Hydrogen-Induced Enhancement of Interdiffusion in Cu-Ni Diffusion Couples

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Drastic enhancements of the interdiffusion were observed in Cu-Ni diffusion couples when samples were heated under high hydrogen pressures (~5 GPa). Interdiffusion coefficients measured between 600–800 °C were increased by $\sim 10^4$ times on the Ni-rich end and by ~10 times on the Cu-rich end. The observation is explained in terms of superabundant vacancy formation in the presence of interstitial hydrogen atoms. [S0031-9007(98)06440-0]

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A few years ago we discovered a formation of superabundant vacancies in Ni and Pd, amounting to as much as ~10 at.%, when specimens were heated under high hydrogen pressures [1,2]. Subsequent work on less hydrogen absorbing metals, Al [3] and Mo [4], also showed enhanced vacancy concentrations in hydrogen-charged samples amounting to, respectively, 8 and 12 orders of magnitude higher than in vacuum under corresponding p, T conditions. The origin of this superabundant vacancy formation was ascribed to the lowering of the formation energy of a vacancy by trapping hydrogen atoms on its neighboring interstitial sites [4–7].

Since the diffusion of metal atoms generally proceeds via a vacancy mechanism, a concomitant enhancement of the metal-atom diffusion can be expected, and was indeed indicated in the hydrogen-induced acceleration of phase separations in some Pd alloys [8–11]. In a $Pd_{0.8}Rh_{0.2}$ alloy, for example, the interdiffusion coefficient at 600 °C was roughly estimated to be $\sim 10^7$ times larger under 5 GPa of hydrogen pressure than in vacuum [10].

The present work is intended to demonstrate unambiguously the hydrogen-induced enhancement of the interdiffusion, by examining its composition and temperature dependence more quantitatively, using diffusion couples of Cu-Ni.

A specimen consisted of a pair of Cu and Ni disks, each 2.0 mm $\phi \times 0.1$ mm in size, 99.9% and 99.99% in purity, respectively. It was enclosed in an NaCl container (a hydrogen sealant) together with an internal hydrogen source ($LiAlH_4$), and placed at the center of a high-pressure cell. Details of the sample cell design were given elsewhere [12]. The cell, a cube of 8 mm edge length, was compressed from all six sides equally by tungsten carbide anvils of top faces measuring 6 mm × 6 mm, using a cubic-anvil press Oz.F1 of our laboratory.

Experiments were performed in the following way: First, the pressure was raised to 5 GPa, then the temperature was raised to prescribed values (600, 700, 750, 800, 900, and 1000 °C), maintained there for 30 min, and quenched. In the process of heating, a sample was hydrogenated by an irreversible decomposition of the internal hydrogen source at ~300 °C. After the diffusion annealing, the sample was recovered to ambient conditions, and the distribution of Cu across the interface was measured by a scanning electron microscope (JEOL JSM 5400-Link exl). For comparison, control experiments of exactly the same annealing conditions were performed without incorporating a hydrogen source in the cell.

Concentration profiles of Cu observed after annealing in hydrogen of 5 GPa at four different temperatures are shown in Fig. 1, together with the result of a control experiment at 700 °C without hydrogen.

