Oxygen Embrittlement and Effect of the Addition of Ni Element in a Bulk Amorphous Zr–Cu–Al Alloy

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Oxygen embrittlement in Zr-based bulk amorphous alloys is an important problem, which must be solved before the application of the bulk amorphous alloys to industrial materials. In the Zr–Cu–Al ternary system, the cast bulk amorphous Zr50Cu40Al10 alloy near the ternary eutectic composition shows good ductility, in the case of the restriction of crystalline inclusions. Furthermore, the addition of Ni element brings about much higher ductility because of the proof ability against oxygen embrittlement. As a result, the Zr50Cu30Ni10Al10 bulk amorphous alloy exhibits good ductility and proof ability against oxidization.

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1. Introduction

In principle, a high glass-forming ability of multicomponent Zr-based alloys can be enhanced by the basic three elements, and other adding elements can play a role in the further enhancement of glass-forming ability.1–4) Inoue et al. reported the appearance of a wide supercooling liquid region exceeding 80 K in a ternary Zr50Cu25Al10 alloy.5) We have also reported6) that the ternary Zr–Cu–Al alloy system has low melting temperatures in a wide compositional range indicating that the Zr50Cu40Al10 alloy is close to the ternary eutectic composition. The Zr50Cu40Al10 bulk amorphous alloy exhibits high tensile strength over 1900 MPa, but the improvement of ductility is expected to cause a further increase in tensile strength. Because the previous bulk amorphous samples were fractured before significant plastic deformation region. The lack of ductility in Zr-based bulk amorphous alloys has been presumed as follows; (1) homogeneity of structure without second phase and boundary, (2) work softening phenomenon7) and (3) low plastic deformability at room temperature,8) and so on. There might be no factors to stop operable crack propagation in bulk amorphous alloy, whereas the ordinary crystalline materials have obstacles of crack propagation, i.e., grain boundary, dislocation, second phases and so on. However, by taking a balance between the good microscopic deformability around crack tip and high tensile strength due to accumulation of large elastic strain energy, a ductile bulk amorphous alloy is expected to realize. The good ductility should be obtained in metallic glassy materials consisting of metallic bonding.

Furthermore, the lack of ductility is closely related to the existence of crystalline inclusions.9) The formation of crystalline inclusions during metallic mold casting (φ3 mm × 50 mm) process for Zr55Cu17.5Ni10Al1.5 bulk amorphous alloy is enhanced by adding oxygen of the concentration from 0.28 to 0.8 at%.10) In the Zr-based alloys with oxygen concentrations over 0.8 at%, fine quasicrystalline particles are observed. This crystallization phenomenon is an origin for the decrease in ductility of bulk amorphous alloys. However, there have been no data on the influence of oxygen on the Zr–Cu–Al and Zr–Cu–Ni–Al bulk amorphous alloys in the oxygen concentration range below 0.28 at%. In the present study, we examined oxygen-induced embrittlement behavior of the Zr–Cu–Al bulk amorphous alloy by the cyclic melting process. The oxygen embrittlement can be thought as one of the main reasons of the embrittlement phenomenon caused by the remelting process. This is because conventional Zr-based alloys are usually embrittled with oxygen concentrations exceeding 800 ppm.11) The oxygen embrittlement of Zr-based crystalline alloy is originated from the sticking of operable dislocations by oxygen atoms, which are intruded into the dislocation core. For the Zr-based bulk amorphous alloy, dissolved oxygen atoms seem to affect on the amorphous structure. However, structural change in the amorphous phase by adding a small amount of oxygen is too little to detect by conventional X-ray structure analysis. To estimate the ductility of the bulk amorphous alloy in this study, the Charpy impact test was performed using the JIS subsize specimen (with U-notch and 5 mm thickness). Furthermore, we tried to find a useful additional element, which restrains the oxygen embrittlement and enhances mechanical properties.

This paper intends to present the compositional dependence of ductility in the Zr–Cu–Al and Zr–Cu–Ni–Al amorphous alloys. The oxygen embrittlement in the remelting process was also examined, and the less-sensitivity against oxygen embrittlement for the Ni-containing Zr-based amorphous alloy is shown in this paper.

