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Metals and Ceramics Division

Quarterly Progress Report,

July through September, 1979

MASTER

Scientific Editor: John J. Truhan

General Editor: Forest N. Weld

October 25, 1979

Lawrence
Livermore
Laboratory

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FOREWORD

This document is one in the UCRL-50058 series. This series of reports describes progress on energy-related work done by the Metals and Ceramics Division of the LLL Chemistry Department.

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ADVANCES IN MATERIALS SCIENCE

Metals and Ceramics Division

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HIGHLIGHTS

Stainless Steel Strengthening—We have developed a thermomechanical process for obtaining high-strength stainless steel plate. This special process was used to warm roll 21-6-9 and 316 stainless steel to thicknesses of 19.0 and 28.6 mm, respectively; the resulting tensile strengths were over 900 MPa (yield) and over 950 MPa (ultimate), and elongations were 30 and 37%, respectively.

Irradiated Creep Testing—We have studied the creep of niobium during bombardment with 14-MeV neutrons generated by the LLL Rotating Target Neutron Source (RTNS). Our results show that neutron irradiation enhances the creep rate at 550-600°C.

MAGNETIC FUSION ENERGY MATERIALS STUDIES*

SUPERCONDUCTOR DEVELOPMENT PROGRAM

Introduction

Multifilament NbTi is a commercially available superconductor and is being used in the MFE Program's Mirror Fusion Test Facility (MFTF), now under construction at LLL. However, NbTi is limited to applications requiring fields of 9 T or less. LLL has proposed an upgrade of MFTF, called MFTF-B, which will require two transition coils that operate at 12 T. We are following the development of an Nb₃Sn superconductor to meet the 12-T requirements of MFTF-B.

The superconductor Nb₃Sn differs from NbTi in two important respects: Nb₃Sn is a strain-sensitive material that requires special handling and process design to prevent degradation of its superconducting properties. In addition, the matrix around the Nb₃Sn must be bronze rather than high-purity copper, and this introduces a problem in developing a conductor in which the current can transfer from the superconductor to the stabilizing matrix in the event of a fault. LLL has been sponsoring a superconductor-development program in industry since 1974 to ensure that a Nb₃Sn superconductor will be available to meet the requirements of the mirror-fusion program. We are presently working with a commercial supplier on a manufacturing program that will provide an Nb₃Sn superconductor for demonstration in the High Field Test Facility (HFTF). Successful operation of the HFTF will provide the experience necessary for construction of 12-T coils for MFTF-B.

The Nb₃Sn superconductor being developed for the HFTF (Fig. 1) is a compacted cable manufactured by the following steps: niobium rods are loaded into holes drilled in a bronze (Cu-13-wt%-Sn) billet, and a nose and cap are welded onto the bronze to form an extrusion billet. This billet is extruded, drawn, and formed into a hexagonal rod. The rod is cut into short lengths and loaded into a second billet, which is extruded and drawn. The resulting rod is clad with a tantalum diffusion barrier and high-purity copper, after which it is reduced to wire by cold drawing. The wire is wound into a triplet cable, and then six of these are wound together. The resulting 18-strand cable is jacketed with additional copper, compacted, and formed into the rectangular cross section shown in Fig. 1. This component, called the core, is then heat treated so that the tin from the bronze matrix reacts with the niobium filaments to form the Nb₃Sn superconductor. Finally, embossed copper strips are soldered to each side of the core to produce a fully stabilized conductor.

*For more information, contact R. M. Scanlan (422-7002).

FIG. 1. Transverse section of Nb_3Sn superconductor made by wrapping 18 strands of bronze/niobium-filament composite in a copper tube, shaping the tube into a rectangular cross section 4.65×9.47 mm, and then heat-treating this core piece to form Nb_3Sn at the bronze-niobium interfaces. This quarter we measured critical current as a function of strain in samples of this superconductor and evaluated raw materials acquired for making more samples. The samples are being made to develop this superconductor for use in the High Field Test Facility.

Current Progress

This quarter we acquired the raw materials for first-stage extrusions and checked that they were within specification. These materials will be used to make developmental samples of the superconductor. We also evaluated samples of HFTF core that have already been made in the superconductor-development program.

In our raw-materials studies, experiments performed last quarter on extruded niobium indicated that it work-hardened rapidly during the drawing between the first and second extrusions. Furthermore, this niobium did not soften appreciably when annealed, in contrast with prior experience on niobium from other lots. Consequently, this quarter we selected for evaluation several samples from niobium rods acquired from different vendors for the HFTF extrusions. Chemical analysis for impurities indicated that this material was within specification, so the rods were processed to simulate the extrusion and drawing steps. The yield strengths measured after this processing were within the range required for successful extrusion, so two billets are being prepared for extrusion next quarter. If these extrusions are satisfactory, the eight remaining billets will be extruded to provide the material needed for 2000 m of HFTF superconductor.

The bronze for the first-stage extrusions of HFTF material has been procured by the supplier. Four of the bronze billets have been drilled with holes for the niobium rods. Chemical analysis of samples from these billets is in progress to verify that the composition is within specification.

Samples of HFTF superconductor core (Fig. 1) have been evaluated. The critical current at 12 T was measured as a function of applied strain, and the results are shown in Fig. 2. These results show that the critical current is above the specification of 5400 A at 12 T. The current/strain behavior is similar to that measured earlier by Deis on a sub-size HFTF prototype conductor.¹ These results indicate that the properties of the HFTF conductor are adequate; the major hurdle remaining is the manufacture of the long lengths required for HFTF.

FIG. 2. Effect of applied strain on the critical current I_s (normalized to I_0 , the critical current under zero applied strain) in the superconductor Nb_3Sn . We found that the effects of strain are reversible up to greater than 0.7% strain, after which the critical current is permanently degraded. The dashed curve is data obtained earlier by Deis et al. on a subsize HFTF Nb_3Sn superconductor prepared by triple extrusion.¹ Our measurements this quarter indicate that this superconductor will have adequate properties for use in the High Field Test Facility at LLL.

IN SITU CREEP TESTING DURING IRRADIATION WITH HIGH-ENERGY NEUTRONS

Introduction

Reactor experiments have shown that fission neutrons degrade reactor materials. Fusion-reactor neutrons will have a large component of high-energy neutrons and will cause even more severe radiation damage for a given neutron flux.

Because no fusion reactors are currently operational, radiation-damage experiments involving high-energy neutrons must use accelerator-based neutron sources. Currently available high-energy neutron sources are the Be(d,n) source at the University of California, Davis, and the T(d,n) Rotating Target Neutron Source (RTNS-II) at LLL. The Be(d,n) source produces a broad spectrum of high-energy neutrons (energies between 4 and 14 MeV), and RTNS-II generates monoenergetic 14-MeV neutrons. The maximum flux of neutrons above 1 MeV from the Be(d,n) source is about 10^{17} n/m²·s, and the maximum flux of 14-MeV neutrons from RTNS-II is about 10^{17} n/m²·s. These flux levels are 10 to 20 times lower than those anticipated in a fusion power reactor. Studies of radiation damage from high-flux, high-energy neutrons cannot be done until early 1984 when the Fusion Materials Irradiation Test (FMIT) Facility will be completed at Richland, Washington. The predicted peak flux in the FMIT is 10^{19} n/m²·s. Meanwhile, the relatively low-flux but high-energy neutron sources will be used to investigate the nature of high-energy neutron damage.

We have designed and constructed an in situ creep-testing unit to meet the stringent requirements of fully instrumented remote creep testing during irradiation. This creep unit in the past was interfaced with the RTNS-I, a 14-MeV neutron source at LLL, and then more recently with the Be(d,n) source. Exploratory creep tests have been conducted at both facilities.

Current Progress

This quarter, we restructured the in situ creep apparatus to interface with the 230-mm-diameter RTNS-II target. A concerted effort was also made to implement computer control of loading and of data acquisition for remote testing at the RTNS-II facility. In the first in situ creep test at RTNS-II, an annealed niobium specimen was creep tested at temperatures of 550 and 600°C and at stresses near 120 MPa while the neutron flux was cycled on and off. This is the most complex fully instrumented in situ experiment that has been run under 14-MeV neutron irradiation.

The results showed pronounced perturbations in creep behavior produced at 550°C by cycling the high-energy neutron beam quickly on and off the highly stressed minispecimen. Deformation rates jumped momentarily by 30 to 50% when the beam was flashed onto the specimen, and they decreased a similar amount upon beam removal (Fig. 3). We attribute the accelerated creep rates to an instantaneous increase in the concentration of radiation-induced point defects in the material. Decelerated rates apparently result from thermal diffusion rapidly removing excess defects when the beam is abruptly turned off.

FIG. 3. Results of creep testing niobium under 14-MeV neutron irradiation. The flux of $1.1 \times 10^{17} \text{ n/m}^2$ produced significant increases in the creep rate of this specimen at 550°C. These creep tests are being performed in the LLL RTNS-II facility and are part of our research on possible materials for future magnetic fusion reactors.

LASER FUSION ENERGY PROGRAM*

INTRODUCTION

The goal of our experiments for the LLL Laser Fusion Energy Program is to increase the ability of polished glass surfaces to transmit high-energy laser pulses without being damaged (i.e., to raise the laser-damage threshold of the surfaces). Such surfaces have a lower damage threshold than the bulk material, and there is still uncertainty about the causes for this. Two possible causes are surface damage and surface impurities. Previously, in an experiment on a freshly fractured surface of fused silica, we have demonstrated that a surface can have a damage threshold as high as the bulk material. There is speculation that damage and impurities on the surfaces result from the polishing process. Adsorbed gas and surface layers are also suspected of lowering damage thresholds. We are also performing other materials studies for this program upon request.

CURRENT PROGRESS

Electron-Beam Annealing

We are experimenting with using an electron-beam evaporation source to anneal lens surfaces and thus reduce the laser-damage threshold. We are currently investigating the changes that occur as a result of evaporation or viscous flow on the fused-silica surface as a function of electron-beam exposure time and power. The most severe combination of beam-exposure time and power that produces acceptably low changes in surface morphology will be used to anneal a Zygo polished Suprasil lens surface, and the effect on laser-damage threshold will then be evaluated.

This quarter we modified a 5-cm-diameter electron-beam source to accommodate a 5-cm-diameter fused-silica lens mounted on a rotating base. We also performed preliminary experiments, which revealed that the fused-silica lens could be briefly exposed to an 8-kV electron beam with 5 kW of power and not be noticeably distorted.

Chemical Stripping of Optical Coatings

Reworking a damaged or defective polarizer or an aspherical lens coating is both expensive and time consuming. A process that strips the coating from the substrate without requiring polishing would allow the coating vendor to correct bad coatings quickly and save the cost of repolishing.

