MASTERContract DE-A^S002-76ER0293**RADIATION EFFECTS ON BCC METALS
AND ALLOYS****FINAL REPORT**

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ABSTRACT

The concept of micro-mechanical metallurgy using the hot-hardness as a strength microprobe and also as a measure of the uniform elongation of irradiated and unirradiated bcc metals and alloys has been shown to be technically feasible and to be an attractive and practical approach in the mechanical property evaluation of small quantities of material. This is especially true for circumstances where (a) small size irradiation facilities, i.e., the fusion sources, are only available, (b) small quantities of material are used in the course of advanced alloy development, and (c) intense radioactivity from the larger conventional test samples preclude the normal handling of this material in semi-remote facilities.

To contribute to more meaningful and self-consistent deformation and/or strengthening models, use was made of quantitative transmission electron microscopy to obtain the number density and size distribution of the various defect states in the irradiated material. With this information, the influence of defects on dislocation mobility and deformation modes was determined. In addition, by means of high temperature anneals for different time intervals, the original defect states was significantly changed so that the above dislocation-defect interaction models may be tested under many different conditions. Combinations of time at temperature and applied stress has been shown to be extremely important in the dislocation channeling phenomenon, a circumstance that is closely associated with irradiation induced embrittlement.

Detailed resistivity measurements, a technique for determining defect thermal stability and recovery kinetics, was used to establish critical test temperatures. In order to minimize defect variability, during a given study, tests were performed in temperature regions where the recovery process would progress relatively slowly, i.e., in between pronounced recovery peaks. A knowledge of these important recovery peaks and also the detailed quantitative defect data, generated in this program, should also be of help to other investigators in both their experimental and deformation modeling studies.

SUMMARY

Introduction

The main objective of this program was to (a) evaluate the influence of irradiation temperature in a nuclear environment on the substructure of bcc metals and alloys which were irradiated at relatively high fluence levels and (b) to determine the influence of this defect microstructure on the subsequent physical and mechanical properties in the as-irradiated condition and following different time-temperature thermal histories. In particular, the nature and the number density of observable irradiation induced defect clusters was determined by the use of a 200 kV transmission electron microscope (TEM). The study of the defect recovery behavior, as a function of annealing temperatures and times, was investigated principally by the use of TEM, resistivity (R), and microhardness (H) measurements. Other parameters such as void volume (density) and length changes were also considered as a means of further identifying both the nature and the temperature stability of the irradiation induced defects. Finally, the influence of these defects on the plastic flow properties (tensile and creep deformation) of these irradiated metals and alloys was evaluated.

The principal materials evaluated in this program included Nb, Nb-1Zr, Mo, Mo-0.5Ti, W, and W-25Re. Most of the studies concentrated on (a) molybdenum and molybdenum alloys and on (b) those specimens which were irradiated in the EBR-II Facility.* Six different irradiation temperatures, in the range of 455 ± 5 to $1050 \pm 30^\circ\text{C}$, was obtained in the EBR-II capsules. The total neutron fluence was 1×10^{22} neutrons cm^{-2} , $E > 1$ MeV. Through a Thesis Parts Program at Argonne

*(Capsules X-034 and X-035; 11035 and 10618 Megawatt days, respectively; capsules were in the reactor from April 16, 1968 through July 31, 1969).

National Laboratory, one detailed study was made on ion-irradiated molybdenum and several molybdenum alloys at temperatures and equivalent fluences (dpa's) typical of the EBR-II irradiations.

The influence of impurity levels on the resulting irradiation induced defect states in molybdenum was investigated by considering three degrees of purity (i.e. residual resistivity ratios of 60,650 and 6320). These specimens, irradiated in the Oak Ridge Research Reactor at ten different temperatures (220 to 900°C) to a fluence of 1×10^{21} n cm⁻², E>0.1MeV, were furnished to the University of Cincinnati by the Metals and Ceramics Division (Dr. K. Farrell) of the Oak Ridge National Laboratory. In addition to the TEM evaluation, small-angle X-ray scattering (SAXS) and microhardness measurements were considered in these tests.

Some of the EBR-II Mo and W specimens were given to Cornell University (Dr. Seidel) for FIM point defect studies and some Nb specimens were given to ORNL (Dr. C. Coch) for superconductivity measurements.

Publications

In addition to presentations at the TMS-AIME Meetings, ASTM Symposia and other Technical Society Programs, nineteen (19) papers have been published in the open literature, with five (5) papers presently submitted for publication. Thirteen (13) other papers relating to work performed under this contract are in the process of preparation. A listing of paper titles and authors for the three categories is presented in Appendix A of this report.

For completeness, a listing of previous Progress Reports is also included in Appendix A.

An indication of the extent to which the Principal Investigator (John Moteff) was involved in published studies of the effects of irradiation on molybdenum is clearly pointed out in a 1976 review document by Schmunk and Kulcinski

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(UNFDM-161, Survey of Irradiation Data on Molybdenum). An excerpt (Pages 10 and 11) from this document is presented in Appendix B of this Final Report.

Students Associated with Program

Five (5) PhD dissertations, and five (5) MS Theses were completed on work related to the DOE Project. One (1) Senior Project was also related to this program. The students and their respective Research Topics are listed in the table on the following page and the complete Abstracts of each document are given in Appendix C of this report.

All but one of the individuals listed in the table on the following page (R. E. Zielinski) were supported entirely by the AEC/ERDA/DOE Contract AT(11-1)-2093. The senior, C. G. Schmidt*, did not receive financial support during the course of his Senior Project, although materials and supplies needed for this project were funded through this program.

