

Interface-generated vitrification in the Y - Mo system with a small positive heat of mixing

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 L165

(<http://iopscience.iop.org/0953-8984/8/11/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.208

The article was downloaded on 13/05/2010 at 16:22

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Interface-generated vitrification in the Y–Mo system with a small positive heat of mixing

B X Liu and Z J Zhang

Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China, and National Laboratory of Solid-State Microstructure Physics, Nanjing University, Nanjing 200039, People's Republic of China

Received 12 September 1995, in final form 29 January 1996

Abstract. We report, in this letter, the first observation of vitrification in the Y–Mo system with positive heat of mixing, as a function of the number of interfaces or more precisely the fraction of interfacial atoms, in Y–Mo multilayered films. The thermodynamic driving force is the excess free energy originating from the interfaces, which elevates the initial energetic state of the multilayered films beyond that of the amorphous phase. In addition, the role of a large atomic size mismatch in vitrification is discussed.

The first amorphous alloy was obtained by liquid melt quenching in the early 1960s [1]; since then various techniques, e.g. physical vapour deposition (PVD), laser quenching (LQ) and ion beam mixing (IM), have been developed and employed to synthesize new amorphous alloys [2–4], which are expected to feature unique properties in many aspects. Schwarz and Johnson reported, for the first time in 1983, the solid-state vitrification in Au–La multilayered films [5], and from then on, there have been many reports presenting similar results in other binary metal systems [6, 7]. The common characteristics of the systems so far studied on this topic are (i) a small negative heat of mixing calculated by Miedema's model [8] and (ii) one metal diffuses anomalously faster in its partner, but not vice versa. It has been understood that the negative heat of mixing results in a lower free energy of the amorphous phase than that of a mixture of two crystalline phases of the constituent metals, and thus provides a necessary thermodynamic driving force for vitrification upon heating. Kinetically, the diffusional asymmetry, closely related to a large atomic size mismatch between the two constituent metals, prohibits the formation of the intermetallic compounds as possible competing phases hindering amorphization. According to the above argument, vitrification is naturally impossible in a system of positive heat of mixing. To further discuss this issue in terms of free energy considerations, two representative systems were selected for comparison, i.e. the Y–Mo system with a small positive heat of mixing of $+26 \text{ kJ mol}^{-1}$ and the Ni–Hf system with a large negative heat of mixing of -42 kJ mol^{-1} . The respective free energy diagrams were calculated on the basis of Miedema's model [8] and the method developed by Alonso and coworkers [9], and are shown in figures 1 and 2. The shape of the free energy curve of the amorphous phase, one can see clearly from the figures, is convex in the Y–Mo system exhibiting a small positive heat of mixing, while it is concave in the Ni–Hf system of a large negative heat of mixing. Obviously, in the Ni–Hf system, the formation of an amorphous phase is favoured energetically. In contrast, in the Y–Mo system, the free energy of the amorphous state is always much higher than that of a mixture

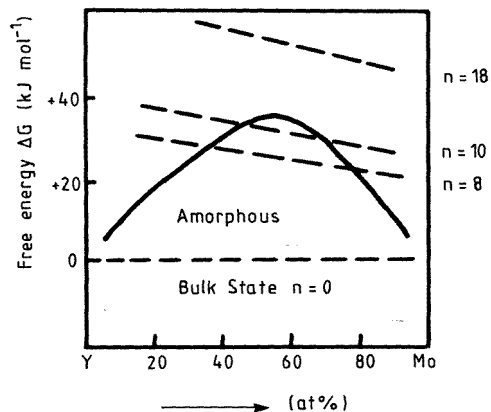


Figure 1. The calculated free energy diagram of the Y–Mo system with a heat of mixing exceeding $+26 \text{ kJ mol}^{-1}$.

