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J. A. Alonso^{ab}, R. Hojvat de Tendler^{cd}

^a Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, Valladolid, Spain ^b

Donostia International Physics Center, Spain ^c Departamento de Ciencias Básicas y Experimentales,

Universidad Nacional del Noroeste de la Provincia de Buenos Aires, Argentina ^d Facultad de Ciencia y

Tecnología, Universidad del Salvador, Argentina

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Mechanism of amorphisation in Cu–Ru, a binary alloy with a positive heat of mixing

J.A. Alonso^{ab*} and R. Hojvat de Tendler^{cd}

^aDepartamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, Valladolid, Spain; ^bDonostia International Physics Center, San Sebastián, Spain; ^cDepartamento de Ciencias Básicas y Experimentales, Universidad Nacional del Noroeste de la Provincia de Buenos Aires, Junín, Provincia de Buenos Aires, Argentina; ^dFacultad de Ciencia y Tecnología, Universidad del Salvador, Buenos Aires, Argentina

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Cu–Ru has a positive heat of formation and does not form equilibrium alloys. Nevertheless, amorphous alloys have been obtained by He (Phys. Rev. B **75**, 045431 (2007)) by ion mixing of multilayers. Analysis of the free energies of the competing phases (the glass and the crystalline solid solutions based on Cu and Ru) leads us to propose that formation of glasses occurs as a result of kinetic frustration between the hcp and fcc solid solutions. These two have lower free energies than the glass, but those free energies are very similar, so a strong driving force for the formation of a particular crystalline phase does not exist. In addition, formation and growth of hcp and the fcc phases appears equally difficult from a kinetic point of view. Very small embryos can form but their growth will be frustrated by the presence of embryos of the other phase.

Keywords: metallic alloys; glass; copper; ruthenium

Copper and ruthenium metals do not mix, that is, these two metals do not form crystalline solid solutions or intermetallic compounds [1,2]. The semiempirical model of Miedema [2] predicts for the equiatomic Cu–Ru alloy a positive heat of formation of 7 kJ mol^{-1} , a value consistent with the absence of crystalline phases. Motivated by the interest in using Ruthenium as a diffusion barrier for Copper in microelectronic circuits, He *et al.* [3] have studied experimentally and theoretically the interfacial reaction and the formation of metastable phases in the Cu–Ru system. Those experiments employed the technique of ion beam mixing (IBM) of thin multilayers. In spite of the positive heat of formation of the alloy, the irradiation by inert gas ions in the IBM technique achieves the intermixing of the two metals and the formation of metastable Cu–Ru amorphous alloys. The reason (although not the mechanism, that will be discussed later) can be understood from Figure 1. We have recalculated the Gibbs free energies of a number of phases of interest for the present discussion, and the results are plotted in Figure 1. The pure Cu and Ru solid metals are taken as the zero of energies.

In the experiment [3], the multilayers are irradiated with a beam of energetic 200 keV Xe^+ ions. The travel of these ions through the system gives rise to collision cascades that displace many Cu and Ru atoms from their original positions and force their intermixing,

