

Hydrogen Enhancement of Interlayer Reaction in Ni/V Bilayer

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X-ray diffraction and Auger-electron spectroscopy depth profiling experiments clearly show that an interlayer reaction in a Ni/V bilayer forming Ni_3V and Ni_2V takes place at a temperature around 823 K when it is annealed in vacuum. However, this reaction temperature is reduced down to around 773 K when it is annealed in 0.5 MPa H_2 . A similar effect has also been observed for a Ni/Nb bilayer previously. These hydrogen-enhanced reactions in the two systems are interpreted to be due to formation of abundant vacancy-hydrogen complexes in the V and Nb layers, which efficiently assist the interdiffusion of the constituent atoms across the interfaces in the two bilayers.

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1. Introduction

The utilization of hydrogen treatment is developing in several fields of material processing in these years, as exemplified by the ultrafine-grain formation in Ti–Al–V alloys which greatly improves their mechanical properties,¹⁾ and the well-known process called HDDR to form submicron-sized grain structures in Nd–Fe–B alloys,²⁾ which are crucial to bestow excellent hard-magnetic properties on them. The solid-state amorphization of intermetallic compounds by hydrogenation³⁾ is another aspect of material processing which may develop as a unique technique for improving the physicochemical properties of the compounds. Furthermore, the control of melting or solidifying temperatures as well as solid-phase transformation temperatures in metals and alloys, which change greatly by hydrogenation,⁴⁾ is also expected to develop as a useful technique of material processing in the future.

Now, we have recently shown that solid-state reactions, as revealed by interlayer reactions in metallic multilayers or bilayers, are strongly influenced by hydrogenation, as listed in Table 1.^{5–10)} For example, in the Ni/Ti^{5,6)} and Pd/Ti^{5,7,8)} systems, solid-state reactions forming homogeneous amorphous alloys take place when they are annealed in vacuum at moderate temperatures, whereas the reactions are completely *inhibited* when annealed in hydrogen atmosphere. A similar trend is observed for the Fe/Ti⁹⁾ system, where FeTi compound is formed after annealing in vacuum whereas the reaction is *inhibited* under hydrogen. However, in the Ni/Nb¹⁰⁾ system, the interlayer reaction forming Ni_3Nb is remarkably *enhanced* by annealing in hydrogen in comparison with that in vacuum. If a solid-state reaction in an alloy is strongly suppressed or enhanced by the hydrogenation, this effect may be efficiently applicable to certain techniques of material processing.

The objective of the present study is to examine in more detail the hydrogen enhancement of the solid-state reactions in transition-metal alloy systems using a Ni/V bilayer, and to discuss a possible underlying mechanism causing this effect in the Ni/Nb and Ni/V systems.

2. Experimental Procedure

The sample used in this experiment was prepared in the same way as employed previously.¹⁰⁾ A Ni/V bilayered film, Ni being the top layer, was deposited on a Si(111) substrate in an Ar-ion-beam sputtering apparatus at ambient temperature. The thickness of each layer was adjusted to 300 nm, so that the net chemical composition of the film was $\text{Ni}_{58}\text{V}_{42}$. The oxygen and carbon contaminations inside the film as checked by Auger-electron spectroscopy depth profiling (AESDP) were small, and were below or comparable to the detection limits (~ 5 at%). The sample, separated into several pieces, was subjected to annealing in vacuum (2×10^{-4} Pa) or in high-purity hydrogen atmosphere of 0.5 MPa at temperatures between 573–873 K for a fixed period of 1.8 ks. The structure of each film was examined with X-ray diffraction (RIGAKU RAD-B) using Cu $K\alpha$ radiation, and the composition distribution inside the film was examined with AESDP (JEOL JAMP-7800), in which the Auger peak intensities of Ni-LMM and V-LMM, as well as those of O-KLL, C-KLL and Si-LMM, were continuously measured as a function of depth from the top surface. The formation of VSi compound at the V/Si-substrate interface was slightly detected by XRD when the films were annealed at temperatures above 823 K. However, it was found from AESDP that this reaction little influenced the interlayer reactions taking place at the Ni/V interface.

3. Results

Figure 1 shows a wide-angle XRD pattern of the Ni/V bilayer annealed at 673 K in vacuum before the onset of interlayer reactions. In addition to a strong diffraction peak of Si(111) from the substrate, diffraction peaks of Ni and V from the bilayer, with preferred orientations of Ni(111) and V(110), respectively, are seen.