We have completed a series of tests to evaluate the effectiveness of stripping TiO_2 and SiO_2 coatings from BK-7 glass using an etching solution of ammonium sulfate in sulfuric acid at about 300°C . We have compared the results of these tests to those obtained with a Gourley etch, which uses an ammonium bifluoride solution and a polishing compound. Although the tests are not complete, the results indicate the following:

- The sulfuric-acid etch can strip a TiO_2 layer (and all layers above it) relatively easily, even if the TiO_2 layer is adjacent to the substrate.
- The sulfuric-acid etch is relatively ineffective in stripping an SiO_2 layer if it is adjacent to the BK-7 substrate. However, for recoating, it may not be necessary to strip such an SiO_2 layer.
- The sulfuric-acid etch does not appear to damage the substrate surface.
- The laser-damage threshold seems to be unchanged by the sulfuric-acid etch, although this result is not conclusive.
- The Gourley etch does remove the SiO_2 film, but it also etches the substrate and is difficult to apply uniformly over a surface.

*For more information, contact R. L. Landingham (422-8022).

Based on these observations and the other test results, we recommend that the first coating (next to the substrate) be TiO_2 or another material that can be stripped easily and not SiO_2 , which is difficult to strip. Another series of tests is needed to further evaluate the effectiveness of using ammonium sulfate in sulfuric acid to strip TiO_2 and SiO_2 films from BK-7 glass. Both roughness and damage-threshold measurements must be refined before any definitive conclusions can be reached. Also, the composition and temperature of the solution must be optimized.

ALUMINUM-AIR BATTERY/VEHICLE PROGRAM*

INTRODUCTION

The ultimate goal of the aluminum-air electric vehicle program is to develop to the point of commercial feasibility a general purpose electric vehicle with the range, acceleration, and rapid refueling capability of today's automobile. The motivation for this goal is the prospect of significant savings in petroleum through the use of practical electric vehicles. Benchmark goals are for the total cost of vehicle operation and total energy use to equal those of vehicles powered by internal-combustion engines using synthetic fuels derived from coal.

Our approach to achieving these goals involves parallel developments of: (1) full-scale automotive propulsion batteries using anodes and air-cathodes adapted from existing technologies and practices, (2) cost-effective anode and cathode materials and structures, and (3) electric propulsion systems optimized for aluminum-air battery characteristics and low cost. The emphasis of our program through FY 1980 rests with the first of these development tasks.

The aluminum-air power cell operates as a fuel cell: Aluminum plates and tap water are mechanically introduced into a hardware device of fixed power limits and are consumed to produce electricity and a reaction product. The reaction product, hydrargillite $[\text{Al}(\text{OH})_3]$, is identical to an intermediate feedstock used in the aluminum-production industry. It is processed on-board the vehicle into a purified, semidry powder, which is periodically withdrawn from the vehicle at service stations for subsequent recycling by the aluminum industry. Waste heat from the battery is used to distill tap water during battery discharge. Using the distilled water as a battery reactant and for washing the hydrargillite maintains high purity in the product—a requirement for economical recycling.

Major parts of this program are carried out on subcontract with private laboratories and consultant firms. We manage this effort and also maintain a sizable in-house effort. This coordinated program is intended to promote and maintain a high level of scientific and engineering capability in the subcontract researchers. Finally, it is our programmatic responsibility to both synthesize a power-cell design and foster commercialization of the battery by promoting industrial participation in the development process and by communicating the results of our dissemination efforts.

CURRENT PROGRESS

Subcontract Status

Lockheed Missiles and Space Company is currently under contract to develop cell hardware beyond the laboratory stage and will soon demonstrate full-scale single-cell hardware together with a method they have developed for rapid refueling. Reynolds Metal Co. is under contract to develop an economical means of producing anode plates from battery-reaction products. Alcoa Aluminum Corporation has been awarded a subcontract to develop processes and components for on-board production of purified hydrargillite; they will commence work as of January 2, 1980. Proposals for air-cathode development have been received and are under review. A draft report has been received from Interplan Corporation (Santa Barbara) concerning an economic analysis of the electric vehicle cost. They predict the battery will be cost-competitive with liquid fuels that cost \$2.25/gal or more. Proposals have been received for an environmental-impact and safety analysis of the aluminum-air electric vehicle and are under consideration.

*For more information, contact J. F. Cooper (422-7168).

Aluminum-Air Cell Testing

Research continued on aluminum-air full- and half-cells, using improved air-cathodes supplied by Prototech, Inc. The new cathodes were equipped with current collectors made of nickel-plated screen and showed excellent polarization properties (200 h of operation, and polarization noble to -0.18 V vs Hg/HgO) and potential for long service life. Sample polarization curves for various air cathodes are shown in Fig. 4; no

FIG. 4. Half-cell polarization of state-of-the-art air-cathodes under operating conditions appropriate to vehicular applications (flowing 6M NaOH solution, 1.5M NaAl(OH)₄, stannate corrosion inhibitor, 60°C). The lower level of electrode potential specified in our request for proposals is indicated. Although they do not meet that goal, present cathodes perform well enough to allow development of a full-scale single-cell.

air cathode has yet (in our laboratory tests) met the performance specifications in the request for proposals, but both the Diamond-Shamrock and the Prototech cathodes are suitable for use in developing practical cell hardware.

Anode Studies

We have completed and tested a flow-channel system for scientific study of battery-anode alloys. The system uses a rectangular flow channel of dimensions $50 \times 3 \times 600$ mm; the channel provides a simple geometry, enabling hydrodynamic conditions to be analytically predicted and readily controlled. Using such a system, we can study the interrelation between anode polarization, hydrodynamics, and solution mass transport.

Mathematical Modeling of Power-Cell Design

We are continuing our computer analysis of the heat- and mass-transport within the battery and between battery and environment. This quarter we defined a domain of operating conditions under which the battery can, while sustaining extreme loads, fulfill the requirements of heat rejection, distilled-water production, and product washing and (partial) dehydration.⁴ We have also completed a similar study of the precipitation of hydrargillite from battery electrolyte.⁵ These studies provide a basis for sizing battery components and for making fundamental choices of battery design. Based on these studies, we have chosen the design shown in Fig. 5. Rather than completely dry the reaction product, the design drains the product under pressure,

FIG. 5. Fundamental battery design chosen on the basis of mathematical modeling of heat transport, mass transport, and hydrargillite precipitation. By producing a hydrargillite powder that is about 14% water instead of completely dry, we were able with this design to significantly simplify the hardware design and increase the system reliability. The mathematical modeling also led to a new scrubber design.

providing a moist powder that contains about 14% water. The elimination of the drying cycle significantly simplifies hardware design and increases system reliability. Also, the mass/enthalpy balance from the computer analyses led to a new scrubber design: tapwater, made alkaline by additions of NaOH (about 0.5–1M), simultaneously cools the battery by evaporation (after absorbing heat from the electrolyte), humidifies the air stream, and scrubs the incoming air to remove dirt and CO₂. A water flow rate of about 30 to 50 ml/s is required.

Economics and Energy-Use Analysis

From a subcontracted study and our own study of the economics of the aluminum–air system, the following scenario has emerged for the competitive implementation of the aluminum–air vehicle:

The aluminum–air battery would be sized for performance competitive with the internal-combustion-engine vehicles and would have a range of 400 km, which is determined by the store of tap water. The refueling with tap water would take place primarily at the vehicle owner's residence. Additional aluminum would be stored on board the vehicle for extended ranges of 1600 km and of 3200–4800 km. The greatest range would require additional aluminum weights of 64 to 128 kg, which would degrade peak power levels by about 7% and increase aluminum fuel consumption per unit of travel distance by about 3 to 4%. The hydrargillite could be withdrawn at the convenience of the vehicle owner. This scenario substantially reduces the service-station infrastructure required for practical use of the vehicle and thus will speed public acceptance of the vehicle.

The recycling of the battery reaction products could involve the aluminum industry in a tolling operation: The vehicle owner would own the aluminum and reaction product, and the aluminum industry would produce new anode plates from this product for a fixed fee. The anode plates would be distributed to the vehicle owner by existing service stations. Such a tolling operation would benefit the aluminum industry by eliminating inventory taxes. Retaining ownership of the product would also be less expensive to the vehicle

FIG. 6. Effect of electricity cost on energy used and cost incurred in reprocessing hydrargillite to aluminum. One of the reasons for this dependence is that the optimum energy density depends heavily on the cost of the electricity used. Higher prices for electricity cause reprocessors to operate the aluminum-production (reprocessing) cell at higher electrical efficiency. Also, a factor in the cost dependence is that only about 10% of the reprocessing cost currently is for electricity.

owner because the competitive price for recycling aluminum from hydrargillite in a tolling setup is the difference between the selling prices of aluminum and hydrargillite, while the competitive price for producing aluminum from hydrargillite *purchased* by the aluminum industry would incur an additional cost, corresponding to the profit of the Bayer industry in producing hydrargillite.

The energy cost of producing aluminum primarily depends on economic factors (chiefly the cost of electricity and capital equipment) and not solely on available technology. The sensitivities of aluminum-production energy and cost to the cost of electricity were derived using methodology developed by Keller⁶ and are shown in Fig. 6. For current technologies of aluminum production, a 100% increase in electricity cost (with constant equipment costs) would increase manufacturing cost of aluminum by about 10 to 15% and decrease energy consumption by about 25%. These analysis results reflect the strong dependence of the optimum operating rate of the aluminum-production cells (i.e., the optimum current density) on the price of electricity. The energy cost of aluminum is directly proportional to production-cell current density because of the high ohmic losses in the battery. The production cost is relatively insensitive to electricity cost for two reasons: higher electricity cost tends to encourage aluminum production under conditions of higher electrical efficiency and the low (10%) fraction of manufacturing cost that is now attributable to electricity.

GEOTHERMAL PROGRAM*

INTRODUCTION

LLL's Geothermal Research Program is aimed at harnessing the total flow of the hot, high-saline brines found in the enormous geothermal resources of Southern California's Salton Sea field. One of the central problems in tapping this energy resource is that the brine passing through the turbine and other equipment causes scaling and corrosion in the materials. To help overcome these problems, we are supporting the program by conducting research in the areas of general corrosion, erosion-assisted corrosion, and stress corrosion.

Currently, our principal concern is the corrosion resistance of materials in the high-temperature leg of a double-stage flashed-steam electrical-generation system. The materials in the high-temperature leg are the production-well casing and the surface piping leading to the steam-brine separators. Currently, we have two experiments in progress to characterize the corrosion performance of well-casing and piping materials.

