

## On the formation of amorphous layers by interdiffusion in zirconium–copper system

K BHANUMURTHY, G K DEY, S BANERJEE, S K KHERA and  
M K ASUNDI

Physical Metallurgy Division, Bhabha Atomic Research Centre, Bombay 400 085, India

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**Abstract.** Formation of amorphous phase by solid state reaction has been observed in bulk copper-zirconium couples. Transmission electron microscopy (TEM), Auger electron spectroscopy (AES) and differential scanning calorimetry (DSC) techniques have been employed to detect and study the amorphous phase. The experimental observations have been explained with a model, which considers the breakdown of the  $\alpha$ -zirconium lattice due to the solute enrichment beyond a certain limit where the nucleation of the amorphous phase becomes thermodynamically possible. The present experiments convincingly show that amorphous phase can form in bulk diffusion couples made from large-grained well-annealed material and conclusively establish that the presence of crystal defects in high concentrations is not a pre-requisite for the formation of amorphous phase.

**Keywords.** Diffusion couples; solid state reaction; amorphous phase; interdiffusion; zirconium-copper system.

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### 1. Introduction

Non-equilibrium cooling techniques either from the melt or from the gaseous phase have been extensively used for the production of amorphous alloys. Anantaraman and Suryanarayana (1987) reviewed the current literature in this area. Some recent studies (Schwarz and Johnson 1983; Schwarz *et al* 1984; Highmore *et al* 1987) have demonstrated that amorphous alloys can also be formed in solid state in some metallic systems by one of the following methods: (a) interface reactions between multilayer deposits of dissimilar metals; (b) mechanical alloying of mixture of metallic elements either by ball milling or by extensive codeformation of filamentary or lamellar composites (van Allman 1987) and (c) introducing hydrogen in certain crystalline alloys (Yeh *et al* 1983). In all these methods the departure from equilibrium, a necessary requirement for the formation of amorphous alloys, is attained by the introduction of both diffusion fluxes and lattice defects.

Amorphous phase formation through solid state interdiffusion (or interface reaction) in a multilayered structure of two-crystalline metals was reported by Atzmon *et al* (1984). However such experiments are confined to evaporation or sputter-deposited multilayered thin film samples. It has therefore not been established whether the defects and high density crystalline interfaces in thin film samples are essential in the formation of amorphous phases in these systems. In the present paper, this point is critically examined by studying the interface reaction in bulk diffusion couples made

from fully annealed pieces of pure zirconium and pure copper sheets of about 0.3 mm thickness.

Metallic glass formation through interdiffusion is attributed to the large negative heat of mixing of the two components (Hallstern and Schultz 1987). The amorphization process can continue at temperatures sufficient for the interdiffusion to occur at a reasonable rate but not sufficient for the nucleation of any competing crystalline intermetallic phases. It is attractive to envisage that amorphization in a diffusion couple can occur when the structure of crystalline solid at the interface breaks down due to the solute enrichment beyond some limiting value. The formation of the amorphous phase in the zirconium  $\alpha$ -copper diffusion couples made from bulk specimens has been analysed in this study from this viewpoint.

## 2. Experimental

High purity copper (99.9%) plates and electron beam-melted zirconium (99.7%) ingots were rolled to obtain sheets of 0.3 mm thickness. These sheets were fully annealed at 1173 K for 3 hr in a vacuum of  $10^{-5}$  torr. Diffusion couples were prepared from these annealed sheets. The mating surfaces of zirconium and copper pieces were prepared by electropolishing and mechanical polishing respectively. Diffusion couples were loaded into a clamping jig under pressure to ensure intimate contact between the two metal surfaces. The entire assembly was placed in a vacuum furnace ( $10^{-5}$  torr) for diffusion bonding at 591 K for 30 minutes. Subsequently the samples were released from the clamping jig, sealed in an inert gas atmosphere and were given diffusion annealing treatments in the temperature range 591 to 923 K for different durations.

