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PREPARED BY:

A. A. HENDRICKSON, PRINCIPAL INVESTIGATOR

D. A. KOSS, PRINCIPAL INVESTIGATOR

MASTER

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I INTRODUCTION

The main purpose of this research was to determine the cause or causes of solid solution strengthening in both fcc and bcc solid solutions. The research was mainly an experimental activity in which careful observations on the deformation characteristics of high purity alloy single crystals were utilized to study mechanisms of solid solutions hardening.

Two general kinds of mechanisms were examined:

1. Mechanisms that result from "direct" solute strengthening effects, i.e., those that involve solute atom-dislocation interactions. The research was concerned with identifying both the interaction (whether the interaction contributing the major strengthening was elastic, chemical, modulus, etc.) and the consequences of the interaction (does the observed strength increase result from dislocation pinning by solute atoms or from solute atoms acting as random obstacles?).
2. Mechanisms that concern "indirect" effects arising from the presence of solute atoms. Here it is anticipated that solute atom additions will cause changes in the elastic moduli, stacking fault energy and the density, arrangement and width of grown-in dislocations. For example, it is possible that larger densities of grown-in dislocations in alloy crystals results in "indirect" solute strengthening.

This report summarizes the important observations and conclusions.

II RESEARCH RESULTS

Solid Solution Strengthening in FCC Alloys

Yield Point Phenomena: Yield point phenomena is commonly observed in substitutional FCC solid solutions; the effects can be observed either in static or dynamic strain aging experiments. Because the magnitude of the effect is concentration dependent (and zero at zero solute concentration), it is undoubtedly a result of interaction between solute atoms and stationary dislocations (static) and moving dislocations (dynamic).

Static strain aging experiments were performed on Ag-Zn and Ag-Sn alloy crystals to observe both the aging kinetics and the magnitude of the yield effects. The main conclusions of the work were:

1. The low activation energies observed (0.44 to 0.60 eV) are due to complex vacancy production during deformation.
2. The magnitude of the yield points observed in Ag-Zn, Ag-Al and Ag-Sn crystals indicated a Suzuki (chemical) interaction as responsible for dislocation immobilization.

Dynamic strain aging behavior studies were made in both the Ag-Zn and Ag-In systems. For the Ag-Zn alloy crystals, measurements of the activation energies supported the idea that the onset of serrations is due to solute atoms gaining sufficient mobility to pin dislocations, and that at the upper critical temperature, solute atoms can diffuse fast enough to drift with moving dislocations. In the Ag-In alloy case, experimental measurements of the temperature and strain rate dependence of the critical strain for the onset of serrations, and stress relaxation experiments gave values of both the activation energy and activation volume. At the critical strain, the alloy's response to strain rate changes altered considerably; this was attributed to increases in solute atom mobility and ability to pin dislocations.

Critical Resolved Shear Stress of Ag Alloy Crystals: Extensive measurements of the dependence of CRSS on solute species, solute concentration and testing temperature were made to test both the nature of solute atom-dislocation interactions and their consequences. Early in the investigation it became clear that because of the inherent weakness of pure fcc crystals, extreme care had to be exercised in preparation and testing; slight mishandling could easily result in strengthening equal to that of a 0.1% solute addition.

In a series of careful experiments, the structure and strength of silver alloy crystals were examined; the following conclusions were drawn:

1. Direct measurements through etch pitting in pure and alloy Ag crystals showed that indirect strengthening due to increased dislocation density is not important.
2. There is no correlation between strength changes and oxygen content variations in Ag and Ag alloy crystals.
3. The concentration dependence of strengthening depends on the interaction strength.
4. Combinations of size and modulus interactions do not account for the relative solute strengthening effects in Ag alloys.

Dislocation Studies: It became apparent that the classical experiments were not going to completely solve the FCC solid solution strengthening problem and that observations of individual dislocation motions were required. In 1968 a program to develop the techniques for obtaining highly perfect Ag and Ag alloy crystals was begun in preparation for motion studies.

As many times happens in basic research, the direction was sidetracked by unexpected discovery; in this case extensive studies of dislocation etch pits and micro-indentation in highly perfect silver crystals resulted in the following findings:

