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FINAL REPORT

January 1, 1960 - December 31, 1962,

IMPERFECTIONS IN METALS

Contract NO. AF 49(638)-790

Principal Investigator C. T. Tomizuka
Report Prepared by C. T. Tomizuka.

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Submitted (6) to:

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J. Description of General Activities

The original research proposal for this contract was submitted from the University of Chicago while the principal investigator was at that institution. In planning a move to the University of Arizona, it was necessary to modify the original research proposal to include the cost and time set aside for the construction of the high pressure systems. The revised contract was submitted from the University of Arizona, approved by the AFOSR, and became effective on 1 January 1960.

The research activity of the past three years sponsored by this contract can be divided into three periods: (1) Design and planning, one year; (2) Construction of the experimental facilities, approximately 15 months; (3) Experimental phase, approximately 9 months. It should be noted that this classification refers only to the high pressure experiments. Other experiments to study the imperfections in metals were initiated during 1960 and experimental results were available in 1961. The relatively long duration of Phase 1 for the high pressure work is due to the fact that the new Physics Building was being built in the year 1960 and the new Physics Machine Shop began its operation on December 13, 1960.

II. Fulfillment of Initial Objectives.

The initial objectives of this research proposal were to provide a set of more direct evidences for vacancies and to supply supplementary results which support the preliminary

evidences. These objectives were to be fulfilled by (1) diffusion experiments in pure noble metals under hydrostatic pressure, (2) diffusion experiments as a function of temperature to obtain the activation energy, (3) internal friction measurements in alpha-brass type alloys and (4) tracer diffusion experiments in alloys to supplement (3), and (5) resistivity increase of quenched-in wires of noble metals under hydrostatic pressure to obtain the activation volume of a vacancy.

All of the items listed above are either under way or are completed. The delay in the execution of some of the plans originally scheduled for completion is due primarily to the experimental difficulty of the problem and in part due to the delay in the construction and testing of the high pressure gas system. (1) All the experimental arrangements have been completed to perform diffusion experiments under hydrostatic pressure. Preliminary runs are underway and this will be continued under AF Grant 105-63. (2) Diffusion experiments involving the diffusion of impurities in copper single crystals were performed. Mercury and selenium were selected as impurities. The results obtained indicate that the existing theories need modifications to include the elastic effect arising from the interaction of closed shells of different radii. This phase of the experiment is regarded as completed. (3) Internal friction measurements were carried out in alpha-brass (15 at.%). The analysis of the results is still underway. It was originally speculated that the isotope effect might be detectable

in the alloys of this type. Preliminary experiments to control the amount of zinc in the alloy proved that it is impossible to control the amount to the precision necessary to detect the isotope effect. The torsion pendulum apparatus constructed for the purpose of measuring the internal friction in alloys is still being used to study the anelastic properties of alloys. (4) Tracer diffusion experiments in alpha-brass was carried out at 15 at.% zinc to compare with the internal friction results. The results are summarized in the following sections. Diffusion of zinc in silver-zinc alloy (15 at.% zinc) was also carried out. (5) In order to quench in anomalous resistivity due to excess vacancies in gold and platinum, it was decided that the pulse-heating was the only solution to the problem since the quenching must take place under high pressure. The electronic apparatus capable of rapid quenching was built and tested. Preliminary experiments are underway and it is expected that this endeavor will continue more actively with the support of the AF Grant 105-63.

. Accomplishments and Summary.

In order to carry out diffusion experiments and other experiments at high pressure, two high pressure systems were constructed. A liquid system capable of 10,000 atmospheres (10 KB) was constructed using the Harwood intensifier with the accompanying priming stage up to 2 KB. This system was later modified to eliminate the priming stage altogether with a much larger

The high pressure gas system is currently operating at the maximum pressure of approximately 8.5 KB. It is possible to obtain 10 KB of pressure in this system for a short period of time. For diffusion anneals at high pressure, however, it is necessary to maintain the pressure at a constant level for a period of a few hours to a few days. For this purpose, approximately 8 KB appears to be the maximum pressure obtainable.

Laboratory equipped to measure radioactive tracer diffusion in metals was designed and constructed. In addition, a new technique was developed to extend the lower limit of measurable diffusion coefficients. With the technique developed in the past few years in our laboratory, it is now possible to measure accurately the diffusion coefficients as small as 10^{-15} or even 10^{-16} cm^2/sec . It is possible to obtain 10 or more sections within a micron of the surface. The impurity diffusion experiments in copper single crystals and the self-diffusion experiments in alpha-brass type alloys were carried out using the conventional tracer-sectioning techniques. The potentiality of the new micro sectioning has not been explored fully.

