NANOCRYSTALS IN ALUMINUM-RICH METALLIC GLASSES

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Abstract

This paper will detail work done on the formation of nanocrystals in aluminum based metallic glasses. Up to 30% increase in tensile strength can be obtained through the formation of nanocrystals surrounded by an amorphous matrix. Glasses that exceed 1200 MPa are obtained for several of the compositions and reveal increased strength values after partial crystallization. Various methods to form nanocrystals of aluminum in an amorphous matrix are discussed and include mechanical and thermal processing.

Introduction

Nanocrystals were first reported in Al-based metallic glasses in 1990 by He, Chen, Shiflet and Poon (1). Following this initial observation the exploitation of nanocrystals towards improving mechanical properties soon followed (2,3). This advance was possible because of the discovery, in 1988, of the family of flexible and strong metallic glasses containing up to 90 at.% Al (4,5). In our group, these Al-rich metallic glasses were discovered during the search for aluminum-rich quasicrystals in the $Al_{20}Cr_2Ce$-type alloys ($Al_{18}Cr_2Mg_3$ structure, 184 atoms per unit cell) (6). In this process, an Al-rich metallic glass of composition $Al_{20}Fe_2Ce$ was obtained, which was produced in continuous ribbons by single-roller melt spinning. This has led to the synthesis of many metallic glasses containing up to more than 90 at.% aluminum. Many of these metallic glasses were found to be flexible with good local ductility, and the amorphous ribbons can be bent 180 degrees without fracture. It was also found that the formation range in this new family of metallic glasses can be as wide as 20 at.% or more.

It is well documented that metallic glasses possess high strength with good bending ductility. The fracture tensile strength of a metallic glass is usually much higher than that of its crystalline state with the same chemical composition. Most metallic glasses lose their high fracture tensile strength and ductility upon crystallization, although there are reports that some metallic glasses still exhibit

high fracture strengths and adequate ductility after partial crystallization by quenching or isothermal annealing near their glass transition temperature. Such a sudden loss of ductility and strength is a severe disadvantage of metallic glasses as engineering materials; the retention of these properties after partial crystallization would obviously be very attractive. Crystallization need not always be deleterious to properties such as strength. In Al-based glasses, partially crystallized material actually increases the fracture strength by ~30%.

This paper will report on the various methods used to produce nanocrystal of aluminum in an amorphous matrix. We have found four different methods of producing nanocrystals. They are: 1) melt-spinning into wholly amorphous material followed by a thermal anneal; 2) melt-spinning with an alloy content rich in aluminum; 3) mechanical alloying; and 4) deformation induced crystallization.

Experimental Procedure

The alloys were prepared by arc melting nominal amounts of elements in an argon atmosphere. Melt spinning was carried out in a partial helium atmosphere using a 0.20 m diameter copper wheel with variable circumferential velocity. Samples are formed with dimensions of 15-250 μm thick, 1-2 mm wide, and up to several meters long. Partially transformed materials were secured by first encapsulating in an argon atmosphere and then isothermally heat treated. Ball milling was performed with a SPEX-8000 laboratory ball mill.

Results and Discussion

Nanocrystals Formed from an Initially Wholly Glassy Material by Thermal Anneal

The first approach taken was to initially obtain wholly amorphous $Al_{90}Fe_5Gd_5$ material through melt spinning, followed by isothermal annealing at 445K, which is just below the crystallization temperature determined by DSC. The mechanical properties of the alloy are included in Table 1. The strength of the isothermally heat treated and partially crystallized $Al_{90}Fe_5Cd_5$ alloy has a fracture tensile strength of 1010 MPA which is much higher than its pure metallic glass form. To follow the crystallization process an $Al_{90}Fe_5Gd_5$ metallic glass was annealed at 170 ^{o}C for increasing times to examine the uniaxial tensile strength as a function of the phase transformation(s) (fig. 1). The fracture tensile strength increases from the as-spun value of 720 MPa to 920 MPa during the first 20 min. of annealing. This increase in strength corresponds with nanocrystalline precipitation. Because of the very high density (10^{23} per cubic meter) and uniform distribution, the efficacy of the nanocrystalline-amorphous matrix material in preventing the onset of fracture is high in this system. As annealing time increases from 20 min to 90 min., the strength decreases dramatically to 330 MPa. A reduced rate of decreasing strength occurs from 90 min. to 350 min. As annealing time exceeds 400 min. the fracture tensile strength remains at about 200 MPa.

