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Journal of Alloys and Compounds 356–357 (2003) 270–273

Journal of ALLOYS AND COMPOUNDS

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Superabundant vacancy–hydrogen clusters in electrodeposited Ni and Cu

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Accepted 26 October 2002

Abstract

Thermal desorption spectra of Ni and Cu were measured on electrodeposited samples and those heat-treated under high hydrogen pressures and high temperatures. Major desorption peaks observed in these two groups of samples agreed reasonably with each other, from which it is concluded that a large number of vacancy–hydrogen clusters are incorporated in the process of electrodeposition.

Keywords: Superabundant vacancies; Vacancy–hydrogen clusters; Electrodeposition; Thermal desorption

1. Introduction

The presence of a fairly large amount of hydrogen in electrodeposited metals is a well-known fact among metallurgists, but its nature has not been clarified so far. Even in metals having limited hydrogen solubilities, the residual hydrogen often amounts to $x=[\mathrm{H}]/[\mathrm{M}]=10^{-4}\sim10^{-3}$, and remains indefinitely—more than 10 years—under ambient conditions. Thermal desorption measurements have shown that in many cases there are distinct desorption stages at 500~900 K. The purpose of this paper is to identify these stages to the release from Vac–H clusters introduced in the process of electrodeposition.

This experiment has been motivated by our discovery of the formation of superabundant vacancies (SAVs) under high hydrogen pressures and temperatures [1–7]. This phenomenon has been shown to be caused by the formation energy reduction of a vacancy by trapping H atoms, which implies that defect structures containing SAVs are in fact the most stable structure of M–H alloys [8–11]. Then it can be expected that these defect structures should be formed in the process of electrodeposition because M and H atoms are deposited simultaneously incorporating M-atom vacancies in appropriate proportions. This is in contrast to our previous experiments where high temperatures were necessary to facilitate introduction of SAVs by solid-state diffusion.

In order to verify this expectation, we have decided to make a detailed comparison of the thermal desorption spectra of electrodeposited samples with those of heat-treated ones under high $p(\mathrm{H_2})$, T for which the conditions of SAV formation are well established. We have examined two metals Ni and Cu in detail, and also made preliminary measurements on Cr, Mn and Fe, all of which have limited hydrogen solubilities under ambient conditions. Results of comparative TDS measurements are described in Section 2, followed by some discussions in Section 3.

2. Results of comparative TDS measurements

Thermal desorption measurements on Ni and Cu were made on specimens prepared by three different methods: (1) Electrodeposited samples under well-defined conditions of electrolysis, (2) commercial electrolytic samples, and (3) heat-treated samples under high $p(\mathrm{H_2})$, T for sufficiently long times for introduction of Vac–H clusters. The high $p(\mathrm{H_2})$, T treatments were performed by our ordinary method (see, e.g. [4–6]), with $\mathrm{NaBH_4+Ca(OH)_2}$ as an internal hydrogen source. For TDS measurements, a sample of 0.02~0.1 g was placed in an evacuated quartz tube, and the amount of hydrogen desorbed in the course of temperature ramping was measured by pressure increase. In order to allow comparison of desorption peak

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0925-8388/02/$ – see front matter
doi:10.1016/S0925-8388(02)01270-7

temperatures, the sample size was made small (powder of 100 mesh or a foil of ≤0.1 mm thick), and the temperature-ramping speed was kept low (5 K/min).

2.1. Ni

Samples for high $p(H_2)$, T treatment were prepared from 0.1 mm thick foil of 99.99% Ni purchased from Johnson-Matthey & Co. Samples were heat-treated under several different $p(H_2)$, T conditions for variable lengths of time, and immediately transferred for TDS measurements. A thermal desorption spectrum measured after a heat treatment at $p(H_2)=3$ GPa, $T=1223$ K for 2 h is shown in Fig. 1(a) [12]. The lowest-temperature peak ($T_{P0}=380$ K), which disappeared in a few days after preparation, is identified to be the desorption of H atoms on regular interstitial sites. The remaining two desorption peaks ($T_{P1}=640$ K and $T_{P2}=800$ K), the magnitude of which changed with holding time and temperature of the heat treatment, are identified to be the decomposition of Vac–H clusters. The amount of hydrogen desorbed in these two peaks is $x=6.8\times10^{-2}$.

