Effect of Al Content on the Microstructure and Tensile Properties of Zr-Co-Al Alloy Prepared by Rapid Solidification

Zixiang Wu 1,2, Wenfei Lu 1,2, Caiju Li 1,2,* , Peng Gao 1, Xin You 1,2 and Jun Tan 3,*

1 Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China
2 Key Laboratory (MOE) of Advanced Materials of Rare and Precious and Nonferrous Metals, Kunming University of Science and Technology, Kunming 650093, China
3 College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China
* Correspondence: lcj@kust.edu.cn (C.L.); j.tan@cqu.edu.cn (J.T.)

Abstract: The Zr_{50−x/2}Co_{50−x/2}Al_{x} (x = 0, 4, 5, 6, 7, 8) alloy sheets were prepared by copper mold suction casting, and the effect of Al content on the mechanical properties and the strengthening mechanism was thoroughly investigated. With Al addition, a Zr_{5}Co_{7}Al_{3} intermetallic compound formed and precipitated at the grain boundaries or inside the grains, which produced strong synergistic effects of secondary phase strengthening, fine grain strengthening and solid solution strengthening. However, the precipitation of intermetallic compounds can lead to the formation of shrinkage cavities at grain boundaries, and the negative effect of adding too much Al is greater than the strengthening effect, resulting in a gradual decrease in strength. Therefore, the best synergistic strengthening effect is achieved when the Al content is 5 at.%, the grain size of the alloy is reduced from 60 µm to 4 µm, and the room temperature tensile strength is increased from 240 MPa to 464 MPa.

Keywords: Zr-based alloys; Al content; microstructure; tensile properties

1. Introduction

Zr-Co(-Al) alloys have attracted attention in the fields of structural materials, biological materials and green-energy material because of their remarkable properties, including high mechanical strength, high corrosion resistance, good biocompatibility and potential for use in hydrogen storage [1–3].

The B2 phase, with a relatively simple structure (CsCl structure), is conventionally considered to have poor plasticity at room temperature due to limited slip systems [4–6]. However, B2-ZrCo is a stable and inherent ductile phase at room temperature [7]. During deformation, the B2 phase is transformed into the B33 phase by martensitic phase transformation, which enhances the mechanical properties of alloys [8–10]. Jansson et al. investigated the effect of different Co/Zr ratios on the structure and properties of alloys, and large Co/Zr ratios were prone to the formation of B33 phases [11]. Chen et al. found noticeable plasticity and work-hardening in Zr-Co-Al bulk metallic glass composites (BMGCs), which was attributed to the higher volume fraction of the B2-ZrCo phase [12]. The same conclusion was obtained for Zr-Cu-Al BMGCs by Kosiba et al. [13].

Alloying is an extremely effective means of toughening intermetallic compounds. By adding a certain amount of solid solution alloying elements to binary alloys, the solute atoms will distort the lattice of the parent phase and act as pinning sites for dislocations, causing a solid solution strengthening effect. When the added solute element exceeds the solid solution degree, the solute element precipitates out as a new phase, which has a precipitation strengthening effect. Li et al. found that minor Al on Zr-Co alloys significantly improved the compressive strength and plasticity of Zr-Co alloys [14]. Li investigated the effect of Cu on the microstructure and mechanical properties of Zr-Co alloys [15]. The addition of Cu elements led to the precipitation of the B33 phase at grain boundaries, and
the minor addition of Cu increased the yield strength, the elastic limit and the Young’s modulus of the alloy [15]. Hossain et al. showed that the addition of different amounts of Ni or Pd elements to ZrCo alloy resulted in different mechanical properties, with a maximal tensile elongation of 22% achieved in Zr_{50}Co_{40}Pd_{10} [4–6,16,17]. The addition of Co and Zn elements to Zr-Cu alloy can enhance the formation ability of the B2 phase [18,19]. The addition of certain amounts of alloying elements such as Cu, Cr, Fe, and Co to NiAl alloy for microalloying will produce disordered γ-phases at the grain boundary between the β-phases with B2 structure, which can coordinate the deformation between adjacent grains and thus improve the plasticity of NiAl alloys [20,21]. Liu et al. found that the addition of Cr effectively increased the decoupling strength of Fe_{3}Al intermetallic compounds, reduced the antiphase boundary (APB) energy and long-range ordering, and altered the dislocation motion and decomposition, which significantly promoted the occurrence of slip bands and cross-slips and improved the plasticity of alloys [22,23]. The minor addition of B element to polycrystalline Ni_{3}Al significantly eliminates brittle intergranular fracture and further improves room temperature plasticity [24]. Similarly, the minor addition of rare earth elements to NiAl alloy can significantly improve its strength and plasticity [25–28]. Wu et al. found that Al elements promoted the formation of the B2 phase in Zr_{50}Cu_{50} alloy and enhanced its mechanical properties [29].

