials.

H. Huang, Rice University, Department of Physics — EXAFS, Absorption Edge Spectroscopy, Near-Edge Fine Structure.

S. Moss, University of Houston, Physics Department — Interstitials in Metals, Amorphous Materials, Intercalation Structures.

R. J. DeAngelis, University of Kentucky, Department of Metallurgical Engineering and Materials Science — Heterogeneous Catalysts and Their Deactivation Processes.

A. Krawitz, University of Missouri, Department of Mechanical and Aerospace Engineering — Structure and Properties of Cemented Carbides, Boron Fibers, Ordering.

L. Blum, University of Puerto Rico, Physics Department — Theory and Structure of Amorphous Materials.

M. I. Kay, University of Puerto Rico, Center for Energy and Environment Research — Time Resolved Studies of Ferroelectrics, Scattering and EXAFS of Liquid and Solid Interfaces under Electric Fields.

N. C. Halder, University of Southern Florida, Physics Department — Structure of Amorphous Materials.

J. E. Spruiell, University of Tennessee, Department of Chemical, Metallurgical, and Polymer Engineering — Defect Structures, Polymers.

H. Steinfink, University of Texas at Austin, Chemical Engineering Department — Fast Phase Transformations, Metal Surface Structures.

J. G. Byrne, University of Utah, College of Engineering — Phase Transformations and Cyclic Deformation.

K. Lawless, University of Virginia, Department of Materials Science — Structure of Thin Films, Corrosion Products.

C. R. Hruska, Virginia Polytechnic Institute and State University, Department of Materials Engineering — Metallic Interfaces, Diffusion, Surface Films.

APPENDIX

1. STAFF CHANGES AND GUEST ASSIGNMENTS

From Materials Science Program

B. S. Borie from X-Ray Scattering Research to University of California, Berkeley, April-June 1980.

P. T. Carlson from Kinetics and Mechanisms of Surface and Solid State Reactions to Conservation Program, Engineering Coordination and Evaluation Group.

G. R. Gessel from Radiation Effects to University of Arkansas.

J. M. Leitnaker from Fundamentals of Welding to Oak Ridge Gaseous Diffusion Plant.

J. P. Moore from Physical Properties Research to Institute für Technische Physik, Kernforschungszentrum, Karlsruhe, FRG, September 1978-August 1979.

T. C. Reiley from Radiation Effects to Institute für Festkörperforschung, Kernforschungsanlage, Jülich, FRG, June 1979-June 1980.

R. A. Vandermeer from Physical Metallurgy to Illinois Institute of Technology, January-May 1980.

H. L. Yakel from X-Ray Scattering Research to Stanford Synchrotron Radiation Laboratory, October 1978-September 1979.

N. J. Zaluzec from AEM-HVEM to Argonne National Laboratory.

To Materials Science Program

(See Chap. 7 for visits by members of users groups.)

B. J. Anderson, Augsburg College, to Metastable Materials, Summer 1980.

F. W. Averill, Judson College, to Theory Group, January-December 1980.

R. J. Bayuzick, Vanderbilt University, to AEM-HVEM, May-August 1980.

T. P. Beaulac, State University of New York-Stony Brook, to Theory Group, February-July 1980.

P. L. Becher from Naval Research Laboratory to Structural Ceramics.

R. B. Benson, North Carolina State University, to AEM-HVEM, Summer 1980.

R. Bullough, Theoretical Physics Division, AERE Harwell, England, to Radiation Effects, July 1979.

J. B. Clark, University of Missouri-Rolla, to AEM-HVEM, May-July 1980.

R. J. DeAngelis, University of Kentucky, to X-Ray Research Using Synchrotron Sources, Summer 1979, Summer 1980.

A. T. Fromhold, Auburn University, to Theory Group, January-September 1980.

M. J. Goringe, Oxford University, to AEM-HVEM, Summer 1980.

K. M. Gupta, University of Delaware, to Small-Angle X-Ray Scattering, 1979-1980.

B. Györfy, University of Bristol, to Theory Group, August-September 1979.

R.O.A. Hall, Chemistry Division, AERE, Harwell, England, to Physical Properties Research, September 1978-April 1980.

J. E. Harris, Central Electricity Generating Board, Berkeley, England, to Deformation Studies, June-September 1979.

J. F. Harris, Institut für Festkörperforschung, Kernforschungsanlage, Jülich, FRG, to Theory Group, June 1978-September 1979.

A. Habenschuss from Chemistry Division, ORNL, to ORNL-ORAU Synchrotron Users Group.

M. R. Hayns, Theoretical Physics Division, AERE, Harwell, England, to Radiation Effects, January 1979-April 1980.

L. L. Horton, University of Virginia, to Radiation Effects, January-December 1980.

G. E. Ice from Stanford Synchrotron Radiation Laboratory to X-Ray Research Using Synchrotron Sources.

W. Kesternich, Institute für Festkörperforschung, Kernforschungsanlage, Jülich, FRG, to Radiation Effects, January 1979-January 1980.

P. D. LaBarbe, University of Montpellier, France, to Small-Angle X-Ray Scattering, March-December 1980.

G. L. Lehman from University of Florida, to ORNL-ORAU SHARE Program.

F. R. Lawless, University of Virginia, to AEM-HVEM, May-June 1980.

P. E. Mackie, Georgia Institute of Technology, to X-Ray Research Using Synchrotron Sources, July-September 1979.

R. L. Mills, Ohio State University, to Theory Group, Summer 1979, Summer 1980.

J. Petermann, University of Saarlandes, Saarbrücken, FRG, to Small-Angle X-Ray Scattering, 1979-80.

F. J. Pinski, State University of New York-Stony Brook, to Theory Group, September 1979-August 1980.

J. M. Schultz, University of Delaware, to Small-Angle X-Ray Scattering, January-May 1980.

S. L. Sommers, Virginia Polytechnic Institute, to Structural Ceramics, June-September 1980.

W. Specking, Institute für Technische Physik, Kernforschungszentrum, Karlsruhe, FRG, to Metastable Materials, June 1978-September 1979.

S. Suehiro, University of Massachusetts and Kyoto University, to Small-Angle X-Ray Scattering, April 1979-May 1980.

V. J. Tennery from Ceramics Technology to Structural Ceramics.

J. M. Vitek from Olins Corporation to Fundamentals of Welding.

R. C. Wasielewski, Virginia Polytechnic Institute, to Structural Ceramics, June-September 1979.

P. Young, University of Massachusetts, to Small-Angle X-Ray Scattering, September 1979-May 1980.

2. UNIVERSITY APPOINTMENTS FOR ACADEMIC YEAR 1979-80

B. S. Borie, Professor, Metallurgical Engineering, University of Tennessee; Visiting Professor, University of California, Berkeley, April-June 1980.

R. W. Carpenter, Adjunct Professor, Materials Science and Engineering, Vanderbilt University.

S. A. David, Adjunct Professor, Metallurgy and Materials Engineering, University of Pittsburgh.

A. DasGupta, Adjunct Professor, Department of Metallurgy and Materials Engineering, Lehigh University.

L. A. Harris, Adjunct Assistant Professor, Department of Geological Sciences, University of Tennessee.

S. H. Jury, Professor, Chemical Engineering, University of Tennessee. Part-time Physical Properties Group.

O. C. Kopp, Professor, Geological Sciences, University of Tennessee. Part-time Preparation of High-Temperature Materials.

C. J. McHargue, Professor, Metallurgical Engineering, University of Tennessee.

J. E. Spruiell, Professor, Metallurgical Engineering, University of Tennessee. Part-time Radiation Effects Program.

R. A. Vandermeer, Professor, Metallurgical Engineering, University of Tennessee; Visiting Professor, Illinois Institute of Technology, January-June 1980.

C. L. White, Adjunct Professor, Materials Science and Engineering, Vanderbilt University.

D. W. Yarbrough, Professor, Chemical Engineering, Tennessee Technological University. Physical Properties Group.

3. SCIENTIFIC AND PROFESSIONAL ACTIVITIES

J. Bentley: ORAU Traveling Lecture Program.

B. S. Borie: Professor, Department of Chemical, Metallurgical, and Polymer Engineering, University of Tennessee; Visiting Professor, Department of Materials Science, University of California (Berkeley).

D. N. Braski: ASTM Technical Committee E. 10.04; 1979 McKay-Helm Award from American Welding Society.

R. W. Carpenter: ORAU Traveling Lecture Program; Adjunct Professor, Materials Science and Engineering, Vanderbilt University; TMS-AIME Physical Metallurgy Committee; TMS-AIME Non-Ferrous Metals Committee;

Chairman, Organizing Committee for Workshop on Analytical Electron Microscopy, SEM, Inc., Chicago, Ill., 1980;

Chairman, Steering Committee ORNL/ORAU SHARE Program;
Director, Electron Microscopy Society of American.

