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DEFORMATION-INDUCED AMORPHIZATION OF CRYSTALLINE PARTICLES IN A CU-TI METALLIC GLASS

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ABSTRACT

Crystalline particles and grains embedded in $\text{Cu}_{35}\text{Ti}_{65}$ glass ribbons have been amorphized by isothermal cold rolling. The structural evolution has been studied by X-ray diffraction and TEM techniques. Initial particle morphologies are spherulitic and spherical, the latter with sizes ranging between 10 and 100 nm. The new amorphous phase seems to nucleate at crystalline-amorphous matrix interfaces. Initially there is a well defined interface between the new and the existing amorphous phases but it disappears as rolling progresses. Crystallites on a nanoscale still present in the final stages of particle amorphization have been observed by convergent beam electron diffraction. After sufficient deformation the consolidated ribbon becomes completely glassy. A morphological description of the transformation process in terms of crystal destabilization and solid-state particle melting is presented.

INTRODUCTION

Amorphous metallic alloys are traditionally produced by rapid solidification and vapor deposition techniques. Several mechanisms of metallic-glass formation via solid-state reactions have recently been discovered and investigated. Experimental observations, and the thermodynamics and kinetics of these solid state amorphization reactions (SSAR) have been reviewed recently [1]. Some of the methods of synthesis are [1]: annealing of diffusion couples; hydrogen absorption and desorption; isothermal annealing of codeformed metal lamellar and filamentary composites; ion and electron irradiation of diffusion couples and homogeneous phases; and mechanical alloying. The first three avenues involves the release of excess chemical enthalpy under isothermal conditions. The last two are representative of externally driven processes

This study is concerned with the complete amorphization of a partially-crystalline metallic-glass ribbon under isothermal rolling conditions. Two important aspects to study are: the microstructural evolution during the accumulation of lattice defects and the nucleation and development of the new amorphous phase. Both aspects have been studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques.

Schwarz and Koch reported the amorphization of the crystalline intermetallics NiTi_2 and $\text{Ni}_{45}\text{Ti}_{45}$ by high energy ball milling [2]. The maximum temperature increase (above the average processing temperature) was calculated to be 38K by allowing the particle to shear under the stress produced by the head-on collision of the steel balls [2]. According to Schwarz and Koch, the amorphization reaction proceeds by a build-

Fig. 1. X-ray diffraction patterns of the starting ribbon and after successive rolling passes (a through d). The reduction ratios are indicated in the figure.

up of lattice defects that destabilizes the crystalline particles in the powder. From our observations, a similar process is proceeding with the rolling of multiphase ribbons. However, particular aspects of microstructural evolution may be totally different for each of this processes.

EXPERIMENTAL

Copper (99.999 % pure) and titanium (99.93 % pure) were levitation melted on a silver boat in an argon atmosphere. The resulting ingot of composition $Cu_{35}Ti_{65}$ was then melt spun under helium into ribbons of about $40 \mu m$ thickness. The resulting morphology is discussed further below. The ribbons were examined on both sides by XRD using $Cu K\alpha$ radiation. The pattern in Fig. 1a identifies the crystalline phases present as $CuTi_2$ and Cu_3Ti_2 .

The ribbons were stacked between two plates of 24 gauge stainless steel and rolled in a standard rolling mill. The rolling conditions are slow and nearly isothermal with a constant rolling direction. The relative degree of deformation is expressed by

the reduction ratio (RR) which is given by the initial sample thickness divided by the final thickness multiplied by the number of layers in the final sample (the last term is denoted as 2^n , where n is the number of folds made).

The as-solidified ribbon and three rolled samples were examined by XRD and TEM techniques. The three rolled samples have reduction ratios of 1.4, 1.7 and 8.5. Fig.1b-d shows XRD patterns taken after each of the foregoing RRs. Amorphization was evident after the first passes. After a $RR = 2.0$, the samples began to fragment, but with further rolling they consolidated into foils of fully amorphous $Cu_{35}Ti_{65}$.

Thin foils suitable for electron microscopy were prepared by cold-stage ion milling in order to avoid microstructural changes in the ribbons. The use of a pair of guns which can be rotated simultaneously makes possible the preparation of specimens representative of either one of the ribbon surfaces (by using one gun only) or specimens representative of the middle of the ribbon (by using both guns). The milling conditions were 5kV at an incidence angle of 14° so as to avoid differential thinning.

The microstructural evolution of particles in the middle of the ribbon after a $RR = 1.4$ is discussed below. A complete description of the process will be given in a subsequent report [3].