CURRENT PROGRESS

Well-Casing Materials

In previous work, we found that the American Petroleum Institute (API) N-80 and C-75 grades of steel performed significantly better than the J-55 grade. These steels were exposed as 9.2 m lengths of 1-1/4-in. well-casing in a 600-m "string," which was suspended in Woolsey I production well for about 1-1/2 months. This quarter we further evaluated the corrosion in this string.

Corrosion was most severe in the bottom 70 m of string. Corrosion attack was in the form of tubercles; the lead sulfide scale was ruptured by expansion of the voluminous corrosion product that formed under it. Apparently, the corrosion product ($\text{Fe}_3\text{O}_4 + \text{FeS}_2$) is much less protective than the lead sulfide that it replaced, resulting in deeply penetrating attack on the steel. As much as half of the tubing-wall thickness was lost during the 2-1/2 month exposure period. This loss corresponds to a penetration rate of 9 mm/y.

While the J-55 lengths were severely corroded, adjacent lengths of N-80 and C-75 showed only small penetrations of attack (on the order of about 50 μm). Metallographic sections of the three steels revealed that the N-80 and C-75 were much finer in grain size and were uniform in microstructure. The structure of the J-55 varied, particularly near the upset ends, and the resulting differences in microstructure of the J-55 appear to have a significant effect on the corrosion behavior of this grade of steel.

To test the effect of microstructure, as well as chemical composition, on the corrosion resistance of steels, we assembled a composite tube string and emplaced it in the Magmamax I well in late August 1979. We expect to leave the string in the well for four months of exposure. The composite string, like previous strings, is made up of 7- to 10-m lengths of 1-1/4-in. tubing. The total length is again about 600 m. The string includes the steels listed in Table 1.

*For more information, contact R. D. McCright (422-7051).

TABLE 1. Steels undergoing four-month exposure to geothermal brine in the Magmamax I well at the Salton Sea Geothermal Field. We selected this range of steels to see the effects that microstructure and chemistry have on corrosion of well-casing steels. This study is part of our effort to characterize materials for their resistance to the corrosive geothermal brine.

Steel	Chemistry or microstructure
API J-55 ^a	Carbon steels, large and varied grain size
API N-80 ^a	Small, consistent grain size
API C-75 ^a	Small, consistent grain size
ASTM A335 P1	1/2% Mo
ASTM A335 P2	3/4% Cr + 1/2% Mo
ASTM A335 P11	1-1/4% Cr + 1/2% Mo
ASTM A335 P22	2-1/4% Cr + 1% Mo
ASTM A335 P5	5% Cr + 1% Mo
ASTM A335 P7	7% Cr + 1/2% Mo
ASTM A335 P9	9% Cr + 1% Mo
ASTM A106 grade B	~0.3% C
ASTM A519 grade 1018	Same as the AISI designation, 0.18% C

^a Numbers indicate minimum yield strength in ksi.

In addition, we obtained "pup" joints (1-m lengths) of API J-55 and N-80 grades and heat treated samples of each by the following four methods:

- Austenitize and air cool (normalize)
- Austenitize and furnace cool
- Spheroidize
- Austenitize, oil quench, and temper

These samples were also placed in the string.

The results from exposure of the composite string should show whether Cr-Mo alloy steels or specially heat treated carbon steels are significantly more corrosion resistant than API J-55, which is the conventional well-casing material.

Surface-Piping Materials

The main concern with piping materials for the high-temperature leg is susceptibility to localized corrosion. Sections of the 10-in. pipe at the San Diego Gas & Electric Co. facility have shown severe attack at elbows and other locations where, presumably, pieces of the lead sulfide scale are dislodged, exposing the underlying steel to attack. We have observed that alloy steels containing up to 9% chromium and 1/2 to 1% molybdenum suffer much less corrosion attack in hypersaline brines, even when the brine is acidified to reduce the scaling rate. However, the Cr-Mo alloy steels do exhibit some tendency to localized attack, in the form of shallow pits. Our concern for piping materials, therefore, was the time dependence of the pitting penetration and whether the pitting will limit use of these steels in geothermal applications. To answer this question, we began an experiment in June of 1979 to measure the general and localized corrosion rates of nine carbon and alloy steels in the geothermal brine.

In this experiment, we have installed flat corrosion coupons in a bypass line connected to the Magmamax I well. The coupons are mounted in a spool piece which slips into a 12-in. by-pass section in the production line from the well. Thus, the coupons are exposed to two-phase fluid at wellhead temperature and pressure.

We installed five identical spool pieces, each containing coupons of all nine steels. The first and second spools were removed, one and two months, respectively, after the five were emplaced. The remaining three will be removed consecutively, after three more one-month periods.

After removing them from the first two spools pieces, we cleaned the individual coupons with 25- μ m glass beads and weighed them to determine the weight loss during exposure. The weight loss was converted into a generalized corrosion penetration rate. Also, we noted the nature of the attack for each specimen. We will also determine the depth of pitting penetration, but the results are not all available yet.

From the data that are so far available, we draw the following conclusions:

- Cr-Mo steels resist general and local forms of corrosion better than the carbon steels.
- The results obtained from the carbon steels are inconsistent between alloys. The 1018 grade, for instance, is much more corrosion resistant than the 1009 grade. Metallographic sections of these two steels showed little difference in the microstructures.

- Mesa-type corrosion was present on the ASTM A106 B steel coupons, and this is consistent with observations made on the production pipeline itself, which is fabricated from this grade of steel. Mesa-type corrosion is the situation where mesas (areas in relief) alternate with attacked areas, which resemble canyon bottoms.

- Corrosion is most severe at the 6 o'clock spool position, where the coupons are fully immersed in brine. It is least in the 10 and 12 o'clock positions, where the coupons are exposed primarily to steam.

- Localized corrosion appears to require longer to initiate on the alloy steels than on the carbon steels.

The third spool piece is due for removal at the beginning of next quarter. Results from this spool should reveal the validity of these trends. In the meantime, we are developing more quantitative methods for assessing the pitting and other localized corrosion attack.

OIL SHALE PROGRAM*

INTRODUCTION

LLL's Oil Shale Program involves an in situ process for recovering crude oil from shale deposits in the western United States. We are supporting this program by performing x-ray diffraction studies to characterize the mineralogy of the raw shales and to determine what chemical reactions these minerals undergo when heated.

CURRENT PROGRESS

We are continuing post-retort diagnostics on the retort run L-3. In this run, two grades of shale were retorted: The lower half of the retort contained shale of about 150-l/Mg quality; the upper half, about 75-l/Mg. The shale came from the C-a tract, not the Anvil Points mine. The feed gas was a 50-50 (vol%) steam-air mixture. The retort run generated usually large amounts of H_2S .

This quarter, we performed x-ray diffraction analyses in an attempt to identify the source of the sulfur generated in the retort. The diffraction patterns of the raw shale are dominated by the presence of minerals that do not contain sulfur: dolomite, calcite, quartz, analcime, albite, buddingtonite, and illite. However, review of the patterns indicates that pyrite, FeS_2 , is probably present in weak amounts in the 75-l/Mg shale and in very weak amounts in the 150-l/Mg shale.

We also analyzed the spent shale by x-ray diffraction. In these analyses, we performed separate tests on spent shale from 40 different levels in the retort. From each level of the retort, shale samples were removed and then carefully blended to give representative samples of each level.

The diffraction analyses indicated the relative abundances of the major raw-shale mineral phases still remaining in the spent shale. The results show that the mineral reactions occurring during retorting are most complete in the lean-grade shale at the top of the retort and are progressively less complete toward the bottom of the retort. Ordinarily, one would have expected just the opposite, because temperatures go up as the combustion zone progresses from lower-grade shale to higher-grade shale. In the L-3 run, to minimize this heating phenomenon, the air was reduced when the combustion zone moved into the richer-grade shale. The results of our x-ray diffraction analyses indicate that the reduction in air flow should probably have been less.

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NUCLEAR WASTE MANAGEMENT*

CORROSION OF NUCLEAR-WASTE STORAGE CANISTERS—NRC

Introduction

The Nuclear Regulatory Commission (NRC) has the responsibility for developing nuclear-waste management regulations concerning high-level and spent-fuel waste, regulatory guides, and licensing in a timely manner consistent with the Department of Energy needs. Previously, our task in this program was to develop macroscopic-element models of the corrosion of waste-storage canisters. Because of NRC policy changes in the NWM program, we are now directed to write regulations and regulatory guides using extremely conservative engineering. The degree of conservatism can later be reduced as research is done and more data becomes available. We are to devise conservative criteria for spent-fuel and high-level waste-burial packages,[†] and to identify research that will provide data for establishing less-conservative acceptance criteria.

Three time ranges are significant in isolating radioactive waste: After about 100 years most of the fission product nuclides generating much heat will have decayed to insignificant levels; after approximately 600 years the highly toxic and heat-generating ⁹⁰Sr and ¹³⁷Cs radionuclides will have decayed to tolerable levels; and after one to several million years the α -emitting actinide nuclides with long half-lives will have decayed to near-background levels.

The ⁹⁰Sr and ¹³⁷Cs isotopes are relatively soluble in water and therefore mobile; thus it is important to confine the waste until these isotopes decay. The actinides are not as soluble or mobile as strontium and cesium; thus they are expected to decay to near background levels before they can enter the biosphere from the underground storage. Also, it would be unrealistic to guarantee several million years containment by a man-made barrier.

Another constraint is imposed on canisters used to contain spent fuel. Because it may eventually be decided to retrieve the spent fuel for reprocessing, the canisters not only must isolate spent fuel from the environment, but also must be retrievable for an extended time. Retrieval is seen as being an option during the first 25 to 50 years of storage. If canisters are not retrieved, permanent disposal is accomplished by sealing the burial site.

Current Progress

We constrained the scope of our analysis to reduce the matrix of interactions to manageable size. The constraints are listed below, along with some definitions and assumptions:

- Only high-level waste and spent fuel are considered.
- Only subterranean and sealed geological sites are considered.
- The role of the canister is to isolate the radioactive waste from the repository environment for approximately 600 years, thus allowing decay of the ⁹⁰Sr and ¹³⁷Cs. (Performance of the canister materials for longer periods would depend on the geological-hydrological stability over these longer periods.)
- The geological-hydrological environment will remain relatively constant for 600 years. There will be no gross breach of repository integrity or diversion of rivers through the repository.
- The hydrology and chemistry of any repository must be defined before materials are selected for canisters.
- The total package includes any or all of the following, moving outward from the waste: canister wall, coating, inner pack, air gap, protective sleeve, coating, protective or sacrificial overpack, air gap, repository medium.

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[†]The term "package" refers to everything between the waste and the repository wall, including canister, coatings, overpacks, and air gaps.