- J. V. Cathcart:** TMS-AIME Corrosion Resistant Metals Committee;
Workshop Solar Materials-DOE.
- W. A. Coghlan:** TMS-AIME Mechanical Metallurgy Committee;
ORNL Ph.D. Recruiting Program.
- A. DasGupta:** TMS-AIME Physics and Chemistry of Metals Committee;
Adjunct Professor, Department of Metallurgy and Materials Engineering, Lehigh University.
- S. A. David:** TMS-AIME Solidification Committee;
ASM Joining Council Member;
Adjunct Professor, Department of Metallurgy, University of Pittsburgh;
1979 McKay-Helm Award from American Welding Society.
- D. S. Easton:** TMS-AIME Mechanical Properties Committee;
Task Group, ASTM Physical/Mechanical Properties of Superconductors;
TMS-AIME Composites Committee.
- K. Farrell:** ASTM Technical Committee E. 10.08;
Consultants Symposium, AERE Harwell, England;
Workshop on Hydrogen in Sirling Engines, DOE;
Task Force for Materials Selection for INTOR.
- L. A. Harris:** EMD-AIME Ad Hoc Committee on Quantitative Process Mineralogy;
Adjunct Assistant Professor, Department of Geological Sciences, University of Tennessee;
Co-organizer, Workshop on Structure of Coal.
- R. W. Hendricks:** Associate Director, National Center for Small-Angle Scattering;
Solid State Sciences Panel, National Academy of Sciences;
Commission on Crystallographic Apparatus, International Union of Crystallography;
Apparatus and Standards Committee, American Crystallographic Association;
Membership Committee, Division of High Polymer Physics, American Physical Society;
TMS-AIME Chemistry and Physics of Metals Committee.
- E. A. Kenik:** ASTM Technical Committee E. 10.06, Task Group 4.

- C. C. Koch: TMS-AIME Alloy Phases Committee;
TMS-AIME Non-Ferrous Metals Committee;
Organizer, Surface Alloying of Refractory Metals for
AIME Annual Meeting;
Organizer, Rapidly Solidified Nonferrous Metals for
TMS-AIME Fall Meeting;
Fellow, American Association for the Advancement of
Science.
- O. C. Kopp: Professor, Department of Geological Sciences,
University of Tennessee;
Abstractor for *Mineralogical Abstracts*.
- D. L. McElroy: ASTM Technical Committee C-16;
Secretary of ASTM Subcommittee C. 16.30;
National Laboratory Accreditation Criteria Committee
(Department of Commerce);
Board of Governors, International Thermal Conductivity
Conferences;
Board of Governors, Symposium on Expansion of Solids;
Vice-President, Energy Conservation Society;
Editorial Board, *International Journal of Thermophysics*.
- C. J. McHargue: Professor, Department of Chemical, Metallurgical, and
Polymer Engineering, University of Tennessee;
Secretary, ASM - TMS-AIME Nuclear Metallurgy Committee;
Visiting Committee, Department of Materials Science and
Engineering, University of Kentucky;
International Metals Review Committee, ASM;
Co-organizer, Workshop on Structure of Coal.
- R. A. McKee: Consultant Symposium, AERE Harwell, England.
- L. K. Mansur: ASTM Technical Committee E. 10.08;
ORAU Traveling Lecture Program.
- J. P. Moore: Secretary, ASTM Technical Committee E. 37.05;
Guest Scientist, Institut für Technische Physik,
Kernforschungszentrum, Karlsruhe, FRG;
Thermal Conductivity Award, 1979.
- N. H. Packan: ASTM Technical Committee E. 10.08.
- T. C. Reiley: ASTM Technical Committee E. 10.08;
Program Committee, ANS-MSTD;
ORNL Ph.D. Recruiting Program;
Guest Scientist, Institute für Festkörperforschung,
Kernforschungsanlage, Jülich, FRG.
- C. J. Sparks: Applied Crystallography Special Interest Group,
American Crystallographic Association;

National Synchrotron Light Source Advisory Committee of Users, DOE Brookhaven National Laboratory;
 National Synchrotron Light Source X-Ray Beam Line Committee, DOE and BNL;
 Science Policy Board, Stanford Synchrotron Radiation Laboratories;
 Steering Committee, ORNL-ORAU Synchrotron Users Group.

- J. O. Stiegler: ASTM Technical Committee E. 10.
 Fellow, American Society for Metals.
- R. A. Vandermeer: Professor, Department of Chemical, Metallurgical, and Polymer Engineering, University of Tennessee;
 ORNL Graduate Fellow Selection Panel;
 TMS-AIME Physical Metallurgy Committee;
 Visiting Professor, Illinois Institute of Technology.
- C. L. White: Adjunct Professor, Vanderbilt University;
 TMS-AIME Heat Treating Committee;
 TMS-AIME Mechanical Metallurgy Committee;
 ASM-MSD Program Committee;
 DOE-BES Workshop on Time-Dependent Deformation;
 Steering Committee ORNL-ORAU SHARE Program.
- H. L. Yakel: Guest Scientist, Stanford Synchrotron Radiation Laboratories;
 Fellow, American Association for Advancement of Science;
 Coeditor *Journal of Applied Crystallography*.
- D. W. Yarbrough: ASTM Technical Committee C. 16;
 Professor, Chemical Engineering, Tennessee Technological University.
- M. H. Yoo: Publication Committee, TMS-AIME, *Metallurgical Transactions A*;
 TMS-AIME Mechanical Metallurgy Committee;
 TMS-AIME Physical Metallurgy Committee;
- C. S. Yust: Program Committee, American Ceramics Society;
 ASTM Technical Committee G. 2;
 NACE Technical Practices Committee T-12A;
 National Material Advisory Board Committee on Dynamic Compaction of Ceramic Powders.

4. PRESENTATIONS AT TECHNICAL MEETINGS

Gordon Conference on Corrosion, New London, New Hampshire, July 6-11, 1979.

R. A. McKee,* "Defect Kinetics and the Oxidation of Metals."

US/USSR Breeder Reactor Core Materials Information Exchange Meeting, Hanford Engineering Development Laboratory, Richland, Washington, July 30-31, 1979.

A. F. Rowcliffe,* E. H. Lee, and P. S. Sklad, "Charged Particle Irradiation in the United States Breeder Reactor Program."

American Crystallographic Association Meeting, Boston, Massachusetts, August 12-17, 1979.

J. E. Epperson,* J. Faber, R. W. Hendricks, and J. S. Lin, "Small Angle Scattering Observations of a Decomposing Ni-Al Alloy."

R. W. Hendricks, J. M. Schultz, J. S. Lin,* J. Peterman, and R. M. Gohil, "Annealing of Polypropylene Films Crystallized From a Highly Extended Melt."

R. W. Hendricks, J. S. Lin,* J. M. Schultz, and R. G. Nepler, "Temperature-Dependent Small-Angle X-Ray Scattering from Poly(Vinylidene Fluoride)."

C. J. Sparks, Jr.,* "Applications of Solid State Detectors to X-Ray Scattering Measurements: Background Reduction and Unique Information."

R. W. Hendricks,* "Small-Angle Scattering Observations of a Decomposing Ni-Al Alloy."

37th Annual Meeting of the Electron Microscopy Society of America (EMSA), San Antonio, Texas, August 13-17, 1979.

J. Bentley* and R. W. Carpenter, "The Dependence of Secondary Electron Image Contrast of Periodic Objects Upon Probe Diameter."

D. N. Braski and J. T. Houston,* "Improved Transmission Electron Microscope Specimen for Semiautomatic Jet Polishing."

R. W. Carpenter* and E. A. Kenik, "The Effect of Displacement Cascades on Chemical Order in Ni_4Mo ."

E. A. Kenik,* B. R. Livesay, and R. W. Carpenter, "High Voltage Electron Microscopy Studies of Hydrogen Storage Materials."

*Speaker

E. A. Kenik,* K. R. Lawless, and R. W. Carpenter, "High Voltage Electron Microscopy In-Situ Oxidation Research on Vanadium and Vanadium-Titanium."

D. N. Braski,* R. W. Carpenter, and E. A. Kenik, "Discontinuous Precipitation in Ordered (Fe,Co)₃V Alloys."

Seminar, AERE, Harwell, England, August 16, 1979.

M. H. Yoo,* "The Role of Divacancies in Loop Growth and Void Swelling."

International Cryogenic Materials Conference, Madison, Wisconsin, August 21-24, 1979.

D. S. Easton, W. Specking,* and P. A. Sanger, "Stress Effects in an Nb₃Sn Conductor Proposed for use in the Magnetic Fusion Energy Program."

Fifth International Conference on Strength of Metals and Alloys, Aachen, West Germany, August 27-31, 1979.

M. H. Yoo,* "A Dislocation Model for Twinning and Fracture and Its Application to H.C.P. Metals."

KFA, Jülich, West Germany, September 3, 1979.

M. H. Yoo,* "A Generalized Rate Theory Model of Void Swelling."

Centre D'Études Nucléaires de Saclay, France, September 6, 1979.

M. H. Yoo,* "Growth Kinetic of Dislocation Loops and Voids."

University of Paris-Sud, Centre D'Orsay, France, September 7, 1979.

M. H. Yoo,* "Slip, Twinning, and Fracture in H.C.P. Metals."

Symposium on Rare Gases in Metals and Ionic Solids, AERE, Harwell, England, September 10-14, 1979.

K. Farrell,* "Experimental Observations of Effects of Inert Gases on Cavity Formation."

American Society for Metals, Bluegrass Chapter, Lexington, Ky., September 12, 1979.

S. A. David,* "Solidification Behavior of Austenitic Stainless Steel Filler Metals."

*Speaker

AIME Fall Meeting, Milwaukee, Wisconsin, September 16-20, 1979.

J. D. Holder* and G. W. Clark, "Synthesis of Oxide-Metal Eutectic Composites by Improved Internal Zone Growth and Skull-Melting Techniques."

