EFFECT OF ANNEALING ON THE SUBSTRUCTURE
OF COLD WORKED FCC METALS AND ALLOYS

FINAL REPORT

D. E. MIKKOLA
DEPARTMENT OF METALLURGICAL ENGINEERING
MICHIGAN TECHNOLOGICAL UNIVERSITY
HOUGHTON, MICHIGAN

JANUARY 1, 1965 - DECEMBER 31, 1974

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION UNDER CONTRACT NO. E(11-1)-1431

DISTRIBUTION OF THIS DOCUMENT UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

The purpose of this research was twofold: first, to obtain information about annealing processes through quantitative examination of structural changes with both x-ray diffraction and transmission electron microscopy and secondly, to relate the changes in structure to changes in properties. For the most part, the studies were centered on materials based on copper and included ordering alloys as well as random solid solution alloys.

This report summarizes the important observations and conclusions resulting from the investigation. These include such topics as: the annealing behavior of stacking faults; the characterization of the nature and stability of dislocation substructures formed in various materials by various modes of deformation; the development of semi-quantitative relationships between strengthening and the nature of dislocation substructures; the relation of atomic displacements associated with solute atoms to strengthening; the effect of dilute solute additions (<100 ppm) on the annealing behavior of pure copper; the kinetics of antiphase domain growth in Cu_3Au in a variety of states: disordered as-quenched, disordered cold-worked, with excess Au, and with Al additions; the development of long period superlattices in $\text{Cu}_3\text{Au} + \text{Al}$ alloys; and the nature of the antiphase domain boundary "maze" pattern observed in Cu_3Au .

LEGAL NOTICE

"This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Energy Research and Development Administration, nor any person acting on behalf of the Administration:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

As used in the above, 'person acting on behalf of the Administration' includes any employee or contractor of the Administration, or employee of such contractor, to the extent that such employee or contractor of the Administration, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Administration, or his employment with such contractor."

I. INTRODUCTION

This research has been concerned with both the mechanisms of annealing and the relation between the structure and property changes occurring during annealing. The research was primarily experimental in nature with x-ray diffraction and transmission electron microscopy being used to examine the changes in substructure as quantitatively as possible. In addition to providing information about annealing processes, these structural observations were combined with observed changes in strength parameters in order to establish semi-quantitative structure-property relationships. The study focused on two groups of materials: (1) pure copper and copper-base solid solutions, and (2) ordering alloys based on the alloy Cu_3Au .

This report summarizes the results of the research which have been for the most part either published in the literature or are currently in some stage of preparation for publication. An important part of the research program not specifically detailed in the published work has been the development of a fine facility for structural characterization of materials. This includes the basic equipment, along with the various modifications developed during the work to provide means for precise and efficient data collection, as well as data analysis techniques involving a variety of complex computer codes.

II. RESEARCH RESULTS

A. Annealing

1. Cu-base Solid Solutions

Much of this portion of the research was concerned with the deformation and annealing behavior of a series of α -Cu-Ge alloys. Detailed studies of the

alloy Cu-8.5 at. % Ge deformed by filing, rolling, and shock loading were carried out. In addition, the effects of changing the Ge content and the deformation temperature on the annealing behavior were also studied. The main conclusions from this work were:

- (a) The disappearance of stacking faults during annealing is generally a two stage process - the second stage being diffusion controlled.
- (b) The stability of stacking faults increases with solute content and with increasing deformation temperature.
- (c) Multilayer faults are more stable than intrinsic stacking faults and can form from intrinsic faults during annealing.
- (d) Recovery processes in annealing involve primarily a relaxation of the non-uniform strains associated with the dislocation substructure.
- (e) The formation and growth of subgrains during the early stage of recrystallization in α -Cu-Ge can only occur after the disappearance of the non-equilibrium stacking faults.
- (f) The stability of deformation substructures is dependent on the mode of deformation.
- (g) An important indicator of the stability of a cold-worked substructure is the level of non-uniform strain, which in turn is determined by the material, strain rate, and the mode and temperature of deformation.