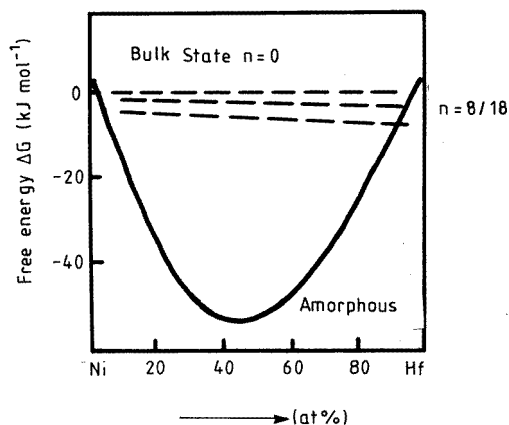


Figure 2. The calculated free energy diagram of the Ni–Hf system with a heat of mixing of -42 kJ mol^{-1} .

consisting of Y and Mo crystalline phases and, as a consequence, no thermodynamic driving force is available for vitrification.

Since all the observed solid-state vitrification took place in multilayered films definitely consisting of a certain number of interfaces, the role of interfaces should have been considered, yet it has been missed in the previous studies. The atoms in the interfacial layers, as well known, are in a metastable configuration and usually possess higher free energy than those in the bulk form. The question is then, for a binary metal system of positive heat of mixing, whether or not the initial energetic state of the multilayered films can be elevated to a state of higher free energy than that of the amorphous phase, by artificially adjusting the number of interfaces, or more precisely the fraction of interfacial atoms in the multilayered films. If the answer is yes, the excess free energy originating from the interfaces can then in turn serve as an effective thermodynamic driving force for the vitrification.

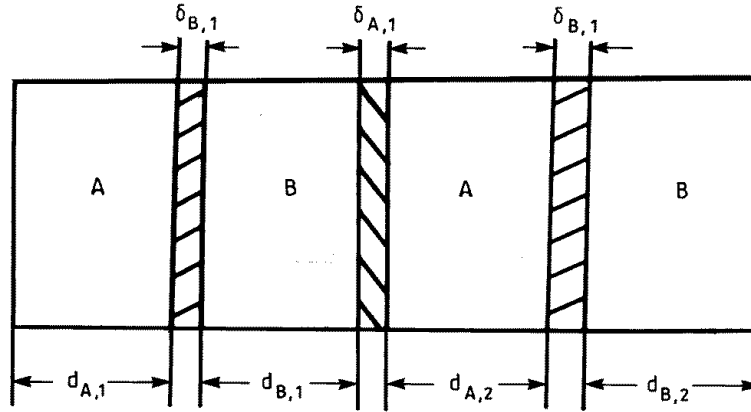


Figure 3. The configuration of the Y–Mo multilayered films and a demonstration of the interfaces involved in the films.