M. H. Yoo,* "The Competitive Role of Deformation Twinning Against Cleavage Fracture."

J. M. Leitnaker, J. Bentley,* and Said Izadi, "Comparative Rates of Precipitation in Cast and Wrought Structures."

D. S. Easton* and W. Specking, "The Effect of Copper Stabilization on the Strain Behavior of Nb₃Sn Multifilamentary Conductors."

D. M. Kroeger,* D. S. Easton, A. DasGupta, J. O. Scarbrough, and C. C. Koch, "The Effect of Stress upon the Scaling Law for Flux Pinning in Bronze Process Nb₃Sn."

C. C. Koch, A. DasGupta,* D. M. Kroeger, J. O. Scarbrough, "The Peak Effect, Summation Problem, and Magnetic History in a Superconducting Nb-38 at. % Hf Alloy."

A. DasGupta,* "Flux Pinning by Grain and Phase Boundaries."

M. B. Lewis,* "Nondestructive Techniques for the Measurement of Oxygen and Hydrogen Profiles Near Metal Surfaces."

Third Europhysics Topical Conference on Lattice Defects in Ionic Crystals, Canterbury, England, September 17-21, 1979.

R. A. McKee* and A. B. Lidiard, "Kinetics and Thermodynamics of the Migration of Interstitial Defects."

Meeting with USSR Delegation on Inelastic Scattering Research, Oak Ridge National Laboratory, September 19-20, 1979.

L. K. Mansur,* "Summary of Theoretical and Experimental Work at ORNL on Irradiation Creep."

Seminar at Lawrence Livermore Laboratory, Livermore, California, on September 20-21, 1979.

R. A. Vandermeer,* "A Report on Recent Studies of Phase Transformations and Shape Memory Effects (SME) in Uranium-Niobium Alloys."

Seminar for Department of Metallurgy, University of Connecticut, Storrs, Connecticut, September 26, 1979.

A. DasGupta,* "Some Aspects of Flux Pinning by Grain Boundaries and Precipitates in Superconductors."

*Speaker

Midwest Solid State Theory Conference, Columbus, Ohio, October 8-9, 1979.

J. S. Faulkner,* "Calculating Properties With the Coherent Potential Approximation."

Poster Session, American Physical Society, Columbus, Ohio, October 8-9, 1979.

F. J. Pinski,* P. B. Allen, W. H. Butler, and J. S. Faulkner, "Electrical and Thermal Resistivities: Solutions to the Boltzmann Equation for Electrons in Metals."

American Ceramic Society Fall Meeting, New Orleans, Louisiana, October 14-17, 1979.

P. Angelini,* R. W. Carpenter, and D. P. Stinton, "High Resolution Analytical Electron Microscopic Analysis of Synroc Nuclear Waste Storage Material."

C. L. Hoenig* and C. S. Yust, "Explosive Compaction and Microstructural Analysis of AlN, Amorphous Si₃N₄, Boron, and Al₂O₃ Ceramics."

Appalachian Regional Electron Microscopy Society Fall Meeting, East Tennessee State University, Johnson City, October 19, 1979.

J. Bentley,* "Analytical Electron Microscopy."

University of Tennessee, Knoxville, October 23, 1979.

W. A. Coghlan,* "A Collection of Technical Highlights from Visits to Laboratories in France, Germany, and Poland."

Seminar at College of Engineering, Vanderbilt University, Nashville, Tennessee, October 24, 1979.

R. W. Carpenter,* "Analytical Electron Microscopy and Modern Materials Science Research."

Geological Society of America National Meeting, San Diego, California, November 5-8, 1979.

H. E. Barrett, O. C. Kopp,* and L. A. Harris, "A Study of Elemental and Maceral Distribution in Coals of Different Paleoenvironments."

16th International Thermal Conductivity Conference, Chicago, Illinois, November 7-9, 1979.

R. S. Graves, R. K. Williams, and J. P. Moore,* "The Thermal Conductivity, Electrical Resistivity and Seebeck Coefficient of Standard Reference Material 735."

*Speaker

D. L. McElroy,* R. K. Williams, F. J. Weaver, and R. S. Graves, "The Physical Properties of $V(Fe,Co,Ni)_3$ Alloys from 300 to 1000 K."

D. W. Yarbrough,* R. K. Williams, and R. S. Graves, "Transport Properties of Concentrated Ag-Pd and Cu-Ni Alloys from 300 to 1000 K."

American Nuclear Society Winter Meeting, San Francisco, November 11-19, 1979.

N. H. Packan* and K. Farrell, "On the Validity of Helium Preinjection in Radiation Damage Simulation."

24th Annual Conference on Magnetism and Magnetic Materials, Cleveland, Ohio, November 14-18, 1979.

W. C. Koehler and R. W. Hendricks,* "The United States National Small-Angle Neutron Scattering Facility."

Materials Engineering Graduate Seminar, VPI, Blacksburg, Virginia, November 15, 1979.

J. D. Holder,* "Preparation of High-Temperature Oxide-Metal Eutectic Composites: A Review."

ORAU Visiting Lecture Program, North Carolina State University, November 20, 1979.

J. Bentley,* "Analytical Electron Microscopy."

Colloquium Series, Case Western Reserve University, Cleveland, Ohio, November 20, 1979.

R. W. Carpenter,* "Convergent Beam Diffraction: Applications and Instrumentation."

Second Japanese Institute of Metals International Symposium on Hydrogen in Metals, Minakami Spa, Japan, November 26-29, 1979.

E. A. Kenik* and B. R. Livesay, "In-Situ Hydriding of Hydrogen Storage Mater 3."

Materials Research Society Meeting, Boston, Massachusetts, November 26-30, 1979.

L. A. Boatner,* G. W. Beall, M. M. Abraham, C. B. Finch, P. G. Huray, and M. Rappaz, "Monazite and Other Lanthanide Orthophosphates as Alternate Actinide Waste Forms."

L. A. Harris and C. S. Yust,* "Transmission Electron Microscopic Characterization of Coals."

*Speaker

D. M. Kroeger,* C. C. Koch, D. S. Easton, and J. O. Scarbrough, "A Study of Arc-Hammer Speeds and Critical Cooling Rates in Amorphous Transition Metal Alloys."

C. C. Koch,* B. C. Giessen, D. M. Kroeger, and J. O. Scarbrough, "Superconductivity in Amorphous Equi-Electronic Transition Metal Alloys."

Seminar at Stanford University, Stanford, California, November 28, 1979.

W. A. Coghlan,* "Growth of Interstitial Loops Under HVE₁ Irradiation."

Seminar at Vanderbilt University, Nashville, Tennessee, December 5, 1979.

J. Bentley,* "Electron Diffraction Techniques in an Analytical Electron Microscope."

ORAU Visiting Lecture Program, University of Kentucky, January 16, 1980.

J. Bentley,* "Analytical Electron Microscopy."

ASM Seminar, Oak Ridge, Tennessee, January 17, 1980.

R. W. Carpenter,* "Analytical Electron Microscopy Techniques and Developments."

Centro Informazion Studi Esperienze (CISE), Milan, Italy, January 21, 1980 and JRC-Ispira, Verese, Italy, January 23, 1980.

T. C. Reiley,* "Irradiation Creep Using Light Ions — Experimental Procedures and Mechanistic Studies."

Seminar, Rockwell Science Center, Thousand Oaks, California, February 18, 1980.

R. W. Carpenter,* "Analytical Electron Microscopy: Electron Energy Loss Spectroscopy and Convergent Beam Diffraction for Phase Identification."

AIME Annual Meeting, Las Vegas, Nevada, February 24-28, 1980.

L. A. Harris* and C. S. Yust, "A Review of Advanced Coal Petrographic Methods in Characterizing and Assessing Coals for Utilization."

W. A. Coghlan,* "The Effect of Applied Stress on the Sink Efficiency of Finite Frank Loops."

R. A. Vandermeer* and J. C. Ogle, "The Kinetics of Void Annealing in Neutron Irradiated Aluminum."

*Speaker

R. W. Carpenter,* "Applications of Microdiffraction to Phase Transformation Research and Lattice Defect Identification in Solids."

N. J. Zaluzec* and R. W. Carpenter, "Light Element Analysis in Structural Alloys and Ceramics by Electron Energy Loss Spectroscopy."

S. A. David* and D. N. Braski, "Solidification Behavior of Austenitic Stainless Steel Filler Metal."

J. Bentley,* "Analytical Electron Microscopy Using a Field Emission Gun."

J. S. Lin,* R. W. Hendricks, J. Bentley, and F. W. Wiffen, "Small-Angle X-Ray Scattering Study on Neutron-Irradiation Effects in Molybdenum and Molybdenum Alloys."

G. R. Gessel* and C. L. White, "Use of Auger Electron Spectroscopy and Residual Gas Analysis to Study Neutron-Irradiation-Enhanced Segregation to Internal Surfaces."

R. W. Hendricks,* "The Use of Small-Angle X-Ray and Neutron Scattering for Characterizing Voids in Neutron-Irradiated Metals and Alloys."

M. B. Lewis* and K. Farrell, "Nuclear Microanalysis as a Probe of Impurity-Defect Interactions."

E. A. Kenik,* K. A. Lawless, and R. W. Carpenter, "Low Pressure in Situ Oxidation of Vanadium and V-20% Ti."

DOE Workshop on Heat Transfer Properties for General Purpose Heat Source Design, Germantown, Maryland, March 5, 1980.

