

Grain boundary amorphization reaction in thin films of elemental Cu and Y

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Compositionally modulated thin films of Cu and Y were prepared in an ultrahigh vacuum dc ion beam deposition chamber. Room-temperature growth of an amorphous Cu-Y phase was observed with interdiffusion of the elemental Cu and Y. Transmission electron microscopy of as-prepared samples revealed a novel growth morphology; amorphous phase formation was observed both at the original Cu/Y interface and between the grains of the elemental Y. Estimates for the thermodynamic and kinetic factors underlying the grain boundary amorphization reaction are presented.

The occurrence of solid-state amorphization reactions (SSAR) during the low-temperature anneal of thin-film metal diffusion couples requires a large thermodynamic driving force for reaction between the starting species and atomic transport at temperatures below that characteristic of crystalline phase nucleation.¹⁻³ The final reaction products coincide with the attainment of a metastable equilibrium condition; coexisting product phases are characterized by equal chemical potentials.⁴ The influence of trace impurities,⁵ defects, dislocations, and grain boundaries⁶ in stabilizing the initial formation of amorphous nuclei or in enhancing interdiffusion of the starting species is of current interest.

Y belongs to a class of materials exhibiting "anomalously" fast tracer diffusion for a group of late transition-metal solutes that include Cu.⁷ The activation energy for interdiffusion in the glass phase formed by SSAR is expected to be similar to that for tracer diffusion within the Y host lattice.¹ The thermodynamic driving force for the interdiffusion of Cu and Y is large and negative as indicated by the equilibrium phase diagram⁸ and Miedema's heat of mixing.⁹ Accordingly, we anticipate that the Cu-Y system is a good candidate for SSAR.

In this letter we describe the growth morphology of amorphous $\text{Cu}_{1-x}\text{Y}_x$ in compositionally modulated thin films of elemental Cu and Y. X-ray diffraction and high-resolution cross-sectional transmission electron microscopy measurements were performed to characterize these samples. The amorphous phase is observed to grow both at the original Cu/Y interface and between grains of the elemental Y. Estimates for the thermodynamic and kinetic factors underlying this first direct observation of grain boundary amorphization in SSAR are presented.

Compositionally modulated Cu-Y multilayer samples were prepared by dc ion beam sputtering using 20 mA, 1 keV Ar^+ , a background Ar pressure of 5×10^{-5} Torr, and a chamber base pressure of 10^{-9} Torr. A description of the sample preparation chamber is contained in Ref. 10. Y (target purity 3N) and Cu (target purity 5N) were alternately deposited with a typical deposition rate of 1.0 \AA/s and with the substrate nominally at room temperature. The overall sample compositions were $\text{Cu}_{50}\text{Y}_{50}$ with a typical total film

thickness of about 2000 \AA . A Cu layer was always deposited last to serve as a barrier to the oxidation of Y during subsequent handling.

Samples were characterized by x-ray diffraction in reflection geometry and by transmission electron microscopy (TEM). TEM samples were prepared in cross section by standard grinding and argon ion milling at 4 keV with liquid-nitrogen cooling. To minimize oxidation after ion milling the samples were then immediately loaded into a Philips EM 430 TEM operated at 300 keV.

X-ray diffraction measurements on as-prepared samples with composition modulation wavelength λ of 150 \AA and less revealed the presence of fcc Y¹¹ with (111) texture and lattice constant of 5.1 \AA and the presence of amorphous Cu-Y. Unamorphized elemental Cu was observed only for as-prepared samples with $\lambda \geq 300 \text{ \AA}$. Real-time, *in situ*, x-ray diffraction measurements¹⁰ revealed a room-temperature onset for the amorphization reaction.¹²

