Effect of Hydriding on Structural Stability of Ni/Ti and Pd/Ti Multilayers

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The structure and composition distribution of Ni/Ti and Pd/Ti multilayers prepared by ion-beam sputtering and their changes with annealing in vacuum and H₂ atmosphere have been investigated using Auger-electron depth profiling, thin-film X-ray diffraction and cross-sectional transmission electron microscopy. Both of these multilayers readily undergo atomic interlayer mixing and solid-state amorphization upon annealing in vacuum at 523 K (Ni/Ti) or at 623 K (Pd/Ti). However, upon annealing in 0.5 MPa H₂ atmosphere at the same temperatures, neither intermixing nor amorphization takes place, although the Ti layers are altered to TiH₂ layers. The stabilization of these multilayers by hydriding is discussed on the basis of calculated free energy diagrams for both systems.

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I. Introduction

The usefulness of applying hydriding/dehydriding technique to material processing has been recognized in certain fields of materials technology in recent years. For example, in the production of Nd-Fe-B ferromagnets, this technique (known as HDDR⁽¹⁾) has provided a significant effect in raising the quality of the ferromagnets by forming ultrafine-grain structures. It has also been proved to be essential for improving the mechanical properties of Ti-base alloys⁽²⁾ because it alters coarse-grain structures into ultrafine ones. Hydrogen-induced amorphization⁽³⁾ seems to be another important effect of this technique, since it may be applicable for developing novel functional materials. The present paper describes a new aspect of hydriding effects on metallic multilayers, where the hydriding is shown to control the structural stability of the multilayers significantly.

Now, in metallic multilayers where one of the layer constituents belongs to a reactive element such as Ti, Zr and rare-earths, atomic interlayer mixing usually takes place at relatively low temperatures, and solid solutions (or amorphous alloys) are formed in the vicinity of the interfaces⁽⁴⁾. In Ni/Ti and Pd/Ti multilayers⁽⁵⁻⁷⁾, for instance, amorphous alloys are readily produced across the layers during deposition around or above 473 K or postdeposition annealing at 523–623 K in vacuum. Thus the structure of these multilayers is less stable in comparison with those devoid of those reactive elements. In this context, it seems interesting to examine the effect of hydriding on the stability of Ni/Ti and Pd/Ti multi-

layers, because hydrogen has a much stronger affinity for Ti than for Ni and Pd, and this may greatly affect the interlayer reactions in the multilayers.

The objective of this study is to make clear the influence of hydriding on the thermal stability of these multilayers. To reveal their compositional and structural changes, Auger-electron depth profiling (AES) and thin film X-ray diffraction (XRD) as well as cross-sectional transmission electron microscopy (TEM) have been used. The results are discussed on the basis of free-energy diagrams for both systems. A preliminary report on the Pd/Ti multilayer has been given elsewhere⁽⁸⁾.

II. Experimental Procedure

The Ni/Ti and Pd/Ti multilayered films used in this experiment were prepared with an ion-beam sputtering technique. They were deposited on slightly oxidated Si(111) substrates at ambient temperatures (below 323 K) under an operating pressure of 3×10^{-2} Pa of Ar in a chamber pre-evacuated to a base pressure of 3×10^{-5} Pa. Raw target materials of 99.99% purity (Ni and Pd) and 99.9% purity (Ti) were sputtered alternatively for appropriate time periods with a 1 keV^{††} ion beam. The thickness of each Ni or Pd layer was 5 nm, and that of Ti layer was 10 nm. Twenty bilayers were stacked attaining the total thickness of 300 nm for each multilayered film. The thickness of the film was measured with a surface roughness meter (Dektak IIA) after the deposition. The net compositions of the films calculated from the thickness were Ni₄₄Ti₅₆ and Pd₃₈Ti₆₂. The topmost layer of the film was chosen as the Ni or Pd to avoid the oxidation. The

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^{††} 1 eV = 1.602×10^{-19} J.

oxygen contamination of the films during deposition as checked by AES was below the detection limit ($< \sim 2$ at%) in both films. Annealing of the films was carried out in vacuum (3×10^{-5} Pa) or in pure hydrogen atmosphere (0.5 MPa H_2) for appropriate time periods at 523 K for the Ni/Ti or at 623 K for the Pd/Ti multilayer.

The composition profiles along the depths of the films were measured with AES using Xe as the etching gas. The peak-to-peak intensities of the Ti-LMM, Ni-LMM, Pd-MNN and O-KLL Auger spectra were monitored for the depth profiling. X-ray diffractographs were measured in both symmetrical geometry ($\theta/2\theta$ scan) with a curved graphite monochromator, and grazing-incidence geometry (2θ scan) with a flat graphite monochromator using Cu K α radiation. High-resolution cross sectional TEM observation was carried out at 200 kV for samples prepared from the films with a dry-etching technique.