Of the five (5) PhD graduates, one is now teaching. He is:

J. F. Stubbins - University of Illinois

Three of the PhD graduates are now working in Industry/National Laboratory. They are:

V. K. Sikka - Oak Ridge National Laboratory

H. Jang - General Electric Company

S. Liu - Special Metals

The fifth student (Frank Lee) just completed his work and graduated in August, 1980. He is presently staying on at the University of Cincinnati in a Post-Doctoral assignment.

*C. G. Schmidt did stay on at the University of Cincinnati to work on his MS degree and was supported on the AT(11-1)-2107 Program. He then went on to Stanford University to get his PhD (1980) and is now working at the General Electric Company in Sunnyvale, California.

STUDENT RESEARCH TOPICS

PhD Dissertation

Vinod K. Sikka, "The Nature and Thermal Stability of Defects in Neutron Irradiated Mo and Mo-0.5% Ti", (1973).

James F. Stubbs, "Heavy Ion Induced Radiation Damage and Void Formation in Molybdenum and its Alloys", (1975).

Ho Il Jang, "Radiation Hardening and Void Swelling of Neutron Irradiated Niobium (Columbium) and Niobium-1% Zirconium Alloy", (1975).

Shaiw-Rong Scott Liu, "The Effects of Interstitial Impurities and Radiation Temperature on Voids Swelling and Irradiation Hardening in the Neutron Irradiated Molybdenum", (1979).

Kang-Jyh Frank Lee, "A Study of the Strength, Substructure, and Their Correlations in Irradiated and Non-Irradiated Molybdenum", (1980).

Master of Science - Thesis

Ho Il Jang, "Dilatometric Measurement of Property Changes in Neutron Irradiated Molybdenum", (1973).

Ashi Malik, "A Correlation of the Dislocation Substructure Associated with Creep-Rupture Tested Polycrystalline Molybdenum", (1974).

J. Matolich, Jr., "Electrical Resistivity Study of the Recovery of Neutron-Irradiated Tungsten and Tungsten-25 Rhenium", (1976).

Ronald E. Zielinski,* "A Study of the Compressive Creep of Irradiated and Un-irradiated Molybdenum at Elevated Temperatures", (1976).

Kang-Jyh Frank Lee, "Electrical Resistivity Study on the Defect Recovery of Neutron-Irradiated Molybdenum", (1976).

Senior Research Project

Charles G. Schmidt, "Hot Hardness of Molybdenum", (1974).

*Part-time graduate student. Work related but not supported by Contract AT (11-1)-2093.

Other personnel assigned to supportive roles on various short-term phases of the AT(11-1)-2093 Project included undergraduate and graduate students on a part-time basis.

Significant Results

In addition to the generation of extensive quantitative experimental data on the observed defect structure of bcc metals and alloys which were irradiated to temperatures up to 1050°C for the case of neutron irradiations and up to 1500°C for the case of ion irradiations, as well as irradiations at neutron fluences up to $1 \times 10^{22} \text{ n cm}^{-2}$, $E_n > 1.0 \text{ MeV}$ (about 29 dpa for the base of Mo) and for ion irradiations up to 57 dpa for the case of Mo, the following significant results are reported:

1. Based on (a) the quantitative (TEM) measurements of various defect states and of their thermal stability, (b) the microhardness experimental data on specimens having the various defect states, and (c) the irradiation induced hardening determined from both the hardness measurements and analytically through dispersion strengthening models shows excellent correlation with corresponding macroscopic tensile/creep tests, it is demonstrated that the concept of a hardness test as a Strength Microprobe is indeed a practical and technically feasible approach for conditions where sample and/or irradiation test facilities (i.e. 14 MeV neutron source) are very small. The fact that ductility may also be determined from the hardness tests makes this concept all the more attractive.
2. Based on the quantitative observed defects (i.e. number density N and size d), the resulting irradiation induced hardening shows excellent correlation with the relationship

$$\Delta\sigma = \alpha Gb\bar{d}^{-1} \quad \text{where}$$

$$\ell = (Nd)^{\frac{1}{2}}$$

where G and b are the shear modulus and Burgers vector respectively and α is a dislocation-defect interaction parameter equal to approximately 0.5 for black spots and loops and to 1.0 for the case of voids.

3. The determination of the ultimate tensile strength (T) from hot-hardness (H) measurements shows excellent correlation with experimental hot-tensile data through the relationship

$$\sigma = (H/3) (n/0.217)^n$$

where n is the strain hardening parameter which can be obtained from a Meyer hardness (m) measurement using $n = m-2$.

4. The embrittlement observed in irradiated bcc metals will always occur when the defect concentration is at or above a given value such that dislocation channeling is the only deformation mode possible under tensile or compressive forces.
5. An anomalous creep behavior occurs when the irradiation induced defect concentration is such that, for a given test temperature and applied stress level, a period of time called the "incubation period" exists where the creep strain is essentially zero. The extent of this incubation period is decreased with an increase in test temperature and/or applied stress. This anomalous creep behavior is directly associated with the time required to initiate dislocation channeling.
6. Dislocation channeling may be observed as coarse planar slip bands on the specimen surface and on the facets of grains in the fracture region as well as on the surface adjacent to the impression of a hardness indentation. As the surface slip lines approach wavy glide features, the irradiated metals become ductile.