Nanocrystals Formed from an Initially Aluminum Supersaturated Liquid Mixture

Another approach is to prepare a slightly aluminum enriched alloy ($Al_{90}Fe_{4.75}Gd_{4.75}$). This results in a partially crystallized alloy directly from melt-spinning without any further heat treatment. The fracture strength of the quenched, partially crystallized $Al_{90.5}Fe_{4.75}Gd_{4.75}$ metallic

glass also exceeds that of the as-spun $Al_{90}Fe_5Gd_5$ metallic glass (Table 1).

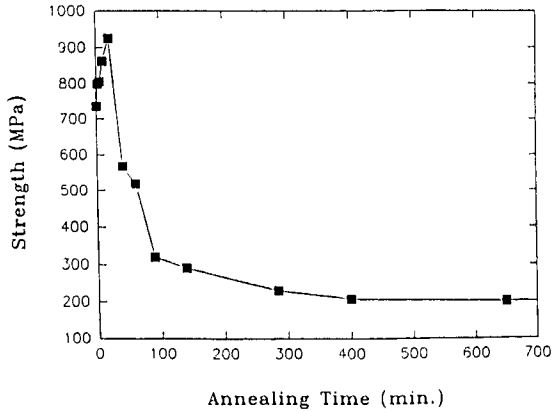

FIGURE 1. Fracture tensile strength of a partially crystallized $Al_{90}Fe_5Gd_5$ metallic glass as a function of annealing time. The annealing temperature is 170 °C.

Microstructure of Nanocrystals in an Amorphous Matrix

The first two methods produce similar microstructures (Figs. 2 and 3). Here the partially crystallized metallic glasses (whether as-spun $Al_{90}Fe_5Gd_5$, annealed at 445 K for 20 minutes or as-quenched $Al_{90.5}Fe_{4.75}Gd_{4.75}$) have the crystalline particles homogeneously embedded in the amorphous matrix. The particle density was estimated from both TEM and X-ray experiments to be about $4x10^{23}$ per cubic meter, which is typical for homogeneous nucleation. Fig. 3 is a HREM image of one of the crystallites. Tilting reveals the crystal structure to be f.c.c. with a lattice parameter of 0.4 nm, suggesting that the crystallites are aluminum. The size of the crystalline particles is about 8 nm and their morphology is roughly spherical.The volume fraction of crystallites for both the annealed alloy and the as-quenched, partially crystallized metallic glass is about 28%.

The final microstructure of an $Al_{90.5}Fe_{4.75}Gd_{4.75}$ alloy, when produce by melt-spinning only, i.e., no subsequent thermal treatment, is identical to Figs. 2 and 3. Indeed, the liquid has sufficient aluminum content that precludes a wholly amorphous material. This results in aluminum precipitates forming uniformly upon quenching. All of the ternary systems could be produced in glassy form only if the ribbon thickness was maintained less than about 20 μm, that is, at high spinning rates.

TABLE 1.

Mechanical Properties of Amorphous and Partially Crystallized (PC) Metallic Glasses (from refs. 3,8,9)

Alloys	Structure	Heat Treatment	Tensile Strength	Elastic Modulus
$Al_{90}Fe_5Gd_5$	PC	445 K, 20 min.	1010 MPa	-
$Al_{90.5}Fe_{4.75}Gd_{4.75}$	PC	as-spun	938	-
$Al_{90}Fe_5Gd_5$	amorphous	as-spun	735	-
$Al_{85}Ni_6Fe_3Gd_6$	amorphous	as-spun	1280	72.7*
$Al_{85}Ni_5Fe_2Gd_8$	amorphous	as-spun	1210	75.3*