R. K. Williams* and R. S. Graves, "Vacuum Contact Conductance Measurements on Interfaces Between Fine-Weave Pierced Fabric" (a graphite fiber composite).

Metallurgical and Materials Engineering Department, Illinois Institute of Technology, Seminar, Chicago, Illinois, March 6, 1980.

R. A. Vandermeer,* "The Kinetics of Void Annealing in Neutron-Irradiated Aluminum."

Seminar University of Virginia, Charlottesville, Virginia, March 17, 1980.

R. W. Carpenter,* "High-Resolution Electron Diffraction Methods in Analytical Electron Microscopy."

*Speaker

American Crystallographic Association Winter Meeting, Gulf Shores, Alabama, March 17-21, 1980.

R. W. Hendricks* and W. C. Koehler, "The National Center for Small-Angle Scattering Research."

American Physical Society, New York, March 24-28, 1980.

A. Goris and G. M. Stocks,* "Total and Component Densities of States in the KKR-CPA† and Average t-Matrix Approximation."

G. M. Stocks* and B. L. Györfy, "Momentum Distribution of Electrons in Random Alloys: The Fermi Surface of $\text{Ag}_c\text{Pd}_{(1-c)}$ Alloys."

J. S. Faulkner* and G. M. Stocks, "New Formulas for Calculating Properties with the KKR-CPA†: Algebraical."

G. M. Stocks* and J. S. Faulkner, "New Formulas for Calculating Properties with the KKR-CPA†: Numerical."

L. A. Boatner,* G. W. Beall, M. M. Abraham, C. B. Finch, P. G. Huray, and M. Rappaz, "The Growth and Characterization of Actinide-Doped Lanthanide Orthophosphate Single Crystals."

S. Suehiro* and R. W. Hendricks, "Dynamic Deformation Device for Small-Angle X-Ray and Neutron Scattering."

R. W. Hendricks and W. C. Koehler,* "The National Center for Small-Angle Scattering Research - A Progress Report."

R. A. McKee,* "Phenomenological Coefficients for Interstitial Diffusion in a Dilute, Two-Component System."

D. M. Kroeger,* D. S. Easton, C. C. Koch, A. DasGupta, and J. O. Scarbrough, "Evidence for Microstructural Changes Under Strain in Bronze Process Nb_3Sn ."

F. J. Pinski,* "Solutions to the Boltzmann Equation for Electrons in a Metal: Energy Dependence."

T. P. Beaulac,* P. B. Allen, and F. J. Pinski, "Calculation of the Low-Field Hall Coefficient in Cu and Nb."

F. J. Pinski, V. S. Kahn, and W. H. Butler,* "Calculation of the Anisotropic Electron-Phonon Mass Enhancement in Cu and Nb."

W. H. Butler,* "Upper Critical Field of Pure Nb: Calculated Temperature Dependence and Anisotropy."

*Speaker

†Korringa-Kohn-Rostoker coherent-potential approximation.

G. M. Stocks* and W. H. Butler, "Residual Resistivity of AgPd Alloys."

A. DasGupta,* D. M. Kroeger, C. C. Koch, and Y. T. Chou, "Flux Pinning by Grain Boundaries in Niobium Bicrystals can be Treated by the First Order Perturbation of Ginzburg-Landau Free Energy."

J. M. Schultz,* J. S. Lin, R. W. Hendricks, J. Petermann, and R. M. Gohil, "Annealing of Polypropylene Films Crystallized from a Highly Extended Melt."

Geological Society of America, Southeastern Division Conference, Birmingham, Alabama, March 27-29, 1980.

O. C. Kopp* and C. B. Finch, "Crystal Growth and Stability of Fayalite (Fe_2SiO_4) Under Controlled $f(\text{O}_2)$ Conditions."

BES/DMS (DOE) Meeting on Coal Structures and Properties, Gatlinburg, Tennessee, April 8-10, 1980.

L. A. Harris and C. S. Yust*, "Transmission Electron Microscopy of Coal."

Seminar, College of Engineering, University of Houston, Houston, Texas, April 10, 1980.

R. W. McClung,* "Current Activities in Nondestructive Testing at ORNL."

Invited talk, American Physical Society, Cornell University, Ithaca, New York, April 11-12, 1980.

C. J. Sparks, Jr.,* "Synchrotron Radiation Sources: Novel Optics and Changed Research Style."

Dynamic Compaction of Metal and Ceramic Powders Committee Meeting, Washington, D.C., April 14, 1980.

C. S. Yust* and L. A. Harris, "Electron Microscope Observations of Explosively Compacted Ceramics."

American Welding Society Annual Meeting, Los Angeles, California, April 14-18, 1980.

L. B. Spiegel and S. A. David,* "Microstructural Study of Laser Beam Welds in Single-Phase Alloys."

Seminar at Max-Planck Institute, Stuttgart, West Germany, April 21, 1980.

J. D. Holder,* "Synthesis of Oxide-Metal Eutectic Composites."

*Speaker

Seminars at Degussa Institute, Frankfurt, West Germany, April 22, 1980; Siemens Research Institute, Erlangen, West Germany, April 23, 1980; and Giesserei, West Germany, April 25, 1980.

J. D. Holder,* "Synthesis and Electronic Applications of Oxide-Metal Eutectic Composites."

Seminar at Laboratory for Physical Chemistry, Eindhoven University, Netherlands, April 28, 1980.

J. D. Holder,* "Synthesis of Oxide-Metal Eutectic Composites."

American Ceramic Society, Chicago, Illinois, April 28-30, 1980.

C. S. Yust* and L. A. Harris, "Transmission Electron Microscopic Analysis of Explosively Compacted Alumina."

P. S. Sklad,* R. W. Carpenter, N. J. Zaluzec, and J. E. Selle, "Phase Identification in $\text{Si}_3\text{N}_4/\text{MgO}$ and $\text{Si}_3\text{N}_4/\text{Y}_2\text{O}_3$ Compacts by Convergent-Beam Diffraction and Energy Loss Spectroscopy."

P. Angelini, D. P. Stinton, R. W. Carpenter, J. S. Vavruska, and W. J. Lackey,* "Phase Identification and Partitioning of Elements in Sol-Gel-Derived Synroc."

KFK-Karlsruhe, West Germany, April 29, 1980.

T. C. Reiley,* "Recent Experiments in Irradiation Creep Using Light Ions."

Seminar at Michigan Technological University, Houghton, Michigan, May 2-6, 1980.

C. L. White,* "Grain Boundary Segregation and Fracture in Noble Metal Alloys."

Electrochemical Society, St. Louis, Missouri, May 11-16, 1980.

R. E. Pawel* and J. J. Campbell, "Some Experiments and Calculations Regarding the Effect of Specimen Dimensions and Oxygen Solubility on Oxidation Kinetics."

Impromptu presentation at meeting of USA-INTOR Group, University of Wisconsin, May 13, 1980 (INTOR = International Tokamak Reactor).

K. Farrell,* "Neutron Damage Response of Aluminum Alloys in INTOR."

First International Al-Li Conference, Stone Mountain, Georgia, May 19-21, 1980.

C. L. White,* "Grain Boundary Segregation and Intergranular Failure."

*Speaker

International Cryogenics Materials Conference, Brookhaven National Laboratory, May 28-29, 1980.

D. S. Easton,* D. M. Kroeger, and C. C. Koch, "Superconducting and Mechanical Properties of Nb₃Sn Conductors Under Tensile Stress."

D. M. Kroeger,* D. S. Easton, C. C. Koch, and A. DasGupta, "Evidence for Microstructural Change Under Strain in Bronze-Process Nb₃Sn."

International Symposium on Management of Alpha-Contaminated Wastes, Vienna, Austria, June 2-6, 1980, sponsored by International Atomic Energy Agency.

L. A. Boatner,* G. W. Beall, M. M. Abram, C. B. Finch, P. G. Huray, and M. Rappaz, "Lanthanide Orthophosphates for the Primary Immobilization of Actinide Wastes."

Tenth International Symposium on Effects of Radiation in Materials (ASTM), Savannah, Georgia, June 3-5, 1980.

K. Farrell,* "Microstructure and Tensile Properties of Heavily Irradiated 5052-0 Aluminum Alloy."

M. R. Hayns and L. K. Mansur,* "Applications of the Theory of Cavity Growth to Dual-Ion Swelling Experiments."

Sixth International Conference on Vacuum Ultraviolet Spectroscopy, University of Virginia, Charlottesville, Virginia, June 4, 1980.

T. A. Callcott,* J. A. Tagle, E. T. Arakawa, and G. M. Stocks, "Soft X-Ray Emission from Li-Mg and Li-Al Alloys and Comparisons with KKR-CPA† Calculations."

Second International Symposium on Ultrasonic Materials Characterization, National Bureau of Standards, Gaithersburg, Maryland, June 4-6, 1980.

S. Golan, L. Adler, K. V. Cook,* and D. Chwirut, "Ultrasonic Diffraction Technique for Characterization of Fatigue Cracks."

AERE, Harwell, Abingdon, England, June 5, 1980.

T. C. Reiley, "Irradiation Creep Using Light Ions."

National Synchrotron Light Source User's Meeting, Brookhaven National Laboratory, Upton, New York, June 9, 1980.

C. J. Sparks, Jr.,* "Oak Ridge Synchrotron Consortium of Radiation Experiments - X Rays."

*Speaker

†Korringa-Kohn-Rostoker coherent-potential approximation.

