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AN AEM STUDY OF THE SOLID-STATE NUCLEATION OF METALLIC GLASS AT GRAIN BOUNDARIES

E. A. Kamenetzky, W. J. Meng, L. E. Tanner and W. L. Johnson

Amorphous phases can be produced by solid-state interdiffusion reactions of elemental composites or thin film multilayers. The thermodynamics and kinetics of these amorphization reactions in metals have been reviewed by Johnson. Whereas the thermodynamic driving force for the formation of equilibrium phases is greater than that for the formation of metastable amorphous phases, the formation of the metastable phase is enhanced by competing kinetic paths for the formation of the various phases. In particular, the dominant diffusion of one species and the role of interfaces in nucleations kinetics and growth, determine whether an amorphization reaction occurs.

The solid-state amorphization reaction of Ni and Zr has been studied in considerable detail. The driving force of the amorphization reaction is the negative free-energy of mixing.

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of the amorphous (liquid) phase. Since Ni is a fast diffuser in Zr, the relative absence of Zr self-diffusion and Zr diffusion in amorphous Ni-Zr, below the crystallization temperature, inhibits the nucleation and growth of equilibrium phases.

It is interesting to establish the structural aspects of the reaction mechanism of the crystalline to amorphous transition. Cross-sectional TEM investigations reveal that Ni diffuses through the glass via a vacancy mechanism, and that the growth of the reaction product occurs at the a-NiZr/c-Zr interface. However, the nature of the nucleation of glass is not addressed in that study. In particular, grain boundaries might play an important role in the nucleation of glass at the original c-Ni/c-Zr interface. Grain boundaries are regions of disorder and excess free volume which promotes diffusion. They are then the most likely site for the nucleation of the glass. Once the glass is nucleated and, if the Ni can diffuse through the glass, growth can occur at the a-NiZr/c-Zr interface. Since different grain boundaries have different amounts of disorder and free volume, a detailed characterization of grain boundary parameters would give an insight into the reaction mechanism. An indirect confirmation of the role of disorder at the nucleating interface is given by the fact that amorphization does not occur on a Zr (112) single crystal surface but it proceeds with either ion mixing of the interface or deposition of a thin polycrystalline layer of Zr on top of the single crystal. The purpose of this investigation is to establish directly the role of grain boundaries in the nucleation of glass in solid-state amorphization reactions.

Experimental

Zirconium foils, 20 \( \mu \text{m} \) in thickness, were recrystallized at 800 °C for 5 to 10 hrs. under a pressure of the order of \( 10^{-8} \) Torr. The material was 99.9% pure but no detailed chemical analysis was available. The role of impurities in glass nucleation is discussed further below. Without breaking vacuum, a sequential layer of Ni, 0.1 \( \mu \text{m} \) thick, was
sputter deposited at a rate between 3 and 5 A/sec. Thin foils suitable for electron microscopy were prepared by dual-gun cold-stage ion milling. Four annealing treatments were investigated: 275 °C for 3.5 hrs., 300 °C for 3.5 hrs., 325 °C for 2 hrs., 350 °C for 2 hrs. Glass pockets were observed at 275 °C.

**Analysis and Results**

For the samples annealed at 275 °C all glassy regions occur at grain boundaries. A detailed characterization of the type of grain boundaries was carried out as follows. The misorientation between the crystals that compose a grain boundary is determined by electron diffraction. The minimum set of data required is two pairs of diffraction patterns with tilting fixed for each pair. The crystal normal (the direction antiparallel to the beam) is determined by the most suitable method for each diffraction pattern (e.g. intersecting Kikuchi lines, ring of intense spots, etc.). The crystal normals \( \mathbf{h} \) are given in hexagonal coordinates. Their coordinates in orthonormal coordinates is given by

\[
\mathbf{x} = S \cdot \mathbf{h}
\]

(1)

where \( S \) is the structure matrix. In orthonormal coordinates the rotation matrix is the orthogonal matrix that relates the diffraction pairs.

\[
\mathbf{x}_1' = R \cdot \mathbf{x}_1
\]

(2)

where \( \mathbf{x}_1 \) is the normalized crystal normal of grain 1 for the pair sub i, and the primed vectors correspond to grain 2. Since two pairs of vectors \( \mathbf{x} \) are known, a third can be generated by the vector product of the first two. The solution to the rotation matrix is given by three systems of three equations with three unknowns.

In the hexagonal crystal system the basis may be chosen in more than one way because of the symmetry of the crystal. There are 12 symmetry elements that correspond to the rotations of the point group 632. The twelve different descriptions of the rotation matrix
are given by
\[ x_1' = R \cdot S \cdot R_a \cdot S^{-1} \cdot x \]  
(3)

It is common practice to refer to a rotation in terms of the axis and angle of rotation: The axis/angle pairs corresponding to the minimum misorientation angle and the twin description (if it exists) are chosen. These are compared with tables of coincidence-site lattices.\(^5\)

Hexagonal CSLs are approximated by ideal \( c^2/a^2 \) ratios. For Zr, \( c/a = 1.59 \) is approximated by \( \sqrt{5/2} = 1.58 \) or \( \sqrt{18/7} = 1.60 \). If a ratio of larger numbers such as \( \sqrt{33/13} = 1.59 \) is used only CSLs with low coincidence, high \( \Sigma \), are generated. From a physical point of view all the frequently occurring low \( \Sigma \) descriptions are generated by the first two ratios. A boundary is considered to be close to coincidence when its deviation from the exact CSL is given by a small-angle rotation.

\[ R_{exp} = R_{sa} \cdot R_{CSL} \]  
(4)

Only CSLs with \( \Sigma \) lower than 50 were considered.

