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DIFFUSION AND PRECIPITATION
OF INERT GASES IN METALS

Final Report

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FINAL REPORT

COO-1799-11

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INERT GASES IN METALS

ABSTRACT

The behavior of inert gases, particularly helium, in metals has been studied in aluminum, copper, niobium and stainless steel. Emphasis has been upon characterizing the state of helium in the metals and upon following the kinetics of precipitation and coalescence. Experimental techniques which are in most cases new to studies of inert gases in metals have been employed. These include low temperature specific heat, precision lattice parameter measurement, internal friction, computer simulation, and residual resistivity in addition to confirmatory electron microscopy. The single most important finding of this study is that bubble coalescence takes place at rates which are much slower than was previously supposed and that the slow coalescence fits a model in which the bubble mobility required for coalescence is rate-limited by nucleation of facets on the bubble surface. The further understanding and subsequent potential ability to control rates of bubble and/or void coalescence will be important to the design of nuclear fuel and cladding materials.

This report covers the five year period from June 1968 through May 1973 during which studies have been made of the behavior of inert gases, particularly helium, in metals. Termination of the contract for this study was arranged by the principal investigator, J. R. Cost, in order that he could take sabbatical leave.

Communications

The period of time of this study has seen the emergence of strong interest in the study of inert gases in solids since they play such an important role in the behavior of fuel and cladding materials for nuclear reactors. Numerous symposia including two international conferences, Albany in 1971 and Gaithersburg in 1973, have been, at least in part, devoted to this subject. Personnel involved on this project presented and published papers at each of these conferences, and the principal investigator was an active organizer of the latter conference. In addition, numerous talks have been given at various national laboratories and universities and at professional meetings. A listing of the various communications related to this project follows.

A. Talks:

1. "Residual Resistivity Method for Determination of Mobility and Precipitation Kinetics of Inert Gases in Metals," J. R. Cost, AIME Annual Meeting, New York, Feb. 1968.
2. "Specific Heat Study of Helium Bubble Formation in Alpha-Irradiated Aluminum," O. P. Katyal, P. H. Keesom, and J. R. Cost (by O. P. Katyal) International Conference on Voids in Metals, June 1971, Albany, N.Y.
3. "Coalescence of Inert Gases in Metals," J. R. Cost, Materials Science Division Seminar, Argonne National Laboratory, Argonne, Illinois, July 23, 1971.

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4. "Coalescence of Inert Gases in Metals," J. R. Cost, Metals and Ceramics Division Seminar, Oak Ridge National Laboratory, August 4, 1972.
5. "The Formation and Coalescence of Helium Bubbles in Aluminum," K. Y. Chen and J.R. Cost (by K.Y. Chen) AIME Fall Meeting, Detroit, Mich., Oct. 1971.
6. "Coalescence of Inert Gases in Metals," J. R. Cost, Metallurgy Colloquium, University of Illinois, October 25, 1972.
7. "Behavior of Helium in Metals," J. R. Cost, Solid State Seminar, Purdue University, February 2, 1973.
8. "Behavior of Helium in Metals," J. R. Cost, Engineering Materials Seminar, University of Maryland, February 8, 1973.
9. "Characterization and Behavior of Atomic Helium in Niobium," D. L. Johnson and J. R. Cost (by D. L. Johnson), International Conference on Defects and Defect Clusters in B.C.C. Metals and Their Alloys, Gaithersburg, Md., August 1973.

B. AEC Technical Reports:

- COO-1799-1: Technical Progress Report for year beginning June 1968.
- COO-1799-2: Preprint, "Site Occupancy and Bubble Formation of Helium in High Purity Aluminum."
- COO-1799-3: Technical Progress Report for year beginning June 1969.
- COO-1799-4: Preprint, "Specific Heat Study of Helium-Bubble Formation in Alpha-Irradiated Aluminum."
- COO-1799-5: Reprint, "Inert Gases in Metals," Purdue University, Materials Sciences Newsletter, December 1970.
- COO-1799-6: Technical Progress Report for year beginning June 1970.
- COO-1799-7: Reprint, Proceedings of International Conference of Radiation-Induced Voids in Metals, Albany, N.Y., June 1971, "Specific Heat Study of Helium-Bubble Formation in Alpha-Irradiated Aluminum."

- COO-1799-8: Preprint, "Coalescence of Helium Bubbles in Aluminum."
- COO-1799-9: Technical Progress Report for year beginning June 1971.
- COO-1799-10: Reprint, Proceedings of International Conference on Point Defects and Point Defect Clusters in B.C.C. Metals and Their Alloys, Gaithersburg, Md., August, 1973, "Characterization and Behavior of Atomic Helium in Niobium."
- COO-1799-11: Final Report
- COO-1799-12: Preprint (in preparation), "On the Site Occupancy of Atomic Helium in Copper."
- COO-1799-13: Preprint (in preparation), "Coalescence Behavior of Helium Bubbles in 316 Stainless Steel."

C. Publications:

1. J. R. Cost and D. L. Johnson, "Site Occupancy and Bubble Formation of Helium in High Purity Aluminum," J. Nucl. Mat., 36, 230 (1970).
2. O. P. Katyal, P. H. Keesom, and J. R. Cost, "Specific Heat Study of Helium-Bubble Formation in Alpha-Irradiated Aluminum," Radiation-Induced Voids in Metals, USAEC Technical Information Center, Oak Ridge, Tenn., 1971, p. 248.
3. D. L. Johnson and J. R. Cost, "Characterization and Behavior of Atomic Helium in Niobium," Defects and Defect Clusters in B.C.C. Metals and Their Alloys, R. J. Arsenault, Ed., Nuclear Metallurgy Series, Vol. 18, 1973, p. 279.
4. K. Y. Chen and J. R. Cost, "Coalescence of Helium Bubbles in Aluminum," J. Nucl. Mat. (accepted for publication).
5. D. L. Johnson and J. R. Cost, "On the Site Occupancy of Atomic Helium in Copper" (in preparation).
6. K. Y. Chen and J. R. Cost, "Coalescence Behavior of Helium Bubbles in 316 Stainless Steel" (in preparation).

