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Formation of amorphous alloys through the multilayer method in an immiscible Y–Nb system

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Abstract. Amorphization was achieved by room-temperature 190 keV xenon ion mixing of multilayered films in the Y–Nb system, which has a positive enthalpy of formation exceeding +44 kJ mol⁻¹. To give further insight into the singularity of the amorphization behaviour of the system, a Gibbs free-energy diagram of the system was constructed by calculating the free energies of the amorphous phase and those of the as-deposited Y–Nb multilayers, in which the interfacial free energy was estimated and added. The established diagram can explain the irradiation-induced amorphization behaviour in the Y–Nb system well.

In the last 15 years, ion mixing (IM) has been employed as a powerful means of synthesizing a variety of metastable alloys with either an amorphous or a crystalline structure in some 90 binary systems [1, 2]. It is commonly considered that, in IM, a high-energy ion beam is used mainly to trigger atomic collisions, inducing intermixing between alternately deposited metal A and B multilayers, thus forming a uniform A–B alloy. From a physical point of view, IM is a far-from-equilibrium process and is commonly divided into two steps of atomic collision and relaxation. It is accepted that the phase structure of the alloy is formed in the relaxation period, which lasts for only 10⁻¹⁰–10⁻⁹ s [3]. According to a thermal spike concept, an effective cooling speed can be as high as 10¹³–10¹⁴ K s⁻¹ in IM [3]. To date, most research interests of IM have focused on synthesizing amorphous alloys and studying the amorphization mechanism of the binary metal systems, especially of those with a negative enthalpy ΔH_f of formation [4, 5]. It is found that the glass-forming ability (GFA) of binary metal systems is greatly widened by IM and is continuous in composition for the binary metal systems with negative ΔH_f [6].

From the extensive experimental data so far obtained [7], it has been commonly considered that the sign of ΔH_f has some effect on the amorphous alloy formation, as a large negative ΔH_f between the constituents is known to lower the free energy of the amorphous phase with respect to that of a mixture of two crystalline phases of the constituent metals and therefore serves as a thermodynamic driving force. In contrast, a positive ΔH_f always makes the amorphous phase have a higher free energy, hindering amorphization and yet favouring phase separation [8]. It follows naturally that a positive ΔH_f does not favour the formation of an amorphous phase, for which the free-energy curve is convex in shape and always higher than that of the mixture of the two crystalline metals. In this respect, however,

the above argument is based on the thermodynamics of solids dealing with the bulk form of the materials. IM begins with multilayered films, in which the interfaces should play a role in alloying behaviours between the metal layers. Very recently, the present authors' group conducted IM experiments in some positive ΔH_f systems with multilayered films [9, 10], which included a sufficiently high fraction of interfacial atoms, and observed the formation of amorphous alloys in these systems. To make a firm conclusion, more experimental study of positive ΔH_f systems is still of importance. The Y–Nb system, which has a positive enthalpy of formation exceeding $+44 \text{ kJ mol}^{-1}$, was thus selected to investigate the GFA by IM.

Y–Nb multilayered films were prepared by alternating deposition of pure Y and Nb onto newly cleaved single NaCl crystals as substrates in an electron-gun evaporation system. The background vacuum level was of the order of 10^{-7} Torr. The substrates were cooled with running water during evaporation and their temperature was estimated to be below 200°C . The total thickness of the samples was designed to be about 40 nm, which approximately equalled the projected range plus the projected range straggling of the irradiating ions, i.e. 190 keV xenon ions. The multilayered films were composed of 18 layers. The compositions of the deposited films were controlled by adjusting the relative thicknesses of the constituent metals and were later confirmed by wavelength-dispersive spectroscopy analysis with an experimental error of 5%. After deposition, the samples were irradiated by 190 keV xenon ions to doses ranging from 3×10^{14} to $7 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$ at room temperature in an implanter with a vacuum level better than 5×10^{-6} Torr. The ion-beam current density was controlled to be less than $1 \mu\text{A cm}^{-2}$ to avoid overheating. After irradiation, all the irradiated films were analysed by transmission electron microscopy (TEM) and selected-area diffraction (SAD) to identify the structures of the resultant phases.

Table 1 lists the structural changes in the Y–Nb multilayered films under 190 keV xenon IM at room temperature with increasing irradiation dosage. The compositions for this study were intentionally chosen to be of around equiatomic stoichiometry, where the amorphous phase frequently had the highest free energy and therefore was the most difficult to form. From the table, one can see that the $\text{Y}_{56}\text{Nb}_{44}$ and $\text{Y}_{60}\text{Nb}_{40}$ multilayered films were indeed amorphized at doses of $7 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$ and $5 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$, respectively. Figures 1(a) and (b) show the corresponding SAD patterns of the as-deposited and amorphized $\text{Y}_{56}\text{Nb}_{44}$ multilayered films. These results suggest that amorphization can be achieved in the Y–Nb system by IM.