C. J. Sparks, Jr.,* "Some Things About X-ray Optics for Synchrotron Radiation: August 1979 Report."

BES Workshop on Nondestructive Evaluation, Los Alamos Scientific Laboratory, June 17-20, 1980.

C. V. Dodd,* "Long-Range Research Needs for Eddy-Current Testing."

International Conference on Metallurgical Effects of High Strain-Rate Deformation and Fabrication, Albuquerque, New Mexico, June 22-26, 1980.

C. S. Yust* and L. A. Harris, "Observation of Dislocations and Twins in Explosively Compacted Alumina."

International Conference on Dislocation Modeling of Physical Systems, Gainesville, Florida, June 22-27, 1980.

W. A. Coghlan* and M. H. Yoo, "Applications of Theoretical Point Defect-Dislocation Interactions to Physical Problems."

Seventh European Thermophysical Properties Conference, Antwerp, Belgium, June 30-July 4, 1980.

J. P. Moore,* R. S. Graves, and R. K. Williams, "Thermal Transport Properties of Niobium and Some Niobium Base Alloys from 80 to 1600 K."

*Speaker

5. PUBLICATIONS

J. Bentley, "Advantages of a Field Emission Gun for a Combined Analytical and High Resolution Transmission Electron Microscope," pp. 72-73 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claiborne's Publishing Division, Baton Rouge, Louisiana, 1980.

J. Bentley and R. W. Carpenter, "The Dependence of Secondary Electron Image Contrast of Periodic Objects Upon Probe Diameter," pp. 566-67 in *37th Annu. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claiborne's Publishing Division, Baton Rouge, Louisiana, 1979.

J. Bentley and J. M. Leitnaker, "Stable Phases in Aged Type 321 Stainless Steel," pp. 70-91 in *The Metal Science of Stainless Steel*, ed. by E. W. Collins and H. W. King, The Metallurgy Society of AIME, New York, 1979.

J. Bentley, L. L. Horton, and K. Farrell, "Defect Structures in Neutron-Irradiated Iron," pp. 390-91 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claiborne's Publishing Division, Baton Rouge, Louisiana, 1980.

D. N. Braski, H. Schroeder, and H. Ullmaier, "The Effect of Tensile Stress on the Growth of Helium Bubbles in an Austenitic Stainless Steel," *J. Nucl. Mater.* 83(2): 265-77 (September 1979).

R. W. Carpenter and J. Bentley "On the Performance of a Field Emission Gun TEM/STEM," pp. 153-60 in *Proc. Scanning Electron Microscopy, Washington, D.C., April 16-20, 1979*, Scanning Electron Microscopy, Inc., AMF O'Hare, Illinois, 1979.

R. W. Carpenter and D. N. Braski, "Heterogeneous Precipitation of MC 'Carbides' on Extrinsic Stacking Faults in V-Co-Fe Ordered Alloys," pp. 648-49 in *37th Annu. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claiborne's Publishing Division, Baton Rouge, Louisiana, 1979.

R. W. Carpenter and E. A. Kenik, "In-Situ Radiation Response of Nickel-Molybdenum Alloys in an HVEM," pp. 577-80 in *High Voltage Electron Microscopy 1977*, Vol. 22, ed. by T. Imura and H. P. Hashimoto, Japanese Society of Electron Microscopy, Kyoto, Japan, 1977.

R. W. Carpenter and E. A. Kenik, "The Effect of Displacement Cascades on Chemical Order in Ni_3Mo ," pp. 654-55 in *37th Annu. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claiborne's Publishing Division, Baton Rouge, Louisiana, 1979.

R. W. Carpenter, J. J. Wert, and S. G. Caldwell, "Metal Surface Deformation and Subsurface Defect Structure: A Microscopy Correlation Study," pp. 140-41 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claiborne's Publishing Division, Baton Rouge, Louisiana, 1980.

J. V. Cathcart, R. A. Perkins, J. B. Bates, and L. C. Manley, "Tritium Diffusion in Rutile (TiO_2)," *J. Appl. Phys.* 50(6): 4110-19 (June 1979).

J. V. Cathcart and R. E. Pawel, "The Mechanical Behavior of Oxide Scales," pp. 300-29 in *Proc. Corros./Erosion Coal Convers. Syst. Mater. Conf.*, ed. by A. V. Levy, National Association of Corrosion Engineers, Houston, Texas, 1979.

S. A. David and G. M. Goodwin, "Solidification Behavior of Type 308 Stainless Steel Filler Metal," pp. 19-28 in *Weldments: Physical Metallurgy and Failure Phenomena*, ed. by R. J. Christoffel, E. F. Nippes, and H. D. Solomon, General Electric Company, Schenectady, New York, 1979.

S. A. David, G. M. Goodwin, and D. N. Braski, *Solidification Behavior of Austenitic Stainless Steel Filler Metals*, ORNL/TM-7116 (February 1980).

S. A. David, G. M. Goodwin, and D. N. Braski, "Solidification Behavior of Austenitic Stainless Steel Filler Metals," *Weld. J. (Miami)* 59(11): 330-s-336-s (November 1979).

P. J. Durham, D. Chaleb, B. L. Györfy, C. F. Hague, J.-M. Mariot, G. M. Stocks, and W. M. Temmerman, "Soft X-Ray Emission and the Local Densities of States in Cu-Ni Alloys," *J. Phys. F.: Metal Phys.* 9(8): 1719-30 (August 1979).

D. S. Easton, D. M. Kroeger, W. Specking, and C. C. Koch, "A Prediction of the Stress State in Nb_3Sn Superconducting Composites," *J. Appl. Phys.* 51(5): 2748-57 (May 1980).

K. Farrell, *Experimental Observations of Effects of Inert Gas on Cavity Formation During Irradiation*, ORNL/TM-7193 (April 1980).

K. Farrell and J. T. Houston, "Suppression of Radiation Damage Microstructure in Aluminum by Trace Impurities," *J. Nucl. Mater.* 83(1): 57-66 (August 1979).

K. Farrell and R. T. King, "Tensile Properties of Neutron-Irradiated 6061 Aluminum Alloy in Annealed and Precipitation-Hardened Conditions," pp. 440-49 in *Effects of Radiation on Structural Materials*, ASTM Spec. Tech. Publ. 683, J. A. Sprague and D. Kramer, eds., American Society for Testing and Materials, Philadelphia, 1979.

K. Farrell and N. H. Packan, "A Helium-Induced Shift in the Temperature Dependence of Swelling," *J. Nucl. Mater.* 85 & 86(II,B): 683-87 (December 1979).

K. Farrell and A. E. Richt, "Microstructure and Tensile Properties of Heavily Irradiated 1100-0 Aluminum," pp. 427-39 in *Effects of Radiation on Structural Materials*, ASTM Spec. Tech. Publ. 683, J. A. Sprague and D. Kramer, eds., American Society for Testing and Materials, Philadelphia, 1979.

J. S. Faulkner, "Multiple-Scattering Approach to Band Theory," *Phys. Rev. B* 19(12): 6186-6206 (June 1979).

J. S. Faulkner and G. M. Stocks, "Calculating Properties with the Coherent-Potential Approximation," *Phys. Rev. B* 21(8): 3222-44 (April 1980).

C. B. Finch, G. W. Clark, and O. C. Kopp, "Czochralski Growth of Single-Crystal Fayalite Under Controlled Oxygen Fugacity Conditions," *Am. Mineral.* 65(3-4): 381-89 (March-April 1980).

R. W. Gilbert, K. Farrell, and C. E. Coleman, "Damage Structure in Zirconium Alloys Irradiated at 573 to 923 K," *J. Nucl. Mater.* 84(1): 137-48 (October 1979).

B. L. Györfy and G. M. Stocks, "First Principles Band Theory for Random Metallic Alloys," pp. 89-192 in *Electrons in Disordered Metals and at Metallic Surfaces*, ed. by P. Phariseau, B. L. Györfy, and L. Scheire, Plenum Press, New York, 1979.

H. R. Haines, R.O.A. Hall, J. A. Lee, M. J. Mortimer, and D. L. McElroy, "The Low Temperature Specific Heats of Three Plutonium Carbides," *J. Nucl. Mater.* 88(2 & 3): 261-64 (February 1980).

J. Harris, "The Role of Occupation Numbers in HKS-Theory," *Int. J. Quantum Chem. Quantum Chem. Symp.* 13: 189-93 (1979).

L. A. Harris, O. B. Cavin, R. S. Crouse, and C. S. Yust, "Scanning Electron Microscopical Observations and Energy Dispersive X-Ray Analysis of Secondary Mineralization in a Bituminous Coal," *Microsc. Acta* 82(4): 343-49 (January 1980).

L. A. Harris and C. S. Yust, "Transmission IR Microscopy (750-1200 nm) of Semicoke," *Carbon* 17(3): 307 (1979).

R. W. Hendricks, *The ORNL 10-m Small-Angle X-Ray Scattering Camera*, 1. Overview, ORNL/TM-6342 (December 1979).

R. W. Hendricks, P. A. Seeger, J. W. Scheer, and S. Suehiro, *The LASL-ORNL Fast Digital Data Acquisition System*, ORNL/TM-7325, LASL-8260-MS (June 1980).

