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1996 J. Phys.: Condens. Matter 8 L79

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LETTER TO THE EDITOR

Interface enhanced glass forming ability under ion mixing/solid-state reaction in an immiscible Hf–Ta system

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Received 18 October 1995

Abstract. Hf–Ta multilayered films were designed to consist of a total of six layers which added enough interfacial free energy to elevate the initial energetic level of the films to surpass that of the amorphous state. In these multilayered films, amorphization was indeed achieved by room-temperature 200 keV xenon ion irradiation, as well as by room-temperature aging, in a broad composition range from Hf₂₆Ta₇₄ to Hf₉₀Ta₁₀, showing a significant enhancement of the glass forming ability by the interfaces. Moreover, an Hf₂₆Ta₇₄ amorphous alloy was also obtained by thermal annealing of the multilayered films at 315 °C for 3 h.

Ion mixing, employed as a powerful means to study metastable alloy phase formation and glass forming ability of metal systems, has been flourishing since the 1980s [1, 2]. To date, more than 70 binary metal systems have been investigated, most of which feature negative heat of formation (ΔH_f) characteristics. From 1983 on, solid-state reaction (SSR) has also been developed to form amorphous alloys [3] between pairs of metals that have a large negative ΔH_f . It is commonly considered that metastable phases, especially the amorphous phase, are relatively easily formed in the negative ΔH_f systems, while in the systems with a positive ΔH_f amorphous alloys are just obtainable by conventional glass forming techniques such as liquid melt quenching, etc. Consequently, such positive ΔH_f systems have been less studied and, in a few systems, ion mixing induced amorphization was only achieved in narrow composition regimes [4, 5]; e.g. in the Zr–Nb system, amorphous alloys were obtained by ion mixing in two isolated composition regimes [5]. Meanwhile, the glass forming ability predicted for such positive ΔH_f systems by different authors [6, 7] is still an issue of debate to be further clarified.

Very recently, our studies showed that the interfacial free energy in the multilayers could provide a thermodynamic driving force necessary for forming amorphous alloys in the positive ΔH_f systems. Explicitly speaking, by adjusting the number of layers at a fixed total thickness of the multilayered films, one could increase the fraction of interfacial atoms versus the total atoms in the films and therefore elevate the multilayered films to a higher energetic level than that of the amorphous state in a certain composition regime or even over the entire composition range [8], indicating the possibility of producing amorphous alloys with flexible chosen composition in positive ΔH_f systems through interface design.

In the present study, the Hf–Ta system with a positive ΔH_f of +4 kJ mol⁻¹ was selected to study the glass forming ability under ion mixing and SSR as a natural continuity of our previous study of the Zr–Nb system. As the Hf–Ta system has a less positive heat of formation than that of the Zr–Nb system (+6 kJ mol⁻¹), it was thought possible to form amorphous alloys in a broader composition range.

On the basis of the model of Miedema *et al* [9] and the method proposed by Alonso *et al* [10], a thermodynamic calculation was carried out for the Hf-Ta system and a free energy diagram was accordingly constructed, in which the free energy curves of amorphous phase and the as-deposited multilayered films (a total of six layers with Ta as the top layer) including excess interfacial free energy were included. Figure 1 shows the calculated free energy diagram together with the corresponding equilibrium phase diagram of the Hf-Ta system for easy reading.

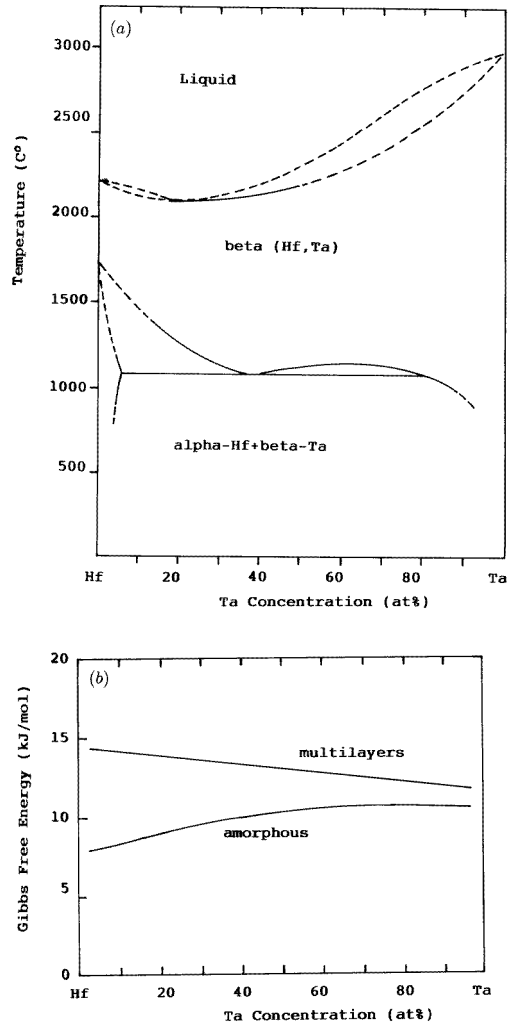


Figure 1. (a) The equilibrium phase diagram of the Hf-Ta system. (b) The calculated free energy diagram of the Hf-Ta system, including the free energy curves of the amorphous phase and the as-deposited multilayered films in which six layers were included.

One sees clearly that, in the Hf-Ta system, a total number of six layers already elevates the energetic level of the multilayers to be higher than that of the amorphous state in the entire composition range. For details of the calculation, the readers are referred to our recent publications [8, 11].