The addition of alloying elements to intermetallic compounds can change the glass forming ability (GFA), the microstructure and the mechanical properties of the alloy. The addition of Al elements to ZrCo alloy was found to change the GFA of the alloy and resulted in Zr-Co(-Al) alloys with different structures ranging from fully amorphous to fully ultrafine crystalline with various mechanical properties [10,30–32]. In Zr-Co-Al alloy systems, higher Al content (more than 14 at.%) usually leads to the formation of fully amorphous structure, while lower Al content (less than 10 at.%) results in full crystallization, and medium Al content results in amorphous matrix composites. The brittleness, work-softening and limited dimensions of BMG and BMGCs prevent engineering applications, and BMGCs always contain a large number of brittle phases [7].

Previous studies on Zr-Co-Al alloys have focused on the GFA and compressive properties of bulk metallic glasses with high Al content. The regulation mechanism of Al on structure and tensile properties in Zr-Co-Al alloys with low Al composition is still unclear. In this work, the microstructure and tensile properties of Zr-Co(-Al) alloys were studied by changing the Al element content. Furthermore, the Strengthening mechanism of mechanical properties was investigated.

2. Experimental Procedures

The Zr_{50−x/2}Co_{50−x/2}Al_{x} (x = 0, 4, 5, 6, 7, 8) master alloys were prepared by arc melting in a Ti-gettered high purity argon atmosphere and were remelted four times to ensure composition homogeneity. The master alloy was suck-casted into a 2 mm × 10 mm × 90 mm alloy sheet by water-cooled copper mold. The phase compositions of the specimens were examined by an X-ray diffractometer (XRD, X’Pert³ Power, PANalytical, Eindhoven, The Netherlands) with Cu Kα radiation (λ = 1.54056 Å) with a 2θ range of 20°–120°. The microstructure and tensile fracture morphology of the Zr-Co(-Al) alloy were observed and analyzed using an optical microscope (OM, Axion Scope A1, Carl Zeiss, Oberkochen, Germany), a scanning electron microscope (SEM, VEGA3 SBH, Tescan, Brno, Czech Republic), a transmission electron microscope (TEM, Tecnai G² F30 S-Twin, FEI, Hillsboro, ON, USA), and Energy Dispersive Spectroscopy (EDS). The Vickers microhardness tester (HVST-1000Z, ZhuoTai, Zhengzhou, China) was used to test the microhardness of the Zr-Co(-Al) alloy specimens. The load of the diamond indenter was 10 g and the holding time was 15 s. Fifteen points were randomly selected on the surface of each sample and the average value was taken as the microhardness of the alloy. The tensile of the Zr-Co(-Al) alloy at room temperature was tested using a universal mechanical testing machine (AG-X-100KN, Shimadzu, Kyoto, Japan). A specimen of the Zr-Co(-Al) alloy was machined into a tensile specimen with a pitch section of 13.3 mm × 2 mm × 2 mm using a wire cutter.
3. Results and Discussion

3.1. Microstructure

In order to determine the deviation between the actual and nominal composition of Zr-Co-Al alloys, Zr_{47}Co_{47}Al_{6} was selected as a representative sample because the raw materials and preparation process of the alloy were identical. The actual elemental mass ratio of a Zr_{47}Co_{47}Al_{6} alloy after melting is Zr:Co:Al = 58.8%:37.5%:2.36% as determined by inductively coupled plasma optical emission spectrometer (ICP-OES). The loss of alloying elements after melting is ignored and basically satisfies the nominal composition.