*determined with ultrasound techniques

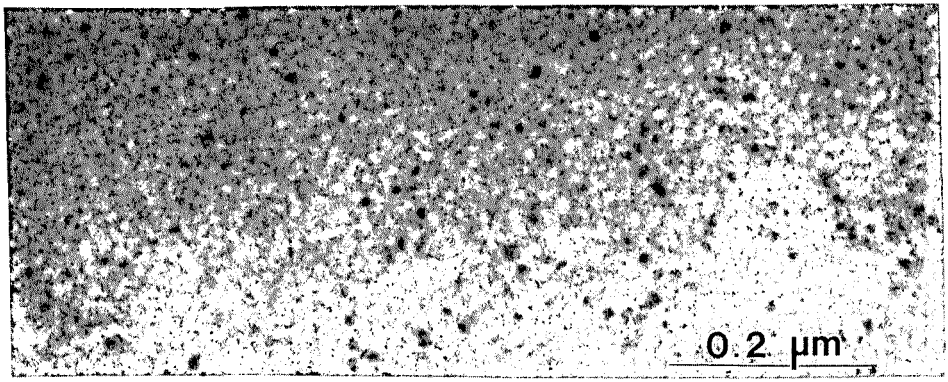

FIGURE 2. TEM image of a partially crystallized $Al_{90}Fe_5Gd_5$ metallic glass which has been annealed at 445K for 20 minutes. The various shades of contrast of the crystallites are due to random orientations of the aluminum crystallites (3).

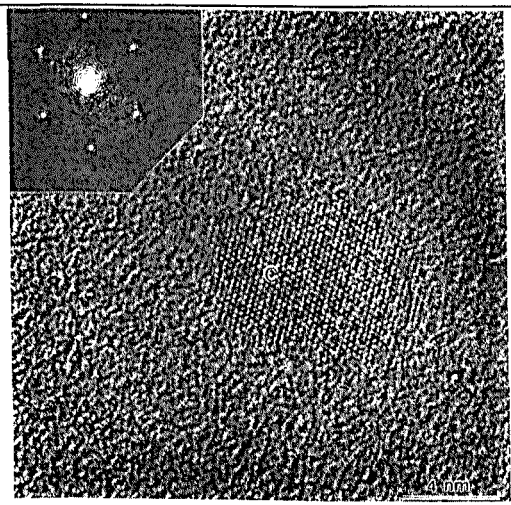

FIGURE 3. HREM image of the rapidly solidified and annealed $Al_{90}Fe_5Gd_5$ alloy. The inset represents the optical diffractogram, which is equivalent to a Fourier transformation and shows that the crystallite in the center of the micrograph is oriented along the 110 direction (1).

Nanocrystals Formed in Material by Mechanical Alloying

Recently, investigations have been carried out on the formation of amorphous phase through solid-state reactions, typically by the use of mechanical alloying and interdiffusion between thin films. Because these solid-state transformations do not rely on high-heat transfer rates, this suggests the possibility of forming bulk amorphous material through powder metallurgy with much larger dimensions than by the rapid-solidification techniques. Mechanical alloying can be performed by any of several methods, but the most common method is ball milling. Using this method, alloys are formed by placing the constituent elemental powders into a hardened metal jar with a number of hard metal balls, then sealing the jar (usually under some inert atmosphere to prevent powder oxi-

dation) and placing the jar into a machine that shakes it for a long period of time, until the elemental powders are so intimately cold-welded and interdeformed that they transform into powdered alloy. In the case of easily amorphizable alloy systems, the powder product is often seen to be the amorphous phase. Never during the process does any material melt, therefore eliminating all consideration of rapid-solidification phenomena. At short milling times, when the elemental powders have not yet interdeformed to the extent that they have lost their individual identities, a fine structure of highly deformed cold-welded elemental layers is observed. Particularly useful is the fact that the milling process itself produces enough localized thermal energy to drive the interdiffusion and lead to amorphization. The structure of the amorphous phase formed in this way is essentially the same as that produced through rapid-quenching (7). Application of this technique to $Al_{80}Ni_8Fe_4Gd_8$ (8) where the elements are mixed and ball-milled up to 20 hours is shown in Fig. 4 where X-ray diffraction traces, as a function of milling time, have previously illustrated the amorphizing of this alloy (8).