We now estimate the interfacial free energy for multilayered films. Figure 3 shows the configuration of a typical A–B multilayer system including several interfaces. The interface is considered as a transient layer with certain thickness. An interface of A growing on B or B growing on A consists of a few atomic layers, as metals A and B are different in atomic size. Consequently, the fraction of the interfacial atoms versus the total atoms denoted as α in the multilayered films is related to the numbers and the thickness of the interfaces. Firstly, the entropy term for an interface can be neglected since it plays only a minor role; the free energy is then equal to the enthalpy change. According to de Boer *et al*, the excess energy of 1 mol interfacial atoms is $\Delta G_F^0 = S^F \gamma^F$ [10], where S^F is the surface area occupied by 1 mol interfacial atoms and γ^F is defined as *the energy per interface area*. As discussed by de Boer *et al*, S^F is calculated by $S^F = C_0 V_A^{2/3}$, where C_0 is a constant, 4.5×10^8 , and V_A is the volume of 1 mol A atoms. For example, S^F is $3.3 \times 10^5 \text{ m}^2$ for Y, and $2.0 \times 10^5 \text{ m}^2$ for Mo. γ^F consists of two contributions, i.e. an elastic term, $\gamma^{mismatch}$, which is closely related to the mismatch between the adjacent lattices and always has a positive sign, and a chemical term, $\gamma^{chemical}$, representing the interaction between the two metals and having the same sign as that of the heat of mixing [10]. Considering interfaces of A growing on B, $\gamma^{mismatch} = 0.5(\gamma_{[A]}^0 + \gamma_{[B]}^0)$, where $\gamma_{[i]}^0$ is *the energy per surface area* of metal i , and for the Y–Mo system is 1125 mJ m^{-2} and 3000 mJ m^{-2} for Y and Mo, respectively; the chemical term is $\gamma^{chemical} = \Delta H_{(A \text{ in } B)}^0 / S_A^F$, in which $\Delta H_{(A \text{ in } B)}^0$ denotes the heat of solution of solid A in solid B. Using the tabulated data from [10], $\Delta H_{(Y \text{ in } Mo)}^0 = 114 \text{ kJ mol}^{-1}$, and $\Delta H_{(Mo \text{ in } Y)}^0 = 81 \text{ kJ mol}^{-1}$; γ^F is then 964 mJ m^{-2} and 1024 mJ m^{-2} for interfaces of Y on Mo and Mo on Y, respectively. For simplicity, the mean values of S^F and γ^F , i.e. $\overline{S^F} = 2.65 \times 10^5 \text{ m}^2$ and $\overline{\gamma^F} = 995 \text{ mJ m}^{-2}$, are used in the calculation of the Y–Mo system. $\Delta G_F^0 = \overline{S^F} \overline{\gamma^F}$ is therefore 264 kJ mol^{-1} for the Y–Mo system. Since the interfacial atoms are only a fraction of the total atoms, the excess interfacial free energy contributed to the total free energy of the multilayered films is then $\Delta G_F = \alpha \Delta G_F^0$. The question for evaluating the initial energetic state of the multilayered films is then the calculation of the fraction of interfacial atoms. Suppose, in an A–B multilayer system as shown by figure 3, N_A and N_B are the numbers of A and B layers, $d_{A,i}$ and $d_{B,i}$ are the thicknesses of the i th layers of A and B metals; n_A and n_B are

the numbers of interfaces A on B and B on A, and $\delta d_{A,j}$ and $\delta d_{B,j}$ are the thicknesses of the j th interface of A on B and B on A, respectively; the fraction of interfacial atoms in the multilayers is then

$$\alpha = X_A \left(\sum_{j=1}^{n_A} \delta d_{A,j} \right) / \left(\sum_{i=1}^{N_A} d_{A,i} \right) + X_B \left(\sum_{j=1}^{n_B} \delta d_{B,j} \right) / \sum_{i=1}^{N_B} d_{B,i} \quad (1)$$

where $N_A + N_B = n_A + n_B + 1$ is naturally held; X_A and X_B are the atomic concentrations of A and B in the multilayered films, respectively.

Since the numbers of interfaces, i.e. $(n_A + n_B)$ can be artificially adjusted, $\delta d_{A,j}$ and $\delta d_{B,j}$ determining the characteristics of the interfaces are therefore of great importance for the calculation of the interfacial free energy. Presumably, $\delta d_{A,j}$ and $\delta d_{B,j}$ can be considered constant since the thicknesses of the metal layers exceed greatly that of the interfaces. It was found in previous experimental studies that the structure of the multilayered films became disordered when the thicknesses of the metal layers were around 5 Å [11], suggesting that 5 Å can be taken as an adaptable measure of the thickness of an interface. Accordingly, the free energy of the Y–Mo multilayers including interfaces was calculated as a function of the total numbers of the metal layers, i.e., $(N_A + N_B)$. *In experiments, the total thickness of the Y–Mo multilayered films is about 400 Å. Based on this thickness, three curves with $(N_A + N_B) = 9, 11$ and 19, corresponding to the interface numbers of $(n_A + n_B) = 8, 10$ and 18, or the fractions of interfacial atoms of 8.1, 10.0 and 18.1 at.% at an equiatomic stoichiometry, were calculated as a function of atomic concentration of the constituent metals and are shown in figure 1 by the dashed lines. For comparison, the same calculation was performed for the Ni–Hf system and the calculated free energy curves of the multilayers with different fractions of interfacial atoms are also added in figure 2 as dashed lines.*