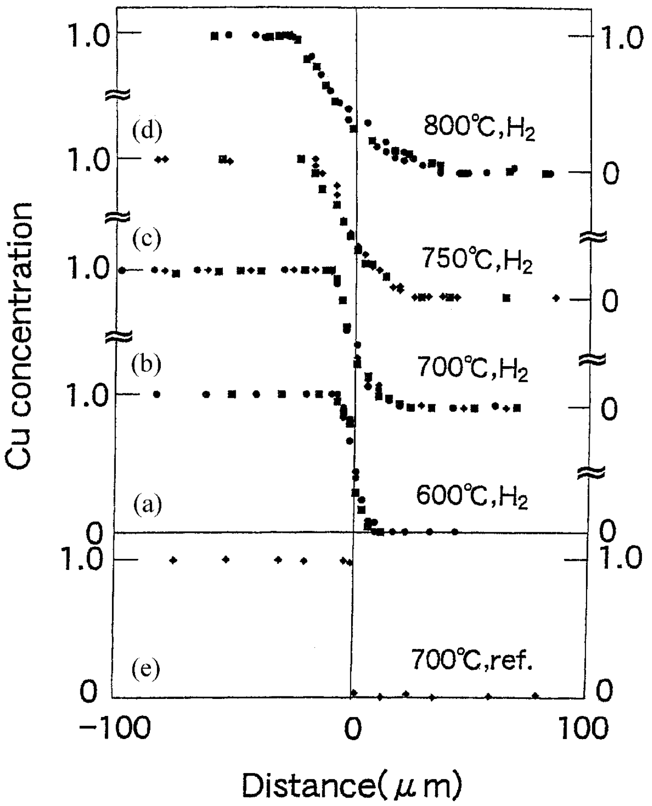

FIG. 1. Concentration profiles of Cu after diffusion annealing for 30 min at (a) 600 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C in 5 GPa of hydrogen, and (e) 700 °C under a mechanical pressure of 5 GPa. The zero of distance is taken at the Boltzmann-Matano interface.

The increase of diffusion lengths in a hydrogen atmosphere is obvious. Even at the lowest temperature of 600 °C, the diffusion length is definitely larger than that of the control experiment, which in fact shows the limit of spatial resolution of approximately 5 μm. The asymmetric shape of the profiles indicates that the observed process was essentially a dissolution of Cu into Ni, without any noticeable Ni diffusion into Cu. Measurements of concentration profiles after annealing above 900 °C were difficult due to excessive deformations of recovered samples. In one of the runs, the recovered sample was roundish in shape, and its concentration profile was nearly flat. These observations indicate that the melting took place at about 900 °C: The melting point was lowered appreciably by hydrogenation, from $T_m = 1260$ °C for Cu and 1630 °C for Ni at 5 GPa [13].

Interdiffusion coefficients obtained by analyzing these concentration profiles by a conventional Boltzmann-Matano method are shown in Fig. 2, together with some reported data obtained under ordinary conditions [14]. The enhancement of interdiffusion coefficients under 5 GPa of hydrogen amounts to $\sim 10^4$ times on the Ni-rich end (extrapolated) and ~ 10 on the Cu-rich end. The curves at different temperatures are nearly parallel to each other, which means that the activation energy is nearly the same at all compositions from Ni to Cu.

