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Formation of superabundant vacancies in M–H alloys and some of its consequences: a review

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Abstract

Superabundant vacancies (SAVs) are the vacancies of M atoms formed in M–H alloys, of concentrations as large as ≲30 at.%. After presenting some results of SAV formation as revealed by X-ray diffraction (XRD) at high temperatures and high hydrogen pressures, its mechanism in terms of vacancy-hydrogen (Vac-H) cluster formation is described, including the underlying information of Vac-H interactions. One of the most important conclusions of the theory is that defect structures containing SAVs are in fact the most stable structure of M–H alloys, and therefore SAVs should be formed whenever the kinetics allow. It is shown subsequently that SAVs can be formed in the process of electrodeposition. Some of the consequences of SAV formation including the enhancement of M-atom diffusion and creep are described, and its possible implication for hydrogen embrittlement of steels is mentioned.

Keywords: Superabundant vacancy; Vacancy-hydrogen cluster; Electrodeposition; Enhancement of diffusion; Enhancement of creep

1. Introduction

In 1993 in the course of structure determination of metal–hydrogen (M–H) alloys at high temperatures and high hydrogen pressures $p(H_2)$, we discovered an intriguing phenomenon that the lattice parameter of Ni and Pd decreased over several hours until it reached a limiting value ~1.5% smaller [1,2]. This was ascribed tentatively to the formation of vacancies, which, however, required incredibly high concentrations of vacancies, as high as ~20 at.%. Thus, in order to provide unambiguous evidence of vacancy formation, specimens of Ni heat treated under such conditions were reheated in vacuum for 15 min at 800 °C, and examined under microscope [3]. The idea was to remove hydrogen after heat treatments to make the existing vacancies over-saturated to precipitate in the form of voids. The voids were indeed observed, and their total volume increased with holding times of the initial heat treatment, exactly as expected. This dependence on the holding time excluded the possibility that the voids were formed by precipitation of hydrogen.

Since these initial experiments, similar observations were made of lattice contractions in the f.c.c. dihydride TiH_2 [4] and monohydrides of Cr [5], Mn [6], Fe [6,7], Co [6], Ni [8], Pd [9,10] and Pd–Rh alloys [11], and of the formation of voids in Al [12] and dislocation loops in stainless steel [13] both due to agglomeration of vacancies. These observations established the generality of this phenomenon, now called the superabundant vacancy (SAV) formation.

For the mechanism of SAV formation, it was immediately inferred that vacancy-hydrogen (Vac-H) binding should be responsible [14]. It had been known from intensive studies of plasma–wall interactions in fusion reactor research that implanted D atoms are trapped by implantation-induced vacancies with rather large binding energies; see the review papers [15–17]. Thus, in the presence of interstitial H atoms vacancies should exist in the form of Vac-H clusters, and their formation energy should be reduced, approximately, by the sum of Vac-H binding energies. Known values of the binding energy indicated that the reduction of the formation energy could be appreciable, and lead to substantial enhancement of the equilibrium concentration of vacancies (Vac-H clusters). Vac-H interactions and a theory giving the equilibrium concentration of Vac-H clusters are described in Section 3.

One of the important recognitions gained from the SAV formation is that the most stable structure of M–H alloys is in fact a defect structure containing a large number of

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vacancies. This implies in particular that high $p(H_2)$, T conditions adopted in our experiments were not essential, needed only for kinetic reasons. High temperatures were necessary to allow vacancies to diffuse into the lattice, and high pressures to confine hydrogen at these high temperatures. The possibility of creating SAVs without any extreme conditions, namely by electrolytic deposition, is described in Section 4. Among the consequences of SAV formation, the most conspicuous is the enhancement of M-atom diffusion, of which some of the results are described in Section 5.