The most ambitious of the proposed programs fell far short of completion due to the intrinsic difficulty of the problem. First of all, by the preliminary experiment carried out by Tomizuka and Lowell at the University of Chicago, it was clear that it is feasible to obtain a sufficiently rapid quenching

rate to quench in vacancies from high temperatures at high pressure. However, further refinement of the experiment was necessary to carry out the precision experiment. For this reason, a pulse-heating method was developed in our laboratory to obtain the rapid heating and the rapid cooling of the specimen which is in the form of a thin wire. The problem of switching several hundred amperes within a fraction of a millisecond and maintaining 30-50 amperes of steady current over a period of 5-100 milliseconds was solved by the use of solid state circuit elements. It is now possible to obtain almost reproducible temperature pulses of the order of 1,000°C. Some minor experimental problems must still be solved in order to obtain numerical results needed for the estimation of the activation volume for the formation of vacancies in noble metals.

In order to extend the scope of the present program to take advantage of the high pressure systems that are available, the entire program was gradually extended to include other solid state phenomena which are pressure sensitive. This part of the program will be expanded in the AF Grant 105-63 to include such phenomena as the pressure effect on the Curie point and the saturation magnetization of ferro- and ferri-magnetic substances. A non-magnetic Be-Cu high pressure vessel was constructed. Also a small steel vessel was constructed to measure the pressure effect on the Curie

temperature of ferrites. Preliminary runs were completed and it is now ready to perform the actual measurements.

Early in 1960 while the high pressure systems were not available, joint experiment was conducted with the University of Chicago high pressure laboratory (director, Professor A. W. Lawson) to determine the activation volume for self-diffusion in silver. The results of this activity are also included in the following summary.

SUMMARY

1. Pressure Effect on the Self-Diffusion Rate in Silver.

Self-diffusion in silver was measured as a function of pressure up to 8 KB at 900°C. From the slope of the $\ln D$ vs. P plot the activation volume for this process was determined to be $9.2 \text{ cm}^3/\text{mole}$ which corresponds to 90.0% of the molar volume (10.34 cm^3).

2. Impurity Diffusion in Copper.

Diffusion of selenium and mercury in single crystals of copper was measured. From the temperature dependence of the diffusion coefficients of mercury into copper, the diffusion coefficients can be expressed as

$$D = (0.183 \pm 0.010) \exp(-42,430 \pm 1400/RT).$$

The diffusion coefficients of selenium in copper can be expressed as

$$D = (0.55 \pm 0.13) \exp(-41,980 \pm 800/RT).$$

The application of LeClaire-Lazarus model gave a fair agreement between the experiment and the theory.

3. Diffusion in Alpha-Brass Type Alloys.

The diffusivity of zinc 65 in an alloy of 17 at. % zinc and 83% copper has been measured using radioactive tracer techniques. The temperature dependence of the diffusion coefficient is given by

$$D = 0.44 \exp(-42,800/RT) \text{ cm}^2/\text{sec.}$$

Corrections of the diffusion coefficients with small differences in specimen composition have been made. The temperature dependence of the exponential correction factor agreed well with theory of Hoffman, Turnbull, and Hart. Comparison of results with other tracer measurements and with chemical diffusion measurements have been made. Diffusion measurements of zinc isotopes in silver-zinc alloys was also carried out. The temperature dependence of diffusion coefficients can be expressed as

$$D = 0.11 \exp(-36,000/RT) \text{ cm}^2/\text{sec.}$$

This value of the activation energy agrees well with the anelastic measurements.

4. High Pressure Technique.

Several new procedures were developed in the laboratory during the construction and testing of the high pressure systems. One is the technique for leak testing of the gas pressure system. The procedure is briefly described elsewhere in this report. A new technique was also developed for a high resistance electrical lead-in for the

liquid high pressure system. This method will eliminate some of the difficulties arising from a frequent large leakage current resulting from the insufficient electrical insulation of a pipestone cone.

5. Pulse-Quenching Technique.

A completely automatic quenching circuit was designed and constructed for the purpose of quenching-in vacancies in gold and platinum under pressure from high temperatures. It is possible to produce a quenching rate of 10^5 deg/sec. In addition to enabling the quenching-in of vacancies from high temperatures, this new technique will enable one to perform isochronal annealing of quenched-in defects or defects introduced by radiation damage at much higher temperatures than were possible by the conventional method of annealing. This will enable one to determine the vacancy jump life-time at high temperatures.

6. A New Sectioning Technique.

A new technique to section the diffusion specimens chemically was developed to extend the present lower limit of measurable diffusion coefficients of 10^{-13} - 10^{-14} cm^2/sec to 10^{-16} - 10^{-5} cm^2/sec . Anomalous behavior of the diffusion penetration curve near the surface was discovered as a result of this newly developed technique.