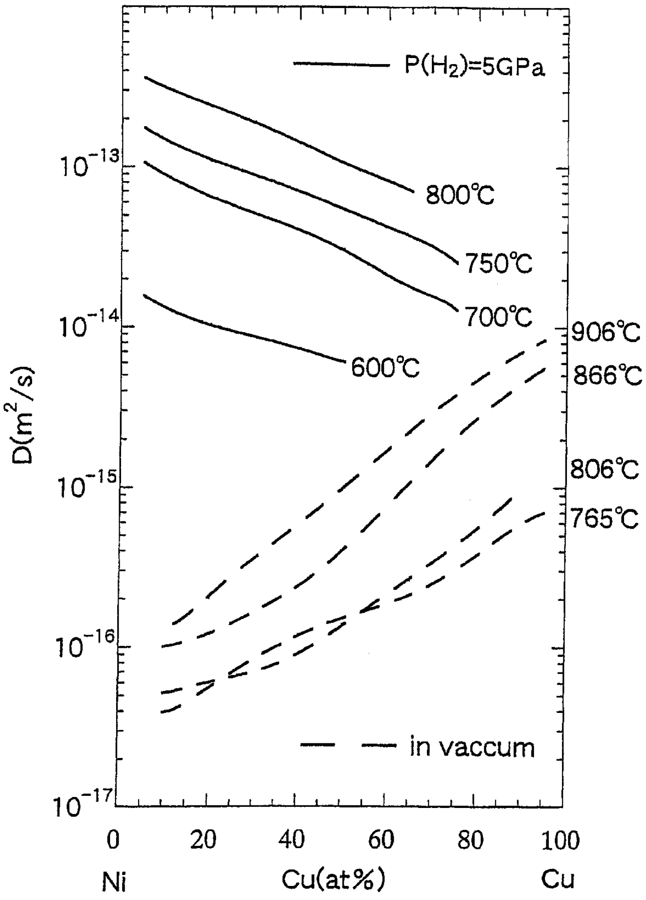

FIG. 2. Interdiffusion coefficients in Cu-Ni alloy. The upper group of curves is the present experimental data obtained in 5 GPa of hydrogen, and the lower group reported data obtained under ordinary conditions [14].

In Fig. 3, the Arrhenius plot is shown of interdiffusion coefficients on the Ni-rich end, i.e., impurity diffusion coefficients of Cu in Ni, which leads to an expression, $D_i' = 4.1 \times 10^{-7} e^{-1.26\,\mathrm{eV}/kT}$ m^2/s.

Implications of these results can be discussed most conveniently in terms of Darken's formula:

$$D = f_{\mathrm{th}}[(1 - y)D_{\mathrm{Cu}} + yD_{\mathrm{Ni}}], \tag{1}$$

where f_{th} is the thermodynamical factor, and D_{Cu} and D_{Ni} are the intrinsic diffusion coefficients of Cu and Ni, respectively, in $\mathrm{Cu}_y\mathrm{Ni}_{1-y}\mathrm{H}_x$.

The effect of hydrogen on f_{th} is estimated to be sufficiently small: $f_{\mathrm{th}} = 1$ for both ends of the alloy composition ($y = 0$ and 1), and $f_{\mathrm{th}} = 1.69$–1.41 for 600–900 °C in the middle ($y = 0.5$). (The values were calculated from the heat of solution of hydrogen in Cu and Ni [15], the Gibbs free energy of the alloy [16], and fluid hydrogen under the relevant range of pressure and temperature [17].)

The intrinsic diffusion coefficients D_{Cu} and D_{Ni} can be written, approximately, as a product of vacancy concentration X_v and vacancy diffusivity D_v, and in view of the rapid motion of hydrogen atoms their effect on D_v can be expected to be reasonably small (see below). Thus, we are left with the enhancement of vacancy concentration as a major cause of the observed diffusion enhancement.

More quantitative discussions can be made by focusing attention on the Ni-rich end, where the interdiffusion is reduced to the impurity diffusion of Cu in a Ni matrix. Taking the ratio of the impurity diffusion coefficient under high hydrogen pressures D_i' to that under normal conditions D_i, we obtain the following expression for the vacancy concentration under high hydrogen pressures:

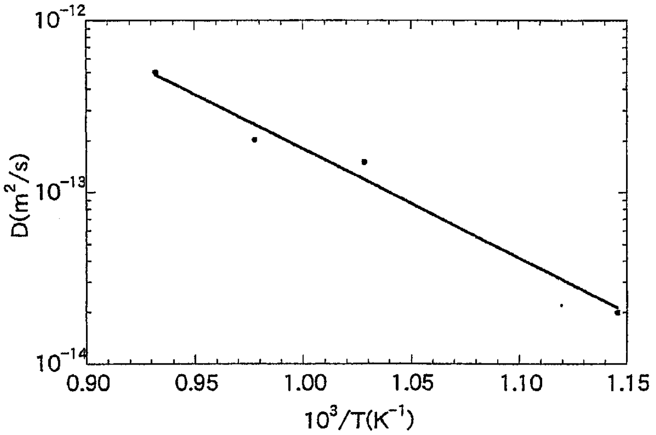

FIG. 3. Arrhenius plot of interdiffusion coefficients in Cu-Ni alloy on the Ni-rich end.

