

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

ZrC 粒子を含む $Zr_{55}Al_{10}Ni_5Cu_{30}$ バルク金属ガラス複合材料
のナノ結晶化挙動

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Abstract: $Zr_{55}Al_{10}Ni_5Cu_{30}$ 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 723K has been investigated by using DSC, X-ray diffraction, TEM and hardness test. It is found that an unknown crystalline phase appears at 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 has a higher hardness than the hardness of 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 723K for 40min, most of the matrix has been transformed into crystalline phases with a final average grain size of about 120nm.

1. Introduction

It has been found that nanocrystals can be dispersed in an amorphous structure by the annealing of amorphous alloys¹⁻⁴⁾. 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 alloys⁴⁾, as compared with those of amorphous single-phase alloys.

Zr-based metallic glass with a high glass-forming ability shows high mechanical strength⁵⁾. 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 particles⁶⁾. It is expected that the properties of the composite can be improved further by obtaining nano-sized

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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 $10\ \mu\text{m}$ were formed by an *in-situ* reaction between Zr-based melt and graphite powder in an argon atmosphere. The melt with nominal composition $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ 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 differential scanning calorimeter (DSC) curve of the composite measured at 723K. 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 X-ray diffractometry and 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 $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ 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.

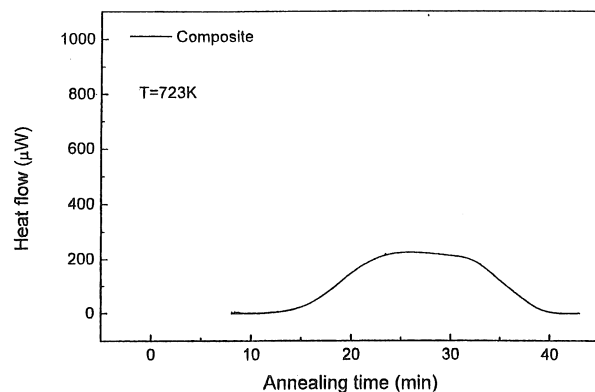


Fig. 1 DSC curve of a $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ bulk metallic glass composite measured at 723K.

X-ray diffraction patterns and TEM micrographs of the composites after annealing at 723 K for the different annealing times are shown in Figs. 2 and 3, respectively. TEM micrograph of the composite annealed at 723K for 20 min is shown in Fig. 3(a). It can be seen that a small volume fraction of crystals with an average size of about 65 nm precipitates in the matrix. According to the electron diffraction pattern of the matrix shown in the bottom-right corner of the photo (Fig. 3(a)), it is known that most of the matrix remains as amorphous phase. On the other hand, an unknown crystalline phase with a width of about 200 nm can be found along the boundary between ZrC particles and the matrix. The X-ray diffraction pattern of the composite reveals that the nanocrystals precipitated in the matrix are composed of ZrNi and Zr_2Ni phases (Figs. 2).

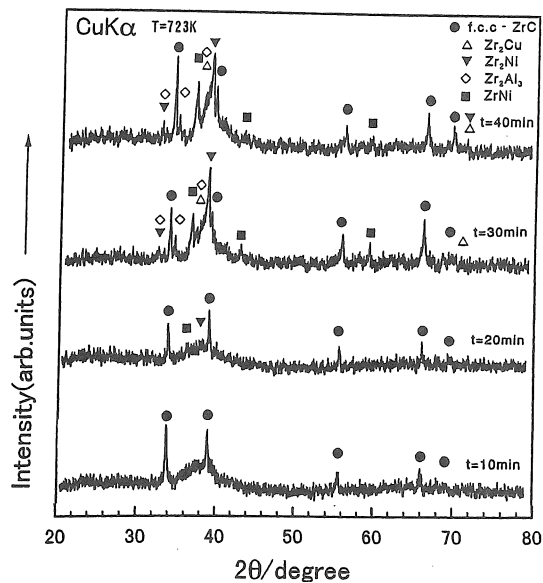


Fig. 2 X-ray diffraction patterns of the composites after annealing at 723K for different durations.

For the composite annealed at 723K 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. 3(b)). The average grain size of the crystals precipitated in the matrix increases to about 100 nm. Crystal growth of the unknown crystalline phase appearing along the boundary between ZrC particle and the

matrix occurred. The X-ray diffraction pattern reveals that two kinds of new crystalline phases, that is Zr_2Al_3 and Zr_2Cu except the existence of ZrNi and Zr_2Ni precipitate in the amorphous phase preserved in the matrix of the composite (Fig. 2).

When the annealing time increases to 40 min, most of the amorphous phase in the matrix is transformed to crystalline phases comprising of ZrNi, Zr_2Ni , Zr_2Al_3 and Zr_2Cu phases with an average size of about 120nm, as shown in Figs. 2 and 3(c). 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. 4. 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

