Internal Friction of Nitrogen-Doped Zr-Based Glassy Composite Alloy

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Internal friction of Zr-based glassy composite alloys containing dispersed-ZrN particles, which were prepared by a powder compact melting and liquid-quenching process using Zr-Al-Ni-Cu glassy alloy and AlN powders as the starting materials, has been investigated using a reed method over the temperature range of ~90–350 K. It should be noted that a broad multi-composed peak was observed around 260 K. The peak internal friction was about $3 \times 10^{-3}$. It was also noteworthy that the so-called $\Delta M$ effect of the Young’s modulus in its temperature dependence was observed. In addition, the internal friction at the peak temperature depended little on the strain amplitude in the range of about ~$1 \times 10^{-5}$ to ~$2 \times 10^{-4}$. These results indicate that the observed internal friction peak is related to the relaxation process. Since the hydrogen content in the sample was very low (0.24 at%H), the observed internal friction peak is suggested to be induced by the interstitially doped nitrogen in the glassy phase. [doi:10.2320/matertrans.MJ200759]

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1. Introduction

Glassy alloys are the focus of many researchers because they have many interesting physical and chemical characteristics different from those of crystalline alloys because of the non-periodicity of their atomic arrangement. There are also reports on glassy composite alloys containing dispersed particles because such particles in the matrix of glassy alloy can improve mechanical properties such as fracture strength and ductility. For example, Kato and Inoue reported the synthesis and mechanical properties of Zr$_{55}$Al$_{10}$Ni$_3$Cu$_{30}$ glassy composite alloys containing ZrC particles. Recently, we have reported the first synthesis of the dispersed-ZrN glassy composite alloys containing pores prepared in ribbons by conventional liquid quenching process using powders of the Zr-based glassy alloy and AlN as starting materials.

The synthesized ZrN particles in the glassy alloy matrix were in ~μm sizes. Their X-ray diffraction peaks were very sharp compared to those of the starting AlN powders, indicating high crystallinity of the ZrN. Many small, almost spherical pores with a diameter of about ~10 μm were also found in the prepared alloy. The mechanical properties of this glassy composite alloy was also investigated. For example, the Vickers hardness was ~560 and larger than that of the Zr$_{55}$Al$_{10}$Ni$_3$Cu$_{30}$ glassy alloys (~470). In this manuscript, internal friction of the glassy composite alloy is described.

There are many reports of the internal friction of the glassy alloys. Especially, hydrogen-induced internal friction of hydrogenated glassy alloys is well investigated. For example, Mizubayashi et al. investigated the hydrogen-induced internal friction behavior of the Zr-based hydrogenated glassy alloys and Hasegawa et al. investigated that of the Ti-rich ones. This internal friction is originated from the relaxation process of the hydrogen atoms absorbed in the glassy structure because hydrogen is an interstitial-type atom. There are also other interstitial-type ones, such as nitrogen and carbon. They also induce relaxation-type internal friction. For example, Fe-Al-C crystalline alloys show high internal friction induced by the carbon. In the process for preparing the dispersed ZrN glassy composite alloys in this study, the starting AlN was decomposed to be Al and N. The decomposed nitrogen atoms usually expected to be used for the formation of the ZrN and N$_2$. This means that there may be no interstitial nitrogen atoms in the glassy structure and that no nitrogen-induced internal friction may be shown. However, it is found in this study that the composite alloy show an internal friction peak in the temperature dependence of the internal friction, which may be induced by the nitrogen atoms interstitially doped in the glassy structure.

2. Experimental Procedure

Alloy ingots with the composition Zr$_{35}$Al$_{10}$Ni$_3$Cu$_{30}$ were prepared in an arc-melting furnace in a purified argon atmosphere. The glassy alloy powder was prepared by a conventional spray method in a purified argon atmosphere. Ribbon samples were prepared by a conventional single-roll spinning method in a purified argon atmosphere using a compacted mixture of the glassy alloy and AlN (2.5 mass%) powders. Phases of the sample were identified by X-ray diffraction method using monochromatized Cu-K$_\alpha$ radiation. Thermal stability was investigated by differential scanning calorimetry (DSC) in a flowing purified argon atmosphere. The heating rate during the measurement was about 0.67 K/s. Morphology was examined using a scanning electron microscope (SEM). Chemical composition was analyzed using a SEM-EDX (Electron Prove Microanalyzer). The hydrogen content of the samples was determined using an inert gas carrier melting thermal conductimetric method.