The following grain boundaries were observed in Zr. Six small-angle grain boundaries with varying degrees of misorientation were studied. They are of mixed tilt and twist components. Glass nucleates in two of these which have misorientations larger than 10°. These two boundaries are shown in Fig. 1, the third boundary in that figure has a misorientation angle of 14°.

The crystallography of six large-angle grain boundaries was also studied. At three large angle grain boundaries which are far from coincidence, glass has been observed to nucleate. At two boundaries which are close to \( \Sigma = 7 \) [0001]/21.79°, glass does not nucleate and similarly at one close to \( \Sigma = 17 \) [10\( \overline{1} \)0]/40.12°. In this notation \( \Sigma \) indicates the volume fraction of coincidence sites.

Glass does not nucleate at twin boundaries. The most commonly observed nucleation site was grain boundary triple junctions. One example is shown in Fig. 2 where all the
boundaries are large-angle and far from coincidence.

The composition of these glassy regions was studied by EDX in a JEOL 200 CX analytical microscope with a high-angle detector and an ultra-thin window detector. Because the glassy regions were thinner than the bulk, the best count rates obtained were 200 c/s with a 600 Å probe. A typical spectra from a glassy region is shown in Fig. 3, were it is shown that the major components are S and Cl. A typical composition of a glassy pocket, in atomic percent is: 31.54 S, 21.19 Cl, 18.80 Zr, 9.45 Si, 8.36 Ni, 5.36 Cu, 2.23 Ti, 1.63 Fe and 1.44 Mn. Spectra taken just outside the glass pockets shown no indications of the presence of elements other than Ni and Zr; in this case the Ni signal originates from regions of the Ni thin film that remain after ion milling. The origin of this complex glass will be discussed.

Discussion and Conclusions

The role of grain boundaries is discussed next. It has been shown in a number of experiments that some grain boundaries with a high degree of coincidence have special properties. Special boundaries have low grain boundary free volume or, equivalently, low grain boundary energy. The variations of grain boundary properties such as corrosion, diffusion and hardening can usually be predicted based on the grain boundary free volume. The grain boundary free volume is plotted in Fig. 5 for an ideal set of boundaries where the axis of rotation is fixed. For small-angle boundaries the free volume follows a Read-Shockley type relationship because it depends on the density of dislocations. Large-angle grain boundaries are open structures except special boundaries which show local minima in the free-volume curve. The open general large-angle boundaries are favorable paths for diffusion. The nucleation of glass at grain boundaries can be understood following a scheme for boundary wetting of ceramics. If the energy of the GB is greater than twice the energy of the crystal/amorphous interface then glass should nucleate. The exact relation between these
two quantities can produce wildly different wetting regimes. This is the simplest view of wetting; a full consideration should take into account the nature of the particular forces at play for a given system. Non-wetting nucleation can always occur at triple junctions. This is in fact the most common form of nucleation observed in the Ni on Zr system.

The volume fraction of glass pockets was estimated to be $10^{-4}$. Thus, the amount of impurities present at the glass pockets can be justified if the impurities are present almost entirely at the same grain boundaries where nucleation occurs. For a well recrystallized foil these impurities which have very low solubilities in Zr will segregate to grain boundaries. In addition, EDX grain boundary profiles show detectable amounts of impurities in only a very few grain boundaries. The glassy pockets are probably a mixed chalcogenide-halide glass. The formation and growth of the glass pockets is dominated by S and Cl, since the glass pocket size for a Ni-Zr glass should be of the order of .1 $\mu$m.$^4$ There are no previously reported Zr-S or Zr-Cl glasses, although many different halide glasses have been investigated recently for their optical properties. However, it is known that that the glass forming tendencies are improved when two or more different halogens are present in a glass.$^9$ As the reaction continues Ni would become the dominant species that diffuses into Zr and a Ni-Zr glass would form.

As discussed above nucleation is heterogeneous. The crystal-glass interface is very sharp. The aspect of the glass pockets (Fig. 1 and Fig. 2) is that of a melting-like reaction. These features are common to the formation of disordered phases in different phase transformations.$^{10}$

It has been shown that grain boundary impurities play a significant role in the nucleation of glass pockets in solid-state amorphization reactions. Grain boundaries act as fast-diffusion paths for the reaction to occur. The grain boundary free volume plays then a dual
role; first facilitating diffusion and then as a preferential site for nucleation. A hierarchy of nucleation sites is observed with nucleation at triple grain boundary junctions being the most commonly observed. Glass pockets occur at grain boundaries far from coincidence but does not occur at near-coincidence and small-angle boundaries.

References


Figure Captions

Fig. 1.-- Nucleation of glass at small-angle grain boundaries; lower glass pocket has a misorientation of 14°, upper glass pockets have misorientations larger than 10°.

Fig. 2.-- Nucleation of glass at triple grain boundary junction; (a) and (b) BF and DF; (c) SAD of glass pocket.

Fig. 3.-- typical EDX spectra of a glass pocket.

Fig. 4.-- EDX spectra just outside the glass pocket.

Fig. 5.-- The wetting regime is determined by the grain boundary free volume.
GLASS POCKETS AT ZR GRAIN BOUNDARIES

Vert = 288 counts

Figure 3.
Figure 4.
Figure 5.

Solid-state wetting regime

\( q \) of boundary energy.

Grain boundary free volume.