The progress of amorphization process was also studied in DSC during heating at a constant rate of 16 K/minute from 300 to 773 K. Because of marked differences in the electropolishing behaviour of zirconium and copper, TEM of the cross-sections of the diffusion couples could not be carried out. Instead several TEM samples were prepared by jet electropolishing of these couples differentially from the copper and zirconium sides. This enabled us to sample areas which are at different distances from the mating surfaces. An electrolyte containing 20% perchloric acid and 80% ethanol maintained at 243 K was used for electropolishing. Electron transparent foils representing areas located at different depths from the interface were examined in an electron microscope operated at 100 kV. However this technique did not permit us to measure these depths with sufficient accuracy.

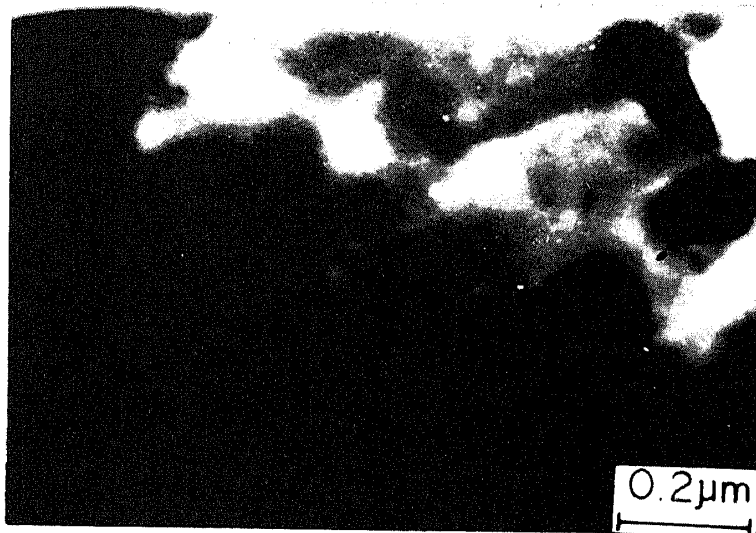
A few diffusion couples were annealed at temperatures higher than 873 K. In these samples layers of ordered intermetallic compounds were found to form to thicknesses which could be analysed by electron beam microanalysis (EPMA).

AES was carried out on the surface opened up by fracturing the couples along the interface plane. The depth distribution of copper in diffusion-annealed samples was carried out by AES in conjunction with argon ion sputtering from the fractured surface.

## 3. Results

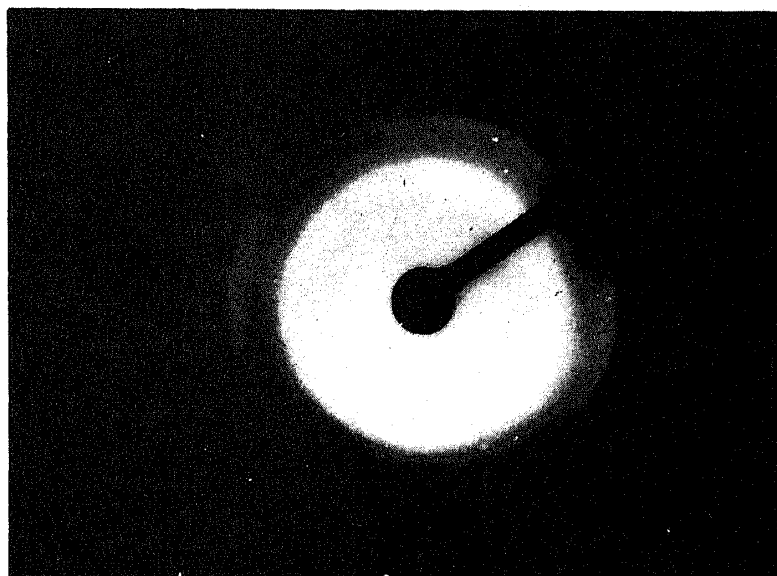
Samples in which electron transparent area corresponds to the region very close to the interface of the diffusion couple formed by annealing at 600 K for 10 h showed the following structural features.

(i) The microstructure (figure 1) was found to be devoid of any contrast features. Tilting of such samples in the electron microscope did not bring out any contrast features like bend or thickness contours and crystal defects.