2. Formation of SAVs under high $p(H_2)$, T

The temperature dependence of the lattice contraction process observed in Ni under 3 GPa is shown in Fig. 1 [8]. The contraction became faster at higher temperatures, but the total magnitude of the contraction stayed nearly constant, as shown in Fig. 2 (on the left-hand scale). Very similar results were obtained for Pd, as also shown in Fig. 2 [9]. The concentration of Vac-H clusters can be estimated using the relation $x_{cl} = 3\,\Delta a/a - v_R/\Omega$, where v_R is the relaxation volume and Ω the atomic volume. Adopting an approximate value of the relaxation volume $v_R/\Omega = -0.35$ for both Ni and Pd, based on calculations for vacancies in pure metals [18], we obtain the concentrations plotted on the right-hand scale of Fig. 2. Apparently the concentration of Vac-H clusters shows a saturation behavior: $x_{cl} \approx 0.3$ for Ni and $x_{cl} \approx 0.1$ for Pd at all temperatures (and hydrogen pressures). Lattice contractions and hence cluster concentrations observed in other f.c.c. hydrides were all similar in magnitude [6].

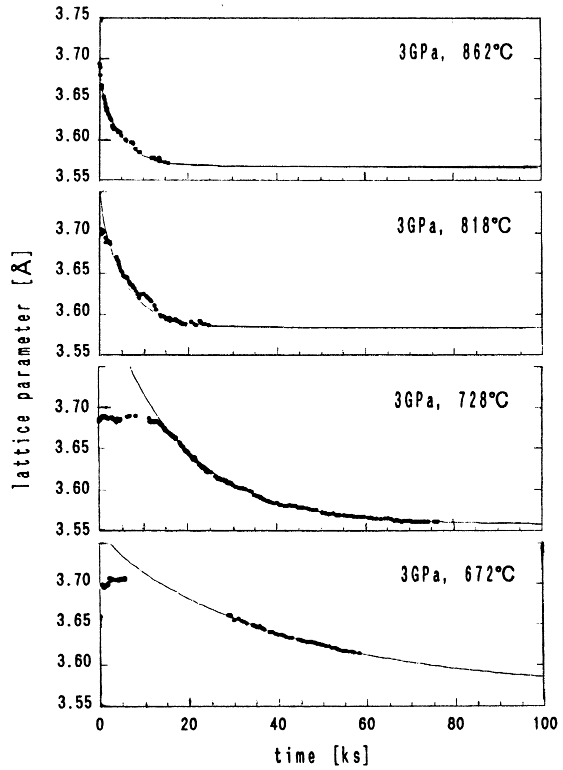

Fig. 1. Examples of measured lattice parameters of Ni as a function of time. Hydrogen concentrations estimated from initial lattice parameter values are in the range $x = 0.57 \pm 0.03$ [8].

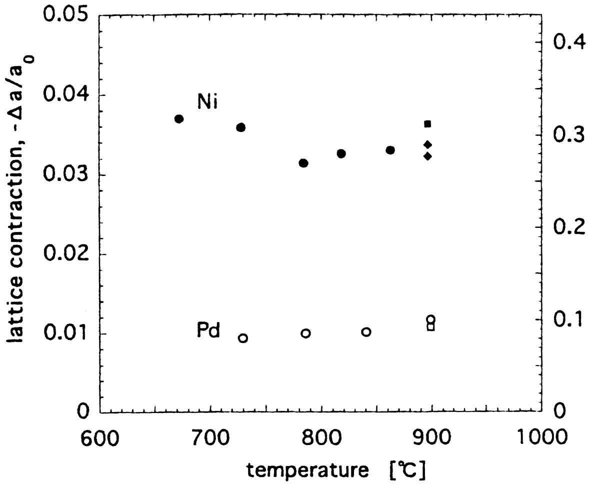

Fig. 2. Measured lattice contractions of Ni and Pd (left scale), converted into concentrations of Vac-H clusters (right scale). Ni: • 3 GPa, ♦ 4 GPa, ■ 5 GPa. Pd: ○ 3 GPa, □ 4.6 GPa [8,9].