The Hf–Ta multilayered films were accordingly prepared by depositing alternately three layers of pure Hf (99.9%) and three layers of pure Ta (99.9%) onto NaCl single-crystal substrates in an electron-gun evaporation system with a vacuum level of the order of 10^{-5} Pa. The total thickness of the films was about 40 nm, which approximately corresponded to the projected range plus projected range straggling of the irradiation ions, i.e. 200 keV xenon ions. The thickness of each layer varied according to the desired composition. As-deposited films were then irradiated at room temperature in an implanter by 200 keV xenon ions to doses from 5×10^{14} to 7×10^{15} Xe^+ cm^{-2} . The vacuum level during irradiation was better than 5×10^{-4} Pa and the ion current density was less than $1 \mu\text{A cm}^{-2}$ to minimize the heating effect. Some multilayered films were subjected to room-temperature aging or thermal annealing. The real compositions of the deposited films were confirmed by wave dispersive spectroscopy (WDS), which has an experimental error of 5%. As-deposited and treated samples were investigated by transmission electron microscopy (TEM) observations and selected area diffraction (SAD) to identify the structure of the resultant phases.

Table 1. WDS determined compositions and ion mixing amorphization in the Hf–Ta multilayered films induced by room-temperature 200 keV xenon ions at a dose of 5×10^{15} Xe^+ cm^{-2} .

	Hf ₂₆ Ta ₇₄	Hf ₃₀ Ta ₇₀	Hf ₄₇ Ta ₅₃	Hf ₅₆ Ta ₄₄	Hf ₇₈ Ta ₂₂	Hf ₉₀ Ta ₁₀
Amorphization	Yes	Yes	Yes	Yes	Yes	Yes

Table 1 lists the WDS determined compositions of the prepared multilayered films and ion mixing results of the amorphization in the films. As indicated in the table, all six samples with the compositions ranging from Hf₂₆Ta₇₄ to Hf₉₀Ta₁₀ were completely amorphized by ion irradiation to a dose of 5×10^{15} Xe^+ cm^{-2} .

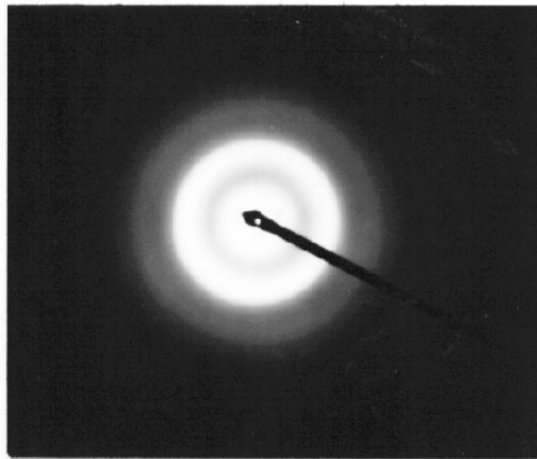


Figure 2. A typical SAD pattern of the obtained amorphous phase in the Hf–Ta system.

Figure 2 shows a typical SAD pattern of an ion mixed amorphous phase. These results indicate that in the Hf–Ta system, even with a positive ΔH_f , the composition range favouring amorphization can be quite broad when the thermodynamic condition is satisfied by including enough interfaces in the multilayered films.

To test the increase of the free energy by the interface in the multilayered films, the

as-deposited Hf–Ta multilayered films were subjected to room-temperature aging and re-examined by TEM each time. It was found that after 6 months, all the films became completely amorphous as evidenced by two or three halos emerging in the SAD patterns. Furthermore, after deposition, one of the Hf₂₆Ta₇₄ samples was immediately put into a furnace for thermal annealing. The vacuum level of the furnace was better than 3×10^{-4} Pa. It was found that after 3 h annealing at 315 °C a unique amorphous phase was also formed. These results confirmed that the interface played an important role in alloying behaviour in a positive ΔH_f system and that the interface greatly enhanced the glass forming ability in this Hf–Ta system.

It should be pointed out that besides the thermodynamic factor discussed above, kinetics is also, by any means, a critical factor for amorphization. As pointed out by Liu in 1986, the amorphous phase is favoured in the two-phase region in the equilibrium phase diagram owing to the frustration of crystallization resulting from the competition of two crystalline phases [12]. In other words, the alloy composition chosen for forming the amorphous alloy should avoid competing with the corresponding simple structured crystalline phase. Accordingly, Liu proposed, a little later, an intrinsic parameter to be a measure of glass forming ability, i.e. MPAR (maximum possible amorphization range) [7], which was defined as 100% minus the maximum solid solubilities observed from the equilibrium phase diagram, suggesting to avoid choosing the alloy composition located within the solid solution region as a solid solution is always of simple structure. Two extreme examples are systems with a continuous solid solution phase diagram and an immiscible system, which have MPAR = 0 and MPAR \approx 100%, respectively. Since the Hf–Ta system is an immiscible one, one can imagine that in terms of kinetics, the amorphous alloy is likely to be formed in a broad composition range, within which there exists no simple structured crystalline phase to compete against amorphization. Consequently, for the positive ΔH_f systems, which have often small solid solubilities, when the thermodynamic condition for amorphization is satisfied by providing enough interfacial free energy in the multilayered films, it is possible to produce the amorphous alloy in a broad composition range by ion mixing or thermal interdiffusion, which has been demonstrated by the experimental results obtained in the Hf–Ta system.

The authors are grateful to the researchers of the TEM Laboratory of Peking University and the Analysis Centre of Tsinghua University for their help. Financial support from the National Natural Science Foundation of China and funding support from Tsinghua University are also appreciated.

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