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Structural difference rule for amorphous alloy formation by ion mixing

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We formulate a rule which establishes a sufficient condition that an amorphous binary alloy will be formed by ion mixing of multilayered samples when the two constituent metals are of different crystalline structure, regardless of their atomic sizes and electronegativities. The rule is supported by the experimental results we have obtained on six selected binary metal systems, as well as by the previous data reported in the literature. The amorphization mechanism is discussed in terms of the competition between two different structures resulting in frustration of the crystallization process.

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It is now established that ion mixing (IM) is well suited to form metastable materials with either crystalline (MX phase) or noncrystalline (amorphous phase) structures. Typically, the experiment consists of first depositing very thin (~ 100 Å) layers of two different metals in alternating sequence on an inert substrate to a total thickness of about 1000 Å. The overall atomic composition ratio is fixed by the thicknesses of the individual layers. This multilayered sample is then irradiated at room temperature or below by inert ions of a range that is commensurate with the thickness of the layer (typically Xe of several 100 keV), and to doses ranging from 10^{15} to 10^{16} ion/cm². Results on IM of binary metal systems have so far been reported on eight combinations, all involving transition metals only. Summarizing the experimental observations, it is found that (i) mixing takes place in each system, (ii) MX phases form in almost every system and typically have the structure of one of the parent metal phases, and (iii) no amorphous phase has been observed in those systems where the two constituent metals have the same crystalline structure (e.g., Au-Ni,¹ Ag-Cu,² and Ag-Ni³), while amorphous alloys were formed in those systems where two metals have different structures (e.g., Au-V,¹ Cu-

Ta,⁴ and Au-Co¹). This observation strongly suggests that a structural difference between the constituent metals plays an important role in ion-induced amorphization.

From a metallurgical point of view, in addition to the structure, atomic size and electronegativity of the constituent metals are the main factors which determine the character of an alloy phase. It is generally accepted that small differences in size and electronegativity favor solid solutions (Hume-Rothery rule), while large differences in these two parameters favor amorphous phases.⁵ We have therefore undertaken to investigate in particular whether structural difference in the parent elements dominates over these other two factors in producing amorphous materials. As most of the metals form in one of the three main structures, bcc, fcc, and hcp, six systems were selected to cover all the three different combinations among these three structures. Additionally, some systems were chosen to have almost identical atomic size, Al-Nb, Mo-Ru, and Ti-Au, or identical electronegativity, Ni-Mo and Mo-Co (see Table I).

Once a system was selected, the appropriate composition for forming an amorphous phase by IM remained to be chosen. It has been established that if the entire composition of the multilayered sample is close to either side of the phase diagram, IM tends to form a supersaturated solid solution (MX phase).¹ It is also possible that an equilibrium com-

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TABLE I. Amorphous alloys formed by room temperature, 300-keV Xe⁺ ion mixing in the selected binary metal systems.

Binary system with different structures	fcc-bcc				bcc-hcp				hcp-fcc			
	Ni-Mo		Al-Nb		Mo-Co		Mo-Ru		Ti-Au		Ti-Ni	
Atomic size $r(\text{\AA})$ and $\frac{\Delta r}{r^*}$	1.24	1.39	1.43	1.46	1.39	1.25	1.39	1.34	1.47	1.46	1.47	1.24
Electronegativity n and $\frac{\Delta n}{n^*}$	1.8	1.8	1.5	1.6	1.8	1.8	1.8	2.2	1.5	2.4	1.5	1.8
Amorphous alloys formed by IM	Ni ₆₅ Mo ₃₅		Al ₅₅ Nb ₄₅		Co ₆₅ Mo ₃₅		Mo ₅₅ Ru ₄₅		Ti ₆₅ Au ₃₅		Ti ₅₀ Ni ₅₀	
	Ni ₅₀ Mo ₅₀				Co ₃₅ Mo ₆₅				Ti ₄₀ Au ₆₀			
	Ni ₁₅ Mo ₆₅											

Note: the larger r and n are used for reference.

pound would be formed by IM if the overall composition is close to that of the compound. An appropriate choice of composition for amorphous alloy formation is therefore away from the pure metals and from equilibrium compound compositions. Accordingly, most of the compositions chosen in this study are those which lie within the two-phase regions of the phase diagrams.

The experimental procedure in this study is similar to that described above. Xenon ions of 300 keV were chosen for irradiation because of their high mass, hence high efficiency in inducing atomic mixing.⁷ The samples were all irradiated at room temperature to doses ranging from 2×10^{14} – 2×10^{16} Xe/cm². Some samples were preannealed, followed by irradiation, to check the effect of the presence of equilibrium compounds on amorphization. All the samples were analyzed by MeV ⁴He⁺ backscattering spectrometry (BS), x-ray diffraction (Read camera), and four-point probe resistivity measurements.

Some ten amorphous alloys have been obtained by IM (see Table I). The amorphous structure was identified by a diffuse band (or halo) on the x-ray diffraction pattern. The resistivities of the mixed films are on the order of 130–320 $\mu\Omega$ cm, which is higher than those expected of crystalline binary alloys, hence lending support to the x-ray data that the films are amorphous.