**Figure 1.** TEM micrograph devoid of any contrast features in the zirconium copper diffusion couple.

(ii) Selected area diffraction patterns (SAD) showed circular intensity halos (figure 2). The radius of the first halo was found to be about  $24.5(\text{nm}^{-1})$  which closely matched with that reported for zirconium-based metallic glasses (Dong *et al* 1981).



**Figure 2.** Electron diffraction pattern from amorphous regions showing broad intensity halos.

Based on the observations it was inferred that a layer of amorphous phase was produced at the interface of diffusion couple formed at 600 K. The interface was

opened up by fracture and depth profile of copper concentration in the  $\alpha$ -Zr phase was obtained by AES. The maximum concentration of Cu was about 4 at.% and the depth of copper in  $\alpha$ -Zr was about 8 nm. A typical AES survey spectra recorded from the interfacial region on the zirconium side of the couple is shown in figure 3.

Samples which represented areas adjacent to the fully amorphous layer exhibited to two-phase microstructure consisting of supersaturated  $\alpha$ -Zr and an amorphous phase (figure 4). SAD patterns (figure 5) from these areas showed arcs of intensity which also extended in the radial direction. The spread of diffracted intensity along the arcs represents the distribution of orientation of crystals present in a given field of view while the radial spread implies a variation in the lattice spacings. These

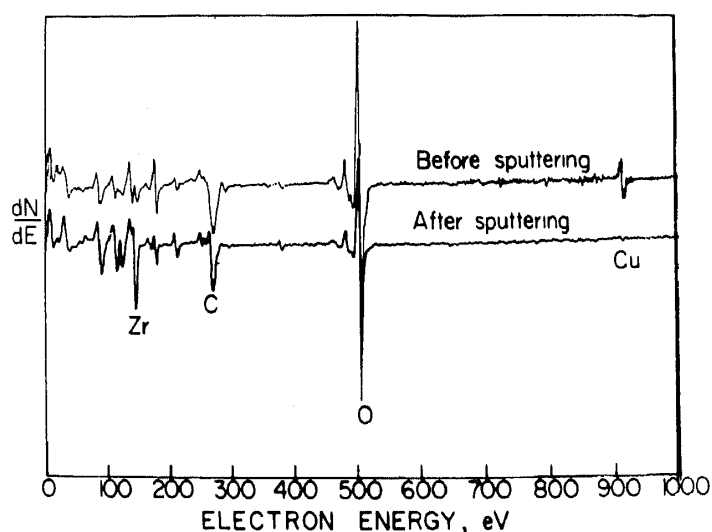


Figure 3. AES survey spectra recorded from the interfacial region on the zirconium side of the couple. The copper signal disappeared after sputtering for 8 min.

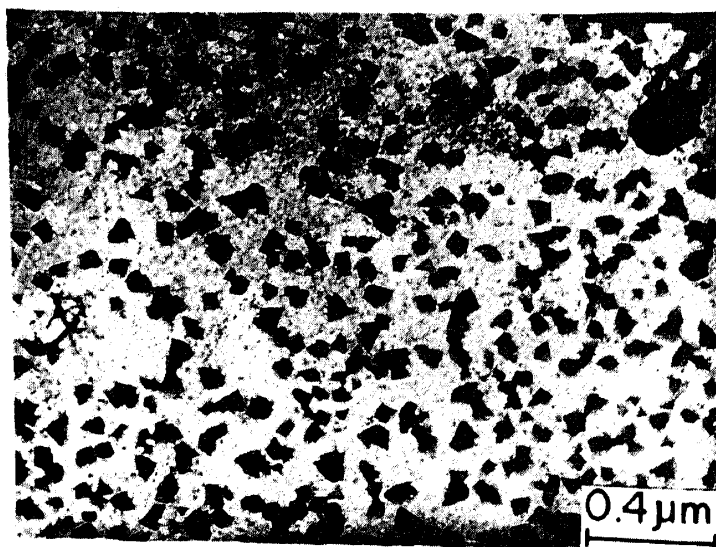


Figure 4. Bright field electron micrograph showing crystalline particles in amorphous matrix.