For the Ni–Hf system shown in figure 2, it appears that the inclusion of the interfacial free energy decreased only slightly the free energy of the multilayered films, yet the multilayered films were still in an energetic state higher than that of the amorphous state. The influence of the interfaces is therefore not significant. For the Y–Mo system shown in figure 1, the situation is sharply different. With increasing fraction of interfacial atoms, the free energy of the multilayered films increases. The figure shows that the free energy curve of the multilayered films intersects with that of the amorphous phase when consisting of eight and 10 interfaces, and eventually the free energy of the multilayered films is higher than that of the amorphous state within the whole composition range when including 18 interfaces, indicating that amorphization of the Y–Mo multilayers becomes possible. Table 1 lists the predicted composition ranges favouring amorphization upon heating for the Y–Mo multilayered films including three different fractions of interfacial atoms. It should be emphasized that although the above calculation was based on semi-quantitative theory and methods, the trend of the changing of the initial energetic state of the multilayered films was believed to be of relevance and correct. Furthermore, in experiment, one can add extra interfaces to ensure the energy level of the multilayered films to be higher than that of the amorphous state. In other words, in checking the idea of interface-generated vitrification, the precision of the calculation is not a crucial issue, though it should be further improved.

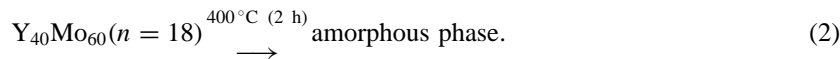
Y–Mo multilayered films including eight, 10 and 18 interfaces were deposited with various compositions in a high-vacuum system. Then the multilayers were annealed *in situ* in a hot stage attached to a transmission electron microscope (TEM) where the vacuum level was of the order of 10^{-7} Torr. TEM observation and selected area diffraction (SAD) were employed to identify the changes of the structures of the multilayered films upon consecutive annealing. For the multilayered films with eight interfaces, it was found that only two multilayered films, i.e. $Y_{80}Mo_{40}$ and $Y_{20}Mo_{80}$, became amorphous after annealing

Table 1. Predicted composition ranges favouring amorphization of the Y–Mo multilayered films with various numbers of interfaces based on the calculations and the confirmation by the experimental results. In the table, α is the fraction of interfacial atoms versus the total atoms in the multilayered films.

Composition	$n = 8$ ($\alpha = 8.1$ at.%)		$n = 10$ ($\alpha = 10$ at.%)		$n = 18$ ($\alpha = 18.1$ at.%)	
	Predicted	Obtained	Predicted	Obtained	Predicted	Obtained
Y ₈₀ Mo ₂₀	Yes	Yes	Yes	Yes	Yes	— ^a
Y ₆₀ Mo ₄₀	No	No	Yes	Yes	Yes	Yes
Y ₅₀ Mo ₅₀	No	No	No	No	Yes	Yes
Y ₄₀ Mo ₆₀	No	No	No	No	Yes	Yes
Y ₂₀ Mo ₈₀	Yes	Yes	Yes	Yes	Yes	—

^a No data obtained.

at 250 °C for 1.5 h, while for those containing 10 interfaces amorphization was achieved in the Y₈₀Mo₂₀–Y₆₀Mo₄₀ and Y₂₀Mo₈₀ multilayered films under similar annealing conditions. It was of importance that when there were 18 interfaces, the Y₅₀Mo₅₀ films transformed into the amorphous state, as evidenced by the haloes observed in the SAD pattern, after a 2 h anneal at 350 °C. Since the free energy of the amorphous state around equiatomic stoichiometry in such a system of small positive heat of mixing has the highest value and thus is most difficult to obtain, another two samples also with 18 interfaces, i.e. Y₄₀Mo₆₀ and Y₆₀Mo₄₀ multilayered films, were prepared and subjected to thermal annealing and they both transformed into the amorphous state after annealing at 400 °C for 2 h. The vitrification of the Y–Mo multilayered films around equiatomic stoichiometry can be illustrated by