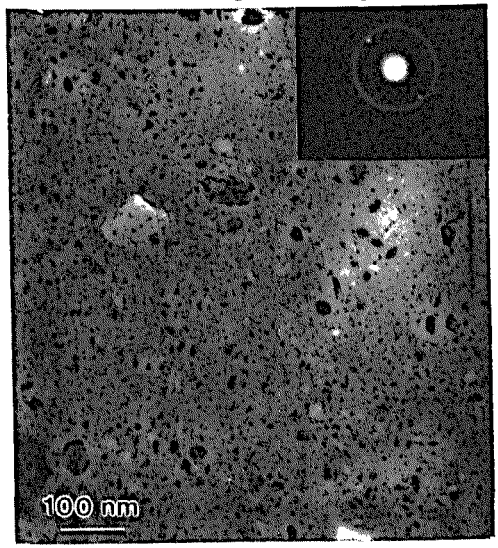

FIGURE 4. TEM image and selected area diffraction (SAD) pattern for $Al_{80}Ni_8Fe_4Gd_8$ sample ball milled for 20 hours (8).

At 80 hours the microstructure approaches its maximum refinement, with only a few very small nanocrystals remaining (generally less than 10 nm in size). Dougherty *et al.* (8) described the microstructural evolution of the amorphous phase to indicate that the initial amorphization reaction takes place between critically thin layers of aluminum and gadolinium after roughly 2 hours of milling. Iron and nickel do not participate in the initial formation of amorphous phase. Aluminum diffuses into neighboring layers of crystalline gadolinium, and when the aluminum concentration becomes a significant fraction of the total composition layer, an amorphous character begins to be seen. The degree of amorphous character appears to be proportional to the aluminum concentration in the gadolinium parent layers.

Nanocrystals Formed by Deformation--Shear Deformation

The formation of localized shear bands and the deformation mechanism of amorphous alloys have been the subject of much theoretical discussion (9-11) and computer simulations (12,13). Local-

ization of plastic flow requires that the material within the shear bands undergoes some structural changes, causing a local softening of the material, so the material inside the shear bands deforms more easily than the rest of the sample. In our experiments we used four different aluminum-based glasses (14), namely $Al_{90}Fe_5Ce_5$, $Al_{90}Fe_5Gd_5$, $Al_{87}Ni_{8.7}Y_{4.3}$ and $Al_{85}Ni_{10}Ce_5$. The ribbons were bent through 180 degrees and the area of the shear band examined with conventional and high resolution TEM. The seemingly "straight" shear bands are shown with SEM in Fig. 5. TEM shows the shear bands not to be straight (as expected) and to contain small precipitates Fig. 6. The apparent width of the shear band is due to tilting the sample in the microscope; tilting for minimum thickness reveals the band to be less than 10 nm. A high resolution image of the shear band precipitates shows they are identical to Fig. 3.

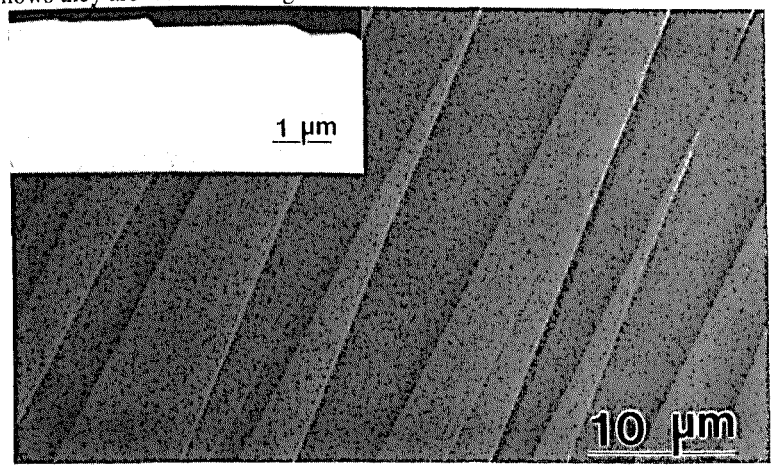

FIGURE 5. SEM picture of the surface of $Al_{90}Fe_5Gd_5$ metallic glass ribbon that has been bent through 180 degrees at room temperature. The straight lines are slip steps which are terminations of the shear bands on the surface. The inset picture is a profile of the surface steps (14).