7. The uniform elongation may be obtained by measuring the height and radius of the peak of the flowed metal adjacent to the impression of a hardness indentation. This technique is especially useful for obtaining preliminary information on ductility changes in radioactive specimens and in those small samples irradiated in fusion environments (14 MeV neutrons).
8. The lower temperature bound for void formation in neutron irradiated bcc metals is shown to be at least $0.19 T_m$, rather than the conventionally reported temperatures of 0.25 to $0.30 T_m$.
9. Based on void superlattice constants and on resistivity recovery data, it has been shown that these parameters can be used to determine the irradiation temperatures of reactor test capsules for cases where general steady state irradiations are considered.
10. For the case of Mo and W, the void volume swelling tends to show two peaks when plotted as a function of irradiation temperature. When the two elements are compared on the basis of the homologous irradiation temperatures, the data superimpose onto a common curve.
11. The void volume swelling based on dimensional measurements ($\Delta l/l_0$ and $(\Delta d/d_0)$ of the length and diameter of the resistivity specimens show good agreement with immersion density data obtained from the same specimens.
12. A comparison of the swelling determined from dimensional changes and immersion density measurements with that obtained from the quantitative TEM results of void number density and size show that the TEM data underestimates the swelling by factors of about 4 or 5. It is believed that the non-observable voids and other defects that are not included in the TEM data analysis account for the discrepancy.

13. The major observable irradiation induced defects are rafts, black spots, loops, voids with the rafts being unstable at irradiation temperature above 455°C, the black spots above 520°C and the loop above 940°C. The voids and dislocation networks were stable up to irradiation temperatures of 1050°C.
14. For identical irradiation conditions W shows a tendency to form two swelling peaks whereas, W-25 Re does not exhibit the lower temperature peak with a slight tendency to form a peak at the higher temperature. The W-25 Re tends to form a second phase, predicted to be an α -Mn type structure, rather than to form voids.

Recommendations for Future Work

Additional work should be performed in the area of micro-mechanical metallurgy using combinations of microhardness and quantitative transmission electron microscopy. This information should then be coupled to macroscopic tensile/creep data on sub-miniature specimens* using the following semi-empirical and/or theoretical approaches:

A. Hot-hardness to uniaxial strength and ductility.

Develop a better understanding of the relationship

$$\sigma = (H/3) (\pi/0.217)^n$$

using continuum mechanics and finite element analysis. Evaluate the limitations on loads and loading rates for both the Vickers and the Meyer hardness values.

*Only 108 of the 256 specimens on hand at the beginning of this program were used. These are unique specimens in that the six irradiation temperatures are well known and they still represent some of the highest neutron irradiations for the bcc metals and alloys to date.

Particular attention should be given to the physics involved in the excellent correlation of the h/r ratio of the flowed metal adjacent to the hardness impression to the uniform elongation in a uniaxial tensile test.

B. Quantitative TEM to uniaxial strength and ductility.

Develop a better understanding of relationships of the type

$$\Delta\tau = \alpha Gb\ell^{-1} = \alpha Gb(Nd)^{1/2}$$

with emphasis on the dislocation-defect interaction parameter (α) and resolved shear stress for the different operating crystallographic slip planes and directions.

The strengthening relationship that may be used when two or three different defects of different strengths are simultaneously present in the test specimen should be further developed.

Finally, the role that dislocation channeling plays in the plastic deformation process and the subsequent ductility of irradiated bcc metals and alloys should be further explored.

APPENDIX A - LIST OF PUBLICATIONS

Papers and Publications

- V.K. Sikka and J. Moteff, "Superlattice of Voids in Neutron Irradiated Tungsten", J. Appl. Phys., 43, 4942 (1972).
- V.K. Sikka and J. Moteff, "Observation of a Void Superlattice Containing a Dislocation in Neutron Irradiated Mo-0.5Ti," Crystal Lattice Defects, 3, 113 (1972).
- V.K. Sikka and J. Moteff, "Stability of the Damage State in Neutron Irradiated Molybdenum", Trans. Am. Nucl. Soc., 17, 142 (1973).
- V.K. Sikka and J. Moteff, "Rafting in Neutron Irradiated Tungsten," J. Nucl. Mater., 46, 216 (1973).
- V.K. Sikka, D.J. Michel and J. Moteff, "Twin-Jet Electropolishing Technique for TEM observation of Tantalum and Niobium", J. Less Common Metals, 31, 311 (1973).
- J. Moteff and V.K. Sikka, "Irradiation Temperature Monitoring by Void Superlattice Constant Measurements", Trans. Am. Nucl. Soc. 16, 97 (1973).
- V.K. Sikka and J. Moteff, "Threshold Temperature for Void Formation in the Group VIA Metals", Trans. Am. Nucl. Soc., 16, 97 (1973).
- J. Moteff, D.J. Michel, and V.K. Sikka, "The Influence of Irradiation Temperature on the Hardening Behavior of the Refractory BCC Metals and Alloys", Defect and Defect Clusters in BCC Metals and Alloys, Nuclear Metallurgy, AIME-IMD, 18, 4942 (1973).
- V.K. Sikka and J. Moteff, "Substructure of Irradiated Molybdenum", Ind. J. of Tech., 11, 541 (1973).
- J. Matolich, H. Nahm, and J. Moteff, "Swelling Characteristics of Neutron Irradiated Tungsten and Tungsten-25% Rhenium, Scripta Met., 8, 837 (1974).
- V.K. Sikka and J. Moteff, "Damage in Neutron Irradiated Molybdenum, Part I, Characterization of As-Irradiated Microstructure", J. Nucl. Mater., 54, 325 (1974).
- V.K. Sikka and J. Moteff, "Identification of α -Mn Crystal Structure in Neutron Irradiated W-Re Alloy", Met. Trans., 5, 14 (1974).
- V.K. Sikka and J. Moteff, "Stability of the Defect State in Neutron Irradiated Molybdenum", J. Nucl. Technology, 22, 52 (1974).
- D.J. Michel and J. Moteff, "Voids in Neutron Irradiated and Annealed Niobium and Niobium-1% Zirconium Alloy", Radiation Effects, 21, 235 (1974).
- F. Lee, J. Matolich and J. Moteff, Swelling in Neutron Irradiated Molybdenum Based on Dimensional Changes, J. of Nuc. Mater., 62, 115 (1976).

Papers and Publications (cont.)