Table 1. Phase changes in the Y–Nb multilayers induced by 190 keV xenon IM at room temperature: PA, partial amorphization; A, complete amorphization.

Dosage ($\text{Xe}^+ \text{ cm}^{-2}$)	Phases in the following multilayers	
	$\text{Y}_{56}\text{Nb}_{44}$	$\text{Y}_{60}\text{Nb}_{40}$
As-deposited	Y + Nb	Y + Nb
3×10^{14}	Y + Nb	Y + Nb
1×10^{15}	Y + Nb	Y + Nb
3×10^{15}	Y + Nb	Y + Nb
5×10^{15}	PA	A
7×10^{15}	A	A

We tried to exclude the possible effect of impurity elements such as O, H, Cl and Na from the substrate and the environment on ion-induced amorphization. It is believed that the Cl and Na atoms did not take part in the phase formation in the Y–Nb multilayered

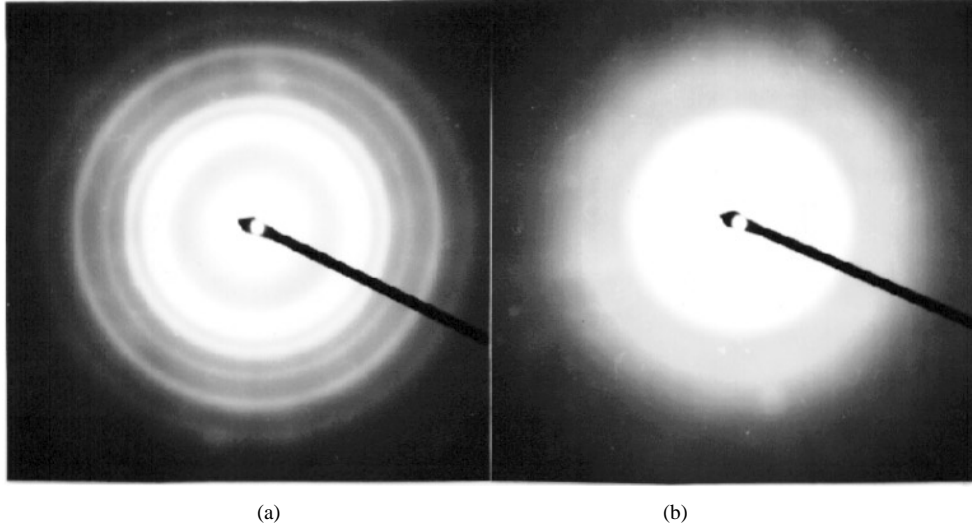


Figure 1. SAD patterns of the $Y_{56}Nb_{44}$ multilayered films with 17 interfaces: (a) as-deposited; (b) amorphized at dose of $7 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$.

films, because the designed thickness of Y–Nb films ensured only a trace amount of Na and Cl atoms were possible to recoil into the films. If there were some Na and Cl atoms involved in the films, they would have preferentially formed NaCl crystals rather than any other complicated compounds, as the binding energy of NaCl is the highest compared with other possible phases. Hydrogen was thought to be a very minor impurity, since the films were held in a dry vacuum chamber, and was found by x-ray photoelectron spectroscopy (XPS) analysis to appear only in the very top surface layer within 10 Å. It was also found in our previous studies by XPS measurements that oxygen atoms were only detected in the surface layer to within 20 Å. In short, the above phase formation resulted from IM.

The Gibbs free energy of a given phase is calculated from $\Delta G = \Delta H - T \Delta S$, where ΔH and ΔS are the enthalpy change and entropy change, respectively. The expression for the entropy change can be taken, as a first approximation, to be that of an ideal solid solution, i.e.

$$\Delta S = -R[x_A \ln(x_A) + x_B \ln(x_B)] \quad (1)$$

in which R is the gas constant and x_A and x_B are atomic concentrations of A and B metals, respectively.