Nanocrystals Formed by Deformation--Ball Milling

The structural changes in Al-based glasses caused by ball milling were investigated to further understand the deformation-induced crystallization observed in some aluminum-based glasses (15). In an amorphous $Al_{90}Fe_5Gd_5$ alloy, ball milling for 2 min. induced the formation of nanocrystalline Al particles (Fig. 7). These nanocrystals are roughly spherical, with a diameter of 10-20 nm, and the crystallographic changes with milling time can be followed employing X-ray analysis. The results are consistent with the observation that nanocrystal formation can be induced within the shear bands of some Al-based glasses after bending, as discussed above. SEM micrographs of ball-milled $Al_{90}Fe_5Gd_5$ amorphous ribbons revealed that the resulting shear bands are similar to those produced by bending. After ball milling for a very short time (30 sec to 2 min), severe shear deformation is readily observed on the ribbon surfaces. The ribbons break into shorter pieces, and cracks are formed. Generally, three types of surface morphology of the deformed ribbons are observed. In some areas narrow shear bands are found which confine the plastic deformation. These shear bands are quite straight and similar to those produced by bending. Different areas reveal shear steps that can be rather wide and more irregular. Another different area where the plastic deformation is still more irregular and severe is also observed. This latter area has features similar to the vein or river pattern commonly observed on the tensile fracture surface of an amorphous

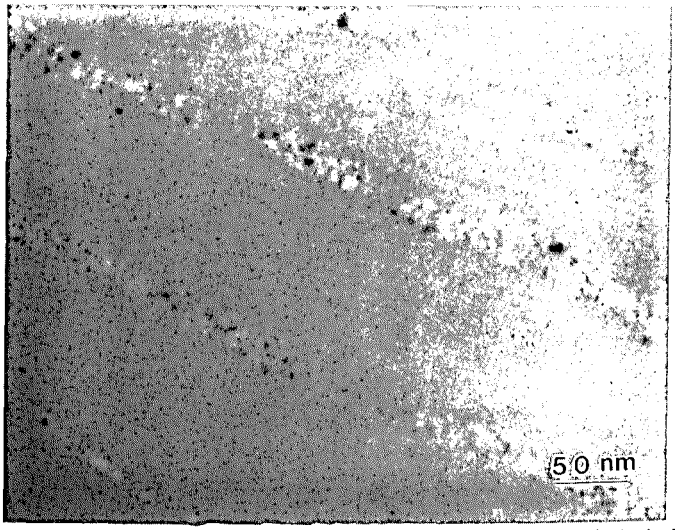

FIGURE 6. TEM micrograph of a slip band shown in Fig. 5. The white and black circles inside the shear band are the crystalline precipitates. The surrounding area is amorphous matrix. HREM images look identical to Fig. 3 (14).

alloy. SEM examination reveals that under ball milling the Al-based metallic glasses can have large plastic strain and the ribbons do not fracture in a brittle fashion. When subjected to prolonged milling (greater than 10 min.) the ribbons become flakes and eventually powders, and the typical particle size after milling for several hours in 10-20 microns. In other samples, with different chemistries, no such ball milling induced crystallization was observed, indicating that the mechanical deformation-induced structural changes are sensitive to the chemical composition and thus the atomic structure and the bonding nature of the metallic glasses. DSC measurements showed that certain structural change occurs in these amorphous alloys after milling even though no crystallization was observed (15). The formation of nanocrystals in the ball-milled amorphous alloys in attributed to the atomic displacements under high stresses during the deformation process. Our results also confirm that the crystallization induced by mechanical deformation is different from that due to a thermal process. Thus, the mechanical process provides a new method of preparing amorphous powders embedded with a nanocrystalline phase. High-strength composite materials containing nanocrystals and amorphous matrix can therefore be synthesized by subsequent consolidation of these powders, using warm pressing, extrusion or explosive compaction processes.

