

# Supercooled melting in multicomponent Zr–Al–Cu–Ni diffusion couples

R. Busch,<sup>a)</sup> E. Bakke, and W. L. Johnson

California Institute of Technology, W. M. Keck Laboratory of Engineering Materials, 138-78, Pasadena, California 91125

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Diffusion couples combining a hcp  $Zr_{90}Al_{10}$  supersaturated solid solution with a fcc  $Cu_{64}Ni_{36}$  solid solution were annealed at 410 °C for different times. The reaction at the interface was investigated by transmission electron microscopy and energy dispersive x-ray spectroscopy. The investigations show the formation of a noncrystalline layer at the interface between the two solid solutions that grows to a maximum thickness of more than 0.3  $\mu\text{m}$ . Concentration profiles reveal that two noncrystalline phases coexist in the diffusion couple. One is Ni-rich and was in the amorphous state during the reaction at 410 °C. The other phase is Zr-rich and grew in its supercooled liquid state. This novel supercooled melting process has not been previously observed in a solid state reaction. Kinetic and thermodynamic aspects that contribute to the high thermal stability of the Zr–Al–Ni–Cu in the supercooled liquid are discussed. © 1996 American Institute of Physics. [S0003-6951(96)00821-2]

Amorphous phase formation in diffusion couples that combine an early transition metal like Zr with a late transition metal like Ni, Co, or Fe is a well-known phenomenon and has been extensively studied in the past.<sup>1–5</sup>

Recently, new families of multicomponent glass formers have been discovered which exhibit a much higher glass forming ability than previously known alloys. Cooling rates of less than 100 K/s are usually sufficient to prevent crystallization and form a glassy state in these alloys, which include Zr–Al–Ni,<sup>6</sup> Zr–Al–Cu–Ni,<sup>7</sup> and Zr–Ti–Cu–Ni–Be.<sup>8</sup> Upon reheating above the glass transition, these bulk metallic glass (BMG) formers show a high thermal stability of the supercooled liquid (sliq) with respect to crystallization. The  $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$  alloy, for example, can be heated to about 130 K above the onset of the glass transition with a rate of 40 K/min into the supercooled liquid before crystallization occurs. Under these conditions, the question arises if it is possible to grow a supercooled molten layer of a BMG forming alloy in a solid state reaction. This would not be an amorphization reaction anymore, but a metastable supercooled melting process far below the equilibrium melting point of the respective alloy composition. We will show that metastable supercooled melting is indeed possible if one chooses a suitable diffusion couple which does not consist of elemental layers attached to each other, but of solid solutions.

In this first attempt to study solid state reactions in bulk glass forming multicomponent systems, we start with a (Zr–Al)/(Cu–Ni) diffusion couple. In this case, the two slow diffusing species Zr and Al are combined as a supersaturated hcp solid solution and attached to the fast diffusing components Cu and Ni that consist of a fcc solid solution. It will be shown by transmission electron microscopy (TEM) and energy dispersive x-ray analysis (EDAX), that noncrystalline layers involving more than two components can grow to thicknesses that were thus far not attained.

$Cu_{64}Ni_{36}$  foils were prepared by the piston and anvil

method in a Bühler rapid quencher under high vacuum conditions ( $<10^{-3}$  Pa). Then one foil was attached to each of the two pistons of the rapid quencher and a  $Zr_{90}Al_{10}$  alloy was rapidly quenched in between these two  $Cu_{64}Ni_{36}$  foils, resulting in a trilayer of  $\sim 150$   $\mu\text{m}$  thickness. The trilayers were cold rolled down to a thickness of 15  $\mu\text{m}$ . The samples were annealed for 20 min, 1, 3, and 9 h at 410 °C in 99.999% Ar atmosphere. To produce TEM samples, the trilayers were cut perpendicular to the plane of the layers by thin sectioning microtomy. The specimens were investigated using a Philips-430-TEM. The EDAX analyses were performed in the scanning-TEM mode of the instrument with a probe diameter of 4 nm.