2. Pure Cu and Dilute Cu-base Alloys

This part of the research was centered on the annealing behavior of high purity Cu as well as the effects of small amounts of solute (<100 ppm

of S, Sn, or Y) on the annealing processes. Deformation was by rolling at room temperature. Some of the important conclusions from these studies were:

- (a) The stability of dislocation substructures both during deformation and annealing is increased with solute additions; i.e., dynamic recovery after large deformations is inhibited and the softening temperature of the cold-worked material is increased.
- (b) The initial stage of annealing in these materials involves a near elimination of non-uniform strains prior to any significant increase in subgrain size (or motion of high angle boundaries).
- (c) Subgrain growth occurs at a lower rate with the addition of solute.
- (d) The effectiveness of a given solute atom in raising the recrystallization temperature cannot be easily related to basic parameters. Many previous correlations in the literature have ignored the fact that comparisons of this type can only be made correctly within the single phase field.
- (e) Based on this study and the work of others, a survey of the effectiveness of various solutes in raising the recrystallization temperature showed three general groups:
 - (1) As, P, Sb, Cd, Ag, and Y giving $\Delta T = 0.25$ to 2°C/ppm ;
 - (2) S, Se, and Te giving $\Delta T \sim 10$ - 15°C/ppm ; and (3) Fe, Ni, and Co causing no effect. The first group gave a maximum $\Delta T \sim 170$ - 200°C for concentrations of $\sim 10^{-3} C_0$ where C_0 is the maximum solubility. Members of the second group,

which all have low solubility, gave a ΔT of only $\sim 50^\circ\text{C}$ at 0.1 to 1.0 C_0 . In general, achieving a high value of ΔT requires the presence of a sufficient amount of solute in solid solution to retard boundary migration. This occurs at $10^{-3} C_0$ with the first group, but is not reached with the second group.

- (f) The addition of 95 ppm Sn to Cu decreased the rate of grain growth in the range 375° to 500°C .
- (g) Solute atom - grain boundary interaction information can be gained from measurements of twin frequencies in dilute Cu-base alloys. Observations of the twin frequency as a function of grain size in Cu, Cu-S, and Cu-Sn showed an increase in the ratio of the twin boundary energy caused by the presence of the S and Sn at the grain boundaries.

B. Structure-Property Relations

Detailed studies of the relation between the various parameters describing the cold-worked substructure and the mechanical properties were carried out on both the Cu-8.5 at. % Ge alloy deformed by shockloading and the pure Cu deformed by rolling. In both cases, substructural data for a large number of specimens given various deformation and annealing treatments were related in a semi-quantitative manner to the mechanical properties. The conclusions from this portion of the work together with those relating to the nature of the as-deformed state were:

- (a) Shockloading of Cu-8.5 at. % Ge in the pressure range 100 to 475 kbars introduces high densities of fairly randomly distributed dislocations. The dislocation

density increases in a uniform manner over this pressure range.

- (b) Stacking faults and twin (or multilayer) faults are also introduced by the shockloading, with the ratio of multilayer faults to stacking faults having a value of approximately four. The amounts of both types of faults increased uniformly with pressure.

- (c) The substructural strengthening as measured by changes in yield strength and hardness can be expressed by the empirical relation:

$$\Delta\sigma = K_1 D^{-1/2} + K_2 \left[\langle \epsilon_L^2 \rangle^{1/2} \right]^{3/2}$$

where D is the mean free path of good crystal and $\langle \epsilon_L^2 \rangle^{1/2}$ is the rms microstrain (K_1 and K_2 are constants).

It should be noted that the parameter D includes the effects of both the faults and the dislocation substructure.

- (d) It is well known that deformation of high purity Cu by rolling produces a dislocation cell structure. Quantitative studies of the substructure of rolled Cu confirmed the fact that the cell size reaches a constant size after ~50% R.A. and more importantly that further strengthening arises from the continued increase in the level of the rms microstrains.

- (e) The results for pure Cu provided the opportunity to confirm the functional form of the dependence of strengthening on the microstrain given by the expression in (c) above. Current interpretation of the expression is that the D term is of the form of the well known Hall-Petch relation,

whereas the microstrain contribution is of the type expected on the basis of various theories dealing with strain center obstacles to dislocation motion.