H. Jang and J. Moteff, Dimensional Stability of Neutron Irradiated Molybdenum, ASTM STP-570, 404, (1976).

F. Lee, J. Matolich and J. Moteff, Irradiation Temperature Determination by Electrical Resistivity Measurements, Nuclear Technology, 39, 207 (1978).

S. Liu, J. Moteff, R.W. Hendricks and J.S. Lin, Small-Angle X-ray Scattering Studies of Voids in Neutron-Irradiated Molybdenum, J. Appl. Cryst.; 11, 597 (1978).

K. Furuya and J. Moteff, Correlation of the Microhardness with the Tensile Properties of Neutron Irradiated Molybdenum, accepted for publication in Metallurgical Transactions (1980).

Papers Submitted for Publication

K. Furuya and J. Moteff, Deformation Behavior of Neutron Irradiated Molybdenum in Tensile Test and Hardness Test".

J. Stubbins and J. Moteff and A. Taylor, "Void Swelling Behavior of Vanadium Ion Irradiated Molybdenum".

J. Stubbins and J. Moteff, "Void Superlattices in Mo and Its Alloys".

J. Stubbins and J. Moteff, "Dislocation Loop Superlattices in Irradiated Cubic Metals".

F. Lee, J. Matolich and J. Moteff, "Defect Recovery Behavior of Neutron Irradiated Molybdenum and Tungsten of Two Purity Levels".

Papers in Preparation

H. Jang and J. Moteff, "Neutron Induced Defect Density and Size Distribution of Nb and Nb-1Zr Specimens Irradiated at Elevated Temperatures".

H. Jang and J. Moteff, "Defect Recovery Behavior of Neutron Irradiated Nb and Nb-1Zr".

H. Jang and J. Moteff, "Influence of Neutron Induced Defects on the Hardness and Resistivity Properties of Nb and Nb-1Zr".

H. Jang and J. Moteff, "Neutron Induced Swelling of Nb and Nb-1Zr Irradiated in EBR II at Temperatures Ranging From 455 to 1050°C".

S. Liu and J. Moteff, and K. Farrell, "Neutron Induced Defect Density and Size Distribution in Molybdenum Having Three Different Impurity Contents".

S. Liu and J. Moteff, "Influence of Purity Level and Irradiation Temperature on Void Volume Changes in Neutron Irradiated Molybdenum".

Papers in Preparation (cont.)

S. Liu and J. Moteff, "Influence of Purity Level and Irradiation Temperature on the Radiation Induced Hardening of Molybdenum".

S. Liu and J. Moteff, "Grain Boundary Denuded Zones in Neutron Irradiated Molybdenum".

F. Lee and J. Moteff, "Subgrain Characteristics of Molybdenum Following Tensile and Creep Deformation at Temperatures from 25 to 2200°C".

F. Lee and J. Moteff, "Anomalous Creep Behavior of Neutron Irradiated Molybdenum".

F. Lee and J. Moteff, "Dislocation Channeling in Neutron Irradiated Molybdenum".

J. Matolich and J. Moteff, "Defect Recovery in Neutron Irradiated Tungsten".

J. Matolich and J. Moteff, "Defect Recovery in Neutron Irradiated Tungsten-25 Rhenium".

Progress Reports

COO-2093-1, December 1970: Annual Progress Report, March 1, 1970 thru November 30, 1970, University of Cincinnati, Cincinnati, Ohio.

COO-2093-7, January 10, 1972: Annual Progress Report, March 1, 1971 thru December 31, 1971, University of Cincinnati, Cincinnati, Ohio.

COO-2093-13, January 2, 1973: Annual Progress Report, January 1, 1972 thru December 31, 1972, University of Cincinnati, Cincinnati, Ohio.

COO-2093-27, January 4, 1974: Annual Progress Report, January 1, 1973 thru December 31, 1973, University of Cincinnati, Cincinnati, Ohio.

COO-2093-29, December 9, 1974: Annual Progress Report, January 1, 1974 thru November 30, 1974, University of Cincinnati, Cincinnati, Ohio.

COO-2093-32, November 30, 1976: Annual Progress Report, December 1, 1974 thru November 30, 1976.

COO-2093-34, December 15, 1977: Annual Progress Report, December 1, 1976 thru December 15, 1977.

COO-2093-41, January 10, 1979: Annual Progress Report, December 16, 1977 thru December 31, 1978.

APPENDIX B

UWEDM-101

Survey of Irradiation Data on Molybdenum

R. K. Schmunk*

G. L. Kulcinski

June 1976

Fusion Technology Program
Nuclear Engineering Department
University of Wisconsin
Madison, Wisconsin 53706

* EG&G, Idaho, Inc., Idaho Falls, Idaho

IV. Summary of Literature by Working Groups

Table IV-1 lists all authors, primary (marked by an asterisk) and secondary, who have contributed to the work on molybdenum over the years. A total of sixty-four working groups are included in the listing. In the case of General Electric Company and Westinghouse, several groups of authors from within each company are listed together.

Table IV-2 shows the distribution of reported work by chronology and laboratory. The total number of investigations per year shows a steady increase from the mid-1950's up to the present time, which at least partially reflects the interest in molybdenum as a potential material for constructing fusion reactors. Most of the investigations have been conducted by a select few laboratories. Battelle's Pacific Northwest Laboratory (PNL) has published the largest number of papers on molybdenum followed by the Harwell group. Nearly equalling the efforts of these two groups are the combined efforts of General Electric (Cincinnati) and the University of Cincinnati which are primarily due to John Moteff. The ten most productive laboratories have produced two thirds of the papers, and the remaining papers are scattered evenly among the other contributors.