Figures 1 and 2 show the OM images and the SEM images of the Zr-Co(-Al) alloys’ microstructures, respectively. The Zr_{50}Co_{50} binary alloy with equal atomic content is composed of a single phase. The grains near the copper die are small, while the internal grains are columnar grains that grow perpendicular to the fine-grained region. The average radial size of these columnar crystals is about 60 µm and the axial size exceeds 1000 µm.

With the increase in Al content, the grain size decreased and then increased. Zr_{47}Co_{47}Al_{6} alloy has the smallest grain size, which reaches about 4 µm. The addition of the appropriate amount of Al element significantly refined the grain size of the alloy, which indicates that Al element plays a significant role in grain refinement in Zr-Co based alloys. Figure 1e,f suggests the formation of dendrites in the Zr_{46.5}Co_{46.5}Al_{7} and Zr_{46}Co_{46}Al_{8} alloys.

![Figure 1. OM images of rapid cooling Zr-Co(-Al) alloys sheet microstructure: (a) Zr_{50}Co_{50} alloy; (b) Zr_{48}Co_{48}Al_{4} alloy; (c) Zr_{47.5}Co_{47.5}Al_{5} alloy; (d) Zr_{47}Co_{47}Al_{6} alloy; (e) Zr_{46.5}Co_{46.5}Al_{7} alloy; (f) Zr_{46}Co_{46}Al_{8} alloy.](image)

The size and number of intergranular shrinkage cavities (blue arrows) increased with increasing Al content, as shown in Figure 2. In addition, the quantity and size of the secondary phase (green circles) precipitated at the grain boundaries (GBs) of the Zr_{50-x/2}Co_{50-x/2}Al_{x} (x = 5, 6, 7, 8) alloys were proportional to the increase in Al content. The second phase was identified as a Zr_{5}Co_{7}Al_{3} intermetallic phase by an Energy Dispersive
X-ray Detector [14]. No secondary phase was observed in the Zr_{48}Co_{48}Al_{4} alloy due to its low Al elemental content and rapid solidification, resulting in less precipitation of Al atoms in the matrix. When Al element content exceeded the solid solubility in the ZrCo matrix, solute atoms gathered at the solid–liquid interface, leading to increased constitutional undercooling levels. The convex grains at the solid–liquid interface extended into the melt at large undercooling levels, while forming secondary dendrites in the lateral direction. The crystal branches of the ZrCo phase, grown in a dendritic way, crossed and blocked each other, and the isolated melt was not replenished during solidification, thereby forming a shrinkage cavity.

Figure 2. SEM images of rapid cooling Zr-Co(-Al) alloys microstructure: (a) Zr_{50}Co_{50} alloy; (b) Zr_{48}Co_{48}Al_{4} alloy; (c) Zr_{47.5}Co_{47.5}Al_{5.5} alloy; (d) Zr_{47}Co_{47}Al_{6} alloy; (e) Zr_{46.5}Co_{46.5}Al_{7} alloy; (f) Zr_{46}Co_{46}Al_{8} alloy. The green circles indicate the secondary phase particles, and the blue arrows indicate the shrinkage cavity at the grain boundaries.