1. The accepted etchant for silver revealed only half of the surface intersections of edge dislocations. Use of a modified etchant showed that smaller etch pits are always paired with the large ones, i.e., the modified etchant was equivalent to the Livingston etchant for Cu in that it distinguished edge dislocations of opposite sign.
2. A new dislocation etchant producing conical dislocation etchpits in Ag was discovered; this etchant revealed only edge dislocations of one sign and was thus equivalent to the CP-4 etchant for Ge.
3. In low-dislocation-density ($5 \times 10^4/\text{cm}^2$) 99.999 + % silver crystals, the Vickers hardness on the (111) surface decreases as the indentation size and load are decreased below 18 μ and 5 grams, respectively. The hardness decrease appeared to be associated with a transition in the shear zone from a hemispherical to a rosette configuration.
4. The hardness at loads small enough to yield rosette deformation depends largely on how effectively rosette dislocations are impeded; both crystal defects and surface condition have appreciable effects. The initiation of plastic deformation does not appear to be difficult even when the indentation is made in dislocation-free regions.
5. Indentation creep on (111) surfaces of 99.999 + % silver crystals is observed at room temperature provided that the indentation load does not exceed 5 grams. For a 1-gram load, creep is found if the dislocation density is below about $10^7/\text{cm}^2$. Examination of the shear-zone configuration revealed by dislocation etching shows that indentation creep in low-dislocation-density crystals is associated with rosette shear-zone configurations.

Solid Solution Hardening of BCC Alloys

Substitutional solid solution strengthening of both binary and ternary Nb base alloys has been investigated. The deformation behavior of high purity alloy single crystals has been examined from the standpoint of athermal (900K) as well as thermally activated behavior (77 ~ 900K). Based on information from these studies, some of the important conclusions which may be drawn about substitutional solid solution hardening in Nb base (and likely most other bcc alloys) are*:

- (a) thermally activated and athermal strengthening appears to be primarily dependent on the atomic size misfit between solvent and solute atoms and not on elastic modulus misfit;
- (b) there is no current theory capable to predicting the observed nearly linear dependence of both the thermally activated and the athermal strengths on the binary and ternary solute concentration;
- (c) the principal effect of binary and ternary solute additions on the stress-strain behavior is to raise the yield stress; work hardening behavior increases only slightly, if at all, at high temperatures (900K), while the low temperature data shows work hardening becomes more parabolic with a somewhat higher rate in concentrated Nb-Mo alloys;
- (d) in the ternary Nb-Hf-W and Nb-Mo-W alloys, the rate of a athermal hardening per solute addition is the highest for the most concentrated alloys, but the opposite is observed at low temperatures and solid solution softening is observed at 77K;

*Alloys tested include: Nb-W, Nb-Hf, Nb-Ta, Nb-Mo, Nb-W-Mo, and Nb-W-Hf.

- (e) a phenomenological analysis of solid solution hardening of ternary alloys in terms of binary alloy hardening increments is presented for the cases in which solute atoms have equal as well as unequal strengths as obstacles to dislocation motion;
- (f) the ternary alloy hardening analysis predicts the observed athermal hardening at total solute concentrations of up to 5-6%, but low temperature strengthening behavior deviates rapidly, especially at equal concentrations of solute;
- (g) a non-random solute distribution (likely in the form of solute association), sensitive to heat treatment, is believed to contribute to the formation of solute association sites or zones which in turn cause the high rate of athermal hardening but which "scavenge" the solute atoms causing substitutional solid solution softening at low temperatures;
- (h) in a cooperative program with D. E. Mikkola, measurements of atomic displacements in niobium base alloys show better correlation with observed solid solution strengthening than do observed changes in the lattice parameter.

A more detailed discussion of the studies upon which the previous results are based may be found in the publications and reports.

JOURNAL AND BOOK PUBLICATIONS

- D. A. Koss and J. Hack, "Thermally Activated Solid Solution Hardening of the Ternary System: Nb-W-Mo (submitted for publication).
- Patricia Ruf and Donald Koss, "Solid Solution Hardening of the Ternary System Nb-Hf-W", (submitted for publication).
- R. Mizia and D. A. Koss, "Substitutional Solid Solution Hardening of Ternary Niobium Alloys", Conference Proceedings, Third International Conference on the Strength of Metals and Alloys, (London: The Institute of Metals and the Iron and Steel Institute), p. 525, 1974.
- C. C. Chen and A. A. Hendrickson, "Microhardness Phenomena in Silver", Science of Hardness Testing and its Research Applications, (J. H. Westbrook and H. Conrad, editors) ASM, 1973.
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- B. C. Peters, K. B. Rundman, and A. A. Hendrickson, "Strain Ageing in Ag Base Sn Solid Solutions," Acta Met., v. 13, p. 142-144, 1965.
- G. E. Tardiff and A. A. Hendrickson, "On the Strength of Silver Base Solutions", Trans. Met. Soc. AIME, v. 230, p. 586-587, 1964.

- R. L. Smith and A. A. Hendrickson, "Mechanical Properties of High Purity Metals", Ultra High Purity Metals, ASM, Metals Park, Ohio, p. 85-113, 1962.
- A. A. Hendrickson "Solute Segregation to Stacking Faults", *Acta Met.*, v. 10, p. 900-901, 1962.
- G. E. Tardiff and A. A. Hendrickson "Yield Points in Ag Base Zn Solid Solutions", *Acta Met.*, v. 10, p. 573-574, 1962.