The as-prepared state was investigated by TEM and EDAX analyses (not shown, see Ref. 9). Dark field TEM images of as-prepared samples show that the grain size of the fcc Cu–Ni layer is of the order of 200 nm. The grains in the Zr–Al layer are smaller than 50 nm. The Zr–Al layer consists of a hcp solid solution that is supersaturated with respect to its Al concentration. This follows from x-ray diffraction analyses on separately quenched  $Zr_{90}Al_{10}$  foils, as well as from the diffraction patterns in the TEM. The concentrations in the Cu–Ni and the Zr–Al layer were measured by EDAX analyses. They correspond to the nominal composition of the initial single binary foils.<sup>9</sup>

Annealing of the diffusion couple results in the planar growth of a noncrystalline layer at the interface between the two solid solutions. After 20 min, the thickness of the layer is 180 nm. After 1 h, the overall thickness reaches 300 nm as shown in Fig. 1 by a dark field TEM image. The diffraction pattern clearly reveals the noncrystalline state of the grown layer. The observed noncrystalline layer thickness exceeds those previously obtained in solid state reactions by half an order of magnitude. This enables us to determine the detailed concentration profile across the reacted layer by EDAX analyses.

Figure 2 shows the concentration profile across the noncrystalline layer formed in the solid state reaction after annealing for 1 h at 410 °C. It was constructed from a series of EDAX analyses across the layers while monitoring the loca-

<sup>a)</sup>Electronic mail: busch@hyperfine.caltech.edu

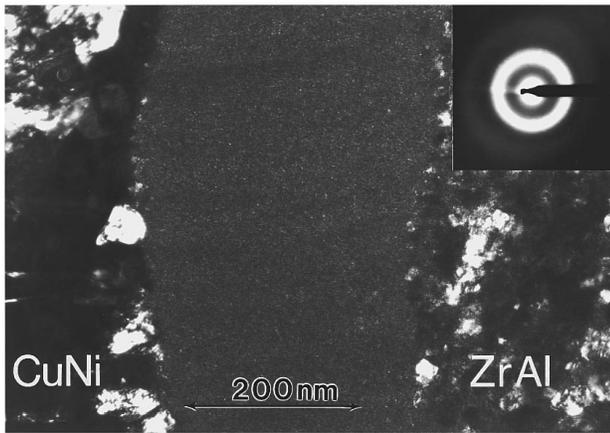


FIG. 1. Dark field TEM image of a diffusion couple that was annealed for 1 h at 410 °C. The diffraction pattern as well as the absence of crystals in the dark field reveal the noncrystalline state of the reacted layer.

tion of the probe in the scanning TEM mode. The concentrations of the elements are cumulatively plotted. The concentration profile reveals that the solid state reaction does not lead to the formation of a Cu-rich noncrystalline alloy as one might have expected from the concentration of the initial Cu–Ni solid solution. The noncrystalline alloy is Cu poor. Ni preferentially diffuses into the layer. In contrast to Cu and Ni, the ratio of Zr and Al stays constant 9/1 throughout the entire layer. The ratio is the same as in the initial Zr–Al solid solution. This indicates that at the reaction temperature, not only the Zr, but also the Al is immobile, which is likely to be a contributing factor to the high resistance of the alloy with respect to crystallization.

From Fig. 2, it is evident that the reacted layer consists of two regions. One is Ni-rich with a relatively small concentration gradient of (Ni+Cu) with respect to (Zr+Al). The other region is Zr-rich, and exhibits a steeper concentration gradient. This observation suggests that two noncrystalline layers coexist in this diffusion experiment.

The measured concentrations throughout the layers were compared with the respective glass transitions that were determined by Inoue and co-workers<sup>10</sup> in the Zr–Ni–Al system. The measured glass transitions in Ref. 10 were determined at a heating rate of 40 K/min in DSC experiments as

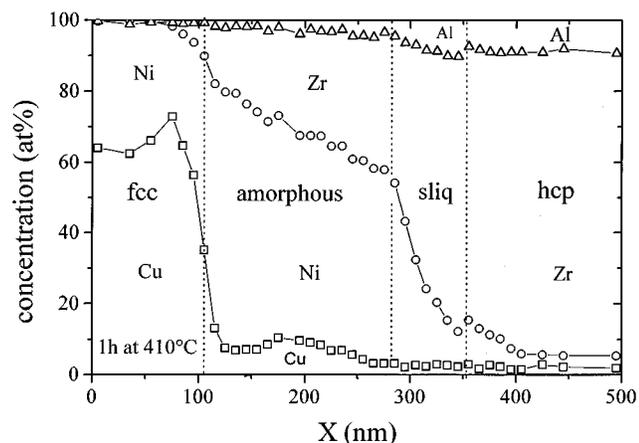


FIG. 2. Concentration profile across the noncrystalline layer formed during annealing of the  $Zr_{90}Al_{10}/Cu_{64}Ni_{36}$  diffusion couple for 1 h at 410 °C.