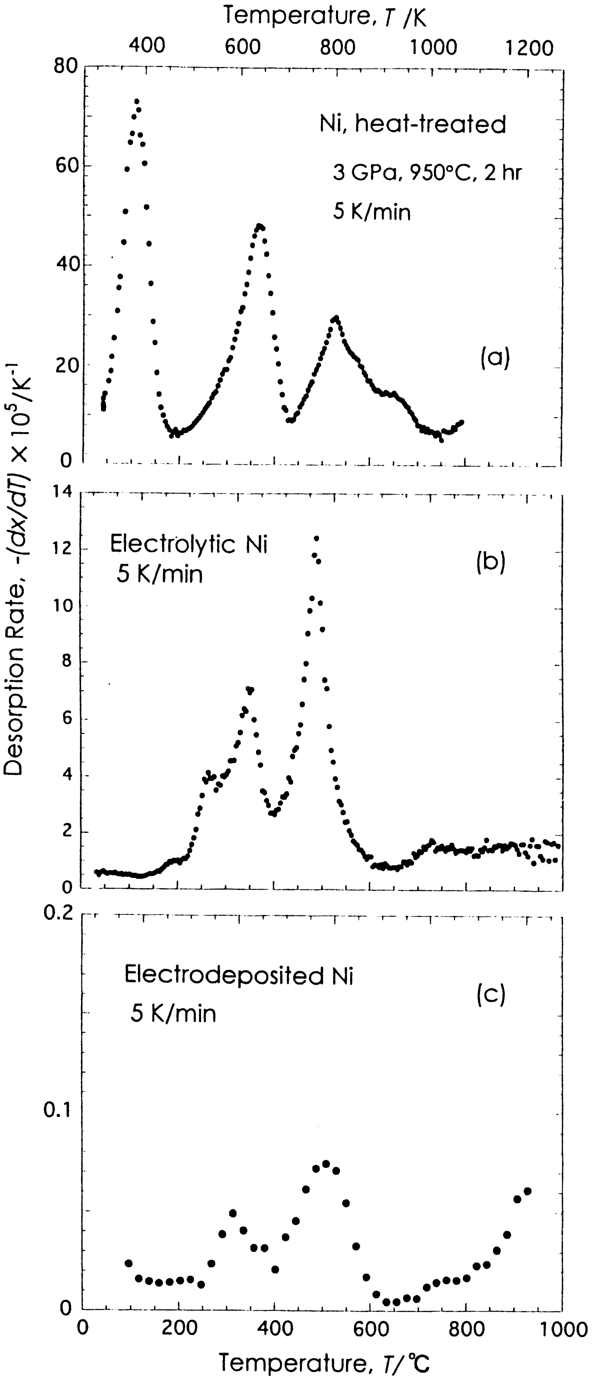

Fig. 1. Thermal desorption spectra of Ni observed in specimens prepared in three different ways: (a) Recovered after heat treatment at high $p(H_2)$, T, (b) a commercial electrolytic Ni aged over 32 years, (c) an electrodeposited sample 7 months after preparation.

Fig. 1(b) shows a desorption spectrum observed with a commercial electrolytic sample aged over 32 years. Two major peaks are located at nearly the same temperatures as above ($T_{P1}=624$ K and $T_{P2}=763$ K), indicating that Vac–H clusters had remained stable over long times. The total amount of desorbed hydrogen was $x=1.5\times10^{-3}$.

A result obtained for an electrodeposited sample is shown in Fig. 1(c). The electrodeposition was performed at 313 K in a solution of 1.0 mol/l $NiCl_2$ and 0.5 mol/l H_3BO_3, at a current density of 500 A/m^2. The thickness of the foil was 25 μm. The peak temperatures 590 K and 780 K agree reasonably well with T_{P1} and T_{P2} of the heat-treated sample, and the total amount of desorbed hydrogen was $x=1.1\times10^{-4}$.

2.2. Cu

An example of TDS measurements on high $p(H_2)$, T treated samples is shown in Fig. 2(a). The sample was a 4–9's foil supplied by Johnson-Matthey & Co., and the heat treatment was performed at $p(H_2)=5$ GPa, $T=1173$ K for 2 h. Comparison to the case of Ni indicates that a pronounced peak corresponds to P_1 ($T_{P1}=550$ K), and a small peak corresponding to P_2 is also visible ($T_{P2}\simeq720$ K). The total amount of desorbed hydrogen ($x=2.8\times10^{-4}$) is much smaller than in Ni, which is consistent with smaller solubilities of hydrogen (and hence smaller Vac–H concentrations) in Cu [13].

Fig. 2(b) shows a spectrum observed with a commercial electrolytic sample aged over 11 years. The position of the pronounced desorption peaks (580 K and 720 K) agrees reasonably with the heat-treated sample, indicating the same origin of the peak, i.e. the decomposition of Vac–H clusters. The amount of hydrogen desorbed in these peaks is $x=2.5\times10^{-3}$. A pronounced peak at ~960 K is due to desorption from H_2 bubbles which precipitated during the long aging time.