In addition to the lattice contraction, superlattice reflections from the contracted lattice were sometimes observed, as shown in Fig. 3 for Ni [8]. The superlattice lines have simple-cubic indices, which indicates the formation of an ordered arrangement of Vac-H clusters most probably of the $L1_2$ structure (Cu_3Au type); Ni_3Vac. Same superlattice reflections were observed in other f.c.c. hydrides Pd–H [2] and Mn–H [19].

These observations suggest that the $L1_2$ structure should be the most stable vacancy-ordered structure in the f.c.c. lattice, and its vacancy concentration $x_v = 1/3$ should be the maximum sustainable by the M lattice. The maximum H concentration in this vacancy-ordered structure can be

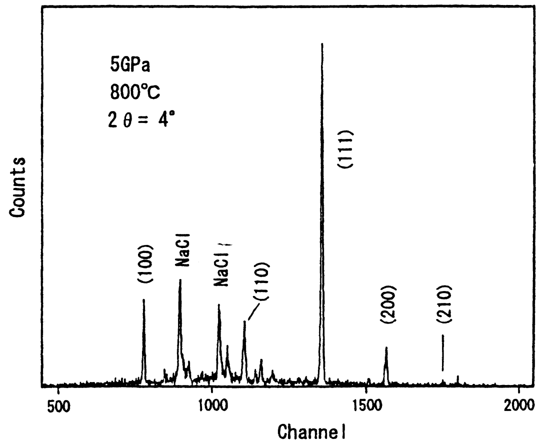

Fig. 3. XRD spectrum of Ni, showing superlattice reflections having simple-cubic indices [8].

attained when all the octahedral sites are filled up, which leads to M_3VacH_4, a superstoichiometric hydride of $x=4/3$. In the case of Pd, electronic calculations showed that the total energy of this vacancy-ordered hydride Pd_3VacH_4 is indeed lower than that of a defect-free stoichiometric hydride PdH of NaCl type [20].

The first observation of a vacancy-ordered hydride structure was made earlier in the near-surface region of ion-implanted Pd hydride [21]. There, one of the two sublattices of the b.c.t. structure was randomly occupied by vacancies to 50%, again forming Pd_3VacH_4. A related structure was observed in the Fe–H alloys at high $p(H_2)$, T, where the superlattice XRD lines having simple-cubic indices were observed in the b.c.c. phase, indicating the preferential occupancy by vacancies of one of the two simple-cubic sublattices of the b.c.c. lattice, forming a $L2_0$ structure (CsCl type) [22].

The appearance of superlattice reflections has been rather sporadic and conditions for their appearance have not been established. Probably, this is due to conflicting requirements that high temperatures are needed to maintain a large number of vacancies whereas low temperatures are needed for these vacancies to order.

Some additional discussions on superstoichiometric hydrides are made in Section 5.1.

3. Vacancy-hydrogen interactions

From intensive studies of D-implantation and annealing in various metals, the following model was derived for Vac-D binding [15]: (i) One vacancy can trap a multiple number of D atoms, up to a maximum of $r=6$, both in f.c.c. and b.c.c. metals. (ii) The binding energy assumes approximately two different values; the larger one assigned to the first two D atoms trapped by a vacancy, and the smaller one to the remaining four D atoms. The binding energies thus obtained are compiled in Table 1.

