Crystallization of $Zr_{55}Al_{10}Ni_5Cu_{30}$ Bulk Metallic Glass Composites Containing ZrC Particles

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$Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass composite containing 10 vol% crystalline ZrC particles was prepared by an *in-situ* reaction between Zr-based melt and graphite powder being followed by an injection casting into a copper mould. The crystallization process of the composites during annealing at 723 K has been investigated by using DSC, TEM and microhardness test. It is found that an unknown crystalline phase appears first along the interface between ZrC particle and the matrix of the composite, and then a homogeneous nanocrystallization occurs in the matrix. The nanocrystalline phase precipitated in the matrix is determined to have orthorhombic structure by using TEM diffraction. It has a higher hardness than the amorphous phase which remained in the matrix. Hardness of the matrix increases with increasing the volume fraction of the nanocrystalline phases. After annealed at 723 K for 40 min, most of the matrix has been transformed into crystalline phases with a final average grain size of about 120 nm.

(Received September 10, 2001; Accepted November 5, 2001)

Keywords: zirconium-based metallic glass, zirconium carbide, composites, nanocrystallization, transmission electron microscope observation

1. Introduction

It has been found that nanocrystals can be dispersed in an amorphous structure by annealing amorphous alloys.¹⁻⁴⁾ Some amorphous alloys containing nanocrystals exhibit excellent properties, for example, high strength and good ductility in the case of Al-based and Mg-based amorphous alloys,^{1,2)} and high permeability in the case of Fe-based alloys,⁴⁾ as compared with those of amorphous single-phase alloys.

Zr-based metallic glasses with a high glass-forming ability show high mechanical strength.⁵⁾ The crystallization behavior of the Zr-based metallic glasses has been studied.⁶⁾ Recently, $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass composite containing ZrC particles formed by an *in-situ* reaction between Zr-based melt and graphite powder is prepared, and it exhibits higher strength and larger elongation than the Zr-based metallic glass without ZrC particles.⁷⁾ It is expected that the properties of the composite can be improved further by obtaining nano-sized crystalline precipitations by use of annealing the amorphous matrix. The purpose of the present paper is to investigate thoroughly the crystallization behavior of the composite during annealing process.

2. Experimental Procedure

Crystalline ZrC particles with an average diameter 10 μm were formed by an *in-situ* reaction between Zr-based melt and graphite powder in an argon atmosphere. The melt with nominal composition $Zr_{55}Al_{10}Ni_5Cu_{30}$ containing 10 vol% ZrC particles was then injected into a copper mould, resulting in a bulk metallic glass composite of 2 mm in diameter and 40 mm in length. For studying the crystallization process of the composite, annealing time was changed from 15 to 40 min under a constant annealing temperature, being based on the differen-

tial scanning calorimeter (DSC) curve of the composite measured at 723 K. After annealing at a constant temperature of 723 K for different durations, the hardness of the matrices of the composites was tested at room temperature by a Vickers microhardness tester with the load of 0.49N, and the structures of the composites were examined using TEM observation. Furthermore, *in-situ* TEM observation during the annealing process of the composite was also carried out in order to study the crystallization procedure in real time.

3. Results and Discussion

The DSC curve of the $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glass composite containing 10 vol% ZrC shows that crystallization occurs during an annealing time ranging from 10 to 42 min at a constant temperature of 723 K, as shown in Fig. 1.

TEM micrographs of the composites before and after annealing are shown in Figs. 2, 3 and 6, respectively. It is seen that the composite consists of amorphous matrix and crystalline ZrC particles, as shown in Fig. 2. After the composite

Fig. 1 DSC curve of a $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass composite containing 10 vol% ZrC measured at 723 K.

Fig. 2 TEM micrograph of the composite before annealing.

Fig. 3 TEM micrograph of the composite annealed at 723 K for 20 min and the corresponding diffraction pattern of the composite matrix.

is annealed at 723 K for 20 min, it can be seen that a small volume fraction of crystals with an average size of about 65 nm precipitates in the matrix (Fig. 3). According to the electron

Fig. 4 Selected area diffraction patterns taken from one of the particles precipitated in the amorphous matrix and the corresponding patterns calculated, (a) [001] zone, (b) $[-111]$ zone, (c) $[-110]$ zone and (d) $[-120]$ zone.

diffraction pattern of the matrix shown in the bottom-right corner of the photo, it is known that most of the matrix remains as amorphous phase. On the other hand, another kind of phase with a width of about 200 nm precipitates along the boundary between ZrC particles and the matrix.