Looked at another way, Table IV-3 indicates that TEM as an investigative technique has been used twice as much as the other methods. Those laboratories which have been most productive in terms of publications (PNL and Harwell) have concentrated their efforts in the use of TEM, reporting nearly half the work published for that technique. Resistivity work has been conducted primarily at Harwell and d'Orsay, France, although the publications reflect a slow steady effort. Mechanical property data have been generated principally

by Moteff and co-workers followed by Oak Ridge National Laboratory and the USSR Academy of Science.

Turning to Table IV-4, neutron irradiations have been involved in approximately three-fourths of all irradiation experiments conducted on molybdenum. Of that effort, only one paper has been published to date for which irradiations were made with 14 MeV neutrons. All other neutron irradiations utilized either thermal or fast fission reactor facilities. The electron irradiations have been used for resistivity studies while the proton, deuteron and alpha particle irradiations were conducted mainly for blistering or gas re-emission studies. The more recent heavy ion irradiations have been used for damage simulation studies.

Nearly half of the published irradiation effects work on molybdenum has been done in the United States. Principal U. S. research groups include PNL, Moteff and co-workers (both at G. E. and Univ. of Cincinnati) and ORNL. About twenty percent of the publications are from the U. K. and these are primarily from Harwell as cited earlier. A note of caution is in order with regard to drawing close comparison between different tables. Some publications include the use of more than one investigative approach and a number of papers are included, such as theory, which did not involve any irradiations. Hence, one cannot be too definitive about the comparison of the number of papers from table to table.

APPENDIX C

Title Pages and Abstracts
of
PhD Dissertations
and
MS Theses

THE NATURE AND THERMAL STABILITY OF DEFECTS
IN NEUTRON IRRADIATED Mo AND Mo-0.5% Ti

Volume I

A dissertation submitted to the

Department Of Materials Science And Metallurgical Engineering
College of Engineering
Division of Graduate Studies
UNIVERSITY OF CINCINNATI

In partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

1973

by

Vinod K. Sikka

B.S. (Chem. Hons)	Delhi University
Delhi (India), 1965.
B.E. (Met. Engrg.)	Indian Institute of Science
Bangalore (India), 1968.
M.S. (Met. Engrg.)	University of Cincinnati
Cincinnati, OH, 1970.

ABSTRACT

The as irradiated microstructure formed during the fast neutron irradiation of molybdenum and molybdenum-0.5% titanium at temperatures in the range of ~ 70 to 1000°C and fast neutron fluences of 4.2×10^{19} (ETR) to $\sim 1 \times 10^{22}$ (EBR-II) n cm^{-2} ($E > 1 \text{ MeV}$), has been characterized using the transmission electron microscope. The effect of neutron irradiation on the physical and mechanical properties have been studied using electrical resistivity, bulk density and microhardness.

The as irradiated microstructure has been classified into black spot clusters, dislocation loops, rafts and voids. The raft formation occurred in the temperature range of ~ 70 to 500°C . A fast neutron fluence of 1.1×10^{20} n cm^{-2} ($E > 1 \text{ MeV}$) has been shown to be the threshold fluence for raft formation at $\sim 70^{\circ}\text{C}$. Threshold temperature for void formation is shown to be as low as $0.19\text{-}0.24 T_m$. Voids have been observed to form a three dimensional bcc void lattice. The ordered void lattice increases linearly with increasing irradiation temperature and thus has been suggested as a temperature monitoring device in the reactor. The effect of 0.5% titanium addition to molybdenum is to increase the temperature for ordered void formation and to decrease the or-

dered void lattice parameter.

The various recovery stages observed in the microhardness curves as a function of annealing temperature have been characterized by transmission electron microscope observations. The black spot clusters have been shown to exist at temperatures $< 700^{\circ}\text{C}$ ($0.34 T_m$), loops $< 1200^{\circ}\text{C}$ ($0.51 T_m$) and voids $< 1450^{\circ}\text{C}$ ($0.6 T_m$). The void annealing has been explained by the bulk diffusion mechanism.

The ordered void lattice parameter and the void density have been shown to be a sensitive function of the displacement rate. All the void data reported in the literature have been corrected to the displacement rate used in this investigation. The significant effect of the ordered void lattice formation is to saturate the void volume swelling to $\sim 1\%$.

HEAVY ION INDUCED RADIATION DAMAGE AND
VOID FORMATION IN MOLYBDENUM AND ITS ALLOYS

A dissertation submitted to the
Department of Materials Science and Metallurgical Engineering
College of Engineering
Division of Graduate Studies
UNIVERSITY OF CINCINNATI

in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

1975

by

James F. Stubbins

B.S. University of Michigan 1970

M.S. University of Cincinnati 1972

ABSTRACT

Heavy Ion Induced Radiation Damage and Void Formation in Molybdenum and Its Alloys.

by

James F. Stubbins

Chairman: John Moteff

Void and other defect agglomerate microstructures produced in molybdenum (Mo), molybdenum - .5 wt % titanium (Mo-.5Ti) and molybdenum - .5 wt % titanium - .1 wt % zirconium (TZM) by bombardment with 3.1 MeV $^{51}\text{V}^+$ ions were characterized using transmission electron microscopy (TEM). The development of defect microstructure with irradiation dose and irradiation temperature was studied for doses up to 60 displacements per atom (dpa) and at temperatures ranging from 750°C (.35 Tm) to 1500°C (.61 Tm). Specifically, quantitative and qualitative data were obtained for the void, dislocation loop and line, and precipitate populations; and the void volume fractions (swelling) were calculated.

The dose dependence of swelling was studied for Mo, TZM and Mo-.5Ti SG (Mo-.5Ti with 1 μm grain diameter) between 850°C (.39 Tm) and 1120°C (.48 Tm), and at 905°C for Mo-.5Ti LG (Mo-.5Ti with 23 μm grain diameter). The void volume fraction was found to be a linear function of dose for Mo over the entire temperature range. At 900°C, Mo developed a void

volume fraction of 2.7% by 50 dpa. At higher temperatures the swelling increased more rapidly with dose.