A result obtained for an electrodeposited sample is shown in Fig. 2(c). The electrodeposition was performed at 313 K in a solution of 0.9 mol/l $CuSO_4$ and 0.6 mol/l H_2SO_4 with 120 ppm Cl^- ions, at a current density of

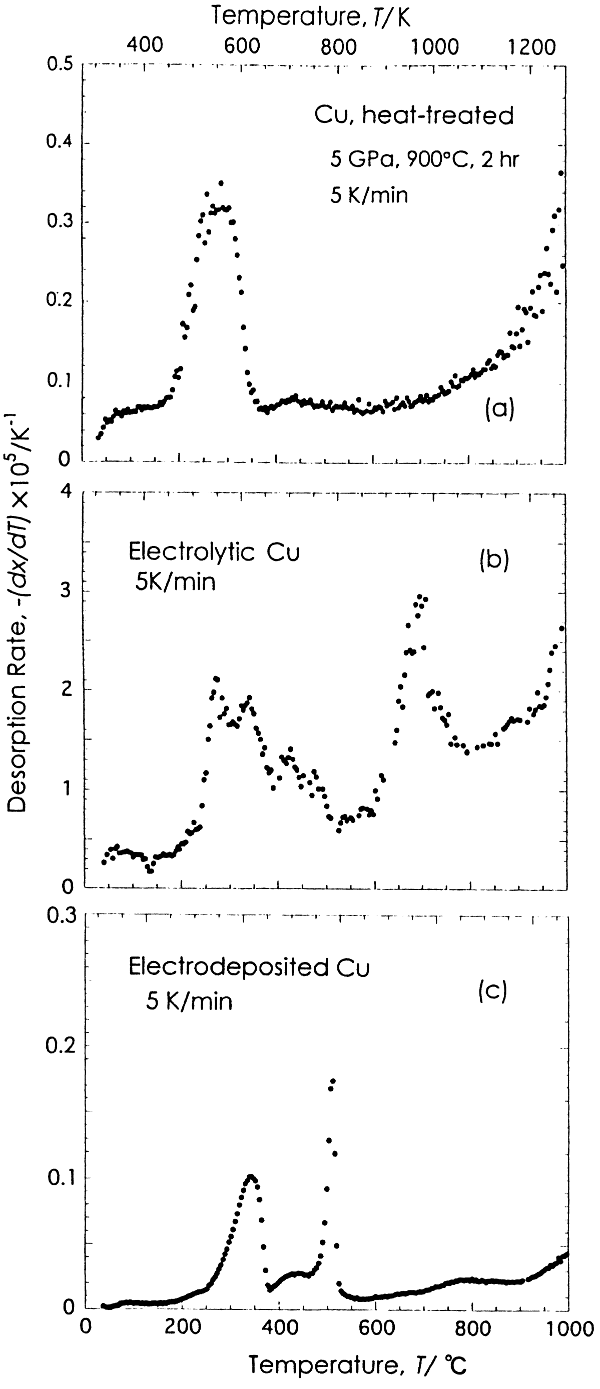

Fig. 2. Thermal desorption spectra of Cu observed in specimens prepared in three different ways: (a) Recovered after heat treatment at high $p(H_2)$, T, (b) a commercial electrolytic Cu aged over 11 years, (c) an electrodeposited sample 4 months after preparation.

2000 A/m^2. The thickness of the foil was 80 μm. Except for a sharp peak at 780 K, the shape of the spectrum is similar to the case of the heat-treated sample, with two remaining peaks located at 610 K and 710 K. The amount of desorbed hydrogen in these two peaks is $x=0.9\times10^{-4}$, an order of magnitude smaller than in Ni. The origin of the 780 K peak, which appeared sporadically, is unknown. The sharpness of the peak suggests decomposition of some unstable hydride phase, but the decomposition temperature of CuH is reported to be much lower (≤400 K) [14].

2.3. Other metals

Preliminary results of thermal desorption measurements on commercial electrolytic samples of Cr, Mn and Fe showed that in all the cases, a pronounced peak existed at 500–900 K. Although a detailed comparison with heat-treated samples is hampered in these metals by structural transitions during and after high $p(H_2)$, T treatments, the observed range of the desorption peak temperatures strongly suggests the release from Vac–H clusters. (The release from voids and grain boundaries usually occurs at much higher temperatures, and the release from impurities at lower temperatures.)