- Retrieval is not considered, only isolation.
- Failure is the first penetration through the canister wall.
- In the case of spent fuel, the fuel cladding is not relied on for containment.

Thus we define the corrosion-resistance criterion as no penetration during first 600 years of storage. Criteria for storage canisters would be specific to given sites, but general principles of selection can be established on the basis of our present knowledge.

This quarter we began delineating the principles for evaluating the corrosion resistance of waste-storage canisters. We consider uniform and nonuniform corrosion separately, since the problems of designing to prevent them are distinctly different. Rates of uniform corrosion are to some degree predictable by experiment and modeling, and corrosion of metal can be accommodated by increasing the thickness of the canister wall. Nonuniform corrosion rates are less predictable. The factors leading to nonuniform corrosion are difficult to measure: alloy inhomogeneity, stress concentrations, formation of concentration cells, etc. Also, some forms of nonuniform corrosion are autocatalytic. Thus penetration rates from nonuniform corrosion cannot be reliably predicted. However, nonuniform corrosion can be minimized by proper materials selection and canister design and fabrication.

Uniform corrosion can be predicted by a combination of laboratory testing, site testing, and modeling. To pass uniform-corrosion standards a metal must be either thermodynamically stable in its environment or limited in the amount of corrosion that can take place during a given time. Limiting of corrosion can be either by the amount of reactants present or by the speed of the reaction.

If a metal is thermodynamically stable in the repository environment, compounds of the metal tend to be reduced and theoretically no corrosion is possible. However, radiolysis of chloride-containing groundwaters can produce oxidizing compounds and radicals and highly corrosive oxychloro compounds. To prevent such phenomena, lead shielding might be used inside the canister to reduce radiolysis.

Corrosion that is limited by the amount of reactant present may be capable of a moderately fast rate, on the order of 0.5 to 1.5 mm/yr, but the total amount of corrosion will be limited by the small amount of corrodant present. Such would be the situation if brine were isolated from the canister, either by allowing it to collect in a sump or by scavenging it with a reactive overpack. While air might still corrode the canister material, it could corrode only a limited amount.

Limitation of corrosion by the speed of reaction occurs with metals and alloys that are passivated in oxygenated solutions by the formation of an insulating oxide film. This film prevents charge transfer by electrons or ions, but corrosion still can proceed at a very slow rate, probably by slow dissolution of the protective passivating film into the surrounding solution. However, radiolysis of chloride-containing groundwaters can produce oxidizing and highly corrosive compounds. These compounds can break down the passivating film and may thus increase corrosion rates by perhaps an order of magnitude. To allow for such an accelerated corrosion rate, the canister wall thickness would have to be increased by at least an order of magnitude.

Because nonuniform corrosion is less predictable, it must be analyzed in great detail. The forms of nonuniform corrosion that must be considered are: crevice corrosion, stress corrosion cracking, pitting corrosion, galvanic corrosion, selective leaching, and intergranular corrosion. This quarter we outlined an approach to be used in formulating regulations that will prevent failure by these modes.

We have found that certain research is needed to reduce uncertainties in the judging of canister materials. The following information and techniques (listed in order of priority) are needed to better understand aspects of both internal and external canister corrosion:

- (1) Sensitive corrosion-detection techniques for very slow processes
- (2) Appropriate accelerated testing methods
- (3) Identification of long-term corrosion mechanisms for candidate materials
- (4) Effects of radiation and radiolysis on corrosion in intermediate-level to high-level waste streams.
- (5) Identification of solid-metal embrittlement problems associated with metal matrices.
- (6) Effects of actual production processing (unanticipated phase separations, etc.).

MINERAL WASTE-FORM DEVELOPMENT FOR U.S.-DEFENSE NUCLEAR WASTES

Introduction

A new program has been initiated by the Department of Energy to study mineral ceramics as hosts for long-term solid storage of U.S.-defense high-level nuclear wastes. The program includes the following:

(1) A study of powder coprecipitation techniques to synthesize multicomponent oxide mineral systems containing key radionuclides in homogeneous solid solution.

(2) Phase-equilibria studies to determine the most thermodynamically stable and leach-resistant mineral ceramic waste form for the diverse compositions of defense wastes. Initially, the program will be concerned with ceramic storage of the wastes now stored at the Savannah River Plant in South Carolina. The program will study whether a titania-based mineral system called "Synroc"² can be adapted for storing these wastes.

(3) Processing studies to determine the optimum high-temperature fabrication methods for producing phase-equilibrated, high-strength, high-density products suitable for long-term storage.

(4) Aqueous-leaching studies both in high-temperature, high-pressure accelerated modes and in long-term modes to determine the behaviors of various host minerals and to compare these behaviors with those of other potential waste forms, such as glass.

This project is a joint effort with the Earth Sciences Division at LLL. Our part is to prepare and characterize Synroc samples. We are currently using x-ray diffraction to examine starting materials and hot-pressed and sintered samples in order to determine phase formations and transformations that occur during fabrication. The Earth Sciences Division will be examining leaching characteristics of Synroc samples.

Current Progress

This quarter we prepared a Synroc composition consisting of a barium-hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$) solid solution, zirconolite ($\text{CaZrTi}_2\text{O}_7$), and perovskite (CaTiO_3). We prepared the Synroc both by a urea-coprecipitation process³ and by a technique of mixing oxides and hydroxides. We calcined the coprecipitated powders at various temperatures from 500 to 1000°C in air and characterized them by x-ray diffraction, surface area, particle density, scanning-electron microscopy, and thermogravimetric analysis. For powders prepared by the urea process and calcined at 500°C, x-ray diffraction showed broad, weak lines of the three mineral phases. In contrast, powders calcined in the range 800–1000°C show complete, well-defined patterns. Powders prepared by long-term grinding in mortar and pestle and calcined at 880°C were not as well combined, and strong patterns of the individual minerals were still present.

However, surface areas of precipitation-prepared powders ranged from 24 to 81 m²/g, in contrast to about 6 m²/g for calcined oxide mixtures. Also, thermogravimetric analysis of the precipitated powders showed a pronounced weight loss in air at 400 to 500°C.

We also hot pressed samples of each powder in graphite and sintered samples of each in air at temperatures in the range 1100–1300°C. Sintering at the higher temperatures produced essentially the full theoretical density. We are now examining the microstructure of the sintered samples and the hot-pressed samples.

THERMOCHEMICAL CYCLES FOR HYDROGEN PRODUCTION*

INTRODUCTION

We are developing thermochemical cycles for producing hydrogen from water, under funding provided by the DOE Office of Basic Energy Science (OBES) and the Division of Energy Storage Systems (DESS). Hydrogen produced by such cycles would be a renewable resource and would be independent of fossil fuels. The cycles could be powered by heat from such energy sources as the high-temperature gas-cooled fission reactor, fusion reactors, or solar concentrators. A thermochemical cycle consists of a series of chemical reactions operated in a closed loop such that the only inputs are water and heat, and the only outputs are hydrogen and oxygen (in separate streams) and waste heat. All other chemical reagents are recycled within the system.

In the OBES program, we are studying the detailed chemistry of the ZnSe thermochemical cycle. Our objective is to develop a basic understanding of the thermochemistry, kinetics, and mechanisms of several complex reactions in the cycle. The major reaction steps in the cycle are as follows:

We are currently studying reactions (3) and (4).

The DESS program is oriented toward the engineering development of thermochemical cycles. Two cycles have been selected and are being developed on a national basis. Both of these cycles have a step that requires the boiling and subsequent thermal decomposition of sulfuric acid into H_2O , SO_2 , and O_2 . Our current role in this program is to test materials for their potential use in heat exchangers and containers for boiling of 97-wt% H_2SO_4 at 725 K and 2 MPa vapor pressure. These extreme boiling conditions are necessary to minimize energy consumption in the cycle but impose very severe materials requirements for the sulfuric-acid vaporizer.

CURRENT PROGRESS

Decomposition of Zinc Sulfate

Zinc sulfate is decomposed in step (4) of the ZnSe thermochemical cycle to liberate oxygen and to regenerate SO_2 as a reducing agent. This is the most endothermic step in the reaction scheme and requires temperatures in the vicinity of 1200 K. Even at these high temperatures the reaction is kinetically hindered, producing SO_3 rather than the thermodynamically favored SO_2/O_2 gas mixture. These characteristics indicate

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a complex reaction that will require effort to optimize decomposition. Both the thermodynamics and kinetics are being studied in this reaction.

Thermodynamic Study. In studying the decomposition of ZnSO_4 , we are first establishing the thermodynamics of the compounds involved. We cannot extrapolate the high-temperature properties of ZnSO_4 from published data because of the limited heat- and mass-transfer characteristics of previous experimental designs. Also, the formation of an oxysulfate, $\text{ZnO} \cdot 2\text{ZnSO}_4$, and a 1015-K phase transformation of ZnSO_4 cast additional doubt on the validity of extrapolation from lower-temperature data. We previously measured the high-temperature enthalpy of ZnSO_4 , $\text{ZnO} \cdot 2\text{ZnSO}_4$, and the enthalpy of the ZnSO_4 α -to- β transition by drop calorimetry. However, we have discovered a small hole in the sample capsule, and it was thus necessary to repeat the β - ZnSO_4 enthalpy determinations.

This quarter we made four more calorimetry drops on ZnSO_4 using a new sample capsule: three β -phase drops and one α -phase drop. Results of the α -phase drop agreed well with our previous pretransition data, establishing the validity of combining the new β -phase results with most of our previous data. Figure 7 shows the combined data with the previous, suspect β -phase points omitted. We calculate a transformation

FIG. 7. Enthalpy of ZnSO_4 above 298 K shows a 22.3-kJ/mol phase transition at 1015 K. This quarter we repeated measurements of the enthalpy of βZnSO_4 to more accurately determine the enthalpy change of the transition. This is part of our effort to optimize the ZnSO_4 -decomposition step in the ZnSe thermochemical cycle.

enthalpy of 22.3 kJ/mol, about 4.7 kJ/mol higher than we previously estimated using data from the defective capsule and about 2 kJ/mol higher than the vapor-phase estimates of Ingraham and Kellogg.⁷ This information, combined with the enthalpies we had previously measured for zinc oxysulfate, provides us with a complete and accurate background on the thermodynamics of ZnSO_4 decomposition and permits us to more definitely establish the pressures of equilibrium decomposition for ZnSO_4 and zinc oxysulfate.