III. Results

1. Ni/Ti multilayer

Figure 1 shows AES depth profiles of as-deposited and annealed Ni/Ti multilayered films, where the individual AES intensities of Ni, Ti and O have been converted into their relative concentrations using their proper sensitivity factors. In the as-deposited sample (top), a periodic modulation of the Ni and Ti concentrations can be seen from the top surface down to just above the Si substrate (only the upper half of the total layers is shown in the figure). It is noted that the Ni concentration, as well as the Ti concentration, does not attain its full-scale height

Fig. 1 Auger-electron depth profiles of Ni, Ti and O concentrations in as-deposited, vacuum-annealed and H_2 -annealed Ni/Ti multilayers.

at the middle of each layer. This is not due to interlayer mixing which may have occurred during the sputter deposition, but due to a limited depth resolution of the AES technique. This point will be clarified by the TEM observation to be shown later. When the sample is annealed in vacuum at 523 K for 86.4 ks (middle), the modulation amplitude of each layer is much reduced and its average concentration appears to approach the calculated net composition, $\text{Ni}_{44}\text{Ti}_{56}$, although a slight modulation is still remaining. This flattening of modulation amplitude is exclusively due to intermixing taking place between the Ni and Ti layers during annealing, which is expected to continue until a completely uniform distribution is established in the film. The kinetics of this alloying process has been analyzed and the interdiffusion coefficients associated with the process involved have been obtained at temperatures between 523 and 623 K⁽⁶⁾. However, when the sample is annealed in the same condition as above but in a 0.5 MPa H_2 atmosphere (bottom), the original concentration modulation of the as-deposited sample is almost completely preserved. This clearly shows that the hydriding strongly suppresses the interlayer mixing, and hence is quite effective in thermally stabilizing the Ni/Ti multilayer.

Figure 2 shows X-ray diffraction patterns for the same samples as used for AES shown above. The XRD has been measured in the symmetric mode or in the grazing mode. In the former, only the crystallographic planes

Fig. 2 X-ray diffraction patterns of as-deposited, vacuum-annealed and H_2 -annealed Ni/Ti multilayers measured in the symmetric and grazing-incidence modes.

parallel to the substrate give rise to the diffraction, whereas, in the latter, those inclined at large angles from the substrate plane contribute to the diffraction. It can be seen from the figure that the as-deposited sample shows rather broad hcp Ti(002) and Ni(111) peaks in the S-mode, while in the G-mode the Ni(111) peak disappears completely and the Ti(002) peak is also weakened. This means that the Ni layers consist of crystallites with a strong preferred orientation of (111) parallel to the substrate, and the Ti layers also exhibit a (001) preferred orientation although less strong compared with the former. The broadening of these Bragg peaks reflect fine crystallite sizes grown in the thin layers. Now, the annealing in vacuum causes both Ti(002) and Ni(111) peaks to be strongly depressed together with a shift of Ni(111) toward a lower angle in the S-mode. In the G-mode, a very broad peak suggestive of an amorphous alloy is observed. These diffractographs show that the multilayer has transformed into an amorphous alloy as a result of the intermixing, although crystallites of a Ni-Ti alloy and the original Ti are partly present. In contrast, the annealing in H₂ atmosphere causes neither a definite change of Ni(111) in the S-mode nor the appearance of a halo pattern in the G-mode, except for Ti(002) which has been replaced by fcc TiH₂(111) in both modes. These XRD results, in conjunction with the prior AES ones, show that the hydriding of the Ni/Ti multilayer alters the Ti layers into Ti dihydrides which strongly inhibits the intermixing between the original Ni and Ti layers and hence the amorphous alloy formation.

The above effect of hydriding on the stability of the Ni/Ti multilayer is further supported by the cross-sectional TEM observation, as shown in Fig. 3. In the as-deposited sample, a periodic stacking of Ni (dark) and Ti (bright) layers is recognized, whose interfaces are flat and clear although somewhat diffused, indicating that the interlayer mixing has not occurred appreciably during the deposition. The electron diffraction pattern consists of the accumulation of Ni(111) and hcp Ti(002) spots normal to the stacking layers, in agreement with the Ni(111) and Ti(001) preferred orientations as revealed by XRD. Now, when the sample is annealed in vacuum, the periodic contrast of the crystalline layers almost disappears, and a nearly uniform structure is obtained (a trace of the contrast modulation is still remaining). In this condition, the ED pattern exhibits a halo ring of the amorphous matrix with weak Ni(111) and Ti(002) spots of the remaining crystallites. However, when the sample is annealed in the H₂ atmosphere, no definite changes of the layer structure and ED pattern from those of the as-deposited sample have taken place, although the accumulation of Ti(002) spots has now changed to that of fcc TiH₂(111). These TEM observations confirm that the hydriding is quite effective in stabilizing the structure of the Ni/Ti multilayer, although the Ti layers are transformed to those of TiH₂.