The internal friction measurements were carried out on a ~15 mm long ribbon shaped sample using a reed method over the temperature range of ~90–350 K while under vacuum (~$10^{-2}$ Pa). One end of the ribbon sample was clamped tightly while an electrostatic force was used for oscillation excitation of the sample. The electrical capacity of the sample was measured to detect the oscillation of the sample. The internal friction was measured using a resonance oscillation method at a frequency of ~200 Hz. The strain in the width of the sample was measured to be ~$3 \times 10^{-6}$. The details of the instrumental setup and measurement procedure have been described elsewhere.
3. Results and Discussion

Figure 1 shows an X-ray diffraction pattern of the prepared ribbons. Sharp diffraction peaks of the synthesized ZrN are observed accompanied with a halo pattern. The DSC thermal analysis indicated that there was a glass transition and that the glass transition and crystallization temperatures, \( T_g \) and \( T_c \), were 726 K and 782 K. These results mean that the prepared ribbon sample was a composite of ZrN and glassy phases.

Figure 2 shows temperature dependence of internal friction and dynamic Young’s modulus. A broad multicomponent peak of the internal friction is observed around 260 K. The peak internal friction is about \( 3 \times 10^{-3} \). In addition, the so-called \( \Delta E \) effect induced by the internal friction is also observed in the temperature dependence of the Young’s modulus. In order to discuss the mechanism of the observed internal friction peak more, the strain amplitude dependence of the internal friction around the peak temperature (260 K) is also studied. Figure 3 shows internal friction at 260 K as a function of the strain amplitude of the applied vibration. It is found that little dependence of the strain amplitude is observed. These results indicate that the observed internal friction peak is related with the relaxation process, such as jumping process of the interstitial atoms induced by the applied vibration. Zr is an element having the affinity with hydrogen which is interstitial-type atom, and so Zr alloys absorb hydrogen easily. However, the analysis of the hydrogen content of the composite was only 0.24 at%.

In the process for preparing the dispersed ZrN glassy composite alloy, the following melting and decomposition reaction occurred at first during the induction melting:

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\text{glassy-Zr}_{55}\text{Al}_{10}\text{Ni}_{5}\text{Cu}_{30} + \text{AlN} \rightarrow \text{liquid-Zr}_{55}\text{Al}_{10}\text{Ni}_{5}\text{Cu}_{30} + \text{Al} + \text{N}
\]

Then, the nitrogen atom decomposed from the AlN usually expects to be used for the formation of the ZrN or \( \text{N}_2 \). However, since the liquid quenching rate of the single-roll spinning technique is very high, i.e. about \( 10^6 \) m/s, it can be expected that part of the decomposed nitrogen atoms after quenching exist as interstitial atoms in the glassy structure, which do not form ZrN and \( \text{N}_2 \). Such a kind of interstitial nitrogen atoms can induce the relaxation-type internal friction peak. These nitrogen atoms may be metastable and the metastability is not high, because the nitrogen atoms should be intrinsically reacted with Zr and N to form ZrN and \( \text{N}_2 \). In order to confirm this, we also prepared the bulky composite by the Cu-mold casting method of which the
cooling rate is lower than that of the single-roll liquid quenching method and measure the temperature dependence of the internal friction. As shown in Fig. 4, it is found that no internal friction peak is observed and that the result is almost the same as that of the glassy alloy with no ZrN. This result also strongly suggests that the metastable interstitial-type nitrogen atoms in the matrix glassy structure induce the internal friction peak in Fig. 2.

It should be noted finally that there is slight strain amplitude dependence of the internal friction in Fig. 3 and that the small internal friction background is observed in the whole temperature range in Fig. 2. This may be attributable to the boundary between the matrix glassy phase and dispersive ZrN particles because the ZrN particles are in ~µm sizes and dispersed almost homogeneously in the matrix glassy phase as shown in Fig. 5 which shows a SEM image of the cross section etched by the acid solution.

4. Conclusion

Internal friction of Zr-based glassy composite alloys containing dispersed-ZrN particles and N2 pores, which have been prepared by a powder compact melting and liquid-quenching process using Zr-Al-Ni-Cu glassy alloy and AlN powders as the starting materials, has been investigated using a reed method over the temperature range of ~90–350 K. A broad multicomponent peak of the internal friction is observed around 260 K. The peak internal friction is about $3 \times 10^{-3}$. In addition, the so-called $\Delta E$ effect in the same temperature range of the internal friction peak is also observed in the temperature dependence of the Young’s modulus. It is also found that little dependence of the strain amplitude is observed. These results indicate that the observed internal friction peak is related with the relaxation process, such as jumping process of the interstitial atoms induced by the applied vibration. Since the liquid quenching rate of the single-roll spinning technique is very high, i.e. about $10^6$ m/s, it is expected that part of the nitrogen atoms decomposed from AlN exist as interstitial atoms in the glassy structure, which do not form ZrN and N2. Such a kind of interstitial nitrogen atoms can induce the relaxation-type internal friction peak observed in this study. It should be also noted that there is slight strain amplitude dependence of the internal friction and that the small internal friction background is observed in the whole temperature range. This may be attributable to the boundary between the matrix glassy phase and dispersive ZrN particles.
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