Kinetic Study. The second area we are studying for the ZnSe cycle is the kinetics of ZnSO_4 decomposition. We hope to minimize the kinetic barrier to decomposition by experimentally determining favorable conditions for the reaction. This quarter we conducted a preliminary study on the decomposition behavior of ZnSO_4 using a tungsten-lamp furnace as a heat source. The results indicate that the rate of ZnSO_4 decomposition depends markedly on the rate of heating through the ZnSO_4 α -to- β phase transition at 1015 K. The results also provide insight into the test conditions that will be needed in the future to obtain quantitative kinetic information.

Experiments on the kinetics of ZnSO_4 decomposition are complicated by the large endothermic requirements of the reaction. Heat and mass transport associated with the sample severely restrict sample size and configuration. To obtain experience with ZnSO_4 -decomposition behavior, we conducted our preliminary study this quarter. In this preliminary study, we measured sample temperature and decomposition-product evolution at several heating rates. Figure 8 shows a schematic of the test apparatus.

Before each decomposition run, the sample of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was first dehydrated at a low power setting. Two main types of dehydration procedures were used. In one, the $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was dried very slowly under vacuum at minimal temperatures. This produced a fine, freely flowing powder. In the other, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was dried rapidly under a rough vacuum at higher temperatures. This produced a caked material, which, upon being shaken in the vial, became a coarse powder.

FIG. 8. Schematic of apparatus for examining the decomposition behavior of ZnSO_4 . Ellipsoidal mirrors focus the light from 1000-W bulbs onto a tube containing the sample and a thermocouple. This apparatus was used in a preliminary study this quarter to gain experience with ZnSO_4 decomposition and determine the test conditions that will be necessary in our detailed studies to come. This preliminary study demonstrated that the decomposition rate depends on the heating rate through the α -to- β phase transition.

We tested the decomposition rate of two samples of the fine-powder ZnSO_4 , using for one a rapid heating rate (2 min to attain and maintain an internal temperature of 1043 K) and for the other a slower heating rate (15 min to reach and maintain 1043 K). In both tests, once the vial was isolated under a static vacuum we monitored the rate of pressure buildup with a capacitance manometer. The rapidly heated sample completely decomposed within a few minutes, but the slowly heated sample required a few hours. For comparison, we performed the rapid-heating test on coarse particulate ZnSO_4 ; this material showed an initial rapid decomposition rate, which then subsided to a very slow rate before much decomposition had occurred. Figure 9 shows the decomposition curves for these three samples.

These results, although preliminary, strongly suggest that rapid heating of ZnSO_4 through the α -to- β phase transition at 1015 K fractures the ZnSO_4 particulates to form a material of large surface area. The large

FIG. 9. Effect of heating rate and particle size on decomposition rate of ZnSO_4 . A greater heating rate causes a greater decomposition rate for fine particles of ZnSO_4 ; coarse particles of ZnSO_4 decomposed slowly even when heated rapidly. These are preliminary results of our program to study ZnSO_4 decomposition and indicate that a rapid heating rate causes a rapid α -to- β phase transition that fractures the particles of ZnSO_4 , causing more rapid decomposition. Complete decomposition to ZnO should produce about 13 mmol of evolved gases.

surface area then greatly accelerates the subsequent decomposition rate. Further experiments showed that coarse particles do not fracture as much as fine particles in either slow or rapid heating conditions. A recent report establishes that the phase transition in ZnSO_4 is from an orthorhombic CuSO_4 -type structure at the lower temperatures to a cubic high-cristobalite-type structure at high temperatures.⁸ The phase transition is accompanied by a 28% volume expansion, which is extremely large and should promote fracturing with rapid heating rates. However, the energy required for the transition is also quite large (22.3 kJ/mol), as established by our enthalpy measurements, so that high rates of energy input would be needed to achieve a rapid phase transition. We believe that these observations are consistent with our initial decomposition-rate results (Fig. 9), but more work is needed to quantitatively establish the behavior.

The tests we performed this quarter provided other information on the behavior of ZnSO_4 during decomposition:

- Once the oxide decomposition product becomes visible (ZnO is colored when hot) the rate of decomposition usually increases rapidly. This may result from some form of auto-catalysis or just from the development of a hot spot at the decomposition site.

- The reaction is sensitive enough to subtle parameters of particle characteristics that the effects of heating rate or sample size are easily masked.

- Temperature gradients develop within the sample and are large enough to severely complicate accurate measurement and characterization of sample temperatures during decomposition.

These preliminary experiments also indicated several problems in our technique. This experience has allowed us to advance from the tungsten lamps to plans for conducting more quantitative experiments in an isothermal wire-wound furnace. Construction of the apparatus has already begun.

Utilization of Zinc Sulfate in H_2SO_4 -Based Cycles

As part of an effort to further develop thermochemical cycles, this quarter we began outlining a scheme substituting ZnSO_4 for sulfuric acid in the sulfate-decomposition step in H_2SO_4 -based cycles. This modification could be used to overcome many of the difficulties presently associated with sulfate decomposition in these cycles. The substitution is illustrated as follows: The reaction

which would require a reaction vessel made of an extremely inert material, is replaced by the following series of reactions:

Here, a 50-wt% H_2SO_4 solution was chosen for illustration, although other concentrations can be used as well. Reaction (1) is exothermic by 83.7 kJ/mol, and reactions (2) and (3) are endothermic by about 79.5 and 338.9 kJ/mol, respectively. Reaction (1), a combined neutralization and precipitation reaction, would have to be conducted in an autoclave because of the high pressures of water involved. At a temperature of 525 K the solubility of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ in water drops to a very low value,^{9,10} permitting it to be filtered out. In reaction (2), $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ is dehydrated to produce high-temperature process steam, and in reaction (3) the ZnSO_4 is

decomposed to regenerate ZnO(s) . The gaseous products in reaction (3) will also contain some SO_3 , which will have to be recycled in a separate stream. As a variant in reaction (1), some (about 20%) of the ZnSO_4 can be recovered in anhydrous form at 350–380 K,¹¹ which may further improve thermal efficiency.

Many of the advantages given by Bowman and co-workers¹² for the use of $\text{Bi}_2\text{O}_3 \cdot 3 \text{SO}_3$ should apply to ZnSO_4 as well; these are: avoidance of corrosion problems in an H_2SO_4 boiler, reduction of heat penalties associated with drying H_2SO_4 solutions, and the use of lower acid concentrations in the process, hence less energy required to produce the acid. We anticipate that the use of this decomposition step should result in significantly reduced thermal requirements and costs even though it is not our purpose to develop the engineering details. We expect that the use of ZnSO_4 with a solar central receiver as a heat source would be especially advantageous, because of higher rates of energy input available from the solar sources as contrasted with high-temperature gas-cooled reactors.

Materials Corrosion Studies in Hot Concentrated Sulfuric Acid

We are conducting materials-corrosion studies with the goal of evaluating materials as to their suitability for an H_2SO_4 vaporizer. As part of these studies, we previously built an autoclave facility for testing materials such as high-silicon cast irons, SiC , Si_3N_4 , and CrSi_2 -coated Fe–Ni-based alloys in concentrated H_2SO_4 at about 673 K. This quarter, we put into operation a boiling–circulating H_2SO_4 loop and used it to test the behavior of the high-silicon cast iron Durichlor-51. We also acquired CrSi_2 -coated specimens of 304 stainless steel, Inconel 600, and Incoloy 800 and subjected them to static tests in H_2SO_4 at 673 K. The CrSi_2 -coated Incoloy 800 shows good potential as a future heat-exchanger material.

The corrosion test loop (Figs. 10 and 11) is constructed of silica glass and has a boiling chamber and a condensation chamber of the same size. Silica-glass piping joins the top and bottom parts of the two chambers. The assembled loop is mounted inside of an autoclave and placed in the furnace of our H_2SO_4 Corrosion Test Facility. Heat from the autoclave provides the primary heating to the test loop, but secondary heating is also provided by a Nichrome heating element, which is wound around the boiler. An argon pressure of 1.2 MPa inside the autoclave compensates for the boiling pressure of H_2SO_4 inside the silica. The condenser is enveloped in a silica cooling jacket, which is cooled by a high-pressure flowing air stream. A fibrous ZrO_2 blanket insulates the cooling jacket on the outside to keep heat exchange with the autoclave enclosure low. The inlet and outlet air temperatures and the air flow rate in the cooling jacket are measured to calorimetrically determine the amount of heat absorbed from the condenser section. With the H_2SO_4 boiler operating at 673 K, the optimum operating conditions appear to be an air flow rate (at 300 K inlet temperature) of 15 l/min and a temperature rise of 200 K. Using 108.8 kJ/mol for the heat of vaporization of H_2SO_4 , we calculate a boiling (condensation) rate of 200 g of H_2SO_4 /h.

This quarter we began running corrosion tests using the test loop. We placed a rod specimen of Durichlor-51, a high-silicon cast-iron alloy, in the boiler section of the loop. Approximately 40 g of 97-wt% H_2SO_4 in the loop covered about 2/3 of the specimen. We ran a 170-h test at 673 K with a boiling rate of 200 g of H_2SO_4 /h. Visual examination showed evidence of moderate corrosion (discoloration, pitting, and crystallites on the surface) over an approximately 2-cm region in the vicinity of the meniscus. Above this region there was no evidence of attack, and below this region the attack was minimal. The corrosion behavior appears to be identical to that we have observed in earlier experiments, which used static H_2SO_4 in contact with the samples in sealed silica bulbs.

We ran another corrosion test, on CrSi_2 -coated specimens in 97% H_2SO_4 at 673 K for 240 h using pieces of 304 stainless steel, Inconel 600, and Incoloy 800 as substrates. Duplicate samples of each material were run. We stopped the test at 240 h because of high pressure in the autoclave and discovered that one of the capsules had failed sometime after 175 h. This capsule contained one of the coated stainless steel samples.

FIG. 10. Top view of the H_2SO_4 circulating-loop assembly. The support rods would be removed to lower the loop into the autoclave below. We use this loop to study materials for their resistance to corrosion by boiling H_2SO_4 . The object is to find materials suitable for use in an H_2SO_4 vaporizer.

FIG. 11. The H₂SO₄ circulating loop mounted on the autoclave flange. When the loop is in use, the condenser chamber is insulated from the heat in the autoclave by a blanket of fibrous ZrO₂. Heat for boiling the H₂SO₄ around the sample being tested is provided by both the autoclave and the heating element. This quarter we began corrosion testing various materials in this loop.

Figure 12 shows the samples as they appeared after the test. A yellow precipitate had formed in the H_2SO_4 around each of the specimens. The failed sample (coated stainless steel) had lost 0.5 g of its 3.4-g total mass and showed large damaged areas in the CrSi_2 coating and extensive attack of the substrate. The other coated stainless steel sample also showed damaged areas in the coating; here the damage was accompanied by spalling, but apparently the spalling occurred after cool-down, because the areas exposed by it showed no significant attack. The total weight loss for this specimen was only 0.03 of its 3.4 g.