We decided to determine independently the Vac-H binding energies by thermal desorption measurements on specimens heat-treated under high $p(H_2)$, T conditions. An example of thermal desorption spectra (TDS) on Ni is shown in Fig. 4 [26]. This spectrum was obtained after a prolonged heat treatment; after a short heat treatment only a lowest temperature peak (P_0) was observed. Thus we may assign the peak P_0 to desorption of H occupying regular interstitial sites, and the higher-temperature peaks (P_1 and P_2) to detrapping from Vac-H clusters. Assuming that the desorption process is rate-controlled by the migration of individual H atoms, we adopt the following relation

$$\frac{e_{\mathrm{m}}^{\mathrm{H}}}{T_{\mathrm{P0}}}=\frac{e_{\mathrm{m}}^{\mathrm{H}}+e_{\mathrm{b1}}}{T_{\mathrm{P1}}}=\frac{e_{\mathrm{m}}^{\mathrm{H}}+e_{\mathrm{b2}}}{T_{\mathrm{P2}}} \tag{1}$$

and substitute the migration energy of an interstitial H atom $e_{\mathrm{m}}^{\mathrm{H}}=0.41$ eV [29] and $T_{\mathrm{P0}}=380$ K, $T_{\mathrm{P1}}=631$ K, $T_{\mathrm{P2}}=792$ K to obtain two binding energies $e_{\mathrm{b1}}=0.27$ eV and $e_{\mathrm{b2}}=0.43$ eV. (These peak temperatures were determined in the limit of low heating rates to justify the use of Eq. (1).) The values thus obtained, listed in Table 1, are in good agreement with the results of implantation-annealing experiments. The binding energies obtained for Cr [5] are also included in Table 1.

Table 1
Formation energy of a vacancy $e_{\mathrm{f}}^{\mathrm{v}}$ and the Vac-H binding energy e_{b} [eV]

Metal	$e_{\mathrm{f}}^{\mathrm{v}}$	e_{b}	Ref. for e_{b}
Al	0.70	~0.52	[15–17]
V	2.2	0.11	[24]
		0.17	[25]
Cr	2.0	0.89, 0.73	[5]
Fe	1.6	0.63, 0.43	[15–17]
Ni	1.79	0.44, 0.28	[15–17]
		0.44, 0.27	[26]
Cu	1.3	0.42, 0.22	[15–17]
		0.37, 0.22	[27]
Zr	2.0	0.28	[15–17]
Mo	3.2	1.03, 0.80	[15–17]
Pd	1.7	0.23, 0.15	[15–17]
Ta	2.9	0.42	[15–17]
W	4.0	1.43	[28]

The data for $e_{\mathrm{f}}^{\mathrm{v}}$ have been taken from [23]. The existence of two binding energies indicates two distinct trapped states of H atoms.

It must be noted, however, that the above model based on implantation-annealing experiments is not entirely consistent with our TDS results. Whereas the model predicts that Vac-H clusters of high occupancies ($r \geq 3$) should be desorbed successively in two stages P_1 and P_2, and those of low occupancies ($r \leq 2$) in a single stage P_2, the observed detrapping peaks consisted of P_1 and P_2 or simply P_1, but in no case a single stage P_2. The TDS data rather suggest that there are two different trapped states, which desorb independently at different temperatures (P_1

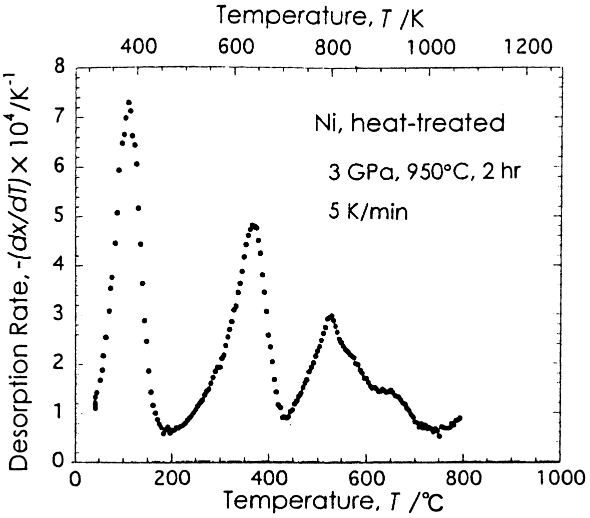

Fig. 4. Thermal desorption spectrum of Ni after heat treatment at 950 °C, $p(H_2)=3$ GPa for 2 h [26]. The heating rate was 5 K/min.

and P_2) without any correlations between the two. The configuration of these two trapped states has not been identified, however.