- (f) As mentioned in connection with the annealing experiments, the level of the microstrains decreases during dynamic recovery. These decreases, which arise largely as a result of stress-induced cross slip, can be inhibited by solute additions.

C. Annealing and Ordering of Cu_3Au

This part of the research was initially concerned with two areas: (1) establishing the details of the ordering process in Cu_3Au , particularly the kinetics of antiphase domain (APD) growth, and (2) examining the effects of composition changes and third element additions on the ordering process. In addition, the interactions between ordering and annealing effects were studied in cold-worked Cu_3Au . The following conclusions summarize some of the important results of this work:

- (a) Antiphase domain growth in Cu_3Au quenched from 450°C ($T_c = 390^\circ\text{C}$) and annealed below T_c is analogous to classical grain growth in that it follows a $D^2 \propto t$ relation. Also, the growth process is diffusion controlled. No change in domain growth kinetics occurs on changing the quenching temperature to 600°C .
- (b) A high degree of order with a very small ($<50 \text{ \AA}$) APD size is established in the early stages of ordering. Subsequent growth of the APD occurs through a coarsening process based on harmonics of the original size. This was established through studies of APD size distributions

determined by quantitative analysis of dark field transmission electron microscope images. The APD structure, which involves primarily {100} type APD boundaries during the early stages of growth, becomes more randomly oriented during the later stages of growth. In general terms, the early stages of ordering in Cu_3Au are analogous to both the initial transient stage and subsequent coarsening processes associated with spinodal decomposition.

- (c) The APD configuration in Cu_3Au forms the well known "maze pattern" when examined in the transmission electron microscope. Several explanations have been given for this phenomenon, such as the presence of appreciable amounts of {100} Type II APDB or a combination of dislocations with {100} Type I APDB. (The latter is possible because the Burgers vector of the dislocations is equal to the antiphase displacement vector.) Detailed examination of the APD structure showed that these effects are not important, rather the maze pattern is most likely caused by invisible non-{100} APDB where the APDB is of the type where the displacement vector is in the plane of the APDB.
- (d) Adding excess Au to Cu_3Au does not change the initial stages of APD growth except that because of the decreased activation energy for diffusion off-stoichiometry a larger APD size results from a given heat treatment. During later stages of APD growth, departures from the $D^2 \propto t$ relation occur in the form of a limiting domain

size which is a function of the excess Au content. Although segregation of the excess Au to the APDB may be important in determining the limiting APD size, analysis shows that most of the excess Au atoms are accommodated within the APD.

- (e) Adding up to 10 at. % Al to Cu_3Au causes several changes in the ordering behavior. For 0.3 and 0.6 at. % Al there is no change in the domain growth process except that the growth rate is lowered slightly. Alloys with 1.6, 6.7, and 9.9 at. % Al all form a one-dimensional long period superlattice on ordering with the modulations occurring along $\langle 100 \rangle$ with spacings of 30, 22, and 15 Å, respectively. The basic APD structure which still persists in these alloys has a random crystallographic orientation of APDB although the APD growth still follows a $t^{1/2}$ dependence.
- (f) Preliminary measurements of the strengthening effects in the long period superlattices showed a large increase in strength on ordering with no tendency to "overage" as in Cu_3Au .
- (g) Initially cold working Cu_3Au causes a larger APD size to be formed by a given heat treatment, although the basic time kinetics of the later stages of the growth process are unchanged. This results from the elimination of APDB by dislocations in the early stage of ordering. As the annealing temperature approaches the critical ordering temperature recrystallization is retarded.

D. Atomic Displacements in Nb-base Alloys

This work was carried out in cooperation with D. A. Koss (ERDA Contract No. E(11-1)-916, "Structure and Properties of Solid Solutions") and involved the determination of the mean-square atomic displacements associated with solute atoms in high purity Nb-W, Nb-Hf, and Nb-Mo alloys. The magnitudes of the atomic displacements were measured from peak depressions observed by x-ray powder pattern diffractometry.

Changes in lattice constant on alloying have been commonly used as a basis for theories of solid solution strengthening; however, in these Nb-base alloys the strengthening effects do not correlate very well with lattice constant changes. A much better correlation exists between the atomic displacements and the strengthening effects.