The microstructures of these samples can be examined more closely by observing magnified images of the above micrographs, as shown in Fig. 4. In the as-deposited sam-

ple, the lattice images of Ni(111) ($d=0.202$ nm) and Ti(002) ($d=0.234$ nm) parallel to the stacking layers can be clearly seen, reflecting the preferred orientations of the layers. In the vicinity of the interfaces, disordered arrays of the lattice images suggestive of the occurrence of a slight interlayer reaction are present. In the sample annealed in vacuum, a high-resolution image typical of an amorphous alloy is seen throughout the sample, although the lattice images of remaining crystallites are also partly mixed. On the other hand, in the sample annealed in H₂, the lattice images of Ni(111) and TiH₂(111) ($d=0.253$ nm) parallel to the stacking layers are seen everywhere in the layers. However, disordered arrays of the lattice images at the interfaces appear to be more spreading than those of the as-deposited sample.

2. Pd/Ti multilayer

The general features of the structural stability of Pd/Ti multilayer upon annealing in vacuum and in hydrogen atmosphere studied by AES, XRD and TEM techniques⁽⁷⁾⁽⁸⁾ are very similar to those of Ni/Ti multilayer described above. Figure 5 shows high-resolution TEM images and the corresponding ED patterns of as-deposited, vacuum-annealed and H₂-annealed Pd/Ti multilayers. The as-deposited sample consists of a periodic stacking of Pd (5 nm) and Ti (10 nm) layers with Pd(111) and Ti(001) preferred orientations parallel to the layers. Upon annealing in vacuum at 623 K for 86.4 ks, atomic interlayer mixing takes place and a nearly homogeneous alloy of amorphous structure is formed. The interdiffusion coefficients corresponding to the mixing process have been determined at temperatures between 523 and 623 K⁽⁶⁾. However, upon annealing in H₂ at 623 K for 86.4 ks, the interlayer mixing is suppressed almost completely and the original stacking of crystalline Pd and Ti layers is preserved, although the latter have been transformed to TiH₂ with a preferred orientation of (111) parallel to the layers. The AES and XRD studies have shown results quite consistent with these TEM observations.

IV. Discussion

The solid-state amorphization reactions (SSAR) in the Ni/Ti and Pd/Ti multilayers can be explained reasonably using calculated free-energy diagrams for the Ni-Ti⁽⁹⁾ and Pd-Ti⁽⁷⁾ systems. In the Ni_{100-x}Ti_x system, the calculated Gibbs free energy at 235 K for the supercooled liquid phase (or amorphous phase) becomes lower than those for the crystalline terminal solid solutions of Ni and Ti for $25 < x < 90$, and a single amorphous phase is expected to be formed, as a metastable phase, for $28 < x < 72$. This composition range of amorphous alloy formation has really been confirmed by a study of mechanical alloying of Ni and Ti powders in Ar atmosphere at temperatures below 240 K⁽⁹⁾, where the SSAR proceeds through mechanical mixing and interdiffusion reaction taking place at or near clean boundaries between the polycrystalline powder materials. The present Ni/Ti

Ni/Ti multilayer

Fig. 3 Cross-sectional transmission electron micrographs and electron diffraction patterns of as-deposited, vacuum-annealed and H₂-annealed Ni/Ti multilayers.

multilayer (Ni₄₄Ti₅₆) is well within the above predicted range of SSAR, and a thermodynamic driving force similar to the one in the mechanical alloying operates to cause the amorphization reaction in the multilayer although only the chemical interdiffusion process is involved here. In the Pd_{100-x}Ti_x system, the calculated free energy diagram is quite similar to that for the Ni-Ti system. As shown in Fig. 6⁽⁷⁾, the free energy, G , at 573 K for the amorphous alloy (curve **b**) is lower than the mixture of crystalline Pd and Ti (line **a**) in a wide range of composition. Although the free energies for the terminal solid solutions

of Pd and Ti have not been calculated, this diagram suggests that a single amorphous phase can be formed in a range $22 < x < 74$. This predicted range is roughly consistent with those found experimentally by mechanical alloying ($42 < x < 85$)⁽¹⁰⁾ and sputtering ($40 < x < 80$)⁽¹¹⁾. The present Pd/Ti multilayer (Pd₃₈Ti₆₂) is well within the predicted amorphizing range.