The equilibrium conditions between H atoms on regular interstitial sites and those trapped by vacancies have been worked out, and led to the following expression for the equilibrium concentration of VacH_r clusters [30],

$$\frac{x_{\text{cl}}}{1+x_{\text{cl}}} = \frac{x_{\text{i}}^{r_{\text{m}}}}{1-x_{\text{i}}}\left(\frac{r_{\text{m}}}{r}\right)^{r_{\text{m}}} \mathrm{e}^{-(g_{\text{f}}^{v}-r_{\text{m}}g_{\text{b}})/kT}, \qquad (2)$$

where r_{m} is the maximum number of H atoms to be trapped by a vacancy, x_{i} is the concentration of H atoms on regular interstitial sites. The energies are defined as follows: g_{f}^{v} is the formation free energy of a vacancy, $g_{\text{f}}^{v} = e_{\text{f}}^{v} + pv_{\text{f}}^{v} - Ts_{\text{f}}^{v}$, g_{b} the binding free energy, $g_{\text{b}} = e_{\text{b}} + pv_{\text{b}} - Ts_{\text{b}}$, and $g_{\text{f}}^{v} - r_{\text{m}}g_{\text{b}}$ $(\equiv g_{\text{f}}^{\text{cl}}) = e_{\text{f}}^{\text{cl}} + pv_{\text{f}}^{\text{cl}} - Ts_{\text{f}}^{\text{cl}}$ may be called the formation free energy of a Vac-H cluster. The binding energies listed in Table 1 show that under ordinary conditions trapping sites around vacancies are occupied almost completely. Even for a relatively small value of $e_{\text{b}} = 0.2$ eV, the deviation of r/r_{m} from 1 is only 5% at $T = 1000$ K and $x_{\text{i}} \sim 0.5$.

Eq. (2) predicts that the equilibrium cluster concentration is proportional to the r_{m}-th power of x_{i}. This strong dependence on H concentration is valid at low cluster concentrations, which is an implicit assumption of Eq. (2). At higher concentrations, the formation energy e_{f}^{cl} should tend to become more positive due to repulsive interactions between the clusters. Existence of repulsive interaction between the clusters is manifested by the formation of ordered arrangements and the existence of limiting concentrations of clusters. Also, the effective number of trapping sites per vacancy becomes smaller as increasingly larger number of trapping sites come to be adjoined by more than one vacancy [30]. In the limit of vacancy-ordered $L1_2$ structure, 75% of the trapping sites are shared by two vacancies, reducing r_{m} to 15/4. Both these effects should tend to weaken the dependence on H concentration.

4. Formation of SAVs in the electrodeposition process

One of the possible ways to obviate the extreme $p(\text{H}_2)$, T conditions for creating SAVs is the electrodeposition process. There, the stable structure should be reached directly as H and M atoms are deposited simultaneously incorporating vacancies in appropriate proportions.

To verify this expectation, thermal desorption spectra were measured on electrodeposited Cu samples and compared with those of heat-treated ones under high $p(\text{H}_2)$, T conditions [27]. Examples are shown in Fig. 5a,b. The samples used were a 0.1 mm thick high-purity sheet of Johnson-Matthey and Co. and a #100 mesh powder of electrolytic Cu aged for more than 10 years. In the electrolytic sample, three desorption peaks are observed at 580, 720 and 970 K. The highest-temperature peak, which showed up most conspicuously in this long-storage sample, is believed to be the desorption from gas bubbles. The lower-temperature peaks, which are also present in the heat-treated sample at 550 and 720 K, are ascribed to desorption from Vac-H clusters. In fact these lower-temperature peaks were observed in all the experiments performed under different conditions of heat treatment and electrodeposition. We estimated the activation energy of these peaks in the electrolytic samples by taking the peak P_0 of Ni as reference, subtracting the migration energy of 0.40 eV [29], and obtained the binding energies $e_{\text{b}} = 0.22$ and 0.37 eV. These values agree reasonably with those deduced from implantation-annealing experiments (Table 1). Similar TDS measurements were made on electrodeposited samples of Cr, Mn, Fe, Ni and in all the cases manifested desorption peak(s) in agreement with those observed in heat-treated samples.