To check the thermal stability of the amorphous alloys obtained at compositions around equiatomic stoichiometry, further annealing of the Y₅₀Mo₅₀ amorphous alloys was conducted, and the recrystallization temperature of the Y₅₀Mo₅₀ amorphous alloy was found to be around 650 °C. Figure 4(a)–(c) shows the SAD patterns of the as-deposited Y₅₀Mo₅₀ multilayers, the amorphous phase formed by annealing and the re-emerging Y+Mo crystalline mixture, respectively. The diffraction lines shown in figure 4(a) and (c) were well indexed to be those from elemental crystalline Y and Mo. The re-emerging Y+Mo crystalline phases in figure 4(c) were certainly the precipitates from the previously obtained amorphous alloy. From the above results it is obvious that the composition range favouring vitrification in this system depends on the fraction of the interfacial atoms versus the total atoms in the multilayers. In particular, when there were sufficient interfacial atoms included in the films, vitrification could take place at compositions around equiatomic stoichiometry. In other words, amorphous alloys can be produced by thermal annealing of multilayers in such a system of small positive heat of mixing. For a clear and explicit comparison with the predictions the thermal annealing results are also listed in table 1.

According to the above calculations, the interfaces behave differently in the vitrification of the Y–Mo and Ni–Hf systems. In the Ni–Hf system with a negative heat of mixing, the interfaces decreased only slightly the thermodynamic driving force. In the Y–Mo system, however, the interfacial free energy arising from the interfaces surpassed that of the amorphous state and served as the driving force for the vitrification. Generally speaking, an interface in an A–B multilayer system prepared by vapour deposition is non-epitaxial if the constituent metals have a large atomic size mismatch, and thus, when one metal grows on the atomic plane of the other metal, lattice mismatch emerges in the interface layer. As