the onset of the endothermic heat effect. In order to decide if a layer was in the supercooled liquid state when it grew in an isothermal experiment, one has to correct the data by taking the width of the glass transition and the lower glass transition in an isothermal measurement into account. Neglecting the influence of the small Cu concentration which usually decreases the glass transition temperature slightly, for all concentrations of the Zr-rich phase, we find that they were not only above the onset of the glass transition, but well within the supercooled liquid state. We can conclude that in this experiment we observed a metastable supercooled melting process, at least in one part of the formed layer. For the Ni-rich portion, the glass transition temperatures as well as the crystallization temperatures are of the order of 500 °C. This part of the layer was in the amorphous state during the reaction.

The diffusion constants in the Ni-rich (amorphous) layer and the Zr-rich (sliq) layer are different. This is reflected by the different concentration gradients in the layers grew. By assuming that the diffusion coefficients of Zr and Al are much smaller than the diffusion coefficients of Ni and Cu [ $(D_{Zr}, D_{Al}) \ll (D_{Ni}, D_{Cu})$ ] and that the ratio of the diffusion coefficients of Ni and Cu are comparable ( $D_{Ni} \cong D_{Cu}$ ), the diffusion constants for Ni (or Cu) in the two regions can be estimated. In the steady state, the flux  $j$  through the layers is

$$j = D_{Ni}^{am} \frac{\partial c_{Ni}^{am}}{\partial x} = D_{Ni}^{sliq} \frac{\partial c_{Ni}^{sliq}}{\partial x}. \quad (1)$$

Using the ratio of the concentration gradients in the two phases, the ratio of the diffusion constants  $D_{Ni}^{am}/D_{Ni}^{sliq}$  is determined to be four. This means that the diffusion of Ni in the Ni-rich amorphous phase is half an order of magnitude faster than Ni diffusion in the Zr-rich supercooled liquid phase, which leads to faster growth of the amorphous layer compared to the supercooled liquid layer.

Surprisingly, the Ni-rich part of the sample which was amorphous during the reaction exhibits a larger Ni diffusion constant than the Zr-rich part which was already in its supercooled liquid state. This indicates that at the reaction temperature the concentration dependence of the diffusion constant has a larger influence on the diffusion constant than the fact of whether the alloy was above or below the glass transition. In turn, the result indicates that the diffusion of Ni in the Zr-rich portion of the layer, which corresponds to concentrations with good BMG forming ability, is sluggish even though the growth took place in the supercooled liquid state.

Ni diffuses preferentially into the amorphous and supercooled liquid layer compared to Cu (Fig. 2). It is unlikely that very different diffusion constants of Ni and Cu are the reason for this, since it is known that all late transition metals observed in a (Zr)-(late transition metal) reaction have similar diffusion constants (see, for example, Ref. 11). However, there is a thermodynamical reason for the observed behavior that originates from the large difference in the Gibbs free

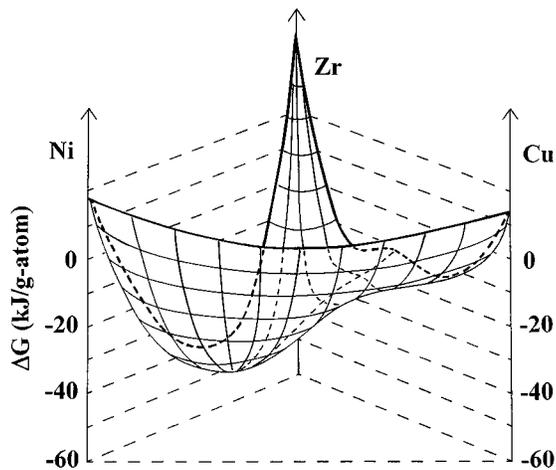


FIG. 3. Schematic Gibbs free energy surface of the supercooled liquid in the ternary Zr–Ni–Cu alloy system at a temperature of 410 °C. The binary Zr–Ni and Zr–Cu curves are drawn according to CALPHAD calculations (Refs. 12 and 13).