Conclusions

The formation of nanocrystals in aluminum glass was shown to be easily obtainable by several techniques. Final processing steps that include either a thermal treatment or heavy plastic deformation (e.g. extrusion) can result with not only a shape change but also an increase in strength. This would be analogous to work hardening in the sense that the final processing steps simultaneously deform, shape and strengthen a material.

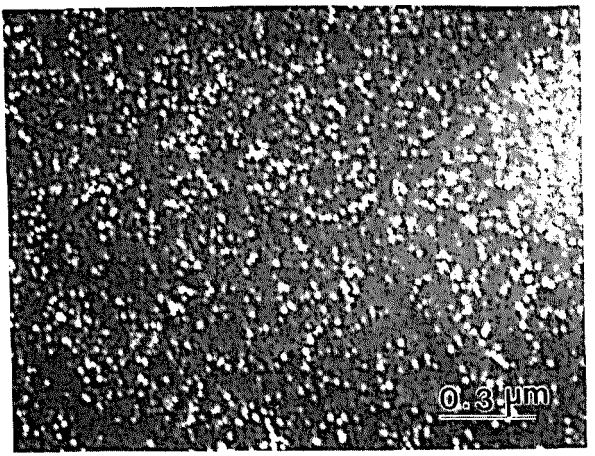

FIGURE 7. TEM dark-field micrograph of a glassy $Al_{90}Fe_5Gd_5$ ribbon after ball milling for 2 minutes. Nanometer size crystals are clearly shown.

Acknowledgment

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CRYSTALLIZATION OF AN AMORPHOUS $Al_{85}Y_8Ni_5Co_2$ ALLOY

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Abstract

The crystallization sequence of amorphous $Al_{85}Y_8Ni_5Co_2$ has been investigated. After rapid solidification the ribbons are fully amorphous. DSC, XRD and TEM investigations show that the alloy crystallizes upon heating as metastable fcc α-Al which decomposes into intermetallic phases and Al. The crystallization sequence occurs in three steps. The first reaction is precipitation and growth of supersaturated fcc α-Al in the amorphous matrix which starts at about 260°C. The second reaction is precipitation of intermetallic phases and further growth of α-Al. This reaction starts at about 310°C. This supersaturated α-Al finally decomposes into intermetallic phases in a less supersaturated α-Al matrix. Several different intermetallic phases are formed and grow during this reaction. The final reaction starts at about 360°C. To study this crystallization sequence in detail the ribbons have been heat treated at 8 different temperatures in the range 240-400°C. The purpose is to investigate if there are any differences in nucleation, composition and structure of the Al-crystals formed in the two first crystallization steps. The microstructure after the first crystallization step consists of a very homogenous distribution of Al-crystals in an amorphous matrix. After the second step the microstructure is more complex. TEM-investigations show that there are other phases than Al precipitating during this step. Similar results have been found by in-situ heat treatment in TEM.

Introduction

Al-base amorphous alloys with transition metals and rare earth metals as alloying elements are characterized by very high strength in combination with good corrosion properties. Al-Y-Ni amorphous alloys were first reported by Inoue et al, [1]. The addition of Co gives and increased endothermal heat exchange due to transformation from amorphous to a supercooled liquid prior to crystallization which is important for successful consolidation of the material. The alloy $Al_{85}Y_8Ni_5Co_2$ (at%) is promising for structural applications because of high hardness and good bending ductility, [2, 3].

The present study is an investigation of the decomposition of amorphous $Al_{85}Y_8Ni_5Co_2$ single phase into fcc Al and intermetallic phases upon heating. The crystallization kinetics of this alloy is imortant to understand for the development of consolidated fully amorphous or partially