The formation of the amorphous alloys in all of the above selected systems clearly demonstrates that the structural difference of the constituent metals plays the key role in ion-induced amorphization and that atomic size and electronegativity effects are minor. It therefore leads us to formulate a rule that an amorphous binary alloy will be formed by ion mixing of multilayered samples when the two constituent metals are of different crystalline structure. We propose to call this the “structural difference rule for amorphous alloy formation” by ion mixing. The experimental evidence presented here allows only the conclusion that the rule is a sufficient condition to assure the formation of an amorphous phase by ion mixing; in fact, cases are known

where binaries of similar structure do form amorphous phases (e.g., Au-Pb, both fcc).

To check the effect of the presence of equilibrium compound on amorphization, one multilayered sample of Ti₆₅Au₃₅ (between neighboring equilibrium compounds Ti₃Au and TiAu) was preannealed at 600 °C for 1 h and Ti₃Au and TiAu were formed as revealed by x-ray diffraction pattern. The preannealed and as-deposited samples were then irradiated at room temperature to the same dose of 5×10^{15} Xe/cm². Amorphous alloys were formed in both cases. This indicates that the presence of equilibrium compounds does not prevent the amorphous alloy formation by IM in this system. However, it has been reported⁸ that in the Fe-W system, if the Fe₇W₆ compound is formed first by preannealing, its presence will hinder the subsequent amorphous alloy formation by IM. The presence of an equilibrium compound therefore varies in its effect from system to system.

The experimental evidence offered thus far in support of the structural difference rule for the formation of amorphous alloys includes the metals with bcc, fcc, and hcp, crystal structures, and the process of IM. Available experimental evidence indicates that the rule is valid beyond these specific conditions. Multilayered samples combining Si (diamond-type fcc) with Au (fcc) up to 70 at % of Au^{9,10}, Mo (bcc) in Mo₅₀Si₅₀ composition,¹¹ and Ru (hcp) in Ru₄₅Si₅₅ composition¹¹ also produced amorphous layers upon Xe irradiation. Ge₈₀Au₂₀ and Ge₆₀Au₄₀ multilayers were also found to amorphize, although the layers recrystallize within a few days at room temperature.¹² It therefore appears that the rule extends at least in part to the diamond lattice structure as well. The case of Si-Ge is exceptional, however, in that these covalently bonded elements can be amorphized already in their elemental form, so that their combination is expected to form amorphous, not polycrystalline films. A recent study of the Fe-W system shows that rf sputtering is capable of producing amorphous layers over a more extended range of composition than IM does.¹³ A study of the

Pt-Si system¹⁴ indicates that vapor quenching of the two elements produces amorphous layers whose properties are altered little upon subsequent irradiation. We therefore believe that the structural difference rule may be useful as well as a guide to the synthesis of amorphous materials by processes other than IM.

We believe that the structural difference rule is closely related to the eutectic criteria for amorphous phase formation first introduced by Turnbull.^{15,16} The simple eutectic phase diagram is formed between two metals (call them *A* and *B*) having a different structure and no intermediate equilibrium compounds. In the two-phase portion of such a phase diagram, any single phase crystalline form of the alloy has a higher free energy than the two-phase equilibrium alloy. Ion mixing of multilayers tends to produce mutual dissolution of the *A* and *B* layers with the composition of each layer gradually moving toward the average composition of the multilayer. Beyond the equilibrium solubility limit of *B* in *A* (for example), the *A* layer (with the structure of pure *A*) becomes metastable. As the *B* concentration further increases, the free energy of the metastable *A* solution rises above that of the equilibrium two-phase material. But the formation of the two equilibrium phases requires nucleation of the *B* phase in the *A* layer. Under conditions of restricted kinetics (ion mixing at suitably low temperatures), the diffusion of *B* atoms required cannot occur. In contrast, the transition to the amorphous state is polymorphic (involves no change in composition) and thus becomes kinetically favored. Viewed in this light, the structural difference rule then formulates conditions where free energy and kinetic considerations favor glass formation. These conditions may occur equally well between two adjacent crystalline phases of any structure in a binary phase diagram. We thus surmise that the structural difference rule will apply also between adjacent equilibrium phases with a phase diagram that are not necessarily the terminal elements. For example, formation of amorphous Zr₁₀Co₉₀ (Ref. 17) and Zr₇₅Co₂₅ (Ref 18) by liquid quenching can be explained in this fashion; Zr and Co are both hcp, but the equilibrium phase diagram is divided into many two-phase regions by several intermetallic compounds. Amorphous Zr₁₀Co₉₀ lies between Co and ZrCo₄ (complex fcc)¹⁹ and Zr₇₅Co₂₅ lies between Zr and Zr₂Co (bc tetragonal).²⁰

According to this view, it is basically the competition between two different structures that results in frustration of the crystallization process and an amorphous phase is ob-

tained.

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