PUBLICATIONS

- W. G. Truckner and D. E. Mikkola, "Strengthening of Copper by Dislocation Substructures," (submitted for publication).
- C. L. Rase and D. E. Mikkola, "Effect of Excess Au on Antiphase Domain Growth in Cu_3Au ," (to be published in *Met. Trans.*).
- S. C. Kolesar and D. E. Mikkola, "Effect of Al Additions on APD Morphology and Growth in Cu_3Au ," *Scandinavian J. Electron Microscopy*, December, 1974.
- D. E. Mikkola, "On the Growth Kinetics and Size Distributions of Ordered Domains in Cu_3Au ," *Scripta Met.* 7 (1973) 1037-1040.
- D. J. Borich and D. E. Mikkola, "The Substructure of Explosively Loaded Cu-8.5 at. % Ge," *Proceedings of TMS-AIME Sandia Laboratories Conference on Metallurgical Effects at High Strain Rates*, Rohde, Butcher, Holland, and Karnes, eds., pp. 587-604, Plenum Press, New York, N.Y., 1973.
- J. W. Kirby, D. J. Borich, and D. E. Mikkola, "Effect of Composition and Deformation Temperature on the Annealing Behavior of Stacking Faults in α -Cu-Ge Alloys," *Met. Trans.* 4 (1973) 1129-1132.
- A. L. Ward and D. E. Mikkola, "A Diffraction Study of the Annealing of Cold-Worked Cu_3Au ," *Met. Trans.* 3 (1972) 1479-1485.
- D. E. Mikkola and K. B. Rundman, "The Kinetics of Ordering and Antiphase Domain Growth vs. the Kinetics of Spinodal Decomposition and Coarsening," *Scripta Met.* 6 (1972) 1095-1098.
- M. Sakai and D. E. Mikkola, "The Growth of Antiphase Domains in Cu_3Au as Studied by Transmission Electron Microscopy," *Met. Trans.* 2 (1971) 1635-1641.
- D. E. Mikkola, M. Sakai, and G. E. Poquette, "Size Distributions of Antiphase Domains in Cu_3Au ," *Proceedings of Third Bolton Landing Conference on Ordered Alloys*, Kear, Sims, Stoloff, and Westbrook, eds., pp. 157-159, Claitor's Publishing, Baton Rouge, La., 1970.
- W. G. Truckner and D. E. Mikkola, "Effect of Annealing on the Substructure of Cold-Worked Cu-8.5 at. % Ge," *J. Appl. Phys.* 40 (1969) 5021-5029.
- G. E. Poquette and D. E. Mikkola, "Antiphase Domain Growth in Cu_3Au ," *Trans. TMS-AIME* 245 (1969) 743-751.

PUBLICATIONS IN VARIOUS STAGES OF PREPARATION

- S. C. Kolesar and D. E. Mikkola, "Effect of Al Additions on Ordering in Cu_3Au ."
- G. P. Shandley, D. A. Koss, and D. E. Mikkola, "Atomic Displacements and Strengthening in Niobium Base Solid Solutions."
- D. J. Borich, E. T. Marsh, and D. E. Mikkola, "Stability of Substructures Formed by Various Modes of Deformation."
- W. G. Truckner and D. E. Mikkola, "Effect of Dilute Solute Additions on the Annealing Behavior of High Purity Copper."

