Effect of Tempering on Microstructure and Mechanical Properties in a Multiphase ZrCuAlNiO Alloy

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The changes in microstructure and mechanical properties of ZrCuAlNiO alloy after tempering were investigated. The morphology of the martensite changes, and both the interfaces of martensite variants and substructural boundaries fade after the tempering treatment. The ZrAl phase precipitates in Zr(Cu, Al, Ni) grains at temperatures higher than 747 K, and its size increases with the tempering temperature, while Zr2Ni phase precipitates in martensite zone at temperatures higher than 1053 K. The mechanical property was improved by the presence of the precipitates after tempering. The correlation between microstructure and property in this alloy was discussed.

KEY WORDS: ZrCuAlNiO alloy; tempering; martensite; precipitate; mechanical property.

1. Introduction

The Zr–Cu(Ni)–Al alloy has been reported as one of the most successful and promising alloys in the formation of bulk metallic glass or a multiphase structure containing martensite due to its excellent good physical and chemical properties.1–6) Also, the Zr–Cu(Ni)–Al alloy is of considerable technological interest for high temperature shape memory and structural applications, and thus was attracted much attention.7,8)

The formation of martensite phases has been observed in a number of Zr–Cu(Ni) based multi-component alloys during rapid cooling or straining.9–15) Previous studies have indicated that the ZrCu phase should be a metastable phase and could be saved by a rapid cooling. If the cooling rate is not large enough, the ZrCu phase with a B2 structure could transform into two martensite phases with the monoclinic symmetry.11–14) One is in a base structure and the other is in a superstructure of the former.12,13) The ZrCu martensites and ZrCu (B2) phases could be used as reinforcement in the Zr–Cu(Ni) based alloys to improve the strength and toughness of the materials.15–21) In addition, the Zr–Cu(Ni) system exhibits particular promise for developing precipitation-strengthened multiphase alloys. However, a problem is the incomplete knowledge of the stability of various phases in Zr–Cu(Ni) system alloy at high temperatures. In this paper, we report the effect of tempering on microstructure and mechanical properties in a multiphase ZrCuAlNiO alloy.

2. Experiment

(Zr55Cu30Al10Ni5)99.1O0.6Fe0.2Zn0.1 alloy (hereafter abbreviated as the ZrCuAlNiO alloy) with nominal composition was prepared by arc-melting of the mixtures of the alloying components (oxygen was added in the form of CuO, while Fe and Zn were the impurities in Zr) in a Ti-gettered argon (99.999 vol%) atmosphere.20) The particular composition of (Zr55Cu30Al10Ni5)99.1O0.6Fe0.2Zn0.1 was selected to trigger the formation of the crystalline phases. The alloy was melted and turned in a water-cooled copper crucible for four times using electromagnetism stirring to ensure chemical homogeneity, and then the master alloy was re-melted in a quartz crucible and cast into a copper mold with a cylindrical cavity of 5 mm in diameter using a spurt casting method. The actual oxygen content in this alloy was analyzed by the pulse heating inert gas fusion-infrared thermal conductivity method, and the value is 0.56 at%.

The spurt-cast samples were tempered under a vacuum of 10⁻³ Pa for 2 h at 573 K, 673 K, 773 K, 873 K, 923 K, 973 K, 1 023 K, 1 053 K and 1 073 K, respectively, and then cooled in furnace (The heating rate is 20 K/min and the cooling rate is 25 K/min). The phases in the spurt-cast sample were identified by X-ray diffraction (XRD, Model D/Max 2500PC, Japan) using Cu–Kα radiation. Microstructural changes after the tempering treatments were examined by transmission electron microscopy (TEM, Model JEM-2000FX, Japan) coupled with energy-dispersive spectrometry (EDS, Model Voyager-3105, UK). The martensitic transformation (MT) cycle was studied using a piece of the as-cast sample about 20 mg by differential scanning calorimetry (DSC, Model JEM-2000FX, Japan) coupled with energy-dispersive spectrometry at a heating rate of 5 K/min. The differential thermal analysis experiments were carried out by differential thermal analysis (DTA, Model Rigaku-8150, Japan) at a heating rate of 20 K/min.