*Corresponding author. Email: jaalonso@fta.uva.es

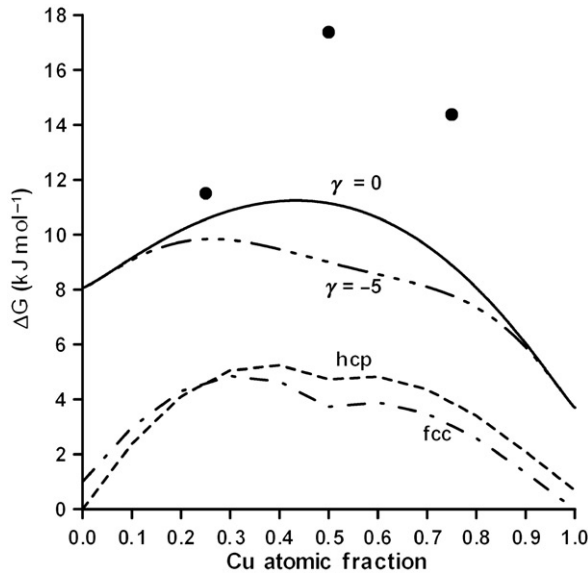


Figure 1. Calculated Gibbs free energies of amorphous and crystalline $\text{Cu}_x\text{Ru}_{1-x}$ solid solutions (hcp and fcc) at 300 K, as a function of the Cu concentration. Two values, $\gamma=0$ and $\gamma=-5$, are taken for the parameter γ of Equation (4) giving the chemical short-range order of the amorphous alloy. Pure Cu and Ru are taken as zero of energies. The black circles are the free energies of systems of Cu–Ru multilayers before irradiation.

producing a hot disordered state. This disordered state cools down very fast with limited local atomic rearrangements and the system is finally quenched in a relaxed state which corresponds to a local minimum of the potential energy hypersurface in the configurational space. Those local potential energy minima which are easy to reach from the hot disordered state represent the competitive phases. The usual competitive phases in methods like IBM are the amorphous alloy and the substitutional solid solutions based on one of the metals. Thermodynamics can be used provided that only those phases are considered whose formation is allowed under the restricted kinetics of the fast quenching methods. Our task is then to calculate and compare the free energies of the competitive phases. The Gibbs free energies of formation of the amorphous alloy and of the substitutional hcp and fcc solid solutions (based on the hcp structure of Ru and the fcc structure of Cu, respectively) are calculated as

$$\Delta G = \Delta H - T\Delta S, \quad (1)$$

where T is the temperature, and ΔH and ΔS are the enthalpy and the entropy of formation, respectively. For ΔS we have used the ideal solution model [4].

The enthalpy of formation of the substitutional solid solutions is the sum of three terms [2,5]

$$\Delta H_{\text{sol}} = \Delta H^{\text{chem}} + \Delta H^{\text{el}} + \Delta H^{\text{str}}. \quad (2)$$

The chemical contribution ΔH^{chem} arises in the model of Miedema from the electronic redistribution near the boundary of the atomic cells in the alloy [2,6].

For a Copper-based alloy, it has the expression (a similar expression holds for a Ruthenium-based alloy)

$$\Delta H^{\text{chem}} = X_{\text{Ru}}(V_{\text{Ru}}(\text{alloy}))^{2/3}f(X_{\text{Ru}}, X_{\text{Cu}})\Delta H^{\text{amp}}, \quad (3)$$

where ΔH^{amp} is an amplitude reflecting the magnitude of the chemical interaction, $V_{\text{Ru}}(\text{alloy})$ is the effective molar volume of Ru in the alloy, and $f(X_{\text{Ru}}, X_{\text{Cu}})$ is a function of the concentrations that accounts for the degree of chemical short-range order. The expression

$$f(X_{\text{Ru}}, X_{\text{Cu}}) = X_{\text{Ru}}^s \left[1 + \gamma (X_{\text{Ru}}^s X_{\text{Cu}}^s)^2 \right], \quad (4)$$

proposed by de Boer *et al.* [2] and Niessen *et al.* [6], describes the degree of chemical short-range order through the parameter γ . The value $\gamma=0$ is appropriate for random solid solutions, and $\gamma=8$ for fully ordered alloys. Intermediate degrees of short-range order have been simulated [7] with intermediate values of γ . The superscript s in the concentrations indicates that X_{Cu}^s and X_{Ru}^s are atomic cell surface area concentrations, that is, the fraction of all cell surface areas for a given species. These are

$$X_{\text{Ru}}^s = \frac{X_{\text{Ru}} V_{\text{Ru}}^{2/3}}{X_{\text{Ru}} V_{\text{Ru}}^{2/3} + (1 - X_{\text{Ru}}) V_{\text{Cu}}^{2/3}} \quad (5)$$