SELECTED PRESENTATIONS

- "Strengthening of Copper by Dislocation Substructures," W. G. Truckner and D. E. Mikkola, to be presented at the Spring Meeting, TMS-AIME, Toronto, Canada, May, 1975.
- "Atomic Displacements in Niobium Base Solid Solution Alloys," G. P. Shandley, D. E. Mikkola, and D. A. Koss, Fall Meeting, TMS-AIME, Detroit, Michigan, October, 1974.
- "Effect of Al Additions on Ordering in Cu_3Au ," D. E. Mikkola and S. C. Kolesar, SCANDEM-74, Scandinavian Electron Microscopy Conference, Helsinki, Finland, June, 1974.
- "Structure-Property Relations," D. E. Mikkola, Helsinki University of Technology, Helsinki, Finland, June, 1974.
- "Order-Disorder Transformations," D. E. Mikkola, University of Groningen, The Netherlands, March, 1974.
- "Substructures Developed by Shock Loading," D. E. Mikkola, The Technical University of Delft, The Netherlands, March, 1974.
- "Effect of Au and Al Additions on APD Growth in Cu_3Au ," D. E. Mikkola, Turku University, Turku, Finland, March, 1974.
- "Shock Strengthening of Metals," D. E. Mikkola, Ovako Steel Corp., Imatra, Finland, February, 1974.
- "Substructural Strengthening," D. E. Mikkola, University of Tampere, Tampere, Finland, February, 1974.
- "Substructure Analysis," D. E. Mikkola, Oulu University, Oulu, Finland, November, 1973.
- "Microstructural Effects of High Rate Deformation," D. J. Borich and D. E. Mikkola, American Society for Mechanical Engineers Meeting, Detroit, Michigan, November, 1973.

- "Effect of Excess Au on Antiphase Domain Growth in Cu_3Au ," C. L. Rase and D. E. Mikkola, International Symposium on Order-Disorder Transformations in Alloys, Tübingen, Germany, September, 1973.
- "Effects of Aluminum Additions on the Ordering Behavior of Cu_3Au ," S. C. Kolesar and D. E. Mikkola, Spring Meeting, TMS-AIME, Philadelphia, Pennsylvania, May, 1973.
- "The Substructure of Explosively Loaded Cu-8.5 at. % Ge," D. J. Borich and D. E. Mikkola, TMS-AIME - Sandia Laboratories Conference on Metallurgical Effects at High Strain Rates, Albuquerque, New Mexico, February, 1973.
- "X-ray Techniques," D. E. Mikkola, invited paper in TMS-AIME Symposium on Modern Techniques in Mechanical Metallurgy, Fall Meeting, TMS-AIME, Cleveland, Ohio, October, 1972.
- "X-ray Study of Annealing in Shock Loaded Cu-8.5 at. % Ge," D. J. Borich and D. E. Mikkola, Spring Meeting, TMS-AIME, Atlanta, Georgia, May, 1971.
- "Electron Microscope Study of the Growth of Antiphase Domains in Cu_3Au ," M. Sakai and D. E. Mikkola, Spring Meeting, TMS-AIME, Las Vegas, Nevada, May, 1970.
- "Size Distributions of Antiphase Domains in Cu_3Au ," Third Bolton Landing Conference on Ordered Alloys, D. E. Mikkola, M. Sakai, and G. E. Poquette, Lake George, New York, September, 1969.
- "Annealing of Cold-Worked Cu_3Au ," A. L. Ward and D. E. Mikkola, Spring Meeting, TMS-AIME, Pittsburgh, Pennsylvania, May, 1968.
- "Effects of Annealing on the Substructure of Cu-8.5 at. % Ge," W. G. Truckner and D. E. Mikkola, Annual Meeting AIME, New York, New York, February, 1968.
- "Antiphase Domain Growth in Cu_3Au ," G. E. Poquette and D. E. Mikkola, Annual Meeting AIME, Los Angeles, California, February, 1967.

GRADUATE STUDENTS SUPPORTED BY THIS PROGRAM

- Edward T. Marsh, M.S., 1972, Ph.D. to be completed in 1975.
- Gary P. Shandley, M.S., 1974, currently with Caterpillar Tractor Co., Peoria, Ill.
- William G. Truckner, M.S., 1966, Ph.D., 1973, currently with Alcoa Laboratories, Alcoa Center, Pennsylvania; employment between M.S. and Ph.D. degrees with Babcock and Wilcox Corp.
- Donald J. Borich, Ph.D., 1973, currently with General Motors Corp., Milford, Mich.
- Craig L. Rase, M.S., 1972, currently with General Motors Corp., Saginaw, Mich.

Masahiro Sakai, currently with Scientific and Technical Information Exchange,
Tokyo, Japan.

Arlyn L. Ward, M.S., 1967, currently with IBM Corporation, Rochester, Minn.

James W. Kirby, M.S., 1967, currently with Ladish Co., Cudahy, Wisconsin.

Gereon E. Poquette, M.S., 1966, currently with IBM Corporation, Boulder, Col.