Electron micrographs taken from samples prepared in cross section show alternating amorphous and crystalline layers. Figure 1 shows a TEM bright field (BF), dark field (DF) pair and diffraction pattern for the as-prepared Cu-Y sample with $\lambda = 150 \text{ \AA}$. The contribution of the amorphous layers can be seen in electron diffraction from diffuse rings and in the BF image from the lack of diffraction contrast. Diffraction contrast can be seen from the crystalline layers and shows the presence of grain sizes from 30 to 60 \AA . The electron diffraction pattern of the multilayer confirmed the presence of strongly textured fcc Y. When viewed with the dominant orientation of the Y grains in a [011] projection, {111} twinning of the fcc Y is revealed. The DF image formed from a (200) reflection (indicated by the arrow) more clearly shows the range of grain sizes and shapes. Figure 2 shows a high-resolution image of the observed amorphization growth morphology. {111} lattice fringes of the fcc Y can be resolved and show that the SSAR has resulted in a nonatomically smooth reaction front. Growth of amorphous $\text{Cu}_{1-x}\text{Y}_x$ is observed both at the original Cu/Y interface and between grains of the elemental Y. This is the first direct observation of grain boundary amorphization in SSAR.

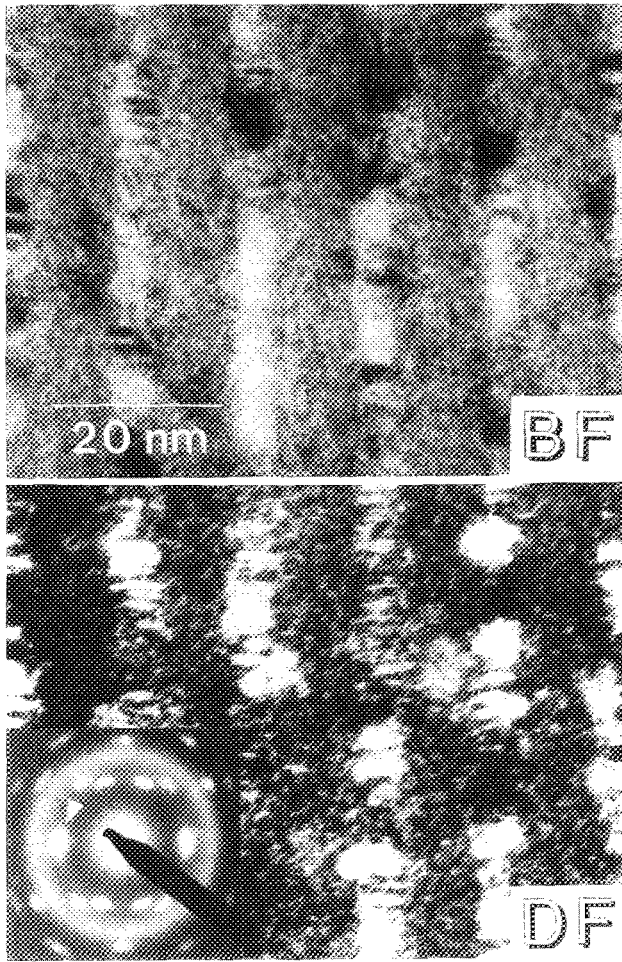


FIG. 1. TEM bright field (BF), dark field (DF) pair and diffraction pattern of the as-prepared (room-temperature annealed) Cu-Y sample with composition modulation wavelength of 150 Å. The light regions in the BF image correspond to fcc Y metal and the grey mottled regions correspond to amorphous $\text{Cu}_{1-x}\text{Y}_x$. The DF image was formed from the Y (200) reflection that is noted by an arrow in the inset diffraction pattern. Nonplanar growth of amorphous $\text{Cu}_{1-x}\text{Y}_x$ and a marked rounding of the Y grains are evident in the DF image.

The Gibbs free-energy change associated with an interfacial layer of amorphous $\text{Cu}_{1-x}\text{Y}_x$ with thickness t in contact with Y metal can be written

$$\Delta g^{\text{Y}(\text{Cu}_{1-x}\text{Y}_x)}(t) = \Delta G(x)t + \gamma_{\text{SL}}^{\text{Y}(\text{Cu}_{1-x}\text{Y}_x)},$$

where $\Delta G(x)$ is the free energy for formation of glassy $\text{Cu}_{1-x}\text{Y}_x$ from the pure elements and $\gamma_{\text{SL}}^{\text{Y}(\text{Cu}_{1-x}\text{Y}_x)}$ is the free energy associated with the Y/ $\text{Cu}_{1-x}\text{Y}_x$ interface. In the following a nominal thickness of 2.5 Å is assigned to the amorphous interfacial layer. This chosen thickness serves to illustrate the primary trends in the following calculation and it corresponds roughly to Spaepen's estimate¹³ for the number of liquid interfacial atoms involved in a monatomic solid/liquid interface. We have estimated $\Delta G(x)$ following Schwarz and Johnson⁴ with the molar volume taken as the composition-weighted average of the molar volumes of the pure components. The resulting $\Delta G(x)t$ for $t = 2.5$ Å and $T = 300$ K is shown in Fig. 3. To estimate the energy asso-