$$X_v' = X_v (D_i'/D_i) \exp[(\Delta h_m - \Delta h_{\mathrm{bvi}})/kT], \qquad (2)$$

where X_v is the equilibrium concentration of vacancies under normal conditions, and Δh_m and Δh_{bvi} are the changes in the enthalpy of migration of the impurity atom (Cu) and of vacancy-impurity binding, respectively, caused by high hydrogen pressures. Substituting the reported data $X_v = 3e^{-1.79\,\mathrm{eV}/kT}$ [18] and $D_i = 6.1 \times 10^{-5} e^{-2.66\,\mathrm{eV}/kT}$ m^2/s [19], and the present expression of D_i', we obtain $X_v' = 2.0 \times 10^{-2} \exp[(-0.39\ \mathrm{eV} + \Delta h_m - \Delta h_{\mathrm{bvi}})/kT]$.

On the other hand, a theory based on vacancy-hydrogen interactions gives the following approximate expression for the concentration of vacancy-hydrogen clusters [4]:

$$X_{\mathrm{cl}} = X_H^6 \exp\left[\Delta S_f/k - \left(h_f - \sum h_b\right) \Big/ kT\right], \qquad (3)$$

where $h_f = e_f + p v_f$ is the heat of formation of a vacancy (1.79 + 0.27 eV at $p = 5$ GPa for v_f equal to 0.8 times the atomic volume [19]), h_b is the binding enthalpy of a hydrogen atom to a vacancy ($e_b = 0.43$ eV for the first two and 0.28 eV for the additional four hydrogen atoms at $p = 0$ [20]), and ΔS_f is the formation entropy of a cluster. X_H is the concentration of hydrogen on (untrapped) solution sites, which can be written approximately as $X_H = 0.3e^{+0.05\,\mathrm{eV}/kT}$ under 5 GPa of hydrogen pressure [17]. Substitution of these values into Eq. (3) leads to $X_{\mathrm{cl}} = 7 \times 10^{-4} \exp[\Delta S_f/k + 0.22\ \mathrm{eV}/kT]$.

Equating the expressions for X_v' and X_{cl}, we obtain $\Delta S_f = 3.3k$ and $\Delta h_m - \Delta h_{\mathrm{bvi}} = 0.61$ eV. The fact that the formation entropy of a cluster is larger than typical values for a vacancy, $(0.5 \sim 1)k$ [19], is reasonable in view of the possible decrease of vibrational energies of hydrogen atoms on trapping. The enthalpy change being of the order of the migration energy of a hydrogen atom ($e_m^H = 0.42$ eV [21]) reflects the dragging effect of trapped hydrogen atoms on the vacancy motion. The remaining terms, $p\Delta V_m$ (ΔV_m: the migration volume) and Δh_{bvi}, are expected to be smaller in comparison, and tend to cancel with each other. ($p\Delta V_m = 0.07$ eV for ΔV_m equal to 0.2 times the atomic volume.)

The fact that the hydrogen-induced diffusion enhancement is small on the Cu-rich end can be naturally understood because hydrogen concentrations in Cu in the present experiments are nearly an order of magnitude smaller [17], leading to a negligibly small number of vacancy-hydrogen clusters [see Eq. (3)].

In summary, the quantitative analysis of the temperature dependence of the diffusivity of Cu in Ni showed that the increase of thermal-equilibrium vacancy concentrations more than compensates for the dragging effect of trapped hydrogen atoms on the vacancy motion. The activation energy of metal-atom diffusion is reduced by $\sum h_b - \Delta h_m + \Delta h_{\mathrm{bvi}} \sim 6e_b - e_m^H$. Since this quantity assumes large, positive values in all of the cases investigated to date, the enhancement of metal-atom diffusion can always be expected, provided hydrogen atoms exist in interstitial sites. The large magnitude of this hydrogen-induced diffusion enhancement strongly indicates its significant implications for wide areas of materials processing.

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