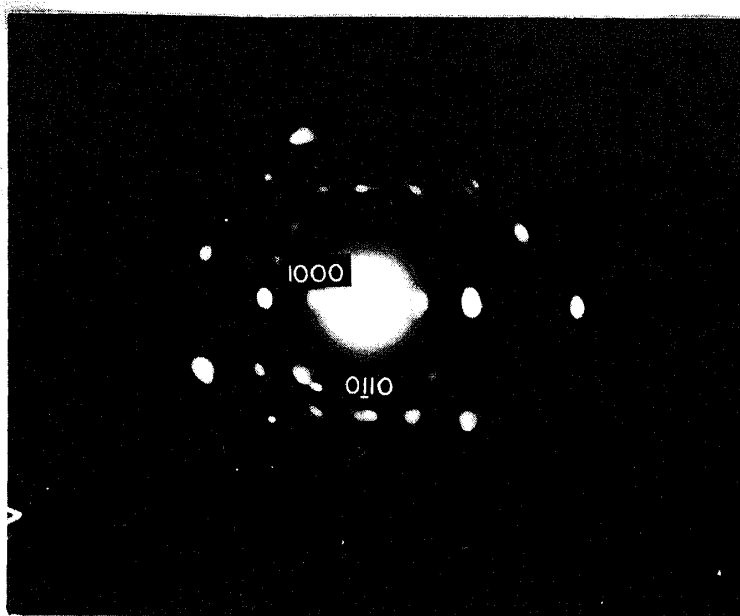


Figure 5. Electron diffraction patterns from a crystalline particle. Zone axis  $[2\bar{1}\bar{1}0]$ .

observations indicate that the  $\alpha$ -crystals present in the given field of view in the matrix of the amorphous phase possess a preferred orientation distribution giving rise to intensity arcs and also a certain variation in the lattice spacings. The average grain size of the  $\alpha$ -Zr sheet used for making the diffusion couples was 0.5  $\mu\text{m}$ . The presence of submicron size  $\alpha$ -crystals in the amorphous matrix, therefore, suggests that the advancing amorphous phase fragments the original  $\alpha$ -grains as copper atoms penetrate into the Zr side. The transition from the crystalline to the amorphous phase, however, was found to be across very sharp interfaces separating  $\alpha$ -crystals from the amorphous matrix. This is not unexpected in view of the first order nature of the crystal to amorphous transition. The large  $\alpha$ -grains get fragmented by the advancing amorphous phase front which is known to exhibit morphological instability. The resulting  $\alpha$ -crystals tend to maintain their original orientations and this causes the presence of preferred orientations of the group of  $\alpha$ -crystals in the same neighbourhood.

The progress of the amorphization process was monitored in the DSC experiments by recording the rate of enthalpy liberation during continuous heating (at a constant heating rate of 16 K/minute) from 300 to 773 K for samples in which thin amorphous layers have been formed by diffusion annealing (at 600 K for 10 h). A typical thermogram in figure 6 indicates two broad exothermic peaks (denoted as I and II). Such exothermic processes were not encountered in a couple which was not given the diffusion annealing treatments. The base line shown in figure 6 illustrates the thermogram of one such couple. These observations suggest that a layer of amorphous phase once formed at the interface can grow during the continuous heating experiment. The enthalpy liberation due to the growth of the amorphous layer is reflected in the appearance of the broad exothermic peak (I) at 543 K. At a higher temperature the amorphous phase crystallizes giving rise to an exothermic peak (II) at 703 K. This temperature closely corresponds to that of crystallization of Zr-Cu glass produced by the melt spinning technique (Freed and Vandarsande 1980).