IV. Significance of Scientific Results.

1. By measuring the pressure effect on self-diffusion, it was discovered that the activation volume for the process is not at all unreasonable. Quite unlike the previous speculation that there might be as much as 50% relaxation around a vacancy, it is now established that for a face-centered cubic system in which a significant closed-shell interaction exists the activation volume for the vacancy formation is approximately $3/4$ of the molar volume. This is in good agreement with the machine calculation by Vineyard and his co-workers at Brookhaven National Laboratory.
2. It is shown definitely that it is possible to quench in vacancies at high pressure from high temperatures with a sufficiently large quenching rate. It is also proved that passing a steady state current to accomplish this is highly unreliable and that the reproducible results can be obtained only through pulse-heating methods.
3. In the field of diffusion, the existing theory on impurity diffusion is only barely adequate and a correction must be made to take the size effect into consideration.
4. Employing the new technique developed in this laboratory, diffusion coefficients can be measured more economically and over a wider range of temperature and pressure.

V. Graduate Students' Training.

This contract sponsored the training and the research which led to the Master's thesis of the following graduate students:

Richard A. Roberts, Diffusion of Zinc in Silver-Zinc Alloy System

James Steedly, Anelastic Relaxation in Alpha-Brass System
(The experimental work was completed but the thesis was not submitted.)

*S. Armijo, Diffusion of Zinc in Alpha-Brass System

*P. H. Kreyne, Diffusion of Selenium in Copper

*R. A. Summerfield, Diffusion of Mercury in Copper

*David L. Styris, A New Sectioning Technique for Measuring Diffusion Coefficients (The experimental work and the thesis are completed. M.S. degree is not yet conferred.)

* Co-sponsored by AEC under Contract AT(11-1)-1041.

The following graduate students have been working on their Ph.D. theses under the sponsorship of this contract:

R. H. Dickerson, Effect of Pressure on the Self-Diffusion Rate in Gold

C. L. Foiles, Pressure Effect on the Curie Temperature and Saturation Magnetization of Some Ferrides.

VI. Work to be Continued.

The following projects will be continued and will be parts of the projects under the sponsorship of the AF Grant 105-63:

1. As was described in the proposal for AF Grant 105-63 the incompleted portion of the pressure effect on self-diffusion rate will be continued.
2. Likewise the quenching-in of vacancies under pressure will be continued.
3. Study of the effect of pressure on other physical properties such as the magnetic properties of solids will be expanded in the new activity supported by the AF Grant.

VII. Publications.

- C. T. Tomizuka and R. A. Roberts, Diffusion in Ag-Zn System, AF Technical Report, no number designated.
- R. M. Emrick, Techniques for Quenching Point Defects in Metal Wires, AFOSR 2581.
- C. T. Tomizuka, Effect of Hydrostatic Pressure up to 8000 Atm. on the Self-Diffusion Rate in Silver Single Crystals. Progress in Very High Pressure Research, John Wiley & Sons, (New York, 1961).
- C. T. Tomizuka (with R. W. Balluffi and J. B. Darby, Jr.) Self-Diffusion in Silver during Plastic Deformation in Torsion, J. Appl. Phys. 32, 840 (1961).

- D. L. Styris and C. T. Tomizuka, Anomalous Diffusion Rate for Small Penetration Distance in Copper. Accepted for publication in Journal of Applied Physics.
- B. E. Abey, R. M. Emrick and C. T. Tomizuka, High Resistance Electrical Leads for High Pressure Applications. Submitted for publication in Reviews of Scientific Instruments
- C. T. Tomizuka, Solid State Reactions under High Pressure, Kagaku (Science) 32, 539 (1962). In Japanese.

APPENDIX

Personnel

The following persons actively engaged in the research activities sponsored by this contract:

C. T. Tomizuka, Professor of Physics, principal investigator.
(No support during academic year, $\frac{1}{2}$ -time support during summer.)

R. M. Emrick, Research Associate & Assistant Professor.
(Full-time support AF contract) Appointed August 1960.

R. C. Lowell, Technician, high pressure laboratory ($\frac{1}{2}$ -time by AF contract) Appointed June 1960.

P. K. Weir, Electronics technician, September 1961 to September 1962. (mostly $\frac{1}{2}$ -time support).

Dorothy Conniff, Secretary, beginning April 1962. (mostly $\frac{1}{2}$ -time support).

C. L. Foiles, graduate student, ($\frac{1}{2}$ -time plus full-time during the summers).

R. A. Roberts, graduate student, left the university in 1962. (mostly $\frac{1}{2}$ -time support).