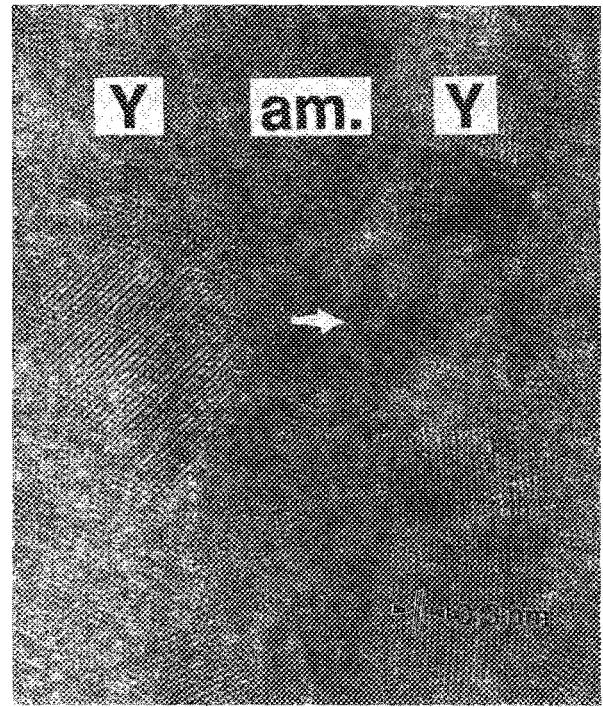


FIG. 2. High-resolution phase-contrast image of the amorphous/crystalline boundary region. {111} lattice fringes of the fcc Y can be resolved and show that the SSAR has resulted in a nonatomically smooth reaction front with the reaction proceeding into the region between Y grains (indicated by arrow).

ciated with the Y/amorphous- $\text{Cu}_{1-x}\text{Y}_x$ interface we extend the procedure developed by Miedema and Broeder¹⁴ for arbitrary solid/liquid metal combinations. We treat the amorphous $\text{Cu}_{1-x}\text{Y}_x$ as an undercooled extension to the

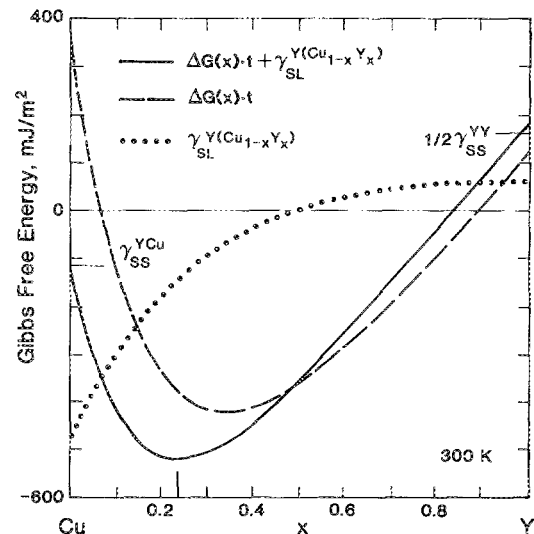


FIG. 3. Gibbs free energy for formation of a thickness $t = 2.5$ Å of amorphous $\text{Cu}_{1-x}\text{Y}_x$, $\Delta G(x)t$, the free energy associated with the Y/amorphous- $\text{Cu}_{1-x}\text{Y}_x$ interface $\gamma_{\text{SL}}^{\text{Y}(\text{Cu}_{1-x}\text{Y}_x)}$, and the result, representing the free energy of the amorphous interfacial layer in contact with Y metal, that is obtained by summing these two terms. Also shown are the energies associated with a high-angle grain boundary in pure Y metal $\gamma_{\text{SS}}^{\text{Y}}$ and with the original Y/Cu interface $\gamma_{\text{SL}}^{\text{YCu}}$.