Summary of Personnel and Activities:

1. D. L. Johnson, graduate student for Ph.D. Supported Sept. 1968 until graduation in Feb. 1973. Studied internal friction, small angle scattering, bubble size distribution, and lattice parameter changes in niobium-helium system, also lattice parameter changes due to helium in copper.
2. O. P. Katyal, post-doctorate research associate. Supported for one year starting in June 1969. Investigated the low temperature specific heat (λ peak) due to helium bubbles in aluminum.
3. K. Y. Chen, post-doctorate research associate. Supported from Oct. 1970 to Aug. 1972. Used computer simulation and electron microscopy to study coalescence of helium bubbles in aluminum and stainless steel.
4. J. R. Cost, professor and principal investigator. Partial support during full term of the contract. Provided technical administration and experimentally studied residual resistivity effects due to implanted helium and made low temperature specific heat measurements.

Summary of Progress:

Progress in the five year term of this project has been quite good. Prior to this study a relatively small amount of information was known about inert gas-metal systems. The general goal of this investigation, was to apply new techniques to the study of helium in these systems in order to provide important new understandings. Several specific goals which were considered to be of special importance, such as the determination of site occupancy and the investigation of bubble coalescence kinetics were given special emphasis, and thus account for the subject matter of most of the publications. The following is a listing of the systems and problems studied and the resulting significant findings:

1. Site occupancy of atomic helium in metals
 - a. Lattice parameter changes in alpha-irradiated aluminum indicated that

atomic helium occupies substitutional lattice sites and, based upon the magnitude of this effect, is probably bound to vacancies.

- b. A similar finding was obtained for the site occupancy of helium in niobium; however, for niobium, the only b.c.c. metal studied, it is believed that the helium leaves the substitutional lattice at a very low temperature (roughly 200°C) to form a sub-microscopic pre-precipitate. Our investigation of internal friction of niobium-helium alloys did not show a Snoek-type of damping peak for this system. This is consistent with the finding of substitutional occupancy.
- c. The above findings relative to the site occupancy question appear to be inconsistent with previous results of Russell and Hastings for copper which indicate interstitial occupancy of atomic helium. Consequently, we decided to also investigate copper. Our study was made upon high purity copper with cyclotron injected helium as opposed to the prior work in which helium was created by an n-type reaction with solutes. Interestingly enough, our results confirmed the previous interstitial occupancy result. This was somewhat unexpected. Based upon a simple size effect argument, one predicts substitutional occupancy since copper is some ten percent smaller than aluminum. Probably the above results will require confirmation by some other experimental methods; field ion microscopy, for instance, could be used to study some metal-helium systems.

2. Bubble Coalescence

- a. Computer-simulated bubble coalescence experiments were conducted with the goal of determining the mechanism of bubble diffusion. These results were compared with electron microscopy studies of the bubble population during annealing of both aluminum and 316 stainless steel.
- b. The above coalescence results were analyzed and found to be consistent with a model for bubble diffusion in which nucleation of facets is the

rate-limiting step. The experimental results were shown to be inconsistent with surface diffusion mechanism for bubble motion. This result is significant since if the former mechanism is operative, then bubble mobility depends exponentially upon bubble size, so that when two bubbles coalesce they can form a single larger bubble which is essentially immobile. This negligible mobility then results in a sharp decrease in the rate of coalescence so that bubbles seldom can grow larger than some effective terminal bubble size. This finding that bubbles (and also in some instances, voids) coalesce at rates which are much slower than predicted is important to nuclear technology since bubble and void growth is usually involved in the failure of fuel rods and claddings, and thus any mechanism which tends to decrease the kinetics of coalescence is potentially of great value.

c. Some specific findings on coalescence are reported below.

- (i) Stainless steel (No. 316), aluminum, and niobium respectively have effective terminal helium bubble sizes when annealed near the melting point (for atomic 100 ppm helium) of 500 A, 200 A, and 40 A.
- (ii) The kinetics of coalescence are in agreement with facet nucleation as the rate-limiting step in bubble diffusion.
- (iii) The appropriate parameter to reduce the coalescence rate, if the facet nucleation is limiting, is the energy per unit length of a ledge of atoms at the bubble surface.

3. General Findings

- a. Two corrections have been made to the constants used in doing basic calculations relative to the concentrations of inert gas atoms in bubbles. These corrections are important in accounting for the fractional amount of helium which at any given time is present as bubbles.
 - (i) In the past the Van der Waals constant has been too high by a factor of roughly 2.5 because it was not corrected for temperature and

pressure. Typical helium concentrations in bubbles are thus corrected downward by roughly one-third.

(ii) The same pressure and temperature corrections are required to the surface energy at the metal-bubble interface. This correction for helium in aluminum results in a helium concentration one-half that previously predicted.

b. A general characterization of the kinetics of the precipitation of helium to form bubbles was obtained. Effects due to temperature, time and concentration were studied. The mechanism of the precipitation process for a gas was examined in contrast to precipitation of condensed phases. The significance of the requirement that a precipitating gas phase requires agglomeration of vacant lattice sites as well as of solute was assessed.