J. D. Holder and G. W. Clark, "New Developments in the IZC of Metal Oxide-Metal Eutectic Composites," pp. 195-207 in *Conference on In Situ Composites-III*, ed. by J. L. Walter, M. F. Gigliotti, B. F. Oliver, and H. Bibring, Ginn Custom Publishing, Lexington, Massachusetts, 1979.

J. D. Holder, G. W. Clark, and B. F. Oliver, "Oxygen Partial Pressure: A Key to Alloying and Discovery in Metal Oxide-Metal Eutectic Systems," pp. 351-56 in *Conference on In Situ Composites-III*, ed. by J. L. Walter, M. F. Gigliotti, B. F. Oliver, and H. Bibring, Ginn Custom Publishing, Lexington, Mass., 1979.

A. Jostsons, P. M. Kelly, R. G. Blake, and K. Farrell, "Neutron Irradiation-Induced Defect Structures in Zirconium," pp. 46-61 in *Effects of Radiation on Structural Materials*, ASTM Spec. Tech. Publ. 683, J. A. Sprague and D. Kramer, eds., American Society for Testing and Materials, Philadelphia, 1979.

E. A. Kenik, "The Influence of Helium on Microstructural Evolution in an Ion-Irradiated Low-Swelling Stainless Steel," *J. Nucl. Mater.* 85 & 86(II,B): 659-63 (December 1979).

E. A. Kenik, K. R. Lawless, and R. W. Carpenter, "High Voltage Electron Microscope In-Situ Oxidation Research on Vanadium and Vanadium-Titanium," pp. 428-429 in *37th Annu. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claitor's Publishing Division, Baton Rouge, Louisiana, 1979.

E. A. Kenik, B. R. Livesay, and R. W. Carpenter, "High Voltage Electron Microscope Studies of Hydrogen Storage Materials," pp. 430-31 in *37th Ann. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claitor's Publishing Division, Baton Rouge, Louisiana., 1979.

E. A. Kenik, J. Mullins, S. Spooner, and B. R. Livesay, "HVEM In Situ Hydriding of Hydrogen Storage Materials," *Trans. Jpn. Inst. Met. Suppl.* 21: 321-24 (1980).

C. C. Koch, "Technetium," pp. 804-06 in *Metals Handbook, Ninth Edition, Volume 2, Properties and Selection: Nonferrous Alloys and Pure Metals*, American Society for Metals, Metals Park, Ohio, 1979.

C. C. Koch, A. DasGupta, D. M. Kroeger, and J. O. Scarbrough, "The Peak Effect, Summation Problem, and Magnetic History in a Superconducting Nb-38 at. % Hf Alloy," *Philos. Mag.* 40(5): 361-87 (November 1979).

D. M. Kroeger, D. S. Easton, A. DasGupta, C. C. Koch, and J. O. Scarbrough, "The Effect of Strain Upon the Scaling Law for Flux Pinning in Bronze Process Nb₃Sn," *J. Appl. Phys.* 51(4): 2184-92 (April 1980).

E. H. Lee, L. K. Mansur, and M. H. Yoo, "Spatial Variation in Void Volume During Charged Particle Bombardment - The Effects of Injected Interstitials," *J. Nucl. Mater.* 85 & 86(II,A): 577-81 (December 1979).

E. H. Lee, A. F. Rowcliffe, and E. A. Kenik, "Effects of Silicon and Titanium on Swelling of AISI 316 Stainless Steel," *J. Nucl. Mater.* 83(1): 79-89 (August 1979).

M. B. Lewis, "A Method for Simulating Fusion Reactor Radiation Damage Using Triple Ion Beams," *IEEE Trans. Nucl. Sci.* 26(1): 1320-22 (February 1979).

M. B. Lewis, "Deuterium Migration and Trapping in Uranium and Uranium Dioxide During D⁺ Implantation," *J. Nucl. Mater.* 88(1): 23-30 (1980).

M. B. Lewis and K. Farrell, "An Ion Beam Technique for the Measurement of Deuterium Diffusion Coefficients," *Appl. Phys. Lett.* 36(10): 819-21 (May 1980).

M. B. Lewis, N. H. Packan, G. F. Wells, and R. A. Buhl, "Improved Techniques for Heavy-Ion Simulation of Neutron Radiation Damage," *Nucl. Instrum. Methods* 167(2): 233-47 (December 1979).

M. B. Lewis and R. A. Perkins, "The Use of Nuclear Reactions to Trace the Source of Oxygen in Anodization," *IEEE Trans. Nucl. Sci.* 26(1): 1818-20 (February 1979).

E. L. Long, Jr., P. Krautwasser, R. L. Beatty, M. J. Kania, C. S. Morgan, Jr., and C. S. Yust, *Characterization and Irradiation Performance of HTGR Biso-Coated Fertile Particles in HFIR Experiments 4T-28, -29, and -30*, ORNL/TM-7298 (July 1980).

L. K. Mansur, W. A. Coghlan, and A. D. Brailsford, "Swelling with Inhomogeneous Point Defect Production - A Cascade Diffusion Theory," *J. Nucl. Mater.* 85 & 86(II,A): 591-95 (December 1979).

L. K. Mansur, "Effects of Point Defect Trapping and Solute Segregation on Irradiation-Induced Swelling and Creep," *J. Nucl. Mater.* 83(1): 109-27 (August 1979).

L. K. Mansur, *Effective Diffusion Coefficients of Point Defects in Impure Materials*, ORNL/TM-7247 (March 1980).

L. K. Mansur and W. G. Wolfer, "Reduction of Irradiation-Induced Creep by Point-Defect Trapping," pp. 624-39 in *Effects of Radiation on Structural Materials*, ASTM Spec. Tech. Publ. 683, J. A. Sprague and D. Kramer, eds., American Society for Testing and Materials, Philadelphia, 1979.

L. K. Mansur and M. H. Yoo, "Advances in the Theory of Swelling in Irradiated Metals and Alloys," *J. Nucl. Mater.* 85 & 86(II,A): 523-32 (December 1979).

P. J. Maziasz and K. Farrell, "The Tensile Properties of High Oxide SAP Containing Helium and Tritium," *J. Nucl. Mater.* 85 & 86(II,B): 913-17 (December 1979).

P. J. Maziasz and R. W. Carpenter, "MC Precipitate Characterization in Austenitic Stainless Steel," pp. 384-85 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claitor's Publishing Division, Baton Rouge, Louisiana, 1980.

M. J. McCready, J. M. Schultz, J. S. Lin, and R. W. Hendricks, "Effect of Crystallization Time on the Properties of Melt-Crystallized Linear Polyethylene," *J. Polym. Sci.: Polym. Phys. Ed.* 17: 725-40 (1979).

D. L. McElroy, "Insulation," pp. 230-31 in *World Book Encyclopedia*, Vol. 10, World Book-Childcraft International, Chicago, 1979.

C. J. McHargue, *Metals and Ceramics Division Materials Science Program Ann. Prog. Rep. for Period Ending June 30, 1979*, ORNL-5589.

J. P. Moore, D. L. McElroy, and S. H. Jury, *A Technique for Measuring the Apparent Thermal Conductivity of Flat Insulations*, ORNL/TM-6494 (October 1979).

J. P. Moore and R. S. Graves, "The Etingshausen-Nernst Coefficient and Transport Properties of Alumel from 200 to 473 K," *J. Phys. Chem. Solids* 41(2): 129-33 (1980).

C. W. Nestor, Jr., C. V. Dodd, and W. E. Deeds, *Analysis and Computer Programs for Eddy Current Coils Concentric with Multiple Cylindrical Conductors*, ORNL-5220 (July 1979).

A. L. Olins, E. Wilkinson-Singley, J. Bentley, D. E. Olins, "Stereo-Electron Microscopy and Energy-Dispersive X-Ray Analysis of Avian Reticulocytes," *Eur. J. Cell Biol.* 19: 239-49 (1979).

N. H. Packan and K. Farrell, "Simulation of First Wall Damage: Effects of the Method of Gas Implantation," *J. Nucl. Mater.* 85 & 86(11,8): 677-81 (December 1979).

N. H. Packan and R. A. Buhl, *A Multispecimen Dual-Beam Irradiation Damage Chamber*, ORNL/TM-7276 (June 1980).

R. E. Pawel, "Oxygen Diffusion in the Oxide and Alpha Phases During Reaction of Zircaloy-4 with Steam from 1000 to 1500°C," *J. Electrochem. Soc.* 126(7): 1111-18 (July 1979).

R. E. Pawel, J. V. Cathcart, and R. A. McKee, "'Anomalous' Oxide Growth During Transient-Temperature Oxidation of Zircaloy-4," *Oxid. Met.* 14(1): 1-13 (1980).

R. E. Pawel, J. V. Cathcart, and R. A. McKee, "The Kinetics of Oxidation of Zircaloy-4 in Steam at High Temperatures," *J. Electrochem. Soc.* 126(7): 1105-11 (July 1979).

F. J. Pinski and W. H. Butler, "Calculated Electron-Phonon Contributions to Phonon Linewidths and to the Electronic Mass Enhancement of Pd," *Phys. Rev. B* 19(12): 6010-15 (June 1979).

D. W. Schaefer and R. W. Hendricks, "Static Correlations in Semidilute Polymer Solutions," *Polym. Prepr. Amer. Chem. Soc. Div. Polym. Chem.* 20: 891 (1979).