liquid phase and ignore the configurational freezing that occurs as the glass transition temperature is approached. The compositional dependence of the resulting $\gamma_{SL}^{Y(Cu_{1-x}Y_x)}$ is due primarily to the variation with x of the chemical interaction between Y and glassy $Cu_{1-x}Y_x$. Following Miedema and Broeder,¹⁴ this chemical interaction is estimated as a fixed fraction of Miedema's heat of solution⁹ of Y in liquid $Cu_{1-x}Y_x$. Shown in Fig. 3 are the values that we obtain for $\gamma_{SL}^{Y(Cu_{1-x}Y_x)}$ and for $\Delta g^{Y(Cu_{1-x}Y_x)} (t = 2.5 \text{ \AA})$. Also shown in Fig. 3 are estimates¹⁴ for the free energy of a high-angle grain boundary in Y metal γ_{SS}^{YY} and the interfacial energy associated with the original Y/Cu interface γ_{SS}^{Cu} . This treatment of interfacial energies, though approximate, provides a consistent framework for a discussion of the present results.

The driving force for the grain boundary amorphization reaction can be expressed:

$$\Delta g(x) = 2[\Delta G(x)t + \gamma_{SL}^{Y(Cu_{1-x}Y_x)}] - \gamma_{SS}^{YY}$$

Figure 3 illustrates that for x somewhat less than 1, $\Delta G(x)t + \gamma_{SL}^{Y(Cu_{1-x}Y_x)} < \gamma_{SS}^{YY}/2$, and that the reaction is thermodynamically favored within this domain. Further, if we suppose that the supply of Cu (and Y) to the grain boundary is not limiting and maintain an interfacial layer thickness of 2.5 \AA , an optimum concentration for the amorphous phase $x \sim 0.2$ is obtained.

A critical thickness t_c of the amorphous grain boundary phase, corresponding to $\Delta g(x) = 0$, can be written:

$$t_c = - (2\gamma_{SL}^{Y(Cu_{1-x}Y_x)} - \gamma_{SS}^{YY})/2\Delta G(x)$$

For $2\gamma_{SL}^{Y(Cu_{1-x}Y_x)} - \gamma_{SS}^{YY} > 0$ and $\Delta G(x) < 0$, t_c represents the critical nucleus size necessary to overcome the energy expended in creating two interfaces at the expense of one interface. Since in the present case $2\gamma_{SL}^{Y(Cu_{1-x}Y_x)} - \gamma_{SS}^{YY} < 0$ for all x , t_c is a measure for compositions with $\Delta G(x) > 0$ of the maximum thickness of amorphous material that can be stabilized by the negative change in interfacial energy. We conclude that there is no nucleation barrier for the grain boundary amorphization reaction and that for compositions $x < 0.06$ and $x > 0.89$ grain boundary stabilization of amorphous $Cu_{1-x}Y_x$ is possible.

The activation energy for grain boundary self-diffusion is typically about 1/2 that for lattice self-diffusion.¹⁵ We observe that the initial diffusion of Cu in Y grain boundaries is also enhanced with respect to Cu diffusion in the Y host lattice. The initial stage of the grain boundary amorphization reaction may then correspond to the case of "supply of Cu nonlimiting" considered above; a consequent enrichment in the Cu concentration of this grain boundary amorphous phase is expected. Subsequent grain boundary diffu-

sion of Cu occurs within this initially formed amorphous $Cu_{1-x}Y_x$ interfacial layer; in the absence of diffusion measurements specific to this process, we anticipate a much reduced Cu mobility.

The room-temperature growth of amorphous $Cu_{1-x}Y_x$ in compositionally modulated thin films of elemental Cu and Y has been described. The amorphization reaction is observed both at the original Cu/Y interface and within the Y grain boundaries. Estimated values of the relevant interfacial energies and a description of the initial growth kinetics underlying the grain boundary amorphization of Y are presented.

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