Figure 2 shows XRD patterns around the Ni(111) peak of the bilayers subjected to annealing at 673–873 K in vacuum (a), compared with those annealed in hydrogen atmosphere (b). Except for slight peak shifts of Ni(111) toward higher angles due to stress relief of the films by annealing, no conspicuous changes in the profile can be seen up to 773 K in

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Table 1 Interlayer reaction characteristics of metallic multilayers or bilayers subjected to annealing in vacuum or hydrogen atmosphere.

Alloy system (Net composition)	Annealing conditions	Reaction products and characteristics		Ref.
		Annealed in vacuum	Annealed in H ₂ (0.5 MPa)	
Ni/Ti multiplayer (Ni ₄₄ Ti ₅₆)	523 K 86.4 ks	Ni–Ti amorphous alloy Homogenized by interlayer reaction.	Ni/TiH ₂ multilayer Interlayer reaction is inhibited.	(5), (6)
Pd/Ti multiplayer (Pd ₃₈ Ti ₆₂)	623 K 86.4 ks	Pd–Ti amorphous alloy Homogenized by interlayer reaction.	Pd/TiH ₂ multilayer Interlayer reaction is inhibited.	(5), (7), (8)
Fe/Ti multiplayer (Fe ₆₀ Ti ₄₀)	523–823 K 10.8–108 ks	FeTi Homogenized by interlayer reaction.	Fe/TiH ₂ multilayer Interlayer reaction is inhibited.	(9)
Ni/Mg multilayer (Ni ₃₄ Mg ₆₆)	323–573 K 10.8–108 ks	Mg ₂ Ni Homogenized by interlayer reaction.	β - or β' -Mg ₂ NiH ₄ Homogenized by interlayer reaction at $T \gtrsim 473$ K, but inhibited at $T \lesssim 373$ K.	(10)
Ni/Nb bilayer (Ni ₆₃ Nb ₃₇)	523–823 K 10.8–108 ks	Ni ₃ Nb Homogenized by interlayer reaction at $T \gtrsim 798$ K.	Ni ₃ Nb Homogenized by <i>enhanced</i> interlayer reaction at $T \gtrsim 723$ K.	(10)
Ni/V bilayer (Ni ₅₈ V ₄₂)	473–873 K 1.8 ks	Ni ₃ V, Ni ₂ V Homogenized by interlayer reaction at $T \gtrsim 823$ K.	Ni ₃ V, Ni ₂ V Homogenized by <i>enhanced</i> interlayer reaction at $T \gtrsim 773$ K.	This work

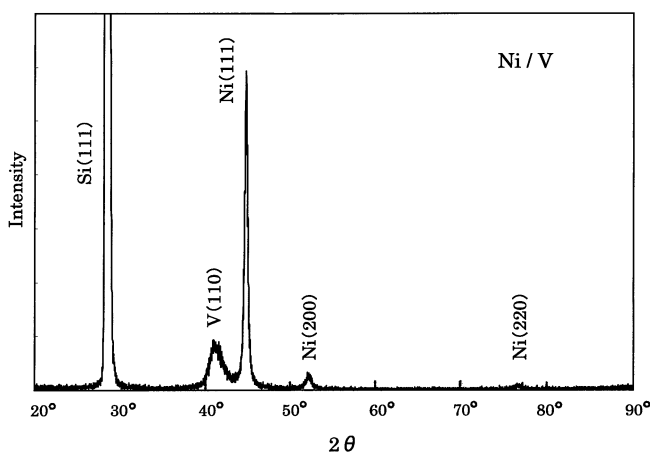


Fig. 1 XRD pattern of a Ni/V bilayer annealed at 673 K for 1.8 ks in vacuum.

both treatments. In the vacuum-annealed samples, a slight hump appears at a lower angle of Ni(111) at 823 K, and it grows to a definite peak at 873 K at the expense of Ni(111). This new peak represents Ni₃V(112) and is accompanied by a secondary very small peak of Ni₂V(100) at a still lower angle. On the other hand, in the hydrogen-annealed samples, the Ni₃V(112) peak grows definitely at 823 K, and becomes a single prominent peak at 873 K accompanied by the definite peak of Ni₂V(100). This XRD result shows that the interlayer reactions forming Ni₃V and Ni₂V in the Ni/V bilayer proceed more rapidly in the hydrogen atmosphere than in vacuum; namely, the interlayer reactions are enhanced by hydrogenation in this system. The unreacted part of the V layer, existing as a hydrogen solid solution VH_x at high temperatures, is altered to V₂H at room temperature in these samples, and the

V(110) peak is shifted toward a lower angle (not shown in the figure).