TZM and Mo-.5Ti LG showed reduced swelling values due to inhibition of void nucleation by alloying content. An incubation period for void nucleation was observed. Nevertheless, the void volume fractions in both materials increased with dose. The small grain size in the Mo-.5Ti specimens enhanced void nucleation and, as a consequence, swelling. The void volume fractions saturated at fairly high (1.5%) values by 15 dpa.

Void formation was found to initiate at 750°C (.35 Tm) in all cases. (There was no helium preinjection, which may have caused voids to form at lower temperatures than 750°C). Voids were found for all irradiations at temperatures in excess of 750°C , the highest being Mo irradiated at 1507°C (.61 Tm).

Peak swelling temperatures were found to be in excess of 1200°C (.51 Tm). A lower temperature, minor swelling peak was found for TZM at 900°C (.41 Tm). Mo and Mo-.5Ti SG exhibited swelling plateaus at temperatures below the peak swelling temperatures.

Ordered defect structures were observed at irradiation temperatures between 900°C (.41 Tm) and 1120°C (.48 Tm). Ordered void superlattices were found in Mo at temperatures between 900°C and 1120°C and in TZM and Mo-.5Ti LG at 900°C . The lattice structure was verified to be body centered cubic (bcc) and matched the atomic lattice orientation and structure

of the host metal. The void superlattice constant was found to be an inverse function of temperature and ordered void lattices were found to become disarranged with increasing irradiation temperature.

Ordered arrays of loops/precipitates were found in TZM irradiated at temperatures between 900°C and 1090°C. These arrays exhibited a bcc structure matching the host metal structure.

RADIATION HARDENING AND VOID SWELLING OF NEUTRON IRRADIATED
NIOBIUM(COLUMBIUM) AND NIOBIUM-1% ZIRCONIUM ALLOY

A dissertation submitted to the

Department of Materials Science and Metallurgical Engineering
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Doctor of Philosophy

1975

by

HO IL JANG

B.S. Seoul National University 1967

M.S. University of Cincinnati 1973

ABSTRACT

Nb and Nb-1Zr irradiated to a fast neutron fluence of $1 \times 10^{22} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$) at 430, 580, 700, 800, 900, and 1050°C have been studied using transmission electron microscopy, microhardness, electrical resistivity, and bulk density change measurements. Voids are observed in as-irradiated Nb specimens at all six irradiation temperatures with the void size and concentration varying from 46 to 458 Å and from 4×10^{16} to 1×10^{14} voids/cm³, respectively. The resultant void swelling is 0.2 - 0.5 % with a maximum swelling occurring at 1050°C. In Nb-1Zr the void swelling varies from 0 to 2%, and the maximum swelling occurs at the irradiation at 800°C. It has been demonstrated that a theoretical model on void swelling by Brailsford and Bullough fits reasonably well with the experimental data on Nb-1Zr, but it overestimates the swelling in Nb by a factor of up to ~ 10, especially at high irradiation temperatures. Void structures show little change during annealing up to 900°C, and completely anneal out thermally at or below 1400°C in most specimens. In addition to voids, other types of defect clusters, e.g. black spots, small dislocation loops, rafts, dislocations, and precipitates have been observed. These defects can serve as obstacles for dislocation movements, and consequently an increase in hardness occurs. Hardness contributions of these defects have been calculated and compared with measured Knoop microhardness data. The magnitude

of radiation-hardening is 34-78% and 6-208% for Nb and Nb-1Zr, respectively. The minimum hardening occurs at 900 and 800°C in Nb and Nb-1Zr, respectively. The radiation hardening in Nb specimens irradiated at low temperatures is mainly due to the high concentration of voids, whereas that in Nb-1Zr specimens is due to black spots and small dislocation loops. The recovery of the radiation-hardening takes place at annealing temperatures between 800 and 1200°C with activation energies 2.23 - 2.35 eV for Nb and 1.77 - 1.94 eV for Nb-1Zr.

THE EFFECTS OF INTERSTITIAL IMPURITIES AND
RADIATION TEMPERATURE ON VOIDS SWELLING AND
IRRADIATION HARDENING IN THE NEUTRON
IRRADIATED MOLYBDENUM

A thesis submitted to the
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DOCTOR OF PHILOSOPHY

in the Department of Materials Science and
Metallurgical Engineering

College of Engineering

1979

by

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ABSTRACT

Molybdenum specimens of three different impurity levels (residual resistivity ratios of 60, 650 and 6520, respectively), irradiated in the Oak Ridge Research Reactor to a fast neutron fluence of $1 \times 10^{21} \text{ n cm}^{-2}$ ($E > 0.1 \text{ MeV}$) at ten different temperatures ranging from 220 to 900°C were studied using transmission electron microscopy (TEM), small-angle x-ray scattering (SAXS) and knoop microhardness measurements.

The TEM results showed that the microstructure consisted of voids, black spots and loops, rafts and dislocation segments. All were present at the lower irradiation temperatures, while only voids and dislocation segments were present at the higher temperatures. SAXS experiments also indicated that voids formed in the specimens irradiated at temperatures ranging from 220 to 900°C. The TEM and SAXS results suggest that the possible threshold temperature of void formation is possibly as low as 150°C ($0.15 T_m$) in molybdenum. The void number densities did not vary significantly but one is consistently higher than another in the specimens of the three impurity levels when compared at the same temperatures; however, the void sizes were largest for the case of the specimens containing the highest void number densities, resulting in a difference in void swelling by factors of 2 to 12 for the differences in impurity levels. Gaseous

impurities account for this deviation in void density for different impurity levels. This difference in void sizes may be explained by the carbon content in the specimens. It concluded that void swelling is a sensitive function of interstitial impurities and depends on the type, nature and form of interstitial impurities.