Now, it has been shown that the hydriding of these multilayers strongly suppresses the SSAR. The origin of this effect may be twofold; namely, kinetic and thermodynamic factors may be involved here. Firstly, the

Ni/Ti multilayer

Fig. 4 High-resolution micrographs of the same samples as shown in Fig. 3.

atomic intermixing between the Ni or Pd and Ti layers at the interfaces may be kinetically hindered due to the formation of TiH_2 . It is noteworthy that neither Ni nor Pd hydride can be formed at the present annealing temperatures and hydrogen pressure. The detail of the mechanism of the hindrance is unclear, but a strong potential barrier for the atomic exchange process could be built at the interfaces by the Ti hydride formation. To examine the validity of this mechanism, further studies are necessary

for revealing the behaviour of hydrided multilayers at higher temperatures. Secondly, the thermodynamic driving force for the atomic intermixing and amorphization may be much depressed owing to the hydride formation. This is simply explained in terms of the free-energy diagram shown above (Fig. 6). The free energy of the mixture of Pd and Ti (line **a**) is lowered to that of Pd and TiH_2 (line **a'**) after hydriding. The free energy of the amorphous alloy (line **b**) may also be lowered to that of a

Pd/Ti multilayer

Fig. 5 High-resolution transmission electron micrographs and electron diffraction patterns of as-deposited, vacuum-annealed and H₂-annealed Pd/Ti multilayers.

hydrided amorphous alloy (curve **b'**); since the latter quantity is difficult to evaluate accurately, the curve **b'** is rather schematic in this figure. The thermodynamic driving force for the SSAR should then change from **ab** before hydriding to **a'b'** after hydriding. Now, if **a'b'** $\ll$ **ab**, the SSAR would be retarded or prohibited by the hydriding. While no thermodynamic data are available on the enthalpy and entropy changes of amorphous alloys upon hydriding, those data on the crystalline compounds, TiM_n (M=Ni, Pd; $n=1, 2, 3, 5$)⁽¹²⁾, suggest that the above

inequality relation would be satisfied for both crystalline and amorphous alloys of the Pd-Ti and Ni-Ti systems. The kinetic and thermodynamic factors mentioned above possibly cooperate to stabilize the Ni/Ti and Pd/Ti multilayers upon hydriding.

It is worth noting here that this stabilizing effect of hydrogen cannot be regarded as a manifestation of a proportionation reaction such as $\text{TiM}_n + \text{H}_2 \rightarrow n\text{M} + \text{TiH}_2$. For this reaction to take place, the free energy of $\text{TiM}_n + \text{H}_2$ must exceed that of $n\text{M} + \text{TiH}_2$.

Fig. 6 Calculated Gibbs free-energy diagram for the Pd-Ti system at 573 K. The free energy, G , is referred to the standard states (298 K, 0.1 MPa (1 atm)) of Pd and Ti gas phases. (a) Mixture of crystalline Pd and Ti; (b) supercooled liquid (amorphous) alloy; (a') mixture of crystalline Pd and TiH_2 ; (b') hydrided amorphous alloy (schematic). The free energies of crystalline compounds are also shown. The predicted amorphous-forming range for Pd-Ti alloy is indicated. The vertical dash-dotted line represents the composition $\text{Pd}_{38}\text{Ti}_{62}$.

However, as shown in Fig. 6, the free energy of TiPd_n , for example, is low enough to prevent this reaction at the present hydrogen gas pressure and temperature. A similar situation is found for TiNi_n ⁽⁹⁾. At much higher pressures and temperatures, the proportionation reaction may take place in both systems, but the original multilayer structure would be destroyed in those conditions.

V. Summary and Conclusions

The composition distribution and microstructure in Ni/Ti and Pd/Ti multilayers subjected to annealing in vacuum or H_2 atmosphere have been investigated using AES, XRD and TEM techniques, and the following

results have been obtained.

(1) The as-deposited multilayers consist of periodic stacking of fine-grained Ni or Pd and Ti layers with Ni(111) or Pd(111) and Ti(001) preferred orientations parallel to the substrates.

(2) Upon annealing in vacuum at 523 K for Ni/Ti or at 623 K for Pd/Ti, atomic interlayer mixing readily occurs and nearly homogeneous alloys of amorphous structure are formed.

(3) However, upon annealing in H_2 atmosphere, the intermixing is suppressed completely and no amorphization reactions take place. The hcp Ti layers are altered to fcc TiH_2 exhibiting a (111) preferred orientation.

(4) The solid-state amorphization in these multilayers is reasonably accounted for in terms of calculated free-energy diagrams for these systems. The suppression of the intermixing and amorphization by hydriding may be explained by taking into account a kinetic effect (diffusion barrier increase at the interface) and a thermodynamic one (depression of the driving force).

(5) Hydriding is quite effective in stabilizing metallic multilayers containing Ti as a layer element.

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