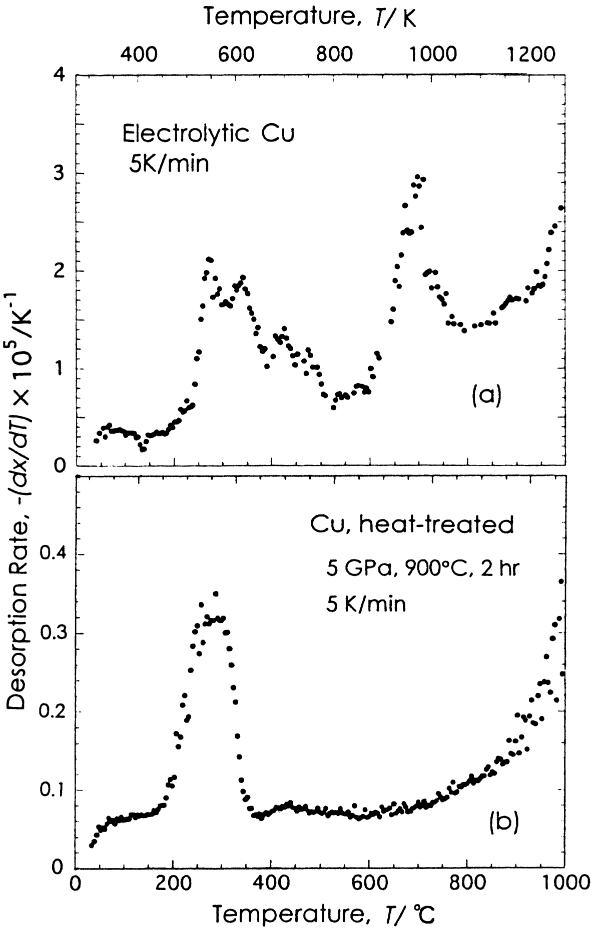

Fig. 5. Thermal desorption spectra of Cu samples (a) electrodeposited, and (b) heat treated at 900 °C, $p(\text{H}_2)=5$ GPa for 2 h [27].

The present result on the long-storage sample shows that, Vac-H clusters, once formed by electrodeposition, remain stable indefinitely under ambient conditions, even after complete loss of H from regular interstitial sites. The presence of fairly large amount of hydrogen in electrolytic metals, a well-known fact among metallurgists, is finally explained in terms of SAV formation. Lastly, it may be mentioned here for fairness' sake that a possibility of defect structure formation in the electrodeposition process was proposed by Roy and Gibb in 1967 [31], but has been largely forgotten since.

5. Some consequences of SAV formation

5.1. Solubility of hydrogen and stability of hydride phases

One of the direct (and most obvious) consequences of SAV formation is the apparent increase of the solubility of hydrogen. At low concentrations, H atoms in trapped states simply add to those on regular interstitial sites. At high H concentrations close to the stoichiometric limit, $x_i \approx 1$, the total concentration becomes $x \approx 1 + x_{cl}$, which implies the formation of a superstoichiometric hydride.