Figure 3 shows AESDP results for the bilayers annealed at 623–873 K in vacuum and in hydrogen atmosphere compared with that of the as-deposited sample. The relative concentrations of Ni and V, obtained from their Auger peak intensities corrected for the sensitivity factors, are plotted against the depth from the top surface in each profile. As can be seen from the figure, the as-deposited sample exhibits a sharp Ni/V interface, which becomes progressively diffuse with increasing annealing temperature. When the sample is annealed in vacuum, the interface begins to deform at 773 K, and the formation of Ni₃V and Ni₂V is indicated across the original interface at 823 K. At 873 K, the two compounds further grow toward both Ni and V sides. On the other hand, when the sample is annealed in hydrogen, the interlayer mixing takes place at temperature as low as 623 K, and the interface becomes more diffuse with increasing temperature. At 773 K, the formation of Ni₃V is clearly indicated in the V side of the bilayer, and at 823 K the formation of Ni₂V and a rapid growth of Ni₃V can be seen. At 873 K, the surface region of the film is severely oxidized owing to the remnant oxygen impurity in the hydrogen gas, leading to a strong enrichment of V over Ni on the surface. However, the interior region is not much disturbed by the surface oxidation, and both Ni₃V and Ni₂V compounds grow further toward the V side more rapidly than those in the vacuum-annealed samples. The onsets of intermixing at 623 K and formation of Ni₃V at 773 K in the hydrogen-annealed samples, both of which occur at definitely lower temperatures than those in the vacuum-annealed samples, evidently show that the interlayer reaction is enhanced by hydrogenation in the Ni/V bilayer.

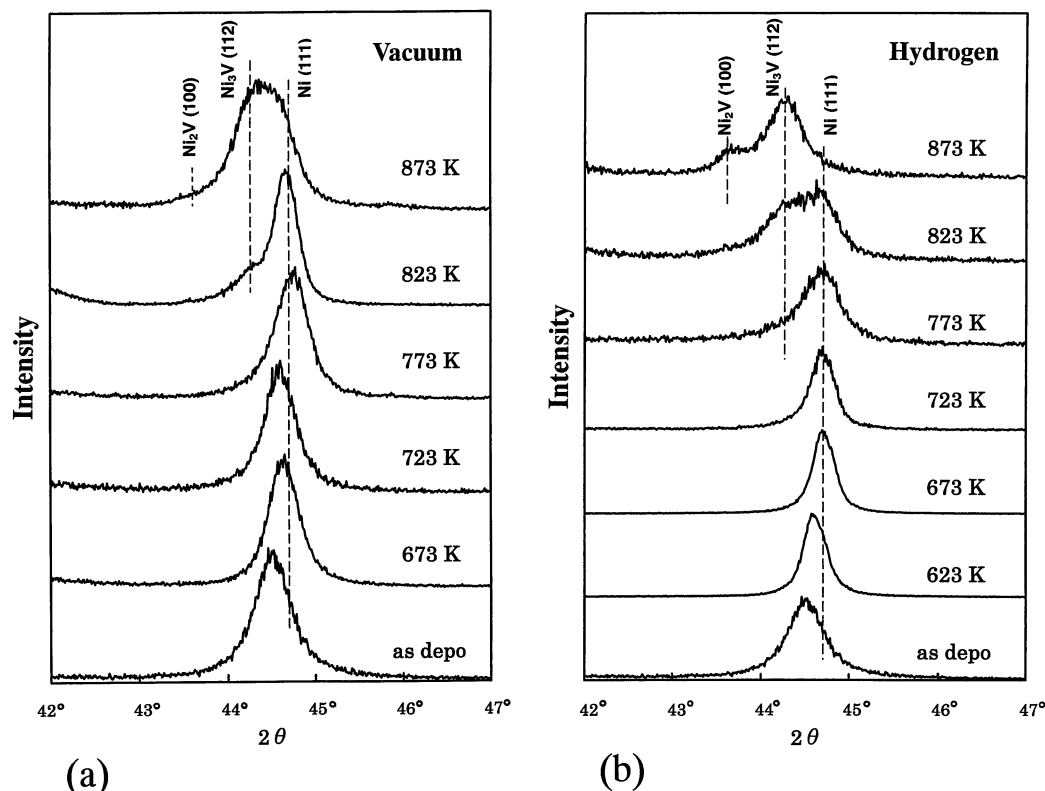


Fig. 2 XRD patterns around the Ni(111) peak of Ni/V bilayers annealed at 673–873 K for 1.8 ks in vacuum (a), compared with those annealed in hydrogen atmosphere (b).