The cylindrical specimens with a diameter of 4.5 mm and a height of 9 mm were prepared by machining from the cylindrical rods with 5 mm in diameter. Both ends of the
specimens were polished to make them parallel to each other prior to the compression test. The uniaxial compressive test was carried out at constant strain rate of $1 \times 10^{-4}$ s$^{-1}$ using a servo-hydraulic materials testing system (Model MTS 810, USA) at room temperature. The microhardness of the specimens was measured by a Vickers hardness tester (Model 1600-5122VD, USA).

3. Results and Discussion

Figure 1 shows a characteristic XRD pattern of the as-cast ZrCuAlNiO sample. The dominant diffraction peaks correspond to tetragonal Zr$_{2}$Cu (space group14/mmm) phase with lattice constants $a=0.3268$ nm and $c=1.1198$ nm. These lattice constants differ from the values of pure Zr$_{2}$Cu ($a=0.3220$ nm and $c=1.1183$ nm), most likely due to the dissolution of Ni and Al atoms into the tetragonal structure. In addition, broad reflections can be allocated to the dissolution of Ni and Al atoms into the tetragonal structure. In addition, broad reflections can be allocated to the monoclinic ZrCu martensite phase (P2$_{1}$/nm and Cm space group). Likewise, the ZrCu martensite is a solid solution of Ni and Al in a monoclinic structure. It has been demonstrated that oxygen impurity at a level of 0.3 at% dramatically reduces the glass forming ability (GFA). Therefore, it can be deduced that the presence of 0.56 at% oxygen in the ZrCuAlNiO alloy deteriorates the GFA and triggers the formation of the crystalline phases. In addition, the oxygen addition may stabilize the ZrCu (B2) crystalline phase.

The formation of the ZrCu (B2) crystalline phase is the prerequisite for the martensitic transformation of ZrCu (B2)$\rightarrow$ martensite under the copper-mold-cooling conditions.

Figure 2(a) shows the DTA curve of the cast ZrCuAlNiO alloy. As can be seen, two weak exothermic peaks appear at $T_1=747$ K and $T_2=1,053$ K, respectively, corresponding to the precipitation of some phases from the matrix. DSC measurement of the complete MT cycle for the cast ZrCuAlNiO alloy is shown in Fig. 2(b). It can be seen that MT in this alloy occurs through one step. The $M_s$, $M_f$, $A_s$, and $A_f$ are 452 K, 408 K, 431 K and 469 K, respectively. For samples tempered at temperatures more than 469 K, one-step reverse transformation occurs upon heating and further the martensitic transformation of B2$\rightarrow$M has taken place during cooling.

Figure 3 shows the TEM bright-field images of the microstructure of the as-cast and tempered ZrCuAlNiO samples. Figures 3(a) and 3(b) correspond to the as-cast sample, and Figs. 3(c)$-$3(f) correspond to the samples tempered at 673 K, 773 K, 973 K and 1,073 K, respectively. As shown in Fig. 3(a), the microstructure is comprised of plate-like martensites with a width of $\sim$100 nm and micrometer-scale Zr$_2$Cu phase. The selected area electron diffraction (SAED) pattern of the Zr$_2$Cu phase obtained from area A clearly shows a symmetrical diffraction. A higher magnification observation [see Fig. 3(b)] shows that the martensite plates exhibit typical preferentially oriented morphologies with well-defined high-angle boundaries, and contain numerous twins. The inset SAED pattern in Fig. 3(b) obtained from area B corresponds to the [213] zone axis of the ZrCu martensite superstructure (Cm space group). The EDS analysis shows that the composition of the plate-like martensite is Zr$_{50}$Cu$_{45}$Al$_{5}$Ni$_{5}$, and that of the Zr$_5$Cu phase is Zr$_{49}$Cu$_{35}$Al$_{7}$Ni$_{9}$, indicating that the martensite phase is Ni-rich, and the Zr$_5$Cu phase is Al-rich. Figure 3(c) shows the microstructure tempered at 673 K. It can be seen that the interfaces of martensite variants, as compared with those in Fig. 3(b), become blurred and flexuous. Further, increasing the tempering temperature makes the martensites variant-crashed/variant-intersect. As shown in Fig. 3(d) (tempered at 773 K), the martensite is no longer in a macrotwin structure, while some nano-scale Zr$_2$Al grains precipitate from the Zr$_2$(Cu, Al, Ni) solid solution during tempering. The SAED pattern (obtained from area C) consists of several discontinuous diffraction rings, indicating an ultrafine grain structure with random crystal orientations. Combining with the DTA result, we speculate that the Zr$_2$Al phase may precipitate from the Zr$_2$(Cu, Al, Ni) solid solution at 747 K. Figure 3(e) shows the microstructure of the sample tempered at 973 K. It can be found that the martensite variants with preferentially oriented morphologies almost disappear. On the other hand, numerous fine grains precipitate in the Zr$_2$(Cu, Al, Ni) solid solution, as shown in the inset graph. Tempering at 1,073 K leads to the formation of a large number of the crystalline Zr$_2$Ni phases [see Fig. 3(f)], which precipitate from the B2 Zr(Cu, Al, Ni) solid solution (high temperature phase). The SAED pattern in the upper inset of Fig. 3(f), obtained from area D, corresponds to a mixture of the [021] zone axis of the Zr$_2$Ni phase (with a strong dif-
fraction intensity) and the [11 \overline{2}] zone axis of the ZrCu martensite superstructure (with a weak diffraction intensity). On the other hand, the Zr2Al precipitates become coarser with the increase in the tempering temperature [see the lower inset of Fig. 3(f)].