The coatings were all intact for the Inconel 600 and Incoloy 800 specimens and showed little visible corrosion, although the yellow precipitate had formed in the bottom of the bulb. Weight losses for the Inconel 600 specimens were 0.034 and 0.056 g of the 3.6-g total sample weights; for the Incoloy 800 specimens weight losses were 0.002 and 0.003 g of the approximately 3-g samples. From these tests, the CrSi_2 -coated Incoloy 800 looks very promising for further development.

FIG. 12. Front and rear views of CrSi_2 -coated specimens of Inconel 600, Incoloy 800, and 304 stainless steel. These specimens were subjected to corrosion by 97% H_2SO_4 at 673 K for 240 h in the H_2SO_4 circulating test loop. Weight losses for the Incoloy 800 specimens were much lower than for the other specimens, and this alloy looks very promising for further testing.

CHEMISTRY AND MATERIALS SCIENCE RESEARCH PROGRAMS

SURFACE SELF-DIFFUSION*

Introduction

We are studying surface self-diffusion on silicon and germanium surfaces to see how this mass-transport process affects the sintering of these two materials. A better understanding of surface self-diffusion should enable methods to be developed by which germanium, silicon, and other covalent materials could be sintered. The experimental approach is to etch a periodic surface profile on a polished single crystal of germanium or silicon and then follow the decay of this profile. Fitting the observed decay behavior to equations derived by Mullins¹³ will give the surface self-diffusion coefficient (D_s).

We have constructed an annealing furnace with controlled atmosphere for this study. The furnace also contains a laser-diffraction system for following surface-profile changes in situ and an Auger electron spectrometer for analyzing the surface composition.

Our first experiments in this system were directed at producing clean germanium surfaces. We found that above about 650°C the oxide film (GeO_2) on germanium is unstable, probably decomposing by reacting with germanium to produce volatile GeO . However, the resulting oxide-free germanium surface remains contaminated with at least a monolayer of carbon. Annealing the sample in vacuum, H_2 , Ar-H_2 , or 1.33×10^{-4} Pa O_2 to 800°C does not remove the carbon.

Current Progress

This quarter, we continued our experiments aimed at removing the carbon from the germanium surface. We were able to remove the carbon by sputtering in argon, but the resulting surface was very rough. We finally produced a carbon-free specular surface on germanium by a brief ion etching with oxygen. The oxygen implanted in the germanium surface is removed afterward by heating the sample above 650°C in vacuum.

Our first diffusion experiment on a clean germanium surface revealed no change in the surface profile after annealing for 80 h at 800°C. This surprising result required that we verify the smoothing we had observed in earlier experiments in Ar-H_2 gas. We annealed a sample for 16 h in Ar-H_2 at 850°C, and its surface smoothed considerably. However, careful observation of the surface revealed the changes to be the result of a chemical vapor-transport process (resulting from reaction with the hydrogen) and not surface diffusion (Fig. 13). These results were confirmed by repeating the experiment in pure argon, where no surface smoothing occurred because no chemical reaction occurred.

We have conducted several further diffusion experiments with (100) germanium samples in vacuum. A 90-h anneal at 900°C showed no change on a profile with a 16- μm wavelength. We are using smaller-wavelength etched patterns because Mullin's theory predicts that the profile smoothing depends directly on the fourth power of the frequency, ω , where $\omega = 2\pi/\lambda$.¹³ A subsequent experiment on a clean germanium surface with a 6- μm wavelength heated for 40 h at 850°C showed only slight rounding. Because surface self-diffusion on the (100) surface of germanium is so slow, a 2- μm -wavelength profile is being prepared to allow changes occurring by surface diffusion to be observed in a shorter annealing time.

*For more information, contact D. M. Makowiecki (422-8007).

FIG. 13. Evidence of vapor-transport mechanisms operating on germanium crystal surface. The original bar-and-groove pattern visible in the center of the photo is lower than the surrounding surface, indicating that the original surface was coated by a vapor-transport process. A surface-diffusion process would leave the original surface higher than the smoothed surface.

METALLIC ALLOY GLASSES*

In this project we are using rapid quenching techniques to produce new materials, mainly alloy glasses, and determining their properties. The goal of the project is to find new materials that have applications both in energy and in the Nuclear Explosives Program.

We are continuing to explore glass formation in the ternary subsystems of the U-Cr-Fe-Si system. This is the first part of a general examination of the U-Cr-Fe-V-Si-P system, in which we hope to find high-strength, oxidation- and corrosion-resistant alloy glasses. Foils are prepared using the arc-hammer method. X-ray diffraction is used to determine whether they are crystalline or glassy; differential scanning calorimetry is used to determine their thermal stability and crystallization behavior; and microhardness and bend ductility are used to estimate their mechanical properties.

This quarter, we prepared 25 additional alloys, bringing to 47 the number of compositions in the U-Cr-Fe-Si ternary subsystems that we have prepared to date (Fig. 14). One composition reliably forms a mixed glassy-crystalline material.

*For more information, contact R. W. Hopper (422-8001).

FIG. 14. Alloys prepared to date in ternary subsystems of U-Cr-Fe-Si system. In the Chemistry and Materials Science Department Metallic Alloy Glasses Program, foils of these alloys have been prepared by the arc-hammer method and characterized by x-ray diffraction, differential scanning calorimetry, microhardness, and bend ductility. This quarter we prepared 25 additional alloys in these subsystems.

We have begun to systematically study the thermal stability of the alloy glasses on time scales of minutes to hours. These studies will eventually allow some predictions concerning the intermediate-time (months) stability of the glasses to be made. Some early thermogravimetric oxidation data collected indicated a slow crystallization occurring during the experiment. Thus, the thermal-stability studies are necessary for the oxidation experiments.

This quarter we also tested the crystalline alloy known as Mulberry (uranium with 7-8 wt% niobium and 2.5 wt% zirconium) for oxidation resistance under conditions similar to those used to evaluate U-Cr-Si glasses (300°C, dry oxygen, for 2-4 h). We found that the Mulberry is at least an order of magnitude more oxidation resistant than the glasses. However, the glass compositions have not yet been optimized for oxidation resistance, and we expect they will be far more resistant than Mulberry.

SOFT FERROMAGNETIC GLASSES*

The soft ferromagnetic glasses program is a joint effort between the Metals and Ceramics Division and the LLL Electrical Engineering Department and will be terminated soon. The program is to develop ferromagnetic glassy-metal alloys for pulsed electronic applications, with emphasis on cores for magnetic switches and linear induction accelerators. The choice of ferrous metal glasses is based on their superior magnetic properties (high saturations and low loss) and their potential for low cost.

The alloy-development program has focused on Fe-Si-based materials. Melt spinning of compositions near $\text{Fe}_{80}\text{Si}_{20}$, which other sources have reported to yield glassy alloy films, has not yielded glassy alloys. However, we have produced ductile magnetic crystalline ribbons of bcc α Fe. This quarter we prepared alloys of $\text{Fe}_{100-x}\text{Si}_x$, where x ranges from 5 to 35. We measured the lattice constants of the resulting alloys and the electrical resistivities of the bcc alloys with silicon contents ranging from 5 to 11 at.% ($x = 5$ to 11). While the electrical resistivity of unalloyed iron (98.99%) is $9.71 \mu\Omega \cdot \text{cm}$, that of $\text{Fe}_{95}\text{Si}_5$ is $48.6 \mu\Omega \cdot \text{cm}$, about a factor of five greater. That of $\text{Fe}_{89}\text{Si}_{11}$ is $81.0 \mu\Omega \cdot \text{cm}$, almost a factor of ten greater. Also, cold rolling of thick ribbon (~ 0.1 cm) has indicated that reductions of thickness of at least 100% are possible.

*For more information, contact C. F. Cline (422-8021).

OFFICE OF BASIC ENERGY SCIENCES (OBES) RESEARCH

RAPIDLY QUENCHED MATERIALS*

Introduction

In 1960 Duwez and co-workers rapidly quenched a Au-Si alloy to liquid-nitrogen temperatures, thereby forming an amorphous solid.¹⁴ The scientific and technological interest in such materials has grown spectacularly since that experiment. These new "metallic glasses" have unique physical and chemical properties not possessed by the corresponding crystalline metal alloys. Compositions near the eutectic are rapidly quenched (10^5 – 10^6 K/s) to suppress the nucleation and growth of the crystalline phase. Although many questions remain to be answered, the rapid-quench techniques are being used to synthesize commercial metallic glasses, and new and specialized applications are being found for these materials. We have focused our attention on alloys containing beryllium because of their possible use as superconducting and high-specific-strength materials.

This quarter, we have been conducting a preliminary investigation of the potentially attractive ternary systems discovered in previous work. We especially studied alloys in the Be-Sc-B, Be-Fe-B, and Be-Ti-B ternary systems.

Current Progress

The Be-Sc binary system appears to have potential because of the low density of scandium. Empirical predictive formulae and actual melt-spinning studies have shown that Be-Sc cannot be melt-spun into an amorphous ribbon. Consequently, we experimented with the Be-Sc-B ternary system. Figure 15 shows the most likely glass-forming regions of this system. This quarter, careful scanning of the system has shown the $\text{Be}_{35}\text{Sc}_{60}\text{B}_5$ and $\text{Be}_{40}\text{Sc}_{55}\text{B}_5$ compositions are partially amorphous when melt-spun. We also formed the $\text{Be}_{40}\text{Sc}_{55}\text{B}_5$ composition by arc-hammering, and the resulting foils are less than 5% crystalline, very close to being entirely amorphous.

We also performed further experiments with Be-Ti-B and Be-Fe-B systems. We used the same melt-spinning procedure as before and, in both systems, found several completely amorphous compositions: x-ray analysis showed that $\text{Be}_{30}\text{Ti}_{65}\text{B}_5$ and $\text{Be}_{35}\text{Ti}_{60}\text{B}_5$ were amorphous, as was $\text{Be}_{20}\text{Fe}_{70}\text{B}_{10}$. We also found that $\text{Be}_{25}\text{Fe}_{65}\text{B}_{10}$ was almost completely amorphous.

We measured some preliminary mechanical-property data on these new metallic glasses and then compared the results with the properties of other high-specific-strength amorphous alloys (Table 2). The material with the highest reported specific strength is the $\text{Be}_{35}\text{Ti}_{60}\text{Si}_5$ composition, as measured by Tanner. If our hardness data is reliable, the $\text{Be}_{40}\text{Sc}_{55}\text{B}_5$ composition has still somewhat higher specific strength. However, our hardness measurements are not conclusive, since they were made on ribbon that still contained some crystalline material.