MICROSTRUCTURAL EVOLUTION

Starting ribbons

A fine crystalline layer forms on the free-surface (FS). The phase observed by TEM is $CuTi_2$ with a grain size of $0.2\ \mu m$. The phase Cu_3Ti_2 was observed only in very small amounts. However, the XRD pattern in Fig. 1a shows large peaks corresponding to this phase; these can be explained in terms of a crystallization texture. In the middle of the ribbon (MR) there is a primary crystallization of $CuTi_2$ particles, with the particles size increasing towards the free surface (FS). In the MR the particle distribution is trimodal with modes at 100 nm, 40 nm, and 10 nm, as shown in Fig. 2. Some of the smaller particles are observed to be twinned; the particles closest to the FS are large 100 nm particles of a spherulitic morphology. Near the wheel surface (WS) only the smallest particles are observed. The structural gradient through the ribbon arises from a pronounced cooling gradient across the ribbon thickness [4]. Additional consideration of the variations of the cooling rate through the ribbon and velocity of the solidification front as affected by heat transfer and recalescence effects, can explain the microstructural variations [5], [6].

Accumulation of defects and nucleation of glass ($RR=1.4$).

After a $RR = 1.4$, XRD indicates a decrease in the amount of crystalline phase present (Fig. 1b). TEM examination of the MR reveals a new glass phase nucleated at the particle boundaries in a melting-like amorphization process. The microstructural aspects of this process are illustrated in Fig. 3 where the new amorphous phase appears as a halo-like region at the outer periphery of each of the various particles. A large spherulitic particle results in an acicular morphology. In the lower right near the crack two particles that are undergoing amorphization are observed; the one on the right shows twinning while the one on the left, in a more advanced stage of amorphization, shows small 5 nm crystalline regions. The amorphization of particles is shown in more detail in Fig. 4 where the central portion of a spherical particle is crystalline

Fig. 2. Particle distribution in MR (a and b). The distribution is trimodal with modes at 100 nm, 40 nm and 10 nm. XBB 860-8812

Fig. 3. Microstructure of the MR after $RR=1.4$. Melting-like amorphization of spherical particles and development of acicular morphology from spherulitic particles are observed. XBB 869-7886

CuTi_2 . The new glass phase nucleated at the interphase interface and migrated inward. At this stage of deformation the interfaces between the matrix and the new amorphous phase are still clearly evident, but they disappear with additional rolling and increased amorphization [3]. Other particles were found to contain several crystals and amorphous regions developed at intrapphase interfaces as well as at the particle surface. A shear band is observed near the particle in Fig. 4 and a crack nucleated within the band that has been formed under tension. Other regions were found where the particles interact with the shear bands. It is clear that particle amorphization is intimately associated with the inhomogeneous distribution of plastic deformation of the glassy matrix.

The foregoing observations are consistent with many previous examples of localized melting and amorphization. In the process of ordinary melting crystalline phases, the liquid phase nucleates readily at free surfaces, and grain boundaries [7]. Similarly, during irradiation of ordered intermetallics, the nucleation of glass has been observed, for example, at antiphase boundaries in Cu_4Ti_3 [8], and at dislocations in NiTi [9]. It has also been shown that during amorphization induced by the dissolution of hydrogen in a crystalline $\text{Zr}_{.75}\text{Rh}_{.25}$ solid solution, the glass phase nucleates at the grain boundaries [10]. Other observations of this nature are discussed in detail by Johnson[1]. All of these investigations point out that enough chemical disorder can be built into an intermetallic compound crystal so that it will melt into a glass that nucleates in the regions of highest disorder. However, as a first approximation, a necessary condition is that the free energy of ordering is greater than the formation energy of the glass. Furthermore, the intermetallic must show a narrow homogeneity

Fig. 4 Melting-like amorphization of spherical particle. A shear band is observed close to the particle. SAD and DF indicate that there is a single crystal of CuTi_2 remaining inside the particle.

XBB 869-7887

range since otherwise, the defect density can be accommodated by a change in stoichiometry rather than leading to solid-state melting. Recently, a description of the SSAR reactions in the language of the theory of melting has been proposed [11].

It is important to note that the nature of the chemical disorder produced depends uniquely on the synthesis method utilized. For deformation induced amorphization of ordered intermetallics compounds, chemical disorder can be introduced by the formation of point defects, dislocations and in particular antiphase boundaries. In this study it was difficult to isolate such defect build-up within the tiny particles but substantial defect accumulation was observed in the more extensive crystalline regions near the FS [3].

An important aspect of the melting of particles is the extent to which crystalline regions are retained (in terms of the smallest crystalline region size). Typical areas in the MR are shown in Fig. 5a and 5b. Two types of particles are shown; in Fig. 5a amorphization has started but large crystalline regions still remain; in Fig. 5b particle amorphization seems complete. This is verified in the electron microscope by the disappearance of Bragg spots in the diffraction pattern, and by the fact that the particles maintain uniform unchanging contrast with specimen tilting through large angles. In order to examine the degree of amorphization in the particles in Fig. 5b, microdiffraction experiments were carried out. The probe diameter utilized is $.2 \mu\text{m}$, which is just slightly larger than the particles so that information from the matrix is minimized. The convergence angle utilized (6.14 mrad) is such that non-overlapping regions occur for the rings from the amorphous matrix.