4. Discussion

The annealing behavior of the Ni/V bilayer in vacuum and hydrogen atmosphere shown above is quite similar to that of a Ni/Nb bilayer,¹⁰⁾ where the formation of Ni₃Nb is initiated at 798 K in vacuum, while it takes place at a temperature as low as 723 K in 0.5 MPa H₂. It has also been found that, while the compound grows almost symmetrically toward both Ni and Nb sides in vacuum, it grows more rapidly toward the Nb side than the Ni side in hydrogen. Thus, the enhanced interlayer reaction and asymmetrical growth of the compound in the Ni/V bilayer observed in this study well conform to those in the Ni/Nb bilayer, and a similar enhancing mechanism appears to be involved in the interlayer reactions in the two systems during annealing in hydrogen. Since the underlying process of the reactions should be interdiffusion of the constituent atoms in the interface region, it is necessary to pursue the enhancing mechanism of interdiffusion by hydrogenation.

The hydrogen concentrations x ($=H/M$) in the Nb and V layers under 0.5 MPa H₂, both of which form hydrogen solid solutions above about 450 K, are considerably high in comparison with that in the Ni layer. For example, at a temperature of 723 K where the interlayer reaction takes place in the Ni/Nb bilayer, the equilibrium concentration of hydrogen in the Nb layer is calculated from Sieverts law as $x = 0.22$, while that in the Ni layer is $x = 0.00007$. Similarly, at 773 K, where the reaction takes place in the Ni/V bilayer, the hydrogen concentration in the V layer is $x = 0.05$, while that in the Ni layer is $x = 0.0005$. To obtain these H-concentrations, the following values of solution en-

tropy ΔS_s and solution enthalpy ΔH_s of hydrogen were used: $\Delta S_s = -8R$ and $\Delta H_s = -34$ kJ/molH (for Nb); $\Delta S_s = -8R$ and $\Delta H_s = -27$ kJ/molH (for V); and $\Delta S_s = -6R$ and $\Delta H_s = 16$ kJ/molH (for Ni), where R is the gas constant.¹¹⁾

Now, Fukai *et al.*¹²⁾ have recently shown that, under a high hydrogen concentration, the formation energy of a vacancy e_f in a metal is effectively reduced as a result of attractive interaction between the vacancy and a hydrogen atom with a binding energy of e_b , and the equilibrium concentration of vacancies c_v trapping r hydrogen atoms is expressed as

$$c_v = \frac{x^r}{1-x} \exp\left(-\frac{e_f - r e_b}{kT}\right), \quad (1)$$

where k is the Boltzmann's constant and T is the temperature. The formation energy of a vacancy is reported as $e_f = 2.6 \pm 0.3$ eV for Nb,¹³⁾ and 2.1 ± 0.2 eV for V.¹³⁾ The binding energy between a hydrogen atom and a vacancy is presently unknown for both Nb and V, except for theoretically calculated values of 0.6–0.7 eV in both metals.¹⁴⁾ We therefore assume that the binding energies are close to that for Ta (0.42 eV),¹⁵⁾ and tentatively take $e_b = 0.4$ eV for both Nb and V. We also assume that a single vacancy can trap up to six hydrogen atoms with this fixed binding energy, a reasonable assumption for both bcc and fcc metals.¹²⁾ By putting these values into eq. (1) and taking $r = 6$, the concentration of the vacancy-hydrogen complexes is calculated as $c_v = 6 \times 10^{-6}$ for Nb at 723 K, and 1×10^{-6} for V at 773 K. It should be noted that these concentrations of the complexes are 10^8 – 10^{12} times higher than those of single vacancies existing in thermal equilibrium in hydrogen-free samples; e.g. $c_v = 1 \times 10^{-18}$ for Nb at 723 K, and 2×10^{-14} for V at 773 K. These abun-