P. S. Sklad, "Observations of Gas Bubbles in an Austenitic Stainless Steel Charged with ^3H ," pp. 388-89 in *38th Annu. Proc. Electron Microscopy Soc. Am.*, ed. by G. W. Bailey, Claitor's Publishing Division, Baton Rouge, Louisiana, 1980.

J. O. Stiegler and L. K. Mansur, "Radiation Effects in Structural Materials," pp. 405-53 in *Annual Review of Materials Science*, Vol. 9, ed. by R. A. Huggins, R. H. Bube, and D. A. Vermilyea, Annual Reviews Inc., Palo Alto, California, 1979.

R. H. Stinson, M. W. Bartlett, Teorin Kurg, P. R. Sweeny, and R. W. Hendricks, "Experimental Confirmation of Calculated Phases and Electron Density Profile for Wet Native Collagen," *Biophys. J.* 26: 209-22 (May 1979).

G. M. Stocks, W. M. Temmerman, and B. L. Györfy, "Aspects of the Numerical Solution of the KKR-CPA Equations," pp. 193-221 in *Electrons in Disordered Metals and at Metallic Surfaces*, ed. by P. Phariseau, B. L. Györfy, and L. Scheire, Plenum Press, New York, 1979.

G. W. Turner and R. W. Hendricks, *An Intelligent CAMAC I/O Module Based on the Signetics 8X300 Microcontroller*, ORNL/TM-6922 (September 1979).

G. W. Turner and R. W. Hendricks, "An Intelligent CAMAC I/O Module Based on the Signetics 8X300 Microcontroller," *Nucl. Instrum. Methods* 169(3): 373-80 (March 1980).

R. A. Vandermeer, "Phase Transformations in a Uranium + 14 at.% Niobium Alloy," *Acta Metall.* 28(3): 383-93 (March 1980).

R. A. Vandermeer and W. B. Snyder, Jr., "Recovery and Recrystallization in Rolled Tantalum Single Crystals," *Metall. Trans.* 10A(8): 1031-44 (August 1979).

R. A. Vandermeer and J. C. Ogle, "The Kinetics of Void Annealing in Neutron Irradiated Aluminum," *Acta Metall.* 28(2): 151-61 (1980).

W. G. Wolfer and L. K. Mansur, *The Capture Efficiency of Coated Voids*, University of Wisconsin Report UWFD-329 (November 1979).

C. F. Yen, C. S. Yust, and G. W. Clark, "The Enhancement of Mechanical Strength in Hot-Pressed TiB₂ Composites by the Addition of Fe and Ni," pp. 317-30 in *New Developments and Applications in Composites*, ed. by D. Kuhlmann-Wilsdorf and W. C. Harrigan, Jr., The Metallurgical Society of AIME, Warrendale, Pennsylvania, 1979.

M. H. Yoo, "A Dislocation Model for Twinning and Fracture and Its Application to H.C.P. Metals," pp. 825-30 in *Strength of Metals and Alloys*, Pergamon Press, Oxford and New York, 1979.

M. H. Yoo, "Growth Kinetics of Dislocation Loops and Voids - the Role of Divacancies," *Philos. Mag. A* 40(2): 193-211 (August 1979).

M. H. Yoo and L. K. Mansur, "The Inclusion of Mobile Helium in a Rate Theory Model of Void Swelling," *J. Nucl. Mater.* 85 & 86(II,A): 571-75 (December 1979).

M. H. Yoo, "The Role of Divacancies in Void Swelling," *Scr. Metall.* 13(7): 635-39 (July 1979).

C. S. Yust, "Unifying Factors in Erosion and the Wear of Machine Elements," pp. 543-53 in *Fundamentals of Tribology*, Massachusetts Institute of Technology Press, Cambridge, 1980.

N. J. Zaluzec, "Quantitative X-Ray Microanalysis in an AEM: Instrumental Considerations and Applications to Materials Science," pp. 121-67 in *Introduction to Analytical Electron Microscopy*, ed. by J. J. Hren, J. I. Goldstein, and D. C. Joy, Plenum Publishing Corporation, New York, 1979.

6. PENDING PUBLICATIONS

L. A. Boatner, G. W. Beall, M. M. Abraham, C. B. Finch, P. G. Huray, and M. Rappaz, "Monazite and Other Lanthanide Orthophosphates as Alternate Actinide Waste Forms," to be published in *Scientific Basis for Nuclear Waste Isolation*, Plenum Press.

B. Borie, "The Observation of Forbidden Reflections in V_3Si ," submitted to *Physical Review Letters*.

W. H. Butler, "Electronic Structure and the Electron-Phonon Interaction," to be published in *Electronic Structure and Properties*, F. Y. Fradin (ed.), Academic Press.

W. H. Butler, "Progress in Calculations of the Superconducting Properties of Transition Metals," to be published in the proceedings of the International Conference on Superconductivity in d - and f -Band Metals, San Diego, California, June 21-23, 1979.

W. H. Butler, "Upper Critical Field of Pure Nb: Calculated Temperature Dependence and Anisotropy," submitted to *Physical Review Letters*.

T. A. Callcott, J. A. Tagle, E. T. Arakawa, and G. M. Stocks, "Soft X-Ray Emission from Li-Mg and Li-Al Alloys and Comparisons with KKR-CPA Calculations," accepted by *Journal of Applied Physics*.

P. T. Carlson, M. R. Hayns, and R. A. McKee, "Trapping Effects on Diffusion in Lead-Base Alloys," submitted to *Physical Review Letters*.

R. W. Carpenter and J.C.W. Spence, "Three-Dimensional Strain-Field Information Inconvergent Beam Electron Diffraction Patterns," accepted by *Acta Crystallographica*.

R. W. Carpenter, "Microdiffraction from Crystals Containing Defects," to be published in the proceedings of the MAS-EMSA Microdiffraction Symposium, San Francisco, August 4-8, 1980.

R. W. Carpenter, "On the Performance of the Field Emission Gun EM-400T," invited for publication in *Norelco Reporter*.

R. W. Carpenter, "Microdiffraction Studies on Semiconductor Materials," to be published in the proceedings of Symposium on Electron Microscopy of Semiconductor Materials, Fall Meeting of the Electrochemical Society, Hollywood, Florida, October 5-10, 1980.

W. A. Coghlan and M. H. Yoo, "Radius Dependence of the Sink Strength of a Dislocation Loop," submitted to *Scripta Metallurgica*.

A. DasGupta, D. M. Kroeger, C. C. Koch, and Y. T. Chou, "Flux Pinning by Small Perturbations of the Order Parameter in Type II Superconductors," accepted by *Philosophical Magazine*.

K. Farrell, "Experimental Observations of Effects of Inert Gases on Cavity Formation," to be published as a Harwell report.

K. Farrell, "Microstructure and Tensile Properties of Heavily Irradiated 5052-O Aluminum Alloy," submitted to *Journal of Nuclear Materials*.

J. S. Faulkner, "Electronic States in Disordered Solids." To be published in the bulletin of the Seventh Annual International Symposium on Electronic Structure of Metals and Alloys, Gaubig, East Germany, April 18-22, 1977.

C. B. Finch, F. L. Ball, and J. B. Bates, "Czochralski Growth of Single-Crystal Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$)," to be published in the proceedings of the International Conference on Crystal Growth VI, Moscow, USSR, September 10-16, 1980.

R. S. Graves, R. K. Williams, and J. P. Moore, "The Thermal Conductivity, Electrical Resistivity and Seebeck Coefficient of SRM-735." To be published in the proceedings of the 16th International Thermal Conductivity Conference, Chicago, Illinois, November 7-9, 1979.

J. Harris and G. S. Yuster, "A Localized Muffin-Tin Orbital Basis for Atomic Cluster Calculations Within the Local Density Formalism," accepted by *Physical Review B*.

L. A. Harris and C. S. Yust, "Transmitted Infrared Light Microscopy: an Improved Method for Viewing Coal Thin Sections," submitted to *Journal of Microscopy*.

L. A. Harris and C. S. Yust, "The Ultrafine Structure of Coal Determined by Electron Microscopy," to be published as chapter of book, *Coal Structure*, part of *Advances in Chemistry Series*.

M. R. Hayns, "A Composite Numerical Scheme for the Nucleation of Secondary Defect Aggregates," to be published as an AERE report.

M. R. Hayns and L. K. Mansur, "Applications of the Theory of Cavity Growth to Dual Ion Swelling Experiments," to be published in the proceedings of the ASTM Tenth International Symposium on Effects of Radiation on Materials, June 3-5, 1980, Savannah, Georgia.

C. L. Hoenig and C. S. Yust, "Explosive Compaction and Microstructural Analysis of AlN, Amorphous Si_3N_4 , Boron, and Al_2O_3 Ceramics," submitted to *Journal of the American Ceramic Society*.

J. D. Holder, R. A. Hartzell, and G. W. Clark, "Eutectics of LaCrO_3 and YCrO_3 with W, Mo, and Cr," submitted to *Journal of the American Ceramic Society*.

J. D. Holder, "Preparation of High-Temperature Oxide-Metal Eutectic Composites: A Review," to be published in *Advanced Fibers and Their Composites for Application at Elevated Temperatures*, AIME.

J. D. Holder, "Soret-Modified Eutectic Constitutional Supercooling Criterion," submitted to *Metallurgical Transactions*.

J. D. Holder, "Synthesis and Electronic Applications of Oxide-Metal Eutectic Composites," to be published in the proceedings of "Verbundwerkstoffe 1980," Konstanz, West Germany, April 17-18, 1980, Deutsche Gesellschaft für Metallkunde.