with a similar expression for X_{Cu}^s . V_{Ru} and V_{Cu} are the molar volumes of Ru and Cu, respectively. Atomic cell surface area concentrations appear in the theory because the electronic redistribution giving rise to ΔH^{chem} occurs as a result of mismatch effects (mismatch of chemical potentials and mismatch of the electron densities) at the boundary of the atomic cells, and the magnitude of those effects is proportional to the total area of contact between Ru and Cu atomic cells. The elastic term ΔH^{el} in Equation (2) accounts for the atomic size mismatch between the solute and the solvent metals in the substitutional solid solution alloy [8], and the structural term ΔH^{str} is due to the different stabilities of the hcp, fcc and bcc structures of transition metals as a function of the number of valence electrons [2,9].

The enthalpy of formation of the amorphous alloy, ΔH_{glass} , only contains the chemical term ΔH^{chem} . The elastic term ΔH^{el} is important for the substitutional solid solutions, but is negligible for the amorphous alloys because the amorphous structure lacks long-range order and, consequently, the atoms are not constrained to fit a fixed volume in a specific structure [4]. Atomic size misfit affects indirectly the glass-forming range through the competition between the free energies of the amorphous and substitutional solid solution phases. That is, a large atomic size mismatch affects negatively the formation of substitutional solid solutions. However, the point we stress here is that there is no direct elastic contribution to ΔH_{glass} .

In order to compare the Gibbs free energies of the solid solutions and the amorphous alloys, ΔG_{sol} and ΔG_{glass} , respectively, the free energy difference between the amorphous and the crystalline states of the pure component metals has to be added to ΔG_{glass} because the crystalline solid metals are taken as the reference state [4,10]. A full explanation of the different terms can be found in the references cited above. Here it is enough to show the results for the Cu–Ru alloy in Figure 1, where the free energies of the amorphous alloy and of the fcc and hcp solid solutions have been plotted and compared. The free energy of the

amorphous alloy has been calculated for two models. One of the curves corresponds to the use of $\gamma = 0$ in Equation (4), assuming ideal short-range chemical disorder. However, in an alloy with a positive heat of formation, like Cu–Ru, the tendency for segregation is strong and one can expect an enhanced number of Cu–Cu and Ru–Ru nearest neighbour pairs (and less Cu–Ru contacts). Consequently, we propose to simulate this segregation tendency by giving a negative value to γ . A curve has been plotted for $\gamma = -5$ and, evidently, ΔG_{glass} is less positive. One can see in Figure 1 that the free energies of the different alloy phases are higher (more positive) than the free energy of the reference system formed by the two separated bulk metals. In other words, it is not possible to form equilibrium Cu–Ru alloys. However, the experiments of He *et al.* [3] were performed by starting with a multilayer configuration of alternating Ru and Cu thin films. In this case, the mismatch between the surfaces of two different metals produces a positive energy contribution that displaces the free energy of the starting unmixed multilayer state from the zero line of Figure 1 (upwards) [3,11–13], rendering the unmixed multilayer configuration highly unstable.

He *et al.* [3] irradiated Cu–Ru multilayers formed by alternating thin Ru and Cu layers with 200 keV Xe⁺ ions. The multilayer films had a number of metal layers between 9 and 18 and the total thickness of the system was around 45 nm. We have calculated the free energy of the multilayers as in ref. [13]. The interfacial free energy of the multilayer system is given by

