Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 38, No. 1, 103–110, January 1967

The Order–Disorder Transformation in Cu_3Au at High Pressure*†

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(Received 1 August 1966)

The order–disorder transformation in the alloy Cu_3Au has been studied at pressures ranging up to 21 kbar by means of electrical-resistance measurements made while the sample is at high temperature and under pressure. The rate of change of the critical temperature with pressure is 2.1°K/kbar from 7 to 21 kbar. The kinetics of the order transformation below T_c are adequately described by the homogeneous reaction rate equation and an activation volume of 6.8 cm^3/mole of atoms. The magnitude of this activation volume indicates that the formation of vacancies on the gold sublattice is the rate-limiting step in the homogeneous ordering process.

INTRODUCTION

APPLICATION of pressure often stabilizes new, equilibrium phases in a substance. An equally important, and as yet hardly studied effect of pressure, is to change phase-transformation kinetics. This paper reports the results of an investigation of the effect of high pressure on the kinetics of the order–disorder transformation in the alloy Cu_3Au. This particular transformation in this particular alloy was chosen because, among all solid-state phase transformations, it is one of the most fully studied and best understood at room pressure.[1] Because of this, identification of the influence of pressure is made easier and more certain than would otherwise be possible.

The rate of the order–disorder transformation in Cu_3Au is most effectively studied by means of isothermal experiments: The alloy is equilibrated at temperature T_1 and then suddenly brought to temperature T_2, which may be higher or lower than T_1, and the progress of the transformation observed over a period of time. If $T_1 > T_c > T_2$, where T_c is the critical temperature for ordering, the transformation involves the heterogeneous growth of small regions of ordered material into the antiphase structure characteristic of the ordered state. However, if T_1, $T_2 < T_c$ and if the alloy has been properly prepared with a large antiphase domain size, the transformation is homogeneous and is fully described by a single rate equation. It is with this aspect of the transformation that we deal in the present work. The theory of the homogeneous change in order within a domain is developed in papers by Rothstein,[2] Dienes,[3] and Nowick and Weisberg.[4] Formulation of the theory in terms of experimentally measurable quantities, as well as comparison with experimental results, is given in a paper by Feder, Mooney, and Nowick.[5] They show that changes in the electrical resistivity of the alloy measured at constant temperature are linearly related to changes in the degree of long-range order and that the time-dependence of the resistivity change at temperature

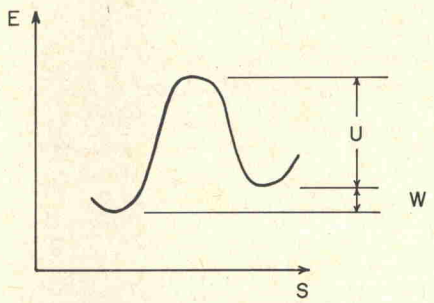

FIG. 1. Energy diagram for the homogeneous ordering step in Cu_3Au. U is the energy barrier to be overcome in taking a pair of atoms from right to wrong sites; W is the resultant change in internal energy of the alloy.

T_2 is given by the equation

$$\frac{R-R_0}{R_e-R_0} = \left\{\begin{matrix}\coth\\ \\ \tanh\end{matrix}\right\} (\alpha t+\beta), \qquad (1)$$

where the coth function applies if $T_2 < T_1$, the tanh functions holds when $T_2 > T_1$, R is the resistance measured at any time t, R_e is the equilibrium resistance at T_2, and R_0 is the resistance of the perfectly ordered alloy at $T = T_2$, and α and β are constants independent of t. It is also shown that, below 320°C, the dependence of the rate constant α on temperature is

$$\alpha = \alpha_0 \exp[(U+W/2)/kT], \qquad (2)$$

where, as indicated in Fig. 1, U is the energy barrier to be overcome in taking a pair of unlike atoms from correct to incorrect lattice sites (the elementary disordering step) and W is the corresponding change in the internal energy of the alloy.

Disordering of Cu_3Au results in a volume increase. Pressure therefore stabilizes the ordered phase and in-