*For more information, contact J. B. Holt (422-8033).

FIG. 15. Region of the Be-Sc-B ternary system most likely to form amorphous metallic alloys by rapid quenching. Two binary points of this region have been estimated from analogous binary systems. This quarter in the OBES Rapidly Quenched Materials Program, we melt-spun the two partially amorphous compositions shown. We also arc-hammered one of the two, and the resulting alloy was more than 95% amorphous.

TABLE 2. Mechanical properties of our new amorphous alloys compared with other high-specific-strength metallic glasses.

Alloy	H_v , kg/mm ²	σ_y , kg/mm ²	ρ , g/cm ³	σ_y/ρ
Formed this quarter				
Be ₃₀ Ti ₆₅ B ₅	610	191 ^a	4.0	48
Be ₂₀ Fe ₇₀ B ₁₀	1030	322 ^a	6.8	47
Be ₄₀ Sc ₅₅ B ₅	520	162 ^a	2.82	57
From the Literature				
Fe ₈₀ B ₂₀	1100	370	7.4	50
Be ₄₀ Ti ₅₀ Zr ₁₀	740	231	4.13	56
Be ₃₅ Ti ₆₀ Si ₅	805	-	3.90	65

^a Calculated from the empirical formula $\sigma_y = H_v/3.2$.

HOT CORROSION*

Introduction

The objective of the hot corrosion program is to develop or extend current quantitative models of hot corrosion. Hot corrosion can be defined as high-temperature attack in a multiple-oxidant system and is usually associated with sulfidation and molten-salt attack. The phenomenon is observed in gas turbines and coal-conversion systems. Because these systems have very complex environments, we are studying in simple, controlled environments pure metals and binaries in order to obtain a detailed model of the attack. The two major experimental techniques used to date are thermogravimetric analysis and electrochemical polarization in molten salts.

Current Progress

This quarter we directed our efforts toward determination of scale chemistry and morphology and determination of growth kinetics, for nickel in molten Na_2SO_4 at 1173 K. We purged the molten salt with argon to drive off any dissolved gases, such as oxygen, that would interfere with the electrode reactions. We then measured anodic and cathodic polarization curves (Fig. 16), which provided a basis for choosing applied potentials to be used for studying the kinetics of scale growth.

As we have reported in previous quarterlies, the anodic branch of the polarization curve shows active-passive behavior. The passive current is high and the passive potential range is small. These characteristics indicate that although a scale forms, as is common in active-passive systems, it does not provide much protection from the corrosion environment.

So far, the applied potentials we have used in studying scale-growth kinetics are the open circuit, or rest potential (E_R), a potential in the passive range (E_1), and a potential in the transpassive (pitting) range (E_2). In future research, we will also apply potentials in the active range.

*For more information, contact J. J. Truhan (422-6925).

FIG. 16. Polarization of Ni in molten NaSO₄ with an argon purge at 900°C. Based on this curve, we chose applied potentials to be used in studying the kinetics of scale growth on nickel in molten H₂SO₄. This quarter we studied the scale growth at the rest potential, E_R , a potential in the passive range, E_1 , and a potential in the transpassive (pitting) range, E_2 .

Figure 17 shows the scale growth as a function of time for E_R , E_1 , and E_2 . These scales were grown by subjecting the nickel to the molten-salt environment for times ranging to 4 h. Figure 17 shows that as the potential shifts in the noble direction the rate of scale growth increases. This increased rate of growth corresponds to the successively higher current density seen in Fig. 16. We measured the rate constant for the scale growth at E_2 to be $1.21 \times 10^{-5} \text{ g/cm}^2 \cdot \text{s}$, which is in excellent agreement with the $1.8 \times 10^{-5} \text{ g/cm}^2 \cdot \text{s}$ calculated using the polarization curve and Faraday's Law.

The scale observed was essentially nickel oxide. We did see some sulfidation under this oxide scale; however it was only about 20 to 40 μm thick, and the thickness showed no dependence on either time of exposure or applied potential.

FIG. 17. Growth of NiO scale on nickel at the rest potential and at the two applied voltages studied this quarter. The scales were formed at 1173 K in molten NaSO_4 purged with argon. Applications of more noble potentials (E_1 and E_2) increase the rate of scale growth. The potentials are measured with respect to a Pt-O half-cell.

The morphology of the nickel oxide did change with applied potential, however. When formed at rest potential, this scale was composed of columnar grains growing perpendicular to the surface (Fig. 18). When formed under applied anodic potentials, the scale appeared layered and porous. The layers were narrow ($\sim 5 \mu\text{m}$ thick) and showed evidence of separation in several areas. Also, the scale contained many voids. In some cases the outermost portion of the top layer had the appearance of the nickel oxide formed at rest potential. We are performing additional metallography to characterize these scales.

This quarter we also carried out several cathodic-polarization experiments and found that cathodic polarization protected the samples from dissolution as does cathodic protection in aqueous environments. These results have exciting potential for the protection of alloys in coal-conversion systems, where salt formation presents a corrosive environment.

We also performed similar experiments with an oxygen purge through the molten salt. The addition of oxygen will shift the rest potential in the noble direction, and we predict from the polarization curve that this shift will provide a more stable oxide. These samples are currently being prepared for metallographic examination.

OPTICAL MATERIALS WITH REDUCED NONLINEAR EFFECTS*

Introduction

The development of high-power lasers, principally for fusion research, places ever more-stringent requirements on the properties of transparent optical materials.¹⁵ The electrical fields associated with such laser beams are so intense that higher-order, nonlinear terms in the polarizability of the material become important. The purpose of this program is to study the effects of these nonlinear terms and search for ways to circumvent or surmount them.

One of the effects of interest is self-focusing caused by nonlinear contributions to the refractive index of a glass. Because of their small predicted nonlinear-index coefficient, fluoride glasses are the most promising candidates for both passive components (such as lenses and windows) and active components (such as the laser-amplifier and Faraday-rotation media) in high-power lasers. Our part in the effort to study these effects is to prepare and characterize beryllium fluoride glasses.

Also, zinc chloride glasses hold interest for laser applications because a ZnCl_2 lattice containing N^{+3} may have narrow fluorescence line widths and thus high laser gain. To support investigation of these glasses, we are attempting to prepare ZnCl_2 glasses doped with NdCl_3 .

Current Progress

This quarter we worked on preparing ZnCl_2 glasses doped with NdCl_3 . We were able to prepare undoped ZnCl_2 by melting anhydrous ZnCl_2 under a flowing atmosphere of either HCl or dry argon. There is evidence of reduction of ZnCl_2 to zinc metal, which has necessitated filtering. The experimental evidence indicates that removing H_2O from the hygroscopic ZnCl_2 makes it more difficult to quench the melt to the glassy state. We have made several experiments to dope ZnCl_2 with 0.5 and 2.0 mol% NdCl_3 without success. Future work will be directed to preparing binary glasses of ZnCl_2 plus KI , as Australian workers have reported success with this binary system. We hope that we will be able to dope this binary glass with NdCl_3 .

*For more information, contact C. F. Cline (422-8021).

NiO
scale

Ni

Formed at rest potential

10 μm

NiO
scale

Ni

Formed under applied anodic potential

10 μm

FIG. 18. Difference in scales formed on nickel at rest potential and under an applied anodic potential (E_2). The nickel was corroded in molten NaSO_4 at 1173 K. Exposure times were 2 h for rest potential and 4 h for E_2 .

FLUORESCENCE-LINE NARROWING OF AMORPHOUS SOLIDS*

Introduction

The objective of this project is to investigate local structure and interactions in glasses by applying laser techniques for fluorescence-line narrowing. Experimental work on this project is being done in Y Division; our part is to model glass structures using a Monte Carlo computer code. In using this code to simulate a glass, we quench several fluid configurations to lower temperatures, where no diffusion occurs. This yields a series of configurations characteristic of a rigid but disordered solid at low temperatures, i.e., a glass. Each configuration represents one of the microscopic structures seen in a glass. The model will be used to relate the experimental results to glass structure.

Current Progress

We are studying the system of BeF_2 doped with the trivalent rare earths, such as neodymium. This quarter we completed several computer simulations of BeF_2 glass doped with a rare earth. The system consisted of 65 beryllium ions, 133 fluorine ions, and 1 rare-earth ion in a box 1.382 nm^2 . We used these simulations to calculate the potential energy from the full Ewald sum; the calculation is exact, assuming the boundary conditions are periodic and the interionic potential is of a specific form. No covalency or polarization is included.

The Be-F radial-distribution function in this system is similar to that of pure BeF_2 . The rare-earth-fluorine radial distribution function g (Fig. 19) shows a peak at 0.235 nm . Note that the function varies widely and thus there is no well-defined coordination number for the rare earth. This results from the average coordination number varying strongly with r for all r . However, for r between 0.30 and 0.35 nm , the average coordination number has a much smaller slope than elsewhere, and thus one can talk vaguely of a rough eight-fold coordination in this region. However, the actual coordination number of particular sites in this region fluctuates between 6 and 10.

*For more information, contact S. A. Brawer (422-8094).

FIG. 19. Rare-earth-fluorine radial distribution function $g(r)$, which is the number of fluorine ions per unit volume at a distance r from the rare earth. Also plotted is the average coordination number $n(r)$, defined as $4\pi \int_0^r r'^2 g(r') dr'$. The plot shows that, because of the wide variation of the average coordination number, there is no well-defined coordination number for the rare earth. This computer simulation is part of an OBES study aimed at investigating the local structure and interactions in laser glasses.

The rare-earth-beryllium distribution function peaks at 0.37 nm and vanishes for rare-earth-beryllium separations smaller than 0.31 nm. Thus, a strong repulsion pushes the beryllium ion away from the rare earth.

The interesting features of the molecular structure about the rare-earth ion are as follows:

- The closer a fluorine is to the rare earth, the more the fluorine tends to be nonbridging (i.e., bonded to only one beryllium). Thus all fluorine ligands within 0.22 nm of the rare earth are nonbridging, but only 50% of those within 0.29 nm are nonbridging.

- With a few exceptions, only one fluorine of any BeF_4 tetrahedron is within 0.35 nm of the rare earth; i.e., those BeF_4 tetrahedra near the rare earth tend to be oriented so that one fluorine is pointed toward the rare earth and the rest are farther away. This structure presumably minimizes the repulsive energy between the rare earth and the beryllium while satisfying the coordination requirements of the rare earth. It also results in more entropy than in the structure where two or more fluorines on the same BeF_4 tetrahedron are rare-earth ligands.