A careful tilting experiment permits determination of the crystal structures of the phases precipitated in the amorphous matrix and at ZrC/matrix interface. Figure 4 is a set of diffraction patterns taken from one of the particles precipitated in the matrix. Their zone axes are [001], $[-111]$, $[-110]$ and

Fig. 5 Selected area diffraction pattern taken from the phase precipitated at the ZrC/matrix interface.

Fig. 7 Hardness of the matrices of the composites annealed at 723 K for different durations.

$[-120]$, respectively. The reciprocal unit cell can be reconstructed from these diffraction patterns. It can be found that it is a C-face center one. Therefore, the phase is determined to have orthorhombic structure with the symmetry of space group CMCN (No. 63), with $a = 0.737$ nm, $b = 0.665$ nm and $c = 0.740$ nm. It is seen that the selected area diffraction patterns of the particle coincide with the ones calculated using the above lattice parameters and space group. The chemical composition of the particles is found to be the same as the matrix by using EDS (TEM). This phase is a new one whose structure has not been reported yet. Other phase which precipitated at the ZrC/matrix interface has been investigated as well. Its chemical composition is also found to be the same as the matrix by using EDS (TEM). According to its selected area diffraction pattern as shown in Fig. 5, this phase seems to have three-fold symmetry. Its structure must be very complicated for analysis and has not been determined yet. Here, we call it “unknown phase”.

For the composite annealed at 723 K for 30 min, the volume fraction of the crystalline phase in the matrix increases remarkably to over 50%, which can be estimated approximately from the area ratio of the precipitated crystalline phases to the remaining as amorphous phase (Fig. 6(a)). The average grain size of the crystals precipitated in the matrix increases to about 100 nm. Crystal growth of the unknown crystalline

Fig. 6 TEM micrographs of the composites annealed at 723 K for (a) 30 min and (b) 40 min, and the corresponding diffraction patterns of the composite matrices.

phase appearing along the boundary between ZrC particle and the matrix occurs. When the annealing time increases to 40 min, most of the amorphous phase in the matrix is trans-

Fig. 8 The micrographs obtained by *in-situ* TEM observation of the composites during annealing: (a) before annealing, (b) annealing at 742 K for 15 min, (c) annealing at 742 K for 17 min and 843 K for 12 min.

formed to crystalline phases with an average size of about 120 nm (Fig. 6(b)). The thickness of the unknown crystalline phase along the boundary between ZrC particle and the matrix increases slightly.

The hardness of the composite matrices as a function of annealing times is shown in Fig. 7. Hardness of the matrices of the composites annealed for more than 20 min increases with increasing annealing times. The hardness of the matrix crystallized increases to the value of 697 Hv, which is much higher than that of the pure amorphous phase with a value of 604 Hv. This hardness increase is considered to be caused by the precipitation of nanocrystalline phases which have a higher hardness than the residual amorphous phase in the matrix. It can be estimated that the precipitation of the nanocrystalline phases in the matrix may contribute to strengthening the metallic glass composites.

In order to clarify the occurring sequence of the aforementioned unknown crystalline phase and the nanocrystalline precipitates, an *in-situ* TEM observation during the heating process was performed on the metallic glass composite. As shown in Fig. 8(a), the microstructure of the composite consists of crystalline ZrC particles and the matrix of amorphous single phase. During the heating process, the unknown crystalline phase appears first along the boundary between ZrC particle and the matrix, and the amorphous single phase is preserved in the matrix (Fig. 8(b)). After that, a homogeneous nanocrystallization starts to occur in the internal region of the matrix (Fig. 8(c)). From Figs. 3, 6 and 8, it can be seen that the nucleation and growth of the unknown crystallized phase appearing along the interface between ZrC particle and the matrix have no effect on those of the nanocrystals appearing in the matrix.

4. Conclusions

The crystallization behavior of $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass composite containing 10 vol% crystalline ZrC particles was investigated. The results obtained are summarized as follows:

(1) In the annealing process of the composite, an unknown crystalline phase appears first along the interface between ZrC particle and the matrix, and then a homogeneous nanocrystallization occurs in the matrix. After the composite is heated at 723 K for 40 min, most of the amorphous phase in the matrix has been transformed into crystalline phases with a final average size of about 120 nm. It is found that the nucleation and growth of the unknown crystalline phase appearing along the interface have no effect on those of the crystalline phases appearing in the matrix.

(2) The nanocrystalline phases precipitated in the matrix have higher hardness than that of the amorphous phase. Their volume fraction begins to increase after the composite is heated at 723 K for 15 min, resulting in an increase in the hardness of the matrix.

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