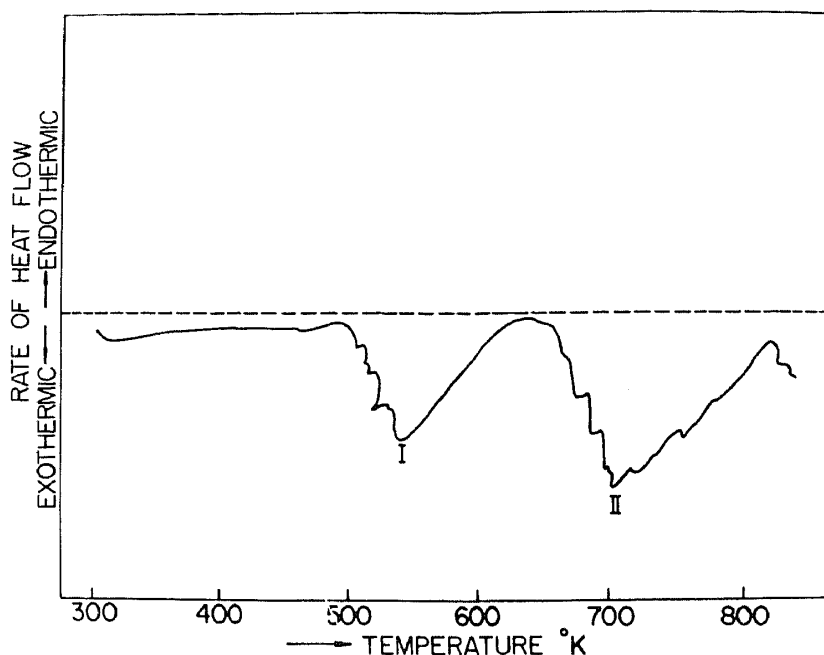


Figure 6. DSC thermogram obtained at a heating rate of 16 K/min. Dotted line indicates thermogram for the couple which was not diffusion-annealed.

#### 4. Discussion

The present experiments indicate that the interface reaction between zirconium and copper results in the formation of intermetallic compounds, when the diffusion annealing temperature is kept at or above 873 K. However, an amorphous phase forms at the interface when the diffusion annealing is carried out at temperatures below 600 K. The observation that an amorphous phase forms instead of stable intermetallic compounds at  $T < 600$  K can be explained in terms of the respective diffusion parameters. It is reported that copper atoms have a diffusivity more than three orders of magnitude greater than the self-diffusivity of zirconium atoms in  $\alpha$ -Zr lattice (Hood and Schultz 1975). The formation of long range ordered intermetallic compounds requires movement of not only copper atoms but also zirconium atoms. At  $T < 600$  K the mobility of zirconium atoms is too small to permit the long range ordering necessary for the formation of equilibrium intermetallic compounds. As a consequence formation of these compounds is suppressed at such low temperatures.

An examination of a hypothetical free energy composition plot (figure 7b) for the  $\alpha$ , the  $\beta$  and the liquid phase reveals that the metastable solubility of copper atoms in the  $\alpha$ -Zr lattice is considerably extended when intermetallic compounds do not participate in the phase equilibrium process. An examination of the boundaries of different phase fields of the phase diagram gives an approximate idea of the metastable solubility limits. The relevant part of the Zr-Cu phase diagram and the hypothetical free energy composition ( $G$ - $X$ ) plots for 600 K, consistent with the phase diagram are shown in figures 7a, b. As the formation of the intermetallic phase  $Zr_2Cu$  is suppressed, the metastable solubility of Cu atoms in  $\alpha$ -Zr increases to the limit shown by the point C at which the line, tangent on the  $G^L$  and  $G^\alpha$  curves, meet the  $G^\alpha$  curve. The  $\alpha$ -Zr phase will continuously decrease its free energy by accepting increasing amounts