Following the suggestion by Niessen and Miedema [11], the calculation of the free energy of the amorphous phase is given by

$$\Delta G_{\text{amorphous}} = \Delta H_c + \beta(x_A T_A + x_B T_B) - T \Delta S \quad (2)$$

where β is an empirical constant equal to $3.5 \text{ J mol}^{-1} \text{ K}^{-1}$, T_i is the melting point of the component i and ΔH_c is the chemical change due to the electron redistribution generated at the boundary for the Wigner-Seitz unit cell when alloying. According to Miedema's model, the chemical change is given by [12]

$$\Delta H_c = \Delta H_{\text{amp}} x_A V_A^{2/3} f_{AB} \quad (3)$$

where ΔH_{amp} is an amplitude reflecting the magnitude of the electron redistribution interaction, x_A is the atomic concentration of metal A in the alloy, V_A is the atomic volume

of atom A, and f_{AB} is a function which accounts for the degree to which atoms A are surrounded by atoms B. In the calculation of the chemical enthalpy, a constant of 5 was taken to describe the degree of the chemical short-range order emerging in the amorphous alloy [13].

Accordingly, the Gibbs free-energy change of the Y–Nb amorphous phase was calculated and is shown in figure 2. The values of the parameters used in the calculation are listed in table 2. From the figure, one may notice that the free-energy curve of the amorphous phase is convex in shape and much higher than that of a mixture of the two pure constituents.

Table 2. Values of the parameters used in calculating the free-energy diagram of the Y–Nb system and the free energy of the as-deposited Y–Nb multilayered films:—data were not used.

Parameter (units)	Value in the following			As-deposited Y–Nb films
	Y	Nb	Amorphous phase	
T_m (K)	1799	2740	—	—
V (cm ³)	19.89	10.81	—	—
γ	—	—	5	—
ΔH_{amp} (kJ mol ⁻¹ m ⁻²)	—	—	20	—
γ^0 (mJ m ⁻²)	1125	2700	—	—
$\Delta H_{(Y \text{ in Nb})}^0$ (kJ mol ⁻¹)	—	—	139	139
$\Delta H_{(Nb \text{ in Y})}^0$ (kJ mol ⁻¹)	—	—	102	102
S_f (10 ⁵ m ²)	3.3	2.2	—	—

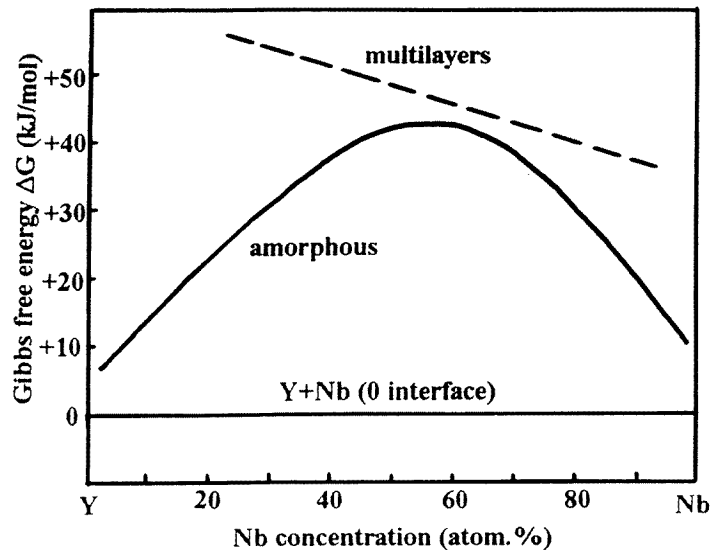


Figure 2. A calculated Gibbs free-energy diagram of the Y–Nb system: — — —, initial energy level of the as-deposited multilayers.

It should be emphasized that multilayered films consisting definitely of a certain number of interfaces can possess a higher free energy than that of the corresponding bulk counterpart, as the interfaces can give rise to an additional interfacial free energy. The additional

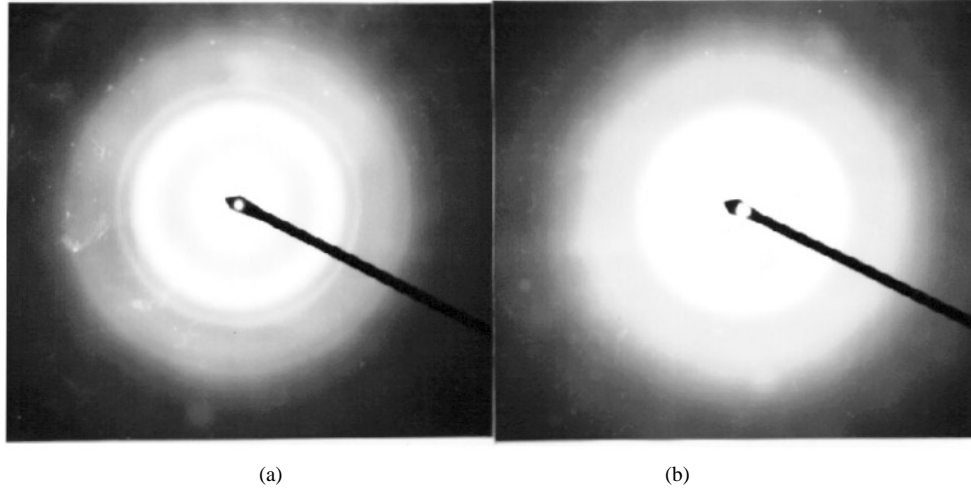


Figure 3. SAD patterns of the $Y_{60}Nb_{40}$ multilayered films with 17 interfaces: (a) as-deposited; (b) completely amorphized at $300\text{ }^{\circ}\text{C}$ for 1.5 h.