Crystalline plus glass diffraction from a particle in Fig. 5a is shown in Fig. 5e; the $[103]$ and $[110]$ discs of CuTi_2 overlap the first amorphous ring. Discs, instead of spots, are observed in the diffraction pattern due to the convergence of the beam. The

Fig. 5. Microdiffraction experiments on the extent of amorphization of particles; (a) arrowheads indicate particles that still have large crystalline regions; (b) arrowheads indicate particles where amorphization seems complete; (c) and (d) microdiffraction pattern from one of the particles indicated in (b), (d) is a different exposure to show the intensity distribution in the center of the diffraction pattern in (c); (e) diffraction pattern from one of the particles indicated in (a); (f) microdensitometer trace of (c); (g) microdensitometer trace of a microdiffraction pattern taken from the amorphous matrix, the limits of the first ring are indicated by the arrows. XBB 860-9597

diffraction pattern from a particle in Fig. 5b is shown in Fig. 5c and also in Fig. 5d with different exposure in order to bring out the intensity distribution within the central region of the pattern. Diffraction was also obtained from the amorphous matrix, using the same beam size and convergence angle for comparison. The significant spacings (obtained by selected area diffraction patterns) from the amorphous matrix and the CuTi_2 particle are shown in Table 1. The breadth of the rings are also indicated in the table. Curves of electron density as a function of the scattering angle $S = 4\pi \sin \theta / \lambda = 2\pi / d$ for linear scans in different directions across each negative were obtained by microdensitometer traces of the diffraction negatives. The densitometer trace from the amorphous matrix is shown in Fig. 5g; the extent of the amorphous ring is indicated by arrows. The densitometer trace from the diffraction pattern of a particle whose amorphization seems complete is shown in Fig. 5f. The extent of the amorphous ring (indicated by the left and right arrows) is the same indicating that the two glassy phases are similar. A dip is observed in the center of the

Table 1
Significant Spacings

Ring or Plane	Spacing (d) or Radius (A)	$S = \frac{2\pi}{d} \text{ in } (\text{\AA})^{-1}$
1	2.05±.10	3.06±.14
2	1.20±.10	5.24±.57
3	.95±.10	6.61±.63
[103]	2.28	2.75
[110]	2.08	3.02

ring (center arrow) which is postulated to be due to the existence of nanocrystalline regions. As noted earlier, the diffraction pattern of a particle with large crystalline regions (Fig. 5e), contains the [103] and [110] spots superimposed on the first amorphous ring. In the case of very small crystalline fragments the spots can not be observed but their presence is revealed in the microdensitometer trace. The dip at the center of the ring is the result of the superposition of the spots intensity distribution with the amorphous ring intensity distribution. The exact position of the dip depends on the relative intensity and position of the two reflections for a particular densitometer trace, and thus it varies within the same diffraction pattern. Although the effect is subtle, it is observed consistently for the particles at this stage of deformation, and it is never observed for the amorphous matrix.

The microdiffraction experiments further illustrate the melting-like nature of the amorphization transformation. Melting proceeds from the particle boundaries and internal interfaces inwards. Approaching the final stages, nanocrystalline regions still remain, but with further deformation these disappear leading to a homogeneous glass. The latter behavior will be described in a subsequent report [3].

CONCLUSIONS

It has been shown that deformation-induced amorphization proceeds by a build-up of local chemical disorder through the creation of a defect structure. These local regions become unstable with respect to an amorphous phase that nucleates preferentially at internal interfaces or particle boundaries. This process can be understood on the basis of the thermodynamic and structural arguments that have been presented in [1].

Results of rapid solidification experiments are usually interpreted in terms of T_0 curves, i.e. the locus of points where the free-energies of two phases are equal [5]. The T_0 curves represent the thermodynamic limit of metastable defect-free crystalline phases with respect to melting. Below the glass transition temperature T_g , the T_0 curves mark the critical conditions for a crystal-to-glass transition.

In the case of line intermetallic compounds it is perhaps more meaningful to consider a $T_0(C_d)$ curve which is a function of the concentration of defects. It indicates the region where a metastable defective phase is preferred over the liquid. Below T_g and outside $T_0(C_d)$ the defective crystalline phase transforms to a glass. As defects are introduced into a line intermetallic phase, the long range order parameter

decreases. Consequently, the ordering enthalpy is released and the compound can be superheated with respect to the glassy phase. If the temperature is low enough so that there is no substantial annealing of defects, a crystal-to-glass transition occurs. These arguments have been used to model the crystal-to-glass transition in intermetallic compounds during ion irradiation [1].

The approach presented above, together with the observations on the heterogeneous nucleation of glass, provide a reasonable model of the amorphization reaction described in this paper. More quantitative modeling should await observations on, for example, the evolution of the long-range chemical order parameter during the mechanical deformation of intermetallic compounds.

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