3. Discussion

The occurrence of distinct desorption stages implies that residual H atoms after electrolysis exist in well defined energy states, and their comparison with those of heat-treated samples leads to the identification that most of these H atoms are in the form of Vac–H clusters. This is a proof of our expectation that a large number of Vac–H clusters should be incorporated in the electrodeposition of metals. In fact, our expectation was preceded by Roy and Gibb [15], who, trying to explain complex structural properties of electrodeposited Cr films, suggested that a defect structure containing vacancies might be formed in the electrodeposition process.

The Vac–H binding energies can be estimated from the observed desorption temperatures taking the lowest-temperature peak (P_0) of Ni as a reference. Assuming a proportionality

$$\frac{e_m^H}{T_{P0}} = \frac{e_m^H + e_{b1}}{T_{P1}} = \frac{e_m^H + e_{b2}}{T_{P2}} \qquad (1)$$

to hold between the three desorption peaks in Fig. 1(a), and substituting the migration energy of H atoms on regular interstitial sites $e_m^H=0.41$ eV [16], we obtain the binding energies $e_{b1}=0.28$ eV and $e_{b2}=0.45$ eV for Ni. Similarly, for Cu, substituting the Ni data $e_m^H/T_{P0}=0.41$ eV/380 K in the left-hand side, and $T_{P1}=550$–610 K, $T_{P2}=710$–720 K (Fig. 2(a)–(c)) and $e_m^H=0.40$ eV [16] in the right-hand sides, we obtain the binding energies $e_{b1}=0.19$–0.26 eV and $e_{b2}=0.36$–0.37 eV. These binding energies agree reasonably well with those deduced from ion implantation-annealing experiments; 0.28 and 0.44 eV for Ni [17], 0.22 and 0.42 eV for Cu [18].

According to the model proposed on the basis of previous ion implantation-annealing experiments, the maximum number of H atoms trapped by a vacancy is 6, of which the first 2 H atoms have a larger binding energy, and the remaining 4 H atoms a smaller one [19,20]. The validity of this model is, however, rather suspect. Our present experiments indicate that the lower-temperature peak P_1 always shows up in the three groups of samples, both in Ni and Cu, whereas the appearance of P_2 is rather variable. In heat-treated samples, P_2 shows up only after prolonged heat treatments at relatively high $p(H_2)$, T, and its magnitude is larger in Ni than in Cu. Apparently, the deep traps are formed only at high hydrogen (and Vac–H cluster) concentrations, which is in marked disagreement with the previous model. The position of P_2 is even more susceptible to the way of sample preparation. Not only the small variations in peak positions but also the splitting into two peaks (at 710 K (P_2') and 860 K (P_2'')) occurred in a few cases in Ni, both in heat-treated and electrodeposited samples, although the condition for its occurrence has not been clarified so far. It may also be noted that in both metals, the peak height of P_2 relative to P_1 is larger in electrodeposited samples than in heat-treated samples.

Based on these observations, we propose the following model for the trapped configurations. The lower-temperature peak P_1 is due to the desorption of H atoms trapped in single vacancies, whereas the higher-temperature peak(s) P_2 (P_2' and P_2'') are due to those trapped by pairs of vacancies. The multiple-vacancy trapping configurations may probably be the consequence of local ordering of vacancies—a precursor to the hydride of $L1_2$ structure (M_3VacH_4) which has been observed from time to time in Pd and Ni at high concentrations of Vac–H clusters [2,6]. In the M_3VacH_4 structure, 75% of O sites are located between two vacancies. This model provides a natural explanation for the relative increase of the P_2 component in electrodeposited samples in comparison to heat-treated ones because the ordered structure should be more easily attainable at lower temperatures. Admittedly, more details of these trapped configurations are yet to be elucidated.

Presence of superabundant vacancies in electrodeposited metals, latent in most cases, may show up under appropriate circumstances to affect some physical properties of the matrix. The enhancement of creep and grain growth in electrodeposited Cu is one such example. Fujikawa et al. [21,22] discovered in their attempt to develop efficient fabricating techniques of fine-scale interconnect layers in ULSIs (Ultra Large Scale Integrated circuits), that electrochemically deposited (ECD) Cu was more easily deformable than physically vapor-deposited (PVD) Cu under subsequent HIP treatment, and capable of filling small holes and trenches having large aspect ratios. They also found that this deformability and acceleration of grain-growth could be transferred from ECD to PVD layers. These phenomena are believed to be the consequence of hydrogen-induced vacancies.

4. Summary and conclusions

It is concluded from close similarities between the thermal desorption spectra measured in electrodeposited samples and high $p(H_2)$, T treated samples that Vac–H clusters are formed in the electrodeposition process and remain as such over indefinite lengths of time.

Acknowledgements

We wish to thank S. Naotsuka for his help in the initial stage of this work.

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