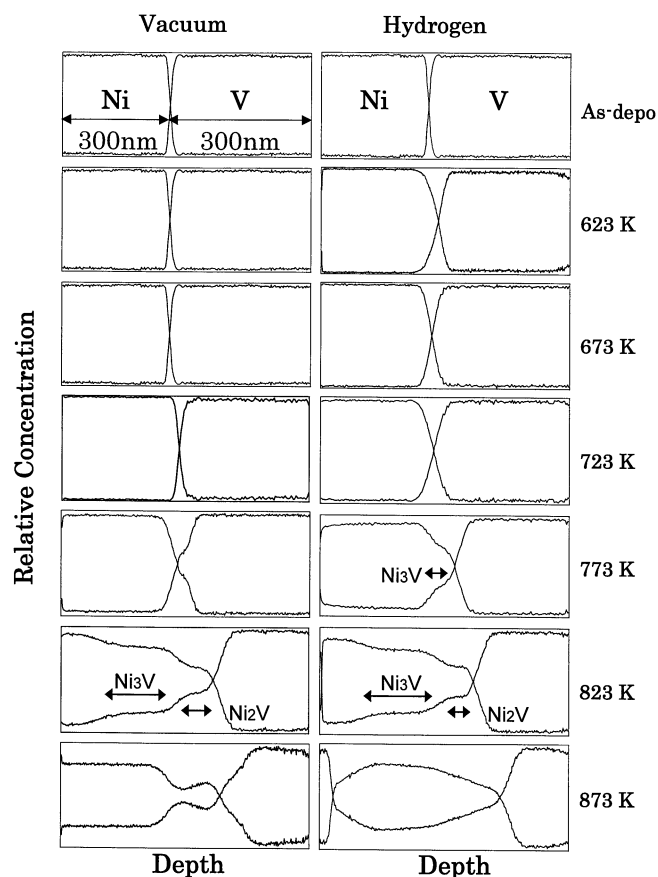


Fig. 3 AESDP results for Ni/V bilayers annealed at 623–873 K in vacuum and in hydrogen atmosphere compared with that of as-deposited bilayer.

dant vacancies introduced by hydrogenation in the Nb and V layers are considered to assist the interdiffusion processes in the interface regions in the Ni/Nb and Ni/V bilayers, resulting in enhancing the formation of Ni_3Nb and Ni_3V compounds as well as their growth toward the Nb and V sides, respectively. Since the hydrogen concentration is too small to form abundant vacancies in the Ni layer, enhancement of the growth of the compounds toward the Ni side is not expected. In fact, the vacancy concentration in the Ni layer at 723–773 K is evaluated, using $e_f = 1.55 \text{ eV}^{16}$ and $e_b = 0.42 \text{ eV}^{15}$ for Ni, as $c_v = (3\text{--}7) \times 10^{-11}$, which is $\sim 10^{-5}$ times smaller than those in the hydrogenated Nb and V layers at the same temperatures. To substantiate the above mechanism of hydrogen-enhanced interlayer reactions, however, analyses on the mobility of vacancy-hydrogen complexes are also required.

In the vacuum-annealed samples, the interlayer reactions take place at 798 K and 823 K in the Ni/Nb and Ni/V bilayers, respectively, as shown by both XRD and AESDP experiments. The vacancy concentrations in the Nb and V layers at these temperatures are $c_v = 4 \times 10^{-17}$ and 1×10^{-13} , respectively, which are still much smaller than the corresponding concentrations of vacancy-hydrogen complexes in the hydrogenated samples at 723 K and 773 K mentioned above. Therefore, we interpret the onset of interlayer reactions in these vacuum-annealed bilayers to be caused not by the vacancy-assisted *intrinsic* interdiffusion within grains of the bilayers but by *extrinsic* interdiffusion through their grain bound-

aries. In the latter mechanism, a rather symmetrical compound growth is expected, and it is qualitatively consistent with the AESDP observations.

5. Conclusions

The interlayer reaction in a Ni/V bilayer forming Ni_3V and Ni_2V compounds at elevated temperatures is appreciably enhanced by a hydrogenation treatment under 0.5 MPa H_2 . This effect is very similar to that found previously for a Ni/Nb bilayer which forms Ni_3Nb compound. This hydrogen-enhanced reaction is commonly interpreted to be due to generation of abundant vacancy-hydrogen complexes in the Nb or V layer, which assist the interdiffusion of the constituent atoms across the interface of the bilayer and enable the formation and growth of the compound at a temperature well below that necessary for the reaction to occur in vacuum. Annealing treatments under higher hydrogen pressures would cause further enhancements of the reaction. This effect appears to be important as a new hydrogen function in various alloy systems, and may be applicable to some related techniques of material processing in the future.

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