energies of mixing of the binary alloys. According to CALPHAD calculations,<sup>12,13</sup> the minimum of the Gibbs free energy of the supercooled liquid in the Zr–Ni system ( $\approx -40$  kJ/g atom) is much lower than in the Zr–Cu system ( $\approx -14$  kJ/g atom). Cu–Ni can be regarded as an ideal solution. These conditions in the binary systems reveal that the Gibbs free energy in the ternary Zr–Ni–Cu system must drop dramatically with increasing Ni content and decreasing Cu content. This is visualized in Fig. 3 by a schematic ternary Gibbs free energy surface of the supercooled liquid. The binary Zr–Ni and Zr–Cu curves are drawn according to Refs. 12 and 13. The diagram shows that the formation of Ni-rich (Cu-poor) alloy leads to the maximum gain in Gibbs free energy and is thermodynamically favored, as observed in the experiments (Fig. 2).

Crystallization starts in the supercooled liquid Zr-rich part of the noncrystalline layer, which has the lowest stability with respect to crystallization (see Fig. 4). However, these compositions are more stable with respect to crystallization than in a binary Zr/Ni diffusion couple without Al, where the Zr-rich part is not a bulk glass former, and starts to

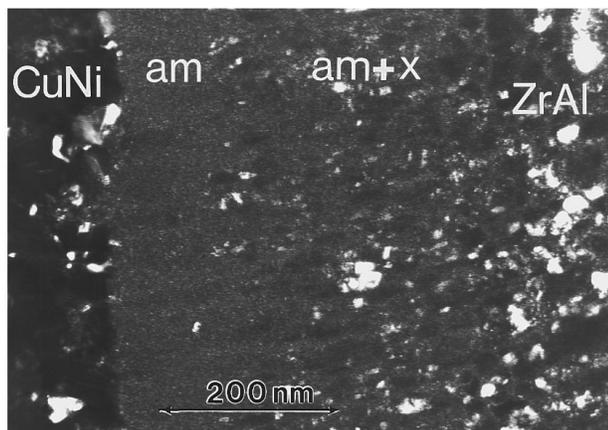


FIG. 4. Dark field TEM image of a diffusion couple that was annealed for 3 h at 410 °C. The crystallization begins in the Zr-rich supercooled liquid layer.

crystallize below the glass transition. This limits the maximum annealing temperature in a Zr/Ni diffusion couple to temperatures far below 400 °C in contrast to our Zr–Al/Cu–Ni diffusion couple.

Figure 4 shows the TEM image of the Zr–Al/liquid/amorphous/Cu–Ni diffusion couple after annealing for 3 h at 410 °C. The crystallization started in the Zr-rich supercooled liquid part of the layer. The Ni-rich part is still amorphous and continues to grow, as TEM images of later stages reveal. In the later stages, formation of a nanocrystalline  $\text{Cu}_{90}\text{Ni}_{10}$  layer at the Cu–Ni/amorphous interface is observed. This is strongly related to the fact that Ni preferentially diffuses into the noncrystalline layer compared to Cu, and Cu piles up at the interface (Fig. 2). This nanophase formation is described elsewhere.<sup>9</sup>

In conclusion, the solid state amorphization reaction was extended to a supercooled melting reaction by combining two binary solid solutions and forming a multicomponent noncrystalline layer at the interface. The resulting layers are about half an order of magnitude thicker than for conventional diffusion couples. Two noncrystalline phases coexist in the particular (Zr–Al)–(Cu–Ni) diffusion couple. One is amorphous and Ni-rich. The other phase is Zr-rich and turns out to be in the supercooled liquid state during the reaction at 410 °C. This metastable supercooled melting where a supercooled molten layer forms far below the melting point has not been previously observed. The present study reveals two kinetically contributing factors to the high thermal stability of supercooled Zr-rich (Zr–Al)–(Cu–Ni) BMG formers. (1) The diffusion constant of Ni and Cu is small in the supercooled liquid even compared to Ni-rich *amorphous* alloys at the same temperature. (2) Aluminum is immobile, which results in a constant ratio between Zr and Al in the reacted layer and kinetically frustrates the system with respect to nucleation of crystalline compounds with a different Zr/Al ratio.

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