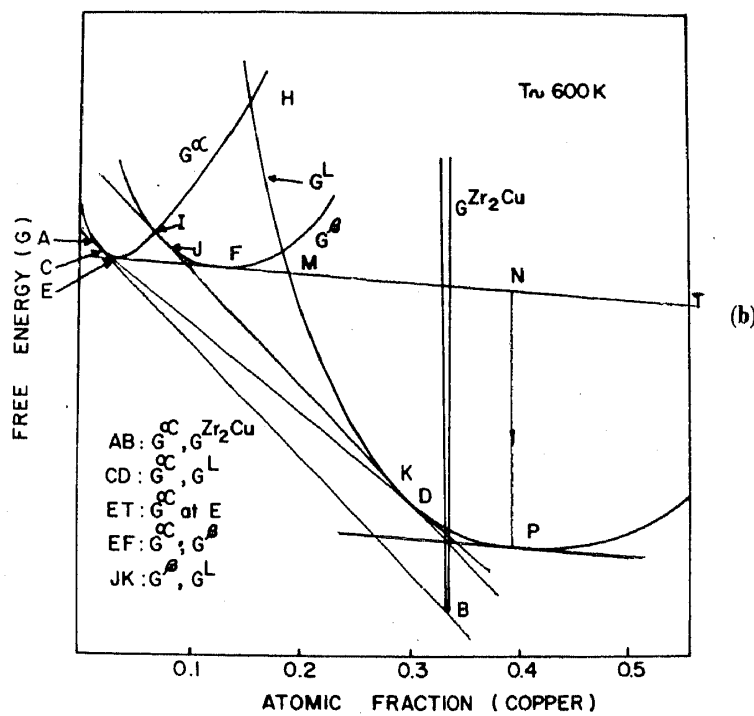
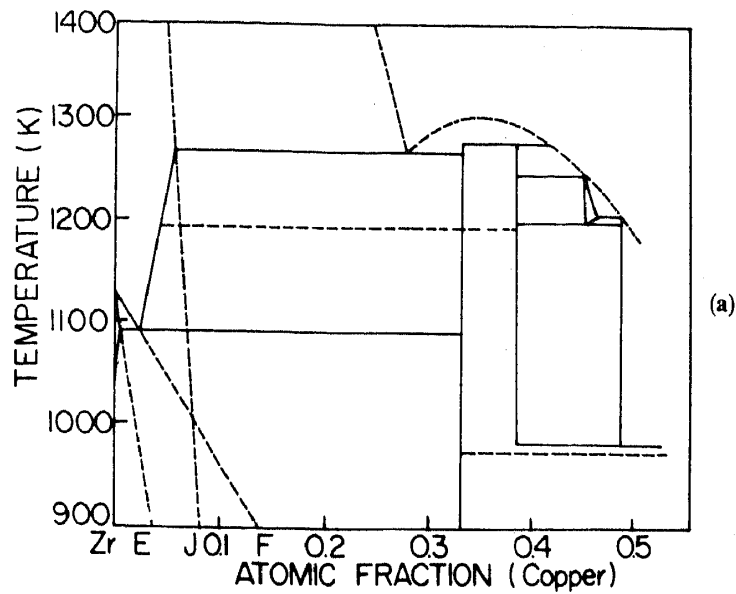


Figure 7. a. Phase diagram of rich portion of zirconium. b. Free energy plot at 600 K for the zirconium/copper system.

of copper till the concentration reaches point C. Further enrichment will make the  $\alpha$ -Zr phase supersaturated with respect to the nucleation of the amorphous phase (L), the free energy for the nucleation for an alloy of composition E being given by the vertical distance between the tangent line ET and the  $G^L$  curve. Though the free energy change (NP) associated with the nucleation will be maximum for the nucleus composition, P, where the tangent to the  $G^L$  curve is parallel to the tangent line ET, the nucleation of amorphous phase becomes thermodynamically possible for the

copper content of the amorphous phase exceeding the point M. Once the amorphous phase is nucleated, it will continue to become richer in copper up to the point D where a metastable equilibrium can be established between supersaturated and the amorphous phase (indicated by the common tangent line CD).

It was earlier proposed by Johnson (1986) that the crystal-to-amorphous transition occurs after solute enrichment goes beyond a level where a composition invariant transition becomes thermodynamically possible. In the present case such a process will require enrichment of  $\alpha$ -Zr beyond the point H where  $G^L$  and  $G^\alpha$  curves intersect. Such a process is unlikely because of the following reasons:

- (a) As indicated earlier,  $\alpha$ -Zr becomes supersaturated with respect to the precipitation of the amorphous phase at a much lower level of copper content (point C).
- (b) Before reaching the point H,  $\alpha$ -Zr goes through point I, where the polymorphic transition from  $\alpha$  to  $\beta$  becomes thermodynamically possible. Such a transition was not observed in the present experiments.
- (c) The maximum concentration of Cu detected in the present experiments in the  $\alpha$ -Zr phase is about 4 at.% which is much below than that corresponding to the point H.