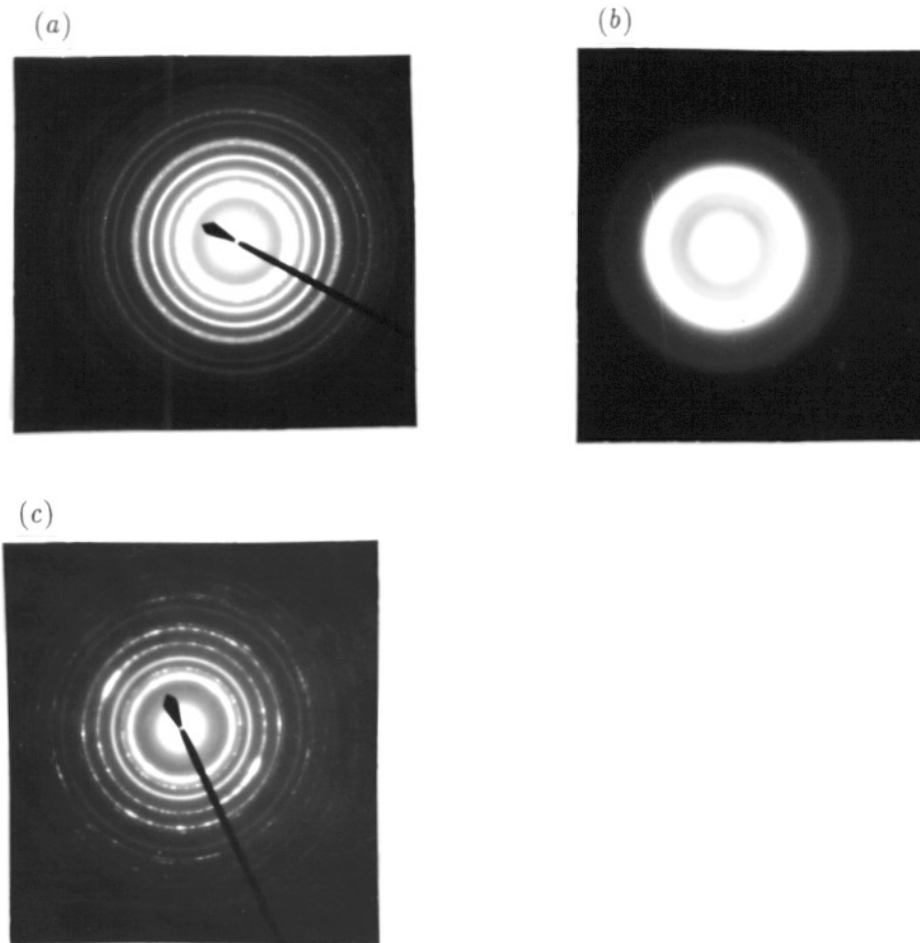


Figure 4. SAD patterns of the $Y_{50}Mo_{50}$ multilayered films with 18 interfaces: (a) as deposited; (b) amorphized at 350 °C for 2 h; (c) recrystallized at 650 °C.

a consequence, there are two contributions to the interfacial free energy if the entropy term is neglected. One is the elastic term of a positive sign due to the lattice mismatch; the other is the chemical term with the same sign as that of the heat of mixing [10]. For the systems with negative heats of mixing, the interfaces have small excess free energy as the signs of the elastic and chemical terms are opposite. The influence of the interfaces is then only a small change of the driving force. However, for the systems with positive heats of mixing, both the elastic and chemical terms are positive in sign and, if the atomic size mismatch of the constituent metals is large enough, the interfacial free energy can surpass that of the amorphous state by artificially increasing the fraction of interfacial atoms, as demonstrated above in a representative Y–Mo system.

In conclusion, the above results demonstrate that a large negative heat of mixing is not a necessary condition for vitrification in metal–metal multilayered films and that vitrification has indeed been achieved in a system of small positive heat of mixing, i.e. the Y–Mo system; this was driven by the excess interfacial free energy. Our calculation shows that

a large atomic size mismatch is of importance, which not only makes it possible for fast diffusion of one metal species into its partner but also determines the sign and size of the excess free energy in the interfaces.

This project is supported in part by the National Natural Science Foundation of China. Financial aid from the Fundamental Research Foundation of Tsinghua University is also acknowledged.

References

- [1] Duwez P, Williens R H and Klement W 1960 *J. Appl. Phys.* **31** 1136
- [2] Buckel W and Hilsch R 1954 *Z. Phys.* **138** 109
- [3] Blatter A and Allmen M V 1985 *Phys. Rev. Lett.* **54** 2103
- [4] Liu B X, Johnson W L, Nicolet M A and Lau S S 1983 *Appl. Phys. Lett.* **42** 45
- [5] Schwarz R B and Johnson W L 1983 *Phys. Rev. Lett.* **51** 415
- [6] Johnson W L 1986 *Prog. Mater. Sci.* **30** 81
- [7] Clemens B M, Johnson W L and Schwarz R B 1984 *J. Non-Cryst. Solids* **61 & 62** 817
- [8] Miedema A R, de Chatel P F and de Boer F R 1980 *Physica B* **100** 1
- [9] Alonso J A, Gallego L J and Lopez J M 1988 *Phil. Mag. A* **58** 79
- [10] de Boer F R, Boom R, Matter W C M, Miedema A R and Niessen A K 1988 *Cohesion in Metals: Transition Metal Alloys* (Amsterdam: North-Holland) ch 2, 4
- [11] Cui F Z, Fan Y D, Wang Y, Verdenberg A M, Draaisma H J G and Xu R 1990 *J. Appl. Phys.* **68** 701