P. H. Karr, P. Predecki, R. W. Hendricks, and J. S. Lin, "Kinetics of Lamellar Thickening During Isothermal Crystallization of Polyoxymethylene from the Melt," submitted to *Journal of Macromolecular Science - Physics*.

C. C. Koch, D. M. Kroeger, J. O. Scarbrough, and B. C. Giessen, "Superconductivity in Amorphous ' T_5 T_9 ' Transition Metal Alloys (T_5 = Nb, Ta; T_9 = Rh, Ir)," submitted to *Physical Review B*.

C. C. Koch, J. O. Scarbrough, D. M. Kroeger, and A. DasGupta, "The Effects of Cold Rolling on Fluxoid Pinning in a Superconducting Metallic Glass," submitted to *Applied Physics Letters*.

M. B. Lewis and K. Farrell, "Nuclear Microanalysis as a Probe of Impurity-Defect Interactions," 109th AIME Annual Meeting, February 24-28, 1980, to be published in the AIME symposium volume on *Advanced Techniques for Microstructural Analysis*.

L. K. Mansur and J. O. Stiegler, "Radiation Effects in Metal and Alloys," submitted to *La Recherche*.

L. K. Mansur, "Effective Diffusion Coefficients of Point Defects in Impure Materials," submitted to *Acta Metallurgica*.

L. K. Mansur, contribution to "Correlation and Interpretation," to be issued as draft of ASTM Recommended Practice.

L. K. Mansur and M. H. Yoo, "Toward a Comprehensive Theory of Radiation-Induced Swelling and Creep - The Point Defect Concentrations," paper presented at and to be published in a supplement to the proceedings of the Conference on Irradiation Behavior of Metallic Materials for Fast Core Components, Corsica, France, June 5-8, 1979.

L. K. Mansur and T. C. Reiley, "Irradiation Creep by Dislocation Glide Enabled by Preferred Absorption of Point Defects — Theory and Experiment," paper to be published in the proceedings of the International Conference on Fundamental Mechanisms of Radiation-Induced Creep and Growth, Chalk River, Ontario, Canada, May 8-10, 1979.

D. L. McElroy, R. K. Williams, F. J. Weaver, and R. S. Graves, "The Physical Properties of $V(Fe,Co,Ni)_3$ Alloys from 300 to 1000 K," to be published in the proceedings of the 16th International Thermal Conductivity Conference, Chicago, November 7-9, 1979.

C. J. McHargue, "Annealing of Defects Produced by Neutron Irradiation," submitted to *International Metals Review*.

R. A. McKee, "Site Blocking and Correlated Defect Motion in Tracer and Chemical Diffusion," submitted to *Physical Review Section B: Solid State*.

R. A. McKee, "Thermodynamics and Kinetics of Interstitial Diffusion in a Two-Component System," submitted to *Physical Review Section B: Solid State*.

R. A. McKee, "Diffusion in a Pure, High Vacancy Content Crystal," submitted to *Physical Review Section B: Solid State*.

F. A. Modine, E. Sonder, W. P. Unruck, C. B. Finch, and E. D. Westbrook, "Phase Transitions in $RbCaF_3$," submitted to *Physical Review Section B: Solid State*.

J. P. Moore, "Analysis of Apparatus with Radial Symmetry for Steady Measurements of Thermal Conductivity," submitted for publication in book titled *The Compendium on Thermophysical Property Measurements Methods*.

J. P. Moore, R. S. Graves, and R. K. Williams, "Thermal Transport Properties of Niobium and Some Niobium-Base Alloys from 80 to 1600 K," submitted to *High Temperatures — High Pressures*.

R. E. Pawel and J. J. Campbell, "The Interaction of Stress and Mechanical Property Effects During Oxidation of Tantalum-Base Alloys," submitted to *Journal of the Electrochemical Society*.

R. E. Pawel and J. J. Campbell, "The Observation of Effects of Finite Specimen Geometry on the Oxidation Kinetics of Zircaloy-4," submitted to *Journal of the Electrochemical Society*.

R. E. Pawel and J. J. Campbell, "A Comparison of the High Temperature Oxidation Behavior of Zircaloy-4 and Pure Zirconium," to be published in the proceedings of the Fifth International Conference on Zirconium in the Nuclear Industry, Boston, August 4-7, 1980.

J. Petermann, R. M. Gohil, J. M. Schultz, R. W. Hendricks, and J. S. Lin, "Small-Angle X-Ray Scattering from Polybutene-1 Films Crystallized from a Highly Extended Melt," submitted to *Journal of Materials Science*.

A. J. Pindor, W. M. Temmerman, B. L. Györfy, and G. M. Stocks, "On the Electronic Structure of $\text{Ag}_c\text{Pd}_{(1-c)}$ Alloys," accepted by *Journal of Physics F: Metal Physics*.

F. J. Pinski, "Solutions to the Boltzmann Equation for Electrons in a Metal: Energy Dependence," accepted by *Physical Review Section B: Solid State*.

F. J. Pinski, P. B. Allen, and W. H. Butler, "Exotic Pairing in Metals: Formalism and Application to Nb and Pd." To be published in the proceedings of the International Conference on Superconductivity in d - and f -Band Metals, San Diego, California, June 21-23, 1979.

F. J. Pinski, W. H. Butler, and P. B. Allen, "Ideal Thermal Conductivity of Pd and Nb," to be published in the proceedings of the 16th International Thermal Conductivity Conference, Chicago, November 7-9, 1979.

T. C. Reiley, R. L. Auble, and R. H. Shannon, "Irradiation Creep Under 60 MeV Alpha Irradiation," submitted to *Journal of Nuclear Materials*.

J. M. Schultz, J. S. Lin, R. W. Hendricks, J. Petermann, and R. M. Gohil, "Annealing of Polypropylene Films Crystallized from a Highly Extended Melt," submitted to *Journal of Polymer Science, Polymer Physics Edition*.

J. M. Schultz, J. S. Lin, R. W. Hendricks, R. R. Lagasse, and R. G. Kepler, "Temperature-Dependent Small-Angle X-Ray Scattering from Poly(Vinylidene Fluoride)," submitted to *Journal of Applied Physics*.

C. J. Sparks, Jr., B. S. Borie, and J. B. Hastings, "X-Ray Monochromator Geometry for Focusing Synchrotron Radiation Above 10 keV," submitted to *Nuclear Instruments and Methods*.

C. J. Sparks, Jr., "X-Ray Fluorescence Microprobe for Chemical Analysis," to be published as chapter for a book on Synchrotron Radiation, Plenum Publishing Corporation.

W. Specking, D. S. Easton, D. M. Kroeger, and P. A. Sanger, "Stress Effects in an Nb_3Sn Conductor Proposed for use in the Magnetic Fusion Energy Program," submitted to *Advances in Cryogenic Engineering*, to be published with proceedings of the International Cryogenic Materials Conference, Madison, Wisconsin, August 21-24, 1979.

G. M. Stocks and B. L. Györfy, "Momentum Distribution of Electrons in Concentrated Random Alloys," to be published in *Journal of Physics F: Metal Physics*.

R. A. Vandermeer, J. C. Ogle, and W. G. Northcutt, Jr., "A Phenomenological Study of Shape Memory Effect (SME) in Polycrystalline Uranium-Niobium Alloys," submitted to *Metallurgical Transactions A*.

L. K. West, P. L. Walne, and J. Bentley, "Trachelmonas Hispida Var. Coronata (Eugleno-Phyceae): III. Envelope Elemental Composition and Mineralization," submitted to *Journal of Phycology*.

C. L. White and C. T. Liu, "Outward Diffusion, and External Oxidation of Thorium in Iridium Alloys," submitted to *Acta Metallurgica*.

C. L. White, T. R. Odom, and R. E. Clausing, "A Study of Grain Boundary Embrittlement in Cu-3Al-1 Si Using AES," submitted to *Microstructural Science*, Vol. 8, American Elsevier.

R. K. Williams and W. D. Philbrook, "The Soret Effect in Molten Ag-Te Solutions," submitted to *Journal of the Electrochemical Society*.

R. K. Williams, D. W. Yarbrough, J. W. Masey, T. K. Holder, and R. S. Graves, "Experimental Determination of the Phonon and Electron Components of the Thermal Conductivity of BCC Iron," submitted to *Journal of Applied Physics*.

H. L. Yakel, "Determination of the Cation Site-Occupation Parameter in a Cobalt Ferrite from Synchrotron-Radiation Diffraction Data," submitted to *Journal of Physics and Chemistry of Solids*.

D. W. Yarbrough, R. K. Williams, and R. S. Graves, "Transport Properties of Concentrated Ag-Pd and Cu-Ni Alloys from 300 to 1000 K," to be published in proceedings of 16th International Thermal Conductivity Conference, Chicago, November 7-9, 1979.

C. F. Yen, H. L. Fuller, and H. K. Bowen, "Electrical Conductivity in the FeO-Fe₂O₃-Al₂O₃-SiO₂ System - Part I. Correlation with Phase Equilibrium in Air," and "Part II. Electrical Conductivity of Iron Aluminosilicate Metals," submitted to *Journal of the American Ceramic Society*.

M. H. Yoo, "Slip, Twinning, and Fracture in Hexagonal Close-Packed Metals," submitted to *Metallurgical Transactions A*.