Figure 4 shows the hardness profile of the as-cast and tempered ZrCuAlNiO samples. The average hardness of the cast sample is 483 Hv. It first decreases, then increases and subsequently decreases again with the increase in the tempering temperature and the maximum value is 544 Hv at the temperature of 973 K. Figure 5 shows the compressive engineering stress–strain curves for the as-cast and tempered ZrCuAlNiO samples. Table 1 summarizes the values of yield stress, fracture strength, elastic strain, fracture strain and Young’s modulus of these samples. Clearly, with the increase in the tempering temperature upon to 673 K, the compressive property decreases. As the tempering temperature increases from 673 to 973 K, the compressive property,
except for elastic strain, increases remarkably. The sample tempered at 973 K exhibits the highest yield stress of 765 MPa and the largest fracture strain of 7.12%. While the sample tempered at 1073 K shows the highest fracture strength of 1912 MPa and the smallest fracture strain of 4.98%. The yield stress changes with the increase in the tempering temperature in a similar manner as that of hardness. Furthermore, the fact that the stress remarkably increases with the increasing strain indicates a strong work-hardening effect.

In a polycrystalline metal, the fundamental unit of deformation is the motion of an individual dislocation. However, a large number of grain and phase boundaries and the stress and strain field caused by solid solution could act as obstacles to restrict the movement of dislocation in the as-cast sample. At low tempering temperatures, the relaxation of point defects, dislocations and grain boundaries occurs, which releases internal stress, and thus leads to the decrease in the hardness, yield stress and fracture strength, and the increase in the fracture strain. The improvement of the compressive properties and hardness for the samples tempered at temperatures between 673 K and 973 K is attributed to precipitation of the Zr2Al phase from the Zr2(Cu, Al, Ni) solid solution and the increase of the volume fraction of Zr2Al with the increase in the tempering temperature, moreover, the complex dislocation interactions and their interactions with the Zr2Al precipitates may also strengthen the mechanical properties of the alloy. The high hardness and fracture strength as well as the decrease in fracture strain for the samples tempered at 1023 K and 1073 K are attributed to the coarsening of the Zr2Al grains and the precipitation of Zr2Ni. Thus, the evolution of the microstructures during tempering is responsible for the change in the mechanical properties.

4. Conclusions

The microstructure and mechanical properties of a cast ZrCuAlNiO alloy after tempering were investigated. The microstructure characteristics depend on the tempering temperature. After tempering, the morphology of the martensite changes, and the interfaces of martensite variants become seriously blurred. The Zr2Al phase precipitates in the Zr2Cu grains after tempering at temperatures higher than 747 K, and it becomes coarser after tempering at higher temperatures. While Zr2Ni precipitates in the martensite zone after tempering at temperatures higher than 1053 K. Tempering at the temperatures between 673 K and 973 K provides a strong precipitation effect for the ZrCuAlNiO alloy, and thus significantly contributes to the mechanical property enhancement. It is concluded that the evolution of the microstructures during tempering is responsible for the change in the mechanical properties. The (Zr55Cu30Al10Ni5)99.1O0.6Fe0.2Zn0.1 alloy is potential to develop precipitation-strengthened multiphase alloys at high temperatures.

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