- The series of Be-F-Be-F-Be bonds linking together fluorines that are within 0.3 nm of the rare earth (i.e., the series of bonds linking the rare-earth ligands) tends to be long, containing three to eight beryllium ions. Occasionally the series contains only two beryllium ions. This has considerable ramifications for the temperature dependence of homogeneous line widths. In particular, for localized lattice vibrations, it is unlikely that the vibrations of the ligands that are within 0.3 nm of the rare earth will be correlated. This means homogeneous line widths will have a weak temperature dependence compared with those in crystals.

Also this quarter, we calculated the energy levels of the $^7\text{F}_1$ manifold of the Eu^{3+} in BeF_2 glass, assuming a second-order crystal field due to point charges and including j-mixing with $^7\text{F}_0$ and $^7\text{F}_2$ manifolds. The results agree qualitatively with experiment, and more detailed and accurate calculations are under way.

MATERIALS RESEARCH NOTES

STAINLESS STEEL COMPATIBILITY WITH HYDROGEN*

We are conducting an experimental program to understand the important parameters contributing to slow crack growth and delayed failures in 21Cr-6Ni-9Mn stainless steel exposed to hydrogen. If we can understand the slow embrittlement process for the 21-6-9 stainless steel then we will be in a better position to understand the limitations of this and other, similar stainless steels.

Our study also includes thermomechanical processing: forging, high-energy-rate forging, rolling, extrusion, and press forming. We are currently concentrating on forging and rolling. We are trying to produce steels that have good mechanical properties and that will likely resist hydrogen embrittlement.

We have made our first try at warm rolling 21-6-9 stainless steel. The rolling was done at Rockwell International Rocky Flats Plant under our direction. The resulting microstructure was nonuniform from one edge to the other, apparently because of a temperature gradient through the thickness of the plate during the rolling operation. At our suggestion, turning, inverting, and reheating of the plate was used to reduce temperature gradients through the thickness. This was very successful; the warm-worked structure had a consistent medium grain size (Fig. 20). The mechanical properties were very attractive and are shown in Table 3.

Since the tensile properties of the 21-6-9 stainless steel looked so attractive, we applied the same thermomechanical processing to 316 VIM/ESR stainless steel. The microstructure of the warm-worked structure is shown in Fig. 21; the tensile properties, in Table 4.

The thermomechanical processing developed for 21-6-9 stainless steel produces very attractive mechanical properties and can be applied with good results to VIM/ESR 316 stainless steel. We will now study the influence of high-pressure hydrogen on the mechanical properties of both of these alloys.

*For more information, contact P. R. Landon (422-7063).

FIG. 20. Consistent, medium-size grains in 21-6-9 stainless steel that was warm-rolled (at 621°C) from 38 to 19 mm thick and water quenched. The mechanical properties of this steel were also very attractive. The special thermomechanical processing that resulted in this steel is part of our effort to improve the compatibility of stainless steels with hydrogen.

TABLE 3. Tensile properties of 21Cr-6Ni-9Mn stainless steel warm rolled to 19.0 mm thick.

	Yield strength, MPa	Ultimate strength, MPa	Elongation		Reduction in area, %
			ϵ_t , %	ϵ_u , %	
Longitudinal	931	986	37	12	71
Transverse	924	965	37	13	67

FIG. 21. Microstructure of warm-rolled 316 stainless steel worked by the same process as the 21-6-9 stainless steel shown in Fig. 20. This 316 sheet was rolled from 57.2 to 28.6 mm thick, and the resulting properties were very attractive. We will now study the compatibility of this and the warm-rolled 21-6-9 stainless steel with hydrogen.

TABLE 4. Tensile properties of 316 stainless steel warm rolled to 28.6 mm thick.

	Yield strength, MPa	Ultimate strength, MPa	Elongation		Reduction in area, %
			ϵ_t , %	ϵ_u , %	
Longitudinal	910	958	37	15	70
Transverse	903	965	37	15	70

UNDERGROUND THERMOCOUPLE PROTECTION*

Underground thermocouples that monitor the in-situ coal-gasification process are subject to severe corrosion and fail quickly. To protect the thermocouples in this environment, a cladding of corrosion resistant material can be used. Currently, we envision this to be a two-layer coating: a stainless steel or nickel-based alloy sheath surrounding the thermocouple and an outside layer of grout for protection from slagging attack.

This quarter we tested the compatibility of several candidate alloys with grout. The grout contained 50% Portland cement and 50% pozzolan. The pozzolan in this grout was derived from fuel ash, and had the following composition:

Fe ₂ O ₂	5 wt%
Al ₂ O ₃	18 wt%
CaO	4.1 wt%
SiO ₂	Balance
MgO	1 wt%
SO ₃	0.5 wt%
Na ₂ O	1.5 wt%
K ₂ O	2.1 wt%
Organics	0.3 wt%

The alloys we tested were low-carbon steel (black iron pipe), 304 stainless steel, 310 stainless steel, Inconel 600, Inconel 625, and Incoloy 800. We embedded a specimen bar of each in grout in a small mullite crucible and heated the crucible in air in an electric furnace.

A heating rate of 250°C/h caused the grout to explode and shatter the crucible. The explosion was caused by water, which evolves from concrete as follows:

at 114°C	free water vaporizes;
at 127°C	hydrate gel of calcium silicate decomposes;
at 147°C	ettringite decomposes; and
at 525°C	Ca(OH) ₂ decomposes

Crucible assemblies for subsequent tests were first baked at 300°C. Baking removed 18 to 21% of the weight of the entire assembly and enabled them to be heated without exploding.

We held crucibles with grout and metal specimens for 24 h at about 1000°C. The grout cracked somewhat and lost most of its strength. It could be powdered between the thumb and forefinger. The low-carbon steel specimens were heavily corroded, but the alloys were only lightly corroded. Corrosion of the alloys was light enough that thermocouple sheaths made of them would survive such a 24-h bake.

However, since the thermocouples could be used eventually up to 1800–1900°C, we carried out higher-temperature experiments. At 1200°C, the grout components reacted, and the grout liquified, overflowed out of the crucible and glazing the ceramic tile underneath. All metal specimens were heavily attacked at this temperature.

We consulted with the manufacturer of the grout, who recommended strongly against using it at high temperatures. They recommend instead another of their products with about 50% silica flour added, or any other refractory cement such as are used in steel mills. Their recommended product contains CaO·Al₂O₃

*For more information, contact W. D. Ludemann (422-7485).

and reacts with SiO_2 to form Ca-Al silicates. Thus, to protect the thermocouples, if Portland cement or the tested grout is to be used, they should be mixed with an equal volume of silica flour, which will tie up the detrimental minerals as silicates.

The manufacturer of the grout also said that, except for free water, water would not cook off of the grout during downhole conditions. However, the free water vaporizing could burst pipes. The grout to be used should pass the American Petroleum Institute zero-free-water test, which is to mix the grout with a given volume of water, e.g., 44%, pour into a graduate, seal it and let it sit for 2 h; then look for free water on top of the grout.

We conclude that this grout will cause some corrosion of thermocouple-sheath materials. However, corrosion will not be catastrophic in 24 h below 1070°C . It would be safer to use neat cement (Portland cement plus water only) or Portland cement plus silica flour. The SO_3 , Na_2O , and K_2O in fly ash pozzolan all degrade protective oxide films on alloy metals.

PRESENTATIONS

R. E. Armstrong	Defocused Electron Beam Welding of Aluminum	American Welding Society Annual Meeting, Detroit, Mich., April 1979
W. L. Barmore	In-Situ Testing with High-Energy Neutrons and Effects of This Irradiation on the Creep of Niobium	1979 TMS-AIME Fall Meeting, Milwaukee, Wis., September 16-20, 1979
S. A. Brawer	The Optical Properties of Mo^{3+} in Phosphate Glass	American Ceramics Society, Cincinnati, Ohio, April 29-May 2, 1979
S. A. Brawer	Computer Calculations of Glass Structures	American Ceramics Society, Cincinnati, Ohio, April 29-May 2, 1979
S. A. Brawer	Fluorescence Line Narrowing, and Hole Burning in Glass	University of Wisconsin, Dynamic Processes Conference, Madison, Wis., June 18-20, 1979
C. F. Cline	Advanced Armor Materials	Ballistic Research Lab Program Review, June 6, 1979
C. F. Cline	Cater Mill Study (Co-chairman of Cater Mill Study)	Defense Advanced Research Projects Agency, Arlington, Va., May 15-17, 1979
C. F. Cline	Explosive Fabrication of Ceramics	Defense Advanced Research Projects Agency Workshop, La Jolla, Calif., July 23-24, 1979
C. F. Cline	Preparation of New Dielectric Films on LSG-91H, LHG-8 and LHG-10 Laser Glasses	National Bureau of Standards Technical Workshop, Laser Glass Meeting, Washington, D.C., August 2-3, 1979
J. F. Cooper and E. Behrin	Aluminum-Air Power Cell Development	Fall Meeting of the American Chemical Society, Washington, D.C., September 13, 1979
J. F. Cooper	Control of Battery Electrolyte Composition through the Precipitation of Aluminum Trihydroxide: Feasibility Study	First International Workshop on Reactive Metal-Air Batteries, University of Bonn, West Germany, July 10, 1979
J. F. Cooper	Economics and Energy Balance of an Aluminum-Air Transportation System	First International Workshop on Reactive Metal-Air Batteries, University of Bonn, West Germany, July 10, 1979

J. F. Cooper	An Aluminum-Air Transportation System: Engineering Design and Concept Analysis	First International Workshop on Reactive Metal-Air Batteries, University of Bonn, West Germany, July 10, 1979
J. F. Cooper	Aluminum-Air Cells: Performance Characteristics	First International Workshop on Reactive Metal-Air Batteries, University of Bonn, West Germany, July 10, 1979
W. R. Holman	CVD Tungsten Coatings on Steel	Integrated Contractors Meeting/SUBWOG, Union Carbide Y-12 Plant, September 25-27, 1979
W. R. Holman	Session Chairman	Symposium on Applications of Refractory Metals in Fusion Reactors, 1979 TMS-AIME Fall Meeting, Milwaukee, Wis., September 16-20, 1979
J. B. Holt and D. M. Makowiecki	Surface Self-Diffusion of Germanium and Silicon	Fifth International Conference on Sintering and Related Phenomena, Univ. of Notre Dame, South Bend, Ind., June 18-20, 1979
O. H. Krikorian	Zinc Sulfate Decomposition Studies	International Energy Agency Hydrogen Workshop, Los Alamos Scientific Laboratory, September 24-27, 1979
O. H. Krikorian	Materials Corrosion Studies in Hot Concentrated Sulfuric Acid	International Energy Agency Hydrogen Workshop, Los Alamos Scientific Laboratory, September 24-27, 1979
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