The formation of superstoichiometric hydrides was indeed observed in the near-surface region of ion-implanted metals, with compositions 1.15±0.07 for Ni [16], 1.32±0.07 [16], 1.6±0.2 [32] for Pd, 2.8±0.4 for Ti [16] and 5.0±0.8 for Zr [16]. These superstoichiometric compositions can be rationalized by assuming a structure similar to mono-, di-, and tri-hydrides formed from a defect $L1_2$ structure having compositions M_3VacH_{4n}, with $n = 1$ for Ni and Pd, $n = 2$ for Ti, and $n = 3$ for Zr.

By far the most important recognitions arising from SAV formation is that quite generally the most stable hydride structure is the defect structure containing SAVs. Consequently, most (or all) of the phase diagrams of M–H systems reported to date are metastable ones because they were determined under conditions where M-atom vacancies could not be introduced. All these metastable hydrides should inevitably tend to approach more stable defect structures in the repetition of hydrogenation–dehydrogenation processes. The real equilibrium phase diagrams allowing for equilibrium concentrations and ordered arrangements of M-atom vacancies have not been obtained so far.

5.2. Enhancement of M-atom diffusion

It may naturally be expected that the formation of SAVs (Vac-H clusters) should induce enhancement of M-atom diffusion. Evidence of diffusion enhancement was provided just before the discovery of SAVs; an accelerated phase separation under hydrogen atmosphere of 5 MPa was observed in Pd alloys and was called hydrogen-induced lattice mobility (HILM) [33,34]. This phenomenon was demonstrated more clearly in $Pd_{0.8}Rh_{0.2}$ alloys [11], where the phase separation at 600 °C occurred in a few minutes under $p(H_2) = 5$ GPa, ~10^5 times faster.

Subsequently, more detailed experiments were performed using Cu–Ni diffusion couples [35]. A sample was maintained at prescribed temperatures for 30 min under high hydrogen pressures, and the concentration profiles of recovered samples were analyzed to deduce interdiffusion coefficients $\check{D}$. The temperature dependence of $\check{D}$ is shown in Fig. 6 [35]. Comparison with previous data obtained under ambient conditions shows that $\check{D}$ is enhanced by 10^4 on the Ni side and by $\lesssim 10$ on the Cu side, resulting in a reversed composition dependence. This is because the solubility of H in Ni ($x = 0.5 \sim 0.7$) is much higher than in Cu ($x = 0.01 \sim 0.05$) under these conditions, and resulted in higher concentrations of Vac-H clusters in the former. The increase of $\check{D}$ with $p(H_2)$ [36], opposite in sense to ordinary pressure dependence, also indicates the effect of SAV formation. The enhancement of the reaction between the deposited layers of Ni/Nb and Ni/V was observed in the hydrogen atmosphere of 0.5 MPa, and was explained in terms of abundant vacancy formation in hydrogen absorbing metals (Nb and V) [37,38].

Admittedly, in a more orthodox approach to interdiffusion, it is necessary to consider the effect of H on the thermodynamics of the binary system—and hence the effect of H on the thermodynamical factor of M-atom diffusion. As it turned out, a deviation of the thermodynamical factor from 1 was reasonably small in the Cu–Ni system, which justifies the above argument [39]. But in cases where the difference of the heat of solution of H in the constituent metals is large, the thermodynamical factor becomes strongly affected by H, and in some cases, interdiffusion can even be retarded by hydrogen. Such cases were indeed observed in the interdiffusion between