2. Experimental Procedure

Ternary Zr–Cu–Al (Zr = 20–75 at%, Cu = 20–70 at% and Al = 10–40 at%) and quaternary Zr–Cu–Ni–Al (Zr = 45–55 at%, Cu = 25–45 at%, Ni = 0–15 at% and Al = 10 at%) alloys were examined in this study. The master alloy ingots were prepared by arc melting the mixtures of pure Zr, Cu, Al, and Ni metals in an argon atmosphere. To suppress the oxidization, special Zr crystal rod (< 0.05 at% oxygen) was used. Subsequently, the master alloy was completely
remelted, then cast into a square rod shape (5 mm × 10 mm × 55 mm) by tilt casting method in an arc-furnace as illustrated in Fig. 1. Oxygen concentration of the bulk amorphous alloys was measured using a fusion in helium gas-infrared absorption method. The cast structure and fracture surface were examined by optical microscopy (OM) and scanning electron microscopy (SEM). The ductility of the bulk amorphous alloys was evaluated by Charpy impact test. The size of Charpy impact test is shown in Fig. 2, which is regarded as the JIS subsize test piece (JIS-G-0202-1313). The tensile strength was measured by Instron testing machine. The hardness was measured by micro Vickers testing machine with a 2.9 N for a loading time of 15 s. The loading condition was determined by the result of the part of load vs. hardness curve not to show the load dependence. The phase characterization of the cast samples was performed by X-ray diffractometry.

3. Results and Discussion

Figure 3(a) shows constitutional diagram of the cast Zr–Cu–Al alloys in the compositional range of 20–75 at% Zr, 20–70 at% Cu and 10–40 at% Al. The single amorphous phase is formed in the wide composition range where the Al content is limited to 8 to 15 at%. The compositional dependence implies that Al plays a significant role in the formation of amorphous structure in the Zr–Cu–Al system. The composition dependence of the Charpy impact value is shown in Fig. 3(b). The highest Charpy impact value region above 60 kJ m⁻² is almost equal to the formation range of the amorphous single phase. The Charpy impact value decreases significantly by the existence of the second crystalline phase. The Charpy impact value decreases significantly by the existence of the second crystalline phase. The Vickers hardness value increases monotonous with increasing Al content as shown in Fig. 3(c). The highest Vickers hardness is obtained near the composition of Zr₅₀Cu₃₅Al₁₅, which is close to a Zr₅(Cu, Al)₄ hexagonal compound with high melting temperature. In the Zr–Cu–Al ternary amorphous alloys, the alloy with the highest ductility and highest strength was determined as Zr₅₀Cu₄₀Al₁₀ alloy. The strength is roughly estimated from Vickers hardness. Both Charpy impact and Vickers hardness values are lower around Zr₅₀Cu₄₀Al₁₅, because the alloy includes well-grown planner shaped Zr₂Cu compounds. However, the ductility of the Zr₅₀Cu₄₀Al₁₀ alloy significantly decreases with an increase of the cycle number of melting, as shown in Fig. 4. This embrittlement tendency is a serious problem for application of the Zr-based bulk amorphous alloy as structural materials. This result suggests that the recyciul uses of the Zr-based bulk amorphous alloy bring about the decrease in ductility, leading to an accidental failure or fracture. In general, the embrittlement of crystalline Zr-based alloys results from the oxygen atoms, which act as the stopping medium of operable dislocations. The oxygen embrittlement in Zr-based crystalline alloys occurs even in a small amount of oxygen content range above 800 ppm. In order to suppress the oxygen embrittlement, Zr–Cu–Ni–Al quaternary amorphous alloys were examined in (Zr₅₀Cu₄₀Al₁₀)₁₀₀–ₓMₓ (M: metallic element, X: 0–5 at%) system. The data are shown in Fig. 5. The samples were prepared in 80 vol.% Ar and 20 vol.% oxygen mixed atmosphere. Only adding Ni, Pd and Pt elements improves the tensile strength of the Zr₅₀Cu₄₀Al₁₀ (O) bulk amorphous alloy in the compositional range of X = 0 to 5 at%. The favorable additional element leading to the suppression of the oxygen embrittlement is limited to Ni, because Pd and Pt metals are...
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Figure 4 Relationship between the Charpy impact value and cyclic remelting numbers of Zr50Cu40Al10 bulk amorphous alloy.