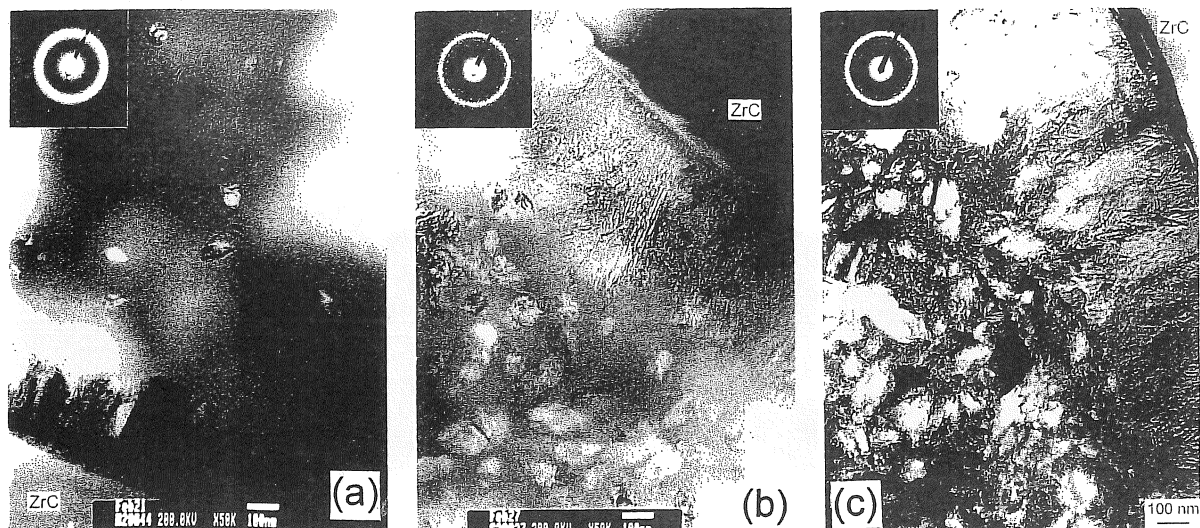


Fig. 3 TEM micrographs of the composites annealed at 723K for (a) 20 min, (b) 30 min and (c) 40 min, and the corresponding diffraction patterns of the composite matrices.

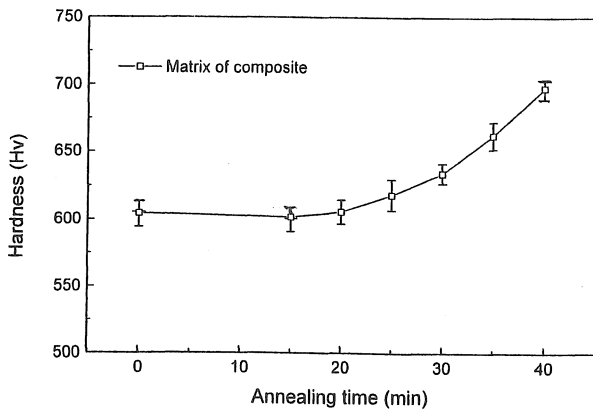


Fig. 4 Hardness of the matrices of the composites annealed at 723K for different durations.

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. 5(a), the microstructure of the composite consists of crystalline ZrC particles and the matrix of amorphous single phase. During

the heating process, at first, the unknown crystalline phase appears along the boundary between ZrC particle and the matrix, and the amorphous single phase is preserved in the matrix (Fig. 5(b)). After that, a homogeneous nanocrystallization starts to occur in the internal region of the matrix (Fig. 5(c)). From Figs. 3 and 5, it can be seen that the nucleation and growth of the unknown crystallized phase appeared along the interface between ZrC particle and the matrix have no effect on those of the nanocrystals which appeared in the matrix.

4. Conclusion

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 at first along the interface between ZrC particle and the matrix, and then a

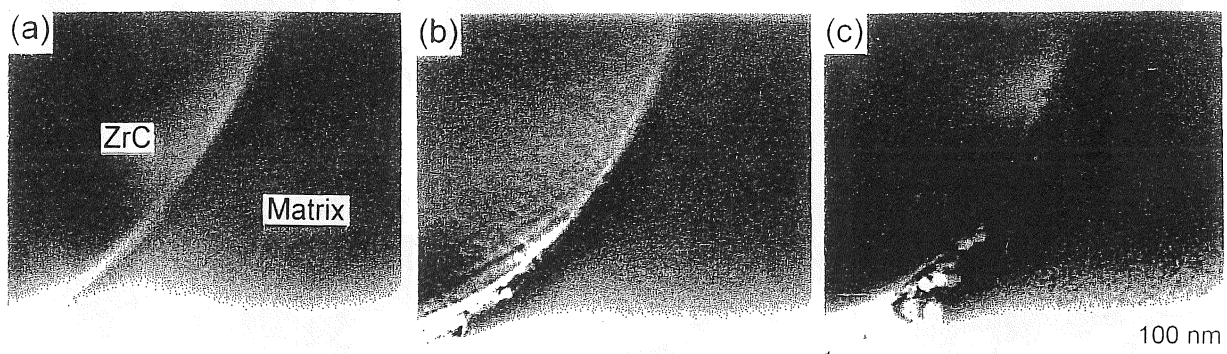


Fig. 5 The micrographs obtained by *in-situ* TEM observation of the composites during annealing: (a) before annealing, (b) annealing at 742K for 15 min, (c) annealing at 742 K for 17 min and 843 K for 12 min.

homogeneous nanocrystallization occurs in the matrix. After the composite is heated at 723K for 40min, most of the amorphous phase in the matrix has been transformed into crystallize phases with a final average size of about 120nm. It is found that the nucleation and growth of the unknown crystalline phase which appeared along the interface have no effect on those of the crystalline phases which appeared 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 723K for 15min, resulting in an increase in the hardness of the matrix.

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