* Supported by the U.S. Office of Naval Research.
† Based on part of a thesis submitted by M. C. Franzblau to the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree.
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[1] L. Guttman, "Order-Disorder Phenomena in Metals," *Solid State Physics*, F. Seitz and E. Turnbull, Eds. (Academic Press Inc., New York, 1956), Vol. 3, p. 145.
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[3] G. J. Dienes, Acta Met. **3**, 549 (1955).
[4] A. S. Nowick and L. R. Weisberg, Acta Met. **6**, 260 (1958).
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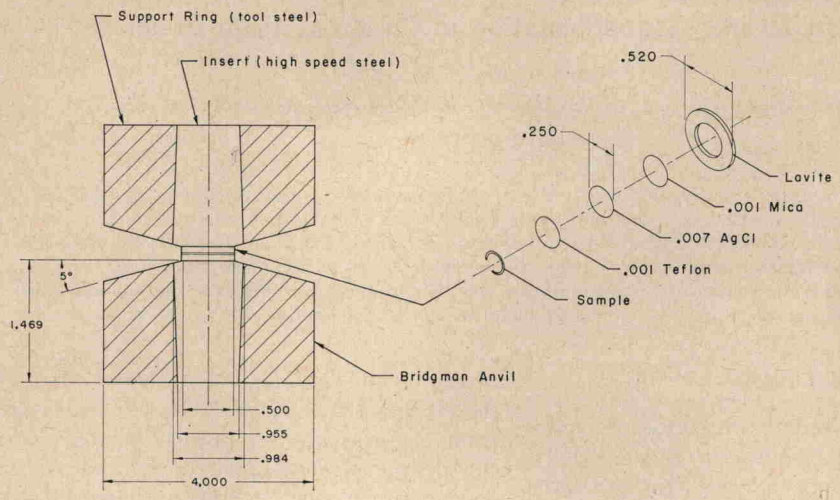

FIG. 2. Bridgman anvil and split-gasket assembly used for the high-pressure measurements.

creases the ordering energy. It will also increase the energy barrier to be overcome in taking a pair of atoms from correct to incorrect lattice sites. To allow for this in Eq. (2), both U and W should be replaced by the free energies G_U and G_W. Since $(\partial G/\partial P)_T = V$ and $(\partial G/\partial T)_P = -S$, a consistent first-order approximation to the effect of pressure will be to add terms PV^* and PV_t to Eq. (2):

$$\alpha = \alpha_0 \exp[(U + PV^* + 1/2W + 1/2PV_t)/kT], \qquad (3)$$

where V_t is the volume increase of transformation for a disordering interchange of a pair of atoms and V^* is the activation volume associated with the activated process represented in Fig. 1. To a higher order of approximation, the pressure- and temperature-dependence of V and S defined by the above equations would have to be considered. However, most high-pressure experiments on atomic mobility are sufficiently accurate to require use of only the first-order approximation. The assumption is made that resistivity mains linearly related to S in the alloy under pressure.

If the activation-volume model of the effect of pressure on the order–disorder transformation is adequate and the resistivity remains linearly related to S, then Eqs. (3) and (1) should fully describe the ordering rate observed at constant temperature and pressure. The first aim of the experiments is to test this; the second is to determine the value of V^*. Knowledge of V^* should help elucidate the nature of the rate-controlling step in ordering.

EXPERIMENTS

The high-pressure technique for the proposed experiment must satisfy a number of requirements. Studies of the effect of pressure on the atomic mobility in fcc metals indicate that pressures of the order of 20 kbar will be required to produce measurable effects on the order–disorder transformation. The pressure must be very nearly a true hydrostatic pressure since the transformation is known to be sensitive to plastic strain. Since electrical resistivity changes are to be used to follow changes in the state of order, four electrical leads as well as four thermocouple leads must be introduced into the sample space. Finally, temperatures up to about 450°C must be attained while the sample is under pressure and it must be possible to both hold the temperature constant for long periods of time and to change it rapidly from one value to another.

APPARATUS

It was found that these requirements could be met economically with Bridgman anvils in conjunction with a multilayered gasket. The anvil and gasket design used is shown in Fig. 2. For the temperature and pressure range of these experiments it is not necessary to use tungsten carbide-anvil inserts; "Hypercut" high-speed steel has the requisite hardness and hot strength. Proper alignment of the anvils is assured by use of a close fitting steel guide. The sample is contained between two halves of a split gasket, each half consisting of mica, AgCl and Teflon discs contained in a lavite washer. The AgCl is used to transmit nearly hydrostatic pressure to the sample while the mica and Teflon discs protect the anvil faces and the sample, respectively, from the corrosive behavior of AgCl at high temperature. Electrical leads are carried between the two lavite rings into the sample space. The thickness of each ring is 0.0125 in. while that of the stack of inner discs is 0.009 in. The extra thickness of the lavite rings is required to avoid overloading the gasket as the sample and electrical leads slightly increase the thickness of the cavity components. When the anvils are forced together, the rings crumble and the high friction between lavite and steel retains the sample by preventing extrusion of the sample cavity materials.

The nature of the pressure distribution in the Bridgman anvil-pressure generator has been treated theoretically by Jackson and Waxman[6] and investi-

[6] J. W. Jackson and M. Waxman, in *High Pressure Measurement* (Butterworths, Washington, 1963), p. 39.