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VACANCY FORMATION IN GOLD UNDER HIGH PRESSURE

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Abstract—High-purity gold wires were resistively heated and quenched in a pure argon gas environment at pressures up to 6 kbars. Quench rates of 10^4 to 5×10^4 °C/sec were obtained by abruptly reducing the heating current. The resistance of both the specimen and an unquenched dummy specimen were measured *in situ* at −38°C with conventional circuits. The logarithm of the quenched-in resistance decreased linearly with increasing pressure at a constant temperature of 600°C. From these data, a formation volume of $0{\cdot}52 \pm 0{\cdot}07$ atomic volume was derived, which was assumed to be associated with the formation of single vacancies. For atmospheric pressure quenches from below 725°C, Arrhenius plots of the quenched-in resistivity for various quenching temperatures yielded an average formation energy for single vacancies of 0·93 eV. Above 725°C, the quenched-in resistivity drops below this line consistent with the complex annealing behavior during the quench observed by others for higher temperature quenches.[1] The measured formation volume indicated a degree of relaxation around a vacancy that is shown to be in accord with previously calculated lattice relaxations obtained using potential function theory.

INTRODUCTION

LARGE elastic strains have been shown to have a significant effect on self-diffusion in several metals.[2–6] Compressive strains resulting from the application of hydrostatic pressures of 5–10 kbars have reduced the diffusion coefficient by as much as an order of magnitude. Theory predicts that the principal manifestation of the strain arises in the exponential part of the diffusion equation associated with the energy required to form a vacancy in the deformed crystal and with the energy an atom requires to surmount a potential barrier along the diffusion path.[7] But this theory does not enable one to predict *a priori* the relative importance of these two effects. However, several quenching and annealing experiments on the noble metals have resulted in the independent determination of the formation energy and migration energy of vacancies in unstrained materials. These techniques have been extended to strained systems for vacancy annealing in gold[8] and at the time of this writing, for quenching in gold.[9] Other methods, the change in macroscopic length[10] and calorimetric measurement of the energy stored in a quenched crystal,[11] have been used to determine, indirectly, the effect of strain on vacancy formation.

The technique reported herein is the most direct; it involves determination of the vacancy concentration by a measurement of the excess electrical resistivity quenched into gold wires that are subjected to large hydrostatic pressures. The data permit the calculation of not only the energy of formation of the vacancy but also the volume change of the crystal accompanying the formation of a vacancy. The volume obtained indicates the degree of relaxation of the lattice atoms around the vacancy. This relaxation is compared with calculated estimates of this quantity obtained using simple pairwise potential function theory.[12]

THEORY

It has been shown that by rapidly quenching fine metal wires from elevated temperature to room temperature or below, a large fraction of the point defects in equilibrium with the crystal lattice at the high temperature, can be retained.[10] The measure of this defect supersaturation at the low

temperature is reflected in an increase in the electrical resistivity of the wire. Annealing of these defects in gold has indicated that defects quenched from below 700°C, at quench rates of 10^3 to 10^5 °C/sec or more, are predominately single vacancies. Above this temperature, more complex defect annealing occurs and has been the subject of several theoretical and experimental studies.[13–15] For simplicity of interpretation, therefore, the quenches under high pressures in this study were done at 600°C.

The number of vacancies n_v, which are in equilibrium with a crystal lattice at absolute temperature T, can be expressed as

$$n_v = N \exp(-\Delta G_f/kT) \qquad (1)$$

where N is the total number of possible lattice sites at which a vacancy can exist and ΔG_f is the change in the Gibbs free energy of the crystal accompanying the formation of a vacancy. Using the thermodynamic relation that the Gibbs free energy is related to the formation energy ΔH_f, or enthalpy, and to the entropy of formation ΔS_f by the expression

$$\Delta G_f = \Delta H_f - T\Delta S_f \qquad (2)$$

and also using the observation that the fractional vacancy concentration quenched into a crystal from a temperature T_Q at pressure p is proportional to the resistivity increase $\Delta\rho_v$ on quenching, one obtains for the quenched-in resistivity,

$$\Delta\rho_v = A\left(\frac{n_v}{N}\right) = A \exp(-\Delta G_f/kT_Q) = A \exp(\Delta S_f/k)\exp(-\Delta H_f/kT_Q) \qquad (3)$$

where A is a constant independent of temperature and pressure. It follows from equation (3) that $\ln \Delta\rho_v$ is linear in $1/T_Q$ with a slope

$$\sum = \frac{\delta(\ln \Delta\rho_v)}{\delta(1/T_Q)} = -\frac{\Delta G_f}{k} = -\frac{\Delta H_f}{k}$$

if ΔS_f is also assumed to be independent of temperature. This last assumption has been justified experimentally, and the energy of formation of a vacancy may be derived from the slope of such a curve.

At constant temperature the derivative of the Gibbs free energy with pressure is a volume, which for ΔG_f has the interpretation of the volume change a crystal experiences on formation of a vacancy. This derivative, from use of equation (3), is

$$\left(\frac{\partial \Delta G_f}{\partial p}\right)_T = \Delta V_f = -kT_Q\left[\frac{\partial(\ln \Delta\rho_v)}{\partial p}\right]_T. \qquad (4)$$

Accordingly, the formation volume can be determined from a plot of $\ln \Delta\rho_v$ against pressure for quenches from a constant temperature.

EXPERIMENTAL

The large hydrostatic pressures required in this experiment were obtained with a Harwood Engineering Company three-stage gas pumping system capable of attaining pressures up to 13 kbars in a cylindrical vessel with internal dimensions of 2 in. dia. and 8 in. high. High-purity argon gas (99·995 %) was used as the high-pressure fluid because it is chemically inert and has favorable thermodynamic properties. Gas chromatographic analysis of the argon confirmed the listed purity. The pressure system was operated with a minimum of lubrication to avoid thermal decomposition of oil on the specimen at elevated temperatures. The high pressures were measured with a calibrated Manganin gage, linear to within 1 per cent in the pressure range used.

The specimen holder used for both the high- and low-pressure quenches is shown in Fig. 1. It is essentially an aluminum housing that encloses horizontally suspended specimen and dummy specimen wires. This enclosure is supported in good thermal contact with a $\frac{7}{8}$ in. (O.D.), $\frac{1}{4}$ in. (I.D.) steel tube that is closed on the lower end. Ethanol cooled to dry-ice-ethanol bath temperature was circulated through this steel 'cold thimble' through a specially designed pressure vessel closure. In this way it was possible to cool the specimen enclosure even when the vessel was at high pressure.

The specimen enclosure was built up in sections to facilitate the insertion and suspension of the specimen and dummy specimen and the mounting of thermocouples. In the finished construction the specimen and dummy specimen wires remained suspended at the center of individual $\frac{1}{4}$-in. cross-sectional annular cavities surrounding the cold thimble. With this arrangement, the temperature of the wires could be precisely maintained near −38°C by heat exchange with the cold walls of the cavities. The enclosure was provided with small baffled vent holes to permit passage of the high pressure gas. The entire specimen holder assembly was surrounded with a Lucite jacket that both insulated the cold assembly from the pressure vessel wall and reduced the dead space in the vessel.

A conventional circuit,[16] shown schematically in Fig. 2, was used in the measurement of the quenched-in resistance. A differential measuring technique, used to improve sensitivity, compared the resistance of the quenched specimen to an unquenched dummy specimen. The dummy specimen also served to compensate for