Figure 5 Change in the tensile strength for the Zr50Cu40Al10 bulk amorphous alloys containing M (M=Ni, Pd, Pt, Co, Rh, Ag, Au, B, Ga and In). $\sigma_0$ is tensile strength of the Zr50Cu40Al10 bulk amorphous alloy containing a small amount of oxygen elements.

very expensive. Figure 6 shows constitutional diagram (a), compositional dependence of Charpy impact value (b) and composition dependence of Vickers hardness (c) in the Zr–Cu–Ni–Al (Al = 10 at% constant) quaternary system. The highest Charpy impact values of over 70 kJ m$^{-2}$ are obtained along the Zr50Cu40–xNi5Al10 ($X = 5$ to 10 at%) compositional line. The Vickers hardness does not change along the Zr50Cu40–xNi5Al10 compositional line. Consequently, it is expected that the oxygen embrittlement of Zr50Cu40Al10 is restricted by partial replacement of Cu for Ni in the Zr–Cu–Ni–Al quaternary alloys.

Figure 7 shows the change in the Charpy impact value with cycle number of remelting for the Zr50Cu40–xNi5Al10 ($X = 0$, 5, 10 and 15 at%) alloys. By adding Ni, the decreasing tendency of Charpy impact values is gradually improved, and the Zr50Cu30Ni10Al10 alloy is seen as oxygen embrittlement even after 5 cycle remelting. The significant decrease in the Charpy impact value due to oxygen embrittlement is presumably caused by the microscopic structural change like an initial stage of crystallization, because all of the samples with Charpy impact values below 20 kJ m$^{-2}$ include fine crystalline inclusions. To clarify the relationship between oxygen content and embrittlement tendency, the oxygen concentration was measured using a part of fractured specimen. Figure 8 shows the relationship between the oxygen and remelting times for the Zr50Cu40–xNi5Al10 ($X = 0$, 5, 10 and 15 at%) alloys. The resistance against oxygen embrittlement for the Zr50Cu30Ni10Al10 alloy is due to the proof ability against oxidation. The crystallization occurs when the oxygen con-
centrations exceed the threshold value of about 0.2 at%. The use of sponge Zr metal may cause the accidental failure due to oxygen embrittlement in Zr–Cu–Ni–Al bulk amorphous alloys, because the sponge Zr usually contains 0.15 to 0.2 at% oxygen. Accordingly, in order to prepare a ductile Zr-based bulk amorphous alloy, we must pay attention to the purity of Zr metal and the suppression of oxidization during cyclic remelting. These data shown in Figs. 7 and 8 were rearranged to examine the relationship between the Charpy impact value and oxygen concentration. As shown in Fig. 9, the Zr–Cu–Ni–Al bulk amorphous alloys show a significant decrease in the Charpy impact value with an increase of oxygen content and the tendency is independent of alloy compositions. The crystalline phase in the bulk amorphous alloys with low Charpy impact values less than 20 kJ m\(^{-2}\) was \(\tau_3\)-phase,\(^6\) which can be formed by partial enriched Al concentration as about 20 at%. Consequently, the oxygen embrittlement without Ni concentration dependence in the Zr–Cu–Ni–Al amorphous alloys implies that the Al plays an important role in the oxygen embrittlement. It is my guess that the additional Ni element may interrupt the chemical interaction between Al and oxygen.

4. Summary

The oxygen embrittlement for Zr-based bulk amorphous alloys is a serious problem for practical use of the alloys. Bulk amorphous Zr–Cu–Al and Zr–Cu–Ni–Al alloys were examined. Zr metal with low oxygen contents (< 0.05 at% oxygen) was used in this study. The ductility of the Zr-based bulk amorphous alloys was estimated by Charpy impact test. The results obtained are summarized as follows.

1) The Zr-based bulk amorphous alloys suffered oxygen embrittlement before crystallization when the oxygen concentration is over 0.2 at%.
2) In the ternary Zr–Cu–Al bulk amorphous alloys, the highest Charpy impact value was obtained around Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\), which is close to the ternary eutectic point.
3) The Zr\(_{50}\)Cu\(_{30}\)Ni\(_{10}\)Al\(_{10}\) bulk amorphous alloy exhibits good ductility because of the proof ability against oxidization.

REFERENCES