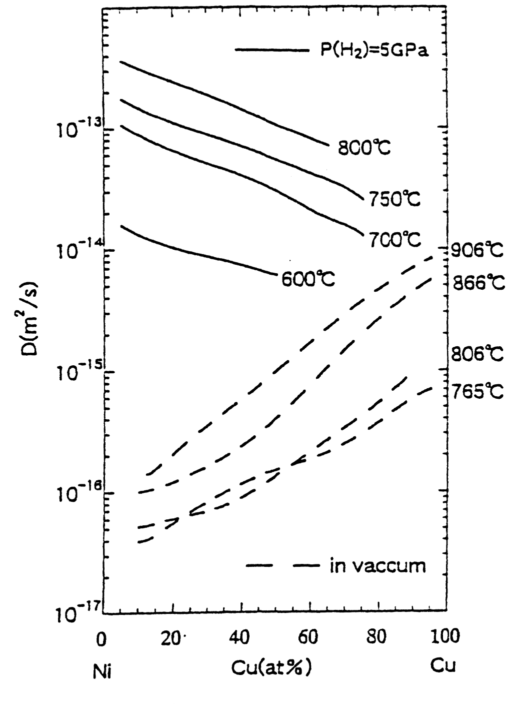

Fig. 6. Interdiffusion coefficients of Ni–Cu alloys under $p(H_2) = 5$ GPa. Diffusion time = 30 min [35].

multiple thin layers of Ni–Ti, Pd–Ti and Fe–Ti, where the interdiffusion was totally inhibited by the formation of TiH_2 [37,40,41].

5.3. Enhancement of creep

Recently, a clear indication of the effect of SAVs was observed by Fujikawa et al. in the creep process of electrodeposited Cu [42]. In the fabrication of Cu wiring for LSIs, they discovered that an electrodeposited Cu film was more deformable than a vapor-deposited one, and amenable to subsequent HIP treatments to fill deep troughs (ditches) of large aspect ratios in the substrate. More interestingly, this deformability could be transferred from an electrodeposited film to a vapor-deposited film during the HIP treatment. These observations can only be explained in terms of enhanced creep motion of dislocations due to SAVs, which was introduced in the electrodeposition. Usually, a creep occurs at high temperatures where thermal vacancy concentrations are high ($\lesssim 10^{-4}$ at the melting point), but Vac-H clusters of these amounts can exist in electrodeposited Cu, as demonstrated in the preceding section, and induce similar creep motion of dislocations.

6. Discussions

Comparison of the SAV formation process observed by lattice contraction on one hand and diffusion enhancement on the other points to the presence of two different vacancy sources. In the slow process of lattice contraction, the source is believed to be the external surface. In Pd, the diffusivity of a cluster D_{cl} deduced from the rate of lattice contraction and particle size was found to be a little smaller than the known diffusivity of a vacancy D_v, a reasonable result considering possible dragging effects of trapped H atoms [9]. (In Ni, a determination of D_{cl} was hampered by more persistent surface-barrier effects [8].) The enhancement of interdiffusion, on the other hand, occurred in much shorter times, and uniformly over the sample. This suggests that there were some internal sources distributed uniformly in space, with capacities limited to $x_{cl} \lesssim 10^{-2}$. Investigations in pure metals have suggested dislocations and grain boundaries as possible internal sources of vacancies, and even a vacancy-interstitial pair creation in perfect crystals [43–45].

It may be added in closing that an implication of SAVs for hydrogen embrittlement (HE) of steels has also been noted. We have performed TDS measurements on Fe after heat treatments at $p(H_2) \lesssim 1.7$ GPa, $T \lesssim 400$ °C, found the SAV formation of concentrations $x_{cl} \lesssim 10^{-2}$, and proposed on this basis that vacancies (Vac-H clusters) formed in front of crack tips should play an important role in modifying the mechanical properties of the matrix [46]. A suggestion along the same line was made by Nagumo [47], who discovered the formation of a large number of vacancies by heavy plastic deformations in the crack-tip region, and suggested that these vacancies stabilized by hydrogen should be playing a decisive role in HE. Thus, a possibility is looming out that the SAV formation in the crack-tip region may provide a clue for solving the long-standing problem of HE in steels.

There may well be many other aspects of SAV formation which still remain to be explored.

7. Summary and conclusions

The defect structures containing superabundant vacancies (SAVs) of M atoms are thermodynamically the most stable structure of M–H alloys. SAVs were introduced by solid-state diffusion at high temperatures, and also in the electrodeposition process. Enhanced M-atom diffusion and creep, which occurred in consequence, are described.

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