Grain boundary void denuded zones were observed in the specimens irradiated above 400°C. The width of the void denuded zone was compared to the existing GB-denuded zone models. The vacancy migration energy was calculated from the width of the void denuded zone by using Konobeev's model and was found to be 1.0 eV for molybdenum.

The present investigation demonstrated that the SAXS method can be used as a rapid and accurate tool in the study of void swelling behavior when specimens containing only voids are used and the experiment is performed under optimum conditions.

According to a dispersed barrier hardening model, the hardness changes due to irradiation induced defects were calculated utilizing the quantitative TEM results, and then compared with the hardness changes determined from microhardness measurements. The calculated hardness changes were in good agreement with the experimental values for conditions where the indentations do not show pronounced cleavage steps around the indentation.

A STUDY ON THE STRENGTH, SUBSTRUCTURE, AND THEIR CORRELATIONS
IN IRRADIATED AND NON-IRRADIATED MOLYBDENUM

A dissertation submitted to the
Department of Materials Science and Metallurgical Engineering
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DOCTOR OF PHILOSOPHY

1980

by

Kang-Jyh Frank LEE

B.S. (Nuc. Eng.)	Tsing-Hua University	1974
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ABSTRACT

Mechanical behavior of arc-cast molybdenum in tension and creep deformation has been determined at temperatures ranging from 25 to 2200°C. Effect of prior testing mechanical-thermal treatment on the properties is significant at temperatures lower than 1200°C (0.5 T_m). The utility of transmission electron microscopy to examine the deformed material has revealed a strong correlation of mechanical properties with substructures. At higher temperatures and lower stresses, well-defined subgrains are formed; whereas jogged and tangled cells are developed at lower temperatures and higher stress levels. The cell or subgrain intercept size, λ , is found to vary with true stress according to the relations,

$$\lambda = 5.5 b \left(\sigma_t / E \right)^{-1}$$

for subgrains and

$$\lambda = 5.6 \times 10^{-3} b \left(\sigma_t / E \right)^{-2}$$

for cells.

A power law equation usually describes the creep rate and stress relationship at elevated temperatures:

$$\dot{\epsilon}_s = 5.2 \times 10^{10} \left(\frac{D_{\text{eff}}}{b^2} \right) \left(\frac{\sigma_t}{E} \right)^{4.83}$$

In the power-law region, subgrains are the main features in substructure and their intercept size is related to stress

and creep rate as follows:

$$\epsilon_s = 3.1 \times 10^8 (D_{\text{eff}}/b^2)(\lambda/b)^3(\sigma_t/E)^{7.83}.$$

Molybdenum specimens irradiated at reactor ambient temperature to a neutron fluence of about $3.0 \times 10^{19} \text{ n cm}^{-2}$, $E > 1 \text{ MeV}$, were creep tested at 600°C in an argon atmosphere with a fixed applied load. In addition to the expected radiation induced hardening, i.e., an increase in the time to rupture, there was a relatively long stress dependent incubation period in which the creep rate was extremely low. This was then followed by an accelerated creep stage terminating in fracture and with little loss in ductility when compared to the unirradiated conditions. Interrupted tests were conducted to different strain levels where TEM examinations were made to investigate the corresponding microstructural changes. It was found that the recovery in the elongation of the irradiated specimen is closely associated with the degree of dislocation channeling.

DILATOMETRIC MEASUREMENT OF PROPERTY CHANGES
IN NEUTRON IRRADIATED MOLYBDENUM

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requirements for the degree of

MASTER OF SCIENCE

1973

by

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ABSTRACT

A dilatometer was constructed to study the length change of recrystallized molybdenum irradiated at several temperatures ($70^{\circ}\text{C} \sim 480^{\circ}\text{C}$) and at fast neutron fluence levels ranging from 1.1×10^{19} to $1 \times 10^{22} \text{ n/cm}^2$ ($E_n \geq 1 \text{ MeV}$). A linear continuous heating from 70° to 900°C of the low irradiation temperature specimens revealed four recovery regions: at about $0.16 T_m$ (Stage III), $0.22 T_m$ (Stage IV), $0.32 T_m$ (Stage V) and $0.36 T_m$ (Stage VI), while the high irradiation temperature specimens revealed fewer recovery regions. It is considered that the Stage III and Stage IV recovery regions result from the recovery of point defects, and that the Stage V and Stage VI recovery regions result from the recovery of defect clusters. The radiation-induced length change increased with the fluence approaching a saturation level.

Transmission electron microscopy, microhardness tests, and density measurements were performed at the same time to help interpret the dilatometric data.

A CORRELATION OF THE DISLOCATION SUBSTRUCTURE
ASSOCIATED WITH CREEP-RUPTURE TESTED
POLYCRYSTALLINE MOLYBDENUM

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Department of Materials Science
and Metallurgical Engineering
College of Engineering
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UNIVERSITY OF CINCINNATI

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Master of Science

1974

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ABSTRACT

Arc-cast and powder metallurgy produced polycrystalline molybdenum specimens, creep tested at varying temperatures over the range 0.32 to $0.86 T_m$, were examined for substructural features. Specimens available for examination were from three different sources and covered different creep test conditions. A brief report of the creep data is presented. Optical microscopy, replica electron microscopy and transmission electron microscopy were used to study the substructure under different ranges of magnification. Observations, results and analysis of the substructure data are presented. The results have been discussed in terms of existing models for substructure formation. Some relationships between the subgrain intercept dimensions and other stress dependent parameters are studied. Quantitative measures of the density of etch pits are reported and discussed with reference to the density of mobile dislocations. An analysis of the dislocation interactions in network boundaries is also illustrated. Statistical techniques have been employed to process data and obtain slopes and intercepts.