interfacial free energy, in some cases, may elevate the multilayers to a state of higher free energy than that of the amorphous phase and thus serves as a major driving force for amorphization. According to Gerkema and Miedema [14], the interfacial free energy is

$$\Delta G^f = \alpha \Delta G_f^0 \quad (4)$$

where α is the fraction of interfacial atoms versus total atoms in the films, ΔG_f^0 is the interfacial free energy per mole interfacial atoms and is calculated from $\Delta G_f^0 = S^{AB} \gamma^{AB}$, where S^{AB} is the surface area occupied by 1 mol of interfacial atoms, γ^{AB} is a constant for a specific system and can be calculated from

$$\gamma^{AB} = 0.15(\gamma_A^0 + \gamma_B^0) + \gamma_{AB}^{chem} \quad (5)$$

where γ_A^0 and γ_B^0 are the surface energies of metals A and B, contributing an elastic term always positive in sign caused by size difference, while γ_{AB}^{chem} is the chemical contribution, which has the same sign as ΔH_f . Consequently, the interfacial free energy for the $\Delta H_f > 0$ system is a sum of two terms, while for the $\Delta H_f < 0$ system it is the difference of two contributions, leading to a minor effect.

Assuming that the thickness of the interface is $4\text{--}6\text{ \AA}$ [15], the fraction of interfacial atoms, i.e. α , can easily be obtained when the total thickness and the number of interfaces are fixed [9].

The interfacial free energies for the as-deposited Y–Nb multilayered films were therefore calculated and the free-energy curve of the Y–Nb multilayers is shown in figure 2 as a broken line, representing the initial energy level of the as-deposited Y–Nb multilayers.

In order to check the relevance of the calculated free-energy diagram, steady-state annealing of as-deposited $Y_{60}Nb_{40}$ multilayered films was conducted with increasing temperature. The films were amorphized after $350\text{ }^{\circ}\text{C}$ annealing for 1.5 h and changed into a mixture of Y + Nb crystalline phases after annealing for 1 h at $600\text{ }^{\circ}\text{C}$. Figures 3(a) and 3(b) show the SAD patterns of the as-deposited and amorphous state of $Y_{60}Nb_{40}$ films. This phase transformation sequence reveals that the initial energy level of as-deposited Y–Nb films, consisting of a sufficiently high interfacial atom fraction, is higher than that of the

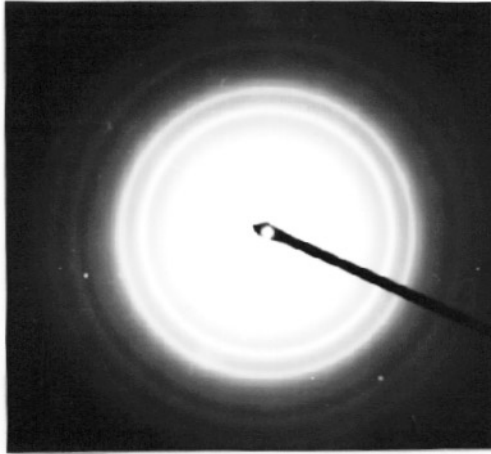


Figure 4. SAD pattern of a mixture of crystalline Y and Nb transformed from the $Y_{60}Nb_{40}$ amorphous films induced by IM and kept at room temperature for 4 months.

amorphous phase, which agrees with, at least in its outline, the calculated results shown in figure 2. Also, the thermal stability of the amorphous phase obtained by IM was also tested by re-examining the films with SAD after the films had been kept at room temperature for 4 months. It turned out that the $Y_{60}Nb_{40}$ amorphous films formed by IM transformed into equilibrium crystalline Y and Nb phases, as evidenced by the corresponding SAD pattern shown in figure 4.

In conclusion, amorphization can be achieved by designing the multilayers to have a sufficiently high fraction of interfacial atoms in the positive Y–Nb system by room-temperature 190 keV xenon ion irradiation, even around the equiatomic stoichiometry region. The major driving force in this case is believed to be from the additional interfacial free energy.

Acknowledgments

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