PRESENTATIONS

(Partial Listing)

- "Atomic Displacements in Niobium Base Solid Solution Alloys" (with G. P. Shandley, D. E. Mikkola and D. A. Koss), to be presented at the AIME Meeting, Detroit, Oct. 1974.
- "Solid Solution Hardening of the Ternary System: Nb-Hf-W" (with Patricia Ruf and D. A. Koss), presented at the AIME-TMS Meeting, Pittsburgh, May, 1974.
- "Substitutional Hardening in Nb-W-Mo Alloys" (with R. Mizia and D. A. Koss), presented at the AIME-TMS, Philadelphia, May, 1973.
- "Substitutional Solid Solution Hardening of Ternary Niobium Alloys" (with R. Mizia and D. A. Koss), Third International Conference on the Strength of Metals and Alloys, Cambridge, England, August, 1973.
- "Solid Solution Hardening of High Purity Niobium Alloys," presented by J. R. Slining and D. A. Koss at the AIME-TMS Spring meeting in Boston, Massachusetts, May 1972.
- "The Microhardness of Silver Single Crystals," Conference on Indentation Hardness of Solids, University of Exeter, Exeter, England, September 1971, C. C. Chen, G. W. Rowe and A. A. Hendrickson.
- "Thermal Activation of Glide in FCC Metals," Department of Physical Metallurgy and Materials Science Seminar, University of Birmingham, England, February 1971, A. A. Hendrickson.
- "Dislocation Etching in Silver," TMS-AIME Spring Meeting, Atlanta, May 1971, C. C. Chen and A. A. Hendrickson.
- "Microhardness Phenomena in Silver," Symposium on the Science of Hardness Testing and its Research Applications, Materials Engineering Congress, Detroit, October 1971, C. C. Chen and A. A. Hendrickson.
- "Mechanical Properties of Co Base Ta and Co Base Mo Alloy Single Crystals," by B. C. Peters and A. A. Hendrickson, presented at the Spring Meeting of AIME, May 1969, Pittsburgh, Pa.
- "Solid Solution Strengthening in Dilute Solutions of Silver," presented by A. A. Hendrickson at the International Conference on the Strength of Metals and Alloys, Tokyo, September 1967 and at Hokkaido University Seminar, Sapporo, Japan, September 1967.
- "Effect of Purity on the Dislocation Density and Strength of Silver Crystals," by R. H. Hammer, W. C. T. Yeh, T. G. Oakwood, and A. A. Hendrickson, presented at the Annual Meeting of AIME, Los Angeles, February, 1967.
- "Solid Solution Strengthening in FCC Metals" Argonne National Laboratory Seminar, October 1963, by A. A. Hendrickson.

"Yield Point Behavior and Solid Solution Strengthening in Ag base Sn Solutions", Fall 1965 Meeting of AIME by K. B. Rundman, B. Peters and A. A. Hendrickson (presented by B. Peters).

"Solid Solution Strengthening in Ag base Systems," Iowa State University Seminar, March 1962, by A. A. Hendrickson.

GRADUATE STUDENT SUPPORT

The following had their graduate research programs supported through

Contract No. AT(11-1)-916 research funds:

Gary Shandley, M.S., 1974; currently with Caterpillar Tractor Co., Peoria, Illinois.

Patricia Ruf, M.S., 1973; currently with Dept. of Mat'l Science and Engineering, University of California, Berkeley, California.

Ronald Mizia, M.S., 1972; currently with Westinghouse Corp, Idaho Falls, Idaho.

James D. Johnson (Ph.D. thesis to be completed); currently with Copper Range Company, White Pine, Michigan.

C. C. Chen, Ph.D., 1971; Senior engineer, Wyman-Gordon Co., Worcester, Mass.

John R. Slining, M.S. 1971; currently with the Materials Laboratory, Standard Oil of California, Richmond, California.

R. A. Strahl, M.S., 1969; Ship Building and Drydock Company, Newport News, Va.

B. C. Young (M.S. incomplete); Metallurgist, Kaiser Aluminum Co., Spokane, Wa.

B. C. Peters, M.S., Ph.D., 1968; now with Dow Chemical Co., Midland, Michigan.

R. H. Hammer, M.S., 1966; currently at General Motors Technical Center, Warren, Michigan.

R. C. Gebeau, M.S., 1965; R & D Center, Carpenter Tech. Corp., Reading, Pa.

W. C. T. Yeh, M.S., 1965; now with Kennecott Copper, Salt Lake City, Utah.

D. G. Harman, M.S., 1963; Oak Ridge National Laboratory, Oak Ridge, Tn.

T. G. Oakwood, M.S., 1963; Research Division, Inland Steel Co., East Chicago, Indiana.

K. B. Rundman, M.S., 1962; Associate Professor, Dept. Met. Engrg., Michigan Technological University, Houghton, Michigan.

G. E. Tardiff, M.S., 1961; Lawrence Radiation Laboratory, Livermore, California.