ELECTRICAL RESISTIVITY STUDY
OF THE RECOVERY OF
NEUTRON-IRRADIATED TUNGSTEN
AND TUNGSTEN-25 RHENIUM

A thesis submitted to the
Department of Materials Science
and Metallurgical Engineering
College of Engineering
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requirements for the degree of

MASTER OF SCIENCE

1976

by

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ABSTRACT

An isochronal electrical resistivity study and ancillary measurements of radiation damage recovery of tungsten and W-25 Re alloy have been made on specimens irradiated at six different temperatures between 460 and 1080°C in the EBR-II facility to a fast neutron fluence of about 1×10^{22} n cm⁻², $E_n > 1$ MeV. The annealing temperatures covered the range from room temperature to 2100°C (0.71 T_m). Resistivity measurements were made at liquid nitrogen temperatures.

For the tungsten specimens the as-irradiated resistivity increases slightly with increasing irradiation temperature to a maximum value of 2.14 $\mu\Omega$ cm at about 0.3 T_m and then drops rapidly to about 0.90 $\mu\Omega$ cm. The unirradiated resistivity (control) has a value of 0.64 $\mu\Omega$ cm.

The irradiation induced defect recovery spectra is quite complex. There are several peaks which overlap, producing a broad band. This band shifts to higher temperatures with increasing irradiation temperatures and the number of peaks decrease. The leading edge of this band becomes a useful measure of the irradiation temperature.

To establish parameters of the various recovery peaks for analysis, an attempt was made to unfold the overlapping recovery spectra. The broad band recovery spectra is consistent with the individual peaks being Gaussian in form and agreeing well with the peaks being due to stages at 0.25,

0.28, 0.31, 0.33, 0.37, 0.41, 0.45, 0.48, and 0.59 T_m .

Unexpectedly, the data require a negative recovery peak at 0.42 T_m suggesting that there is an increase in the resistivity on annealing through this temperature interval, a circumstance which may be attributed to the dissociation of defect-impurity atom complexes and/or compact clusters.

For the W-25 Re alloy the as-irradiated resistivity decreases with increasing irradiation temperature from 22.5 to 13.8 $\mu\Omega$ cm. The unirradiated resistivity (control) has a value of 18.3 $\mu\Omega$ cm.

For the W-25 Re specimens the recoverable radiation damage effects were small and were centered at 800 to 1000°C (0.32 to 0.41 T_m). Recovery was observed only for specimens irradiated below 800°C.

The principal effect of radiation in this alloy is the formation of an unexpected second phase. The second phase precipitate has been identified in the literature but several inconsistencies remain. These are examined in detail.

Based on the electrical resistivity data the precipitate goes back in solution in the temperature range 1000 to 1500°C.

Data are also presented and discussed on length change and swelling behavior as a result of annealing for both tungsten and tungsten-25 rhenium.

A Study of the Compressive Creep of Irradiated
and Unirradiated Molybdenum at Elevated Temperatures

Master's Thesis

Submitted to

The Department of Materials Science
and Metallurgical Engineering

Graduate Division

The University of Cincinnati

1976

Submitted by

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B.S. (Physics) University of Scranton, 1966

ABSTRACT

Compressive creep tests were performed on molybdenum samples exposed to four different pre-test conditions: (1) Annealed; (2) annealed and neutron irradiated at 480°C to a fluence of $5 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$); (3) stress-relieved; and (4) stress-relieved and neutron irradiated at reactor ambient temperature to a fluence of $1 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ MeV}$). The tests were performed in the temperature range of 600 to 900°C with an initial applied stress of 176.5 MPa. Both pre- and post-test specimens were examined using electron microscopy and the relationship between substructure and mechanical properties is discussed. Possible controlling mechanisms of deformation are proposed and activation energies for creep are determined.

ELECTRICAL RESISTIVITY STUDY ON THE
DEFECT RECOVERY OF NEUTRON-
IRRADIATED MOLYBDENUM

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MASTER OF SCIENCE

1976

by

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1974

ABSTRACT

Six molybdenum specimens were irradiated in Experimental Breeder Reactor (EBR-II) to high neutron fluence (1.1×10^{22} neutrons/cm², $E > 1$ MeV) at relatively high temperatures (460-1080°C). The effect of neutron irradiation on the physical properties is studied using electrical resistivity technique.

The radiation-induced defect recovery have been investigated by a series of isochronal annealing and subsequent resistivity measurements. Recovery stages are found to locate at 0.33, 0.36, 0.40, 0.47 and 0.54 T_m (T_m is the homologous melting temperature). One unusual negative peak is observed to be at 0.42 T_m for specimens irradiated at higher temperatures.

SENIOR RESEARCH PROJECT PROPOSAL

"Hot Hardness of Molybdenum"

Name: Charles G. Schmidt

Advisor: Dr. John Moteff

Date: November 12, 1973

Abstract

This investigation determined the influence of carbon content on the hot hardness of molybdenum at temperatures from R.T. to 1200°C. The influence of irradiation temperatures, i.e. at R.T., 380 and 480°C on the hot hardness values was also evaluated. This information was compared to similar data on the hot hardness of Mo-TZM and Mo-0.5Ti.

The determination of the strain hardening exponent, n , based on the Meyer's hardness number m of each specimen, showed good correlation with information obtained from tensile tests of the same material for room temperature conditions. Here $n = m - 1$. Based on the Vickers' (H) and the Meyers (m) hardness numbers, excellent agreement was obtained with the ultimate tensile strength (σ) through the relationship

$$\sigma = (H/3) (n/0.217)^n$$