$$\Delta G_{\text{multilayers}} = \xi \Delta G_{\text{interface}}, \quad (6)$$

where $\Delta G_{\text{interface}}$, the interfacial free energy between the surfaces of the two solid metals in contact, contains lattice mismatch and chemical interaction contributions [11–13], and the parameter ξ gives an account of the fraction of interfacial atoms in the multilayer system. ξ depends on the number and thickness of the layers, and on the thickness $\delta = \delta_{\text{Cu}} + \delta_{\text{Ru}}$ assigned to the Cu–Ru interfaces. A reasonable election for perfect surfaces would be to take for δ_{Cu} and δ_{Ru} the interplanar distances in the pure Cu and Ru metals. This gives a value $\delta = 0.7$ nm, but to allow for the existence of surface imperfections, defects, terraces, etc, we take $\delta = 1$ nm. The three filled circles represented in Figure 1 correspond to concentrations $X_{\text{Cu}} = 0.25, 0.5$ and 0.75 , and a total number of layers $N = 9, 12$ and 13 , respectively, in the multilayer film. A point worth to be noticed is that the total thickness of the multilayer system, around 45 nm, was designed to match the range of the irradiating ions. This means that practically all the Xe⁺ ions go through the multilayers and leave the system from the opposite side. Consequently, gaseous inclusions that might form in thicker samples are not present in this case.

The free energy difference between the starting multilayer films and the various metastable phases shown in Figure 1 provides the thermodynamic driving force for the structural phase transformations of the system under ion irradiation. The experiments of He *et al.* [3] were performed for multilayers corresponding to overall atomic concentrations Cu₂₅Ru₇₅, Cu₅₀Ru₅₀ and Cu₇₅Ru₂₅. In the three cases, amorphous phases were obtained for irradiation doses of 1×10^{15} Xe⁺/cm², 8×10^{14} Xe⁺/cm² and 5×10^{14} Xe⁺/cm², respectively. These results can be understood from the free energy diagram of Figure 1, because the free energies of the glasses are below the free energies of the multilayers. In addition, He *et al.* performed molecular dynamics simulations of the interfacial solid state reaction in Ru–Cu sandwiches using interatomic many-body potentials based on the tight-binding theory [14]. The molecular dynamics simulations at a

temperature of 300 K produced solid state amorphisation that confirms the amorphisation observed in the IBM experiments.

There is, however, an important point that He *et al.* have not discussed in their article. By observing the free energies of the different phases in Figure 1 one can notice that the free energy curves of the crystalline hcp and fcc solid solutions are below the free energies of the glass. The free energy differences between the starting unmixed multilayers and the fcc and hcp solid solutions are 13.7 and 12.6 kJ mol⁻¹ at a concentration $X_{\text{Cu}} = 0.5$, and at the same concentration the free energy differences between the multilayers and the glass are smaller, namely 6.2 and 8.4 kJ mol⁻¹ for the two models of glass (with $\gamma = 0$ and $\gamma = -5$, respectively). Similar conclusions are obtained for other concentrations. Consequently, one could expect that both the IBM experiments and the molecular dynamics simulations would preferentially produce the substitutional solid solution phases, instead of the glass, because the thermodynamic driving force is stronger. It is well-known that the substitutional solid solutions are the main competitors of the amorphous phase in fast quenching methods applied to normal binary alloys, that is, alloys with negative heats of formation [4,10,15]. In those alloys, formation of substitutional solid solutions in regions near the ends of the concentration range, that is, at concentrations substantially rich in one component, restrict the formation of amorphous alloys in those particular regions. The reason is that at those compositions the free energy of the substitutional solid solution based on the structure of one of the metals is more negative than the free energy of the glass and, consequently, the thermodynamic driving force for the formation of the solid solution is stronger. Turning to Cu–Ru, Figure 1 shows that the substitutional solid solutions have lower free energies than the glass in the whole concentration range (the free energy differences are large, $\sim 6\text{--}8$ kJ mol⁻¹). So, the thermodynamic driving force for the formation of metastable solid solutions is there, and formation of solid solutions of Cu in Ru, or Ru in Cu, appears feasible.