In view of the aforementioned arguments the amorphous phase formation at the mating face of Zr-Cu diffusion couples can be envisaged to involve the following steps:

- (i) Diffusion of Cu atoms in  $\alpha$ -Zr resulting in copper enrichment to about 4 at.%.
- (ii) Nucleation of amorphous phase particles in the matrix of  $\alpha$ -Zr.
- (iii) Growth of amorphous regions at the expense of  $\alpha$ -Zr, the amorphous phase gradually becoming continuous by coalescence of independently nucleated amorphous particles. (At this stage  $\alpha$ -Zr particles remain distributed in a continuous matrix of the amorphous phase.)
- (iv) Formation of a fully amorphous layer which remains in contact with the  $\alpha$ -Zr containing about 4% of copper.
- (v) With continuous arrival of copper atoms at the interface between the  $\alpha$ -Zr (Cu-enriched) and the amorphous phase, growth of the amorphous layer continues till the supply of Cu atoms gets restricted due to the formation of Kirkendall pores in the Cu side (Newcomb and Tu 1986). However the evidence for the formation of Kirkendall pores could not be obtained as cross-sectional TEM was not carried out.

The breakdown of  $\alpha$ -Zr lattice first occurs at the nucleation stage when the local composition of a region due to chance fluctuation reaches a composition beyond M as shown in figure 7b. Such a breakdown of the lattice also occurs at the  $\alpha$ -Zr/amorphous interface during the growth of the amorphous layer. The concentration level at which such a breakdown occurs can be estimated from the Egami criteria (Egami and Waseda 1984) of topological stability of a solid solution containing atoms of two different sizes. The maximum concentration,  $C_A^*$ , of the small atoms (A atoms) at which the lattice becomes unstable is approximately given by

$$C_A^* = 2\lambda V_B / (V_B - V_A),$$

where  $\lambda$  is a constant and  $V_A$ ,  $V_B$  are the atomic volumes of A and B atoms.  $\lambda$  has been estimated to be between 0.07 and 0.09 by Liou and Chien (1986). Substituting the following values  $V_A = V_{Cu} = 0.001181 \text{ (nm)}^3$ , and  $V_B = V_{Zr} = 0.002327 \text{ (nm)}^3$  and  $\lambda = 0.07$ , the value of  $C^*$  has been estimated to be 0.28. However experimentally



obtained concentration of Cu in  $\alpha$ -Zr has never been found to exceed 0.04, indicating that the nucleation of amorphous phase can occur at a much lower level of Cu concentration.

In multilayer thin films the growth of the amorphous alloy is terminated by coalescence of adjacent interfaces. However, if a bilayer is used, as in the present case, crystalline compounds can begin to grow by interdiffusion before coalescence intercedes and restrict the growth of the amorphous layer. In the present investigation the formation of intermetallic compounds was not observed in the diffusion-bonded couples presumably because the temperature and the duration of bonding treatment was not sufficient. The formation of crystalline compounds could occur at a higher temperature, as indicated in the DSC and EPMA investigations. DSC trace suggests that the rate of amorphization increases initially and then falls off. The decrease in the amorphization rate at higher temperatures is primarily due to the formation of voids at the interface between the copper and amorphous phases and also due to the formation of intermetallic compounds directly from the elemental phases.

## 5. Conclusions

- (i) The formation of the amorphous phase is possible in the Zr-Cu system in a bulk diffusion couple made from large-grained well-annealed materials.
- (ii) The nucleation of the amorphous phase becomes possible when copper concentration of the  $\alpha$ -phase exceeds a limit defined by a metastable equilibrium between the  $\alpha$  and amorphous phases. This occurs at a much lower copper concentration than that required for the composition-invariant  $\alpha$  to amorphous transition as suggested earlier (Johnson 1986).

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