Turning to kinetics, we first notice that the starting multilayer configuration contains thin films of the pure metals, hcp Ru and fcc Cu. Although thermal diffusion of one metal into the other is slow [16], the molecular dynamics simulations of the thermal annealing of the Cu–Ru multilayers performed by He *et al.* [3] show that some diffusion occurs at the interfaces between the two metals. On the other hand, the IBM irradiation of the multilayers forces the intermixing between Ru and Cu. Consequently, the formation of small local regions (embryos) with the structure of the hcp or fcc solid solutions following the relaxation of the hot disordered mixture induced by the IBM collision cascades should not be too difficult. The reason is that the fcc and hcp are the simplest crystal structures, and limited local atomic relaxations and simple diffusion processes may produce the compact fcc or hcp structures. However, the observed fact is that the substitutional fcc or hcp solid solutions do not form in the experiment. Our purpose is to propose a plausible mechanism for the formation of the glass instead of the solid solutions.

One of the ingredients is to notice that the free energies of the two solid solutions, hcp and fcc, are very similar, with differences smaller than 1 kJ mol⁻¹ (in particular, the free energies of the hcp and fcc phases are equal at 25 atomic % Cu). Those differences are very small compared to the large differences between the free energies of the starting unmixed multilayers and the free energies of the fcc and hcp solid solutions. This indicates that the thermodynamic driving forces for the formation of the hcp and fcc solid solutions are nearly equal, with the net result that a dominant driving force for the formation of a preferred phase does not exist. The other ingredient, more important, is based on

considering the kinetics of the formation of the hcp and fcc solid solutions. The hcp and fcc are the simplest crystal structures (these are also rather similar, because the nearest neighbours around an atom have the same arrangement). Consequently, nucleation of small local regions (embryos) of each phase is expected under the restricted kinetic conditions of the IBM experiment. Each of those embryos will be formed essentially by one central atom and its first coordination shell of 12 atoms in both the fcc and hcp structures. However, the growth of embryos under the fast quenching conditions of the experiment is very difficult because of two reasons. The first is the fast effective quenching rate. The second reason, even more important in our opinion, is that growth of embryos of one phase becomes frustrated by the presence of competing embryos of the other phase. In summary, we propose that the strong mutual competition between the kinetics of formation and growth of the two solid solution phases, hcp and fcc, frustrates the formation of both and this facilitates the formation of the glass. That is, neither the fcc, nor the hcp phases are able to grow, and the system, experiencing only limited atomic relaxation, becomes arrested in the disordered structure induced by the IBM process.

The case of Ru–Cu is very different compared to the usual formation of glasses in alloys with a negative heat of mixing [4]. When the heat of formation of the alloy with respect to the pure metals is negative (these are the normal alloys), the free energy of the glass is lower than the free energy of the substitutional solid solutions except for concentrations rich in one component (near the concentration ends of the free energy diagram). Consequently, for normal alloys the glass forms by the fast quenching techniques at intermediate concentrations but not near the concentration ends. In contrast, in Figure 1 the free energy of the glass is above that of the solid solutions for all concentrations. The formation of the glass in a situation like that in Figure 1 can only be understood as due to a different mechanism, the mutual frustration of the formation of the two solid solutions.

In conclusion, Cu–Ru is a peculiar alloy with a positive heat of mixing, and we propose that the formation of glasses in the IBM experiments performed by He *et al.* [3] for thin Cu–Ru multilayers arises from the mutual frustration between the hcp and fcc substitutional solid solutions. First of all, these two crystalline solid solutions have lower free energies than the glass. However, the free energies of the fcc and hcp phases are very similar, so a strong thermodynamic driving force favouring one phase over the other does not exist. On the other hand, we expect that nucleation of small local atomic arrangements (embryos formed by one atom and its first coordination shell) with the fcc and hcp structures is possible under the restricted kinetic conditions of the IBM experiment, because those structures are very simple. However, the difficulty for the embryos of one phase to grow would be extreme due to the fast quenching conditions and to the strong competition from embryos of the other phase. The consequence is that the mutual kinetic frustration between the two solid solution phases facilitates the formation of the glass under the restricted kinetic conditions of the IBM experiment.

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