Figure 3 shows the XRD patterns of Zr_{50−x/2}Co_{50−x/2}Al_{x} (x = 0, 4, 5, 6, 7, 8) alloys. The Zr_{50}Co_{50} alloy mainly consists of the B2-ZrCo phase and a small quantity of ZrCo_{2} (2θ = 93°) and Zr_{2}Co (2θ = 37°, 50°, 65°) intermetallic compounds. After adding Al, the Zr_{5}Co_{7}Al_{3} brittle phase was precipitated in the Zr_{50−x/2}Co_{50−x/2}Al_{x} (x = 4, 5, 6, 7, 8) alloy, which is in full agreement with the results observed in OM and SEM above. The mixing
enthalpy of Al and Zr is the lowest in the Zr-Co-Al system (Zr-Co: −41 kJ/mol, Zr-Al: −44 kJ/mol, Co-Al: −19 kJ/mol), and Zr and Co are more likely to form intermetallic compounds [7]. The weaker intensity of the Zr₅Co₇Al₃ peak is due to the minor addition of Al elements and rapid cooling, which increases the solid solubility of Al elements in the B₂-ZrCo matrix, further reducing the precipitation of Al-containing intermetallic compounds.

![XRD patterns of Zr₅₀−ₓ/₂Co₅₀−ₓ/₂Alₓ (x = 0, 4, ..., 8) alloys.](image)

**Figure 3.** XRD patterns of Zr₅₀−ₓ/₂Co₅₀−ₓ/₂Alₓ (x = 0, 4, 5, 6, 7, 8) alloys.

### 3.2. Hardness

The Vickers microhardness of the Zr₅₀−ₓ/₂Co₅₀−ₓ/₂Alₓ (x = 0, 4, 5, 6, 7, 8) alloys is shown in Figure 4. As the Al content increased from 0 to 8 at.%, the microhardness increased from 183 HV to 471 HV, indicating that the addition of Al significantly enhanced the hardness of Zr-Co-Al alloys. The addition of Al elements caused lattice distortion and produced solid solution strengthening. In addition, intermetallic compounds also produced a secondary phase strengthening effect, resulting in a significant increase in the hardness of the alloys.

![Vickers microhardness of Zr₅₀−ₓ/₂Co₅₀−ₓ/₂Alₓ (x = 0, 4, 5, 6, 7, 8) alloys.](image)

**Figure 4.** Vickers microhardness of Zr₅₀−ₓ/₂Co₅₀−ₓ/₂Alₓ (x = 0, 4, 5, 6, 7, 8) alloys.
3.3. Tensile Mechanical Properties

The engineering stress–strain curves of Zr$_{50-x/2}$Co$_{50-x/2}$Al$_x$ (x = 0, 4, 5, 6, 7, 8) alloys at room temperature are shown in Figure 5. The Al element adjusts the hardness, the strength, and the elongation of Zr$_{50-x/2}$Co$_{50-x/2}$Al$_x$ alloy. Zr$_{50-x/2}$Co$_{50-x/2}$Al$_x$ alloys have poor plasticity due to internal defects and precipitation at grain boundaries. The ultimate tensile strength (UTS) and ultimate failure strain (UFS) of these alloys are listed in Table 1.

![Figure 5. Engineering stress–strain curves of Zr$_{50-x/2}$Co$_{50-x/2}$Al$_x$ (x = 0, 4, 5, 6, 7, 8) alloys.](image)

### Table 1. Mechanical properties of Zr$_{50-x/2}$Co$_{50-x/2}$Al$_x$ (x = 0, 4, 5, 6, 7, 8) alloys including the ultimate tensile strength (UTS) and ultimate failure strain (UFS).

| Alloys        | UTS (MPa) | UFS (%) |
|---------------|-----------|---------|
| Zr$_{50}$Co$_{50}$   | 240 ± 20  | 6.99    |
| Zr$_{48}$Co$_{48}$Al$_4$ | 304 ± 20  | 3.75    |
| Zr$_{47.5}$Co$_{47.5}$Al$_5$ | 464 ± 20  | 3.93    |
| Zr$_{47}$Co$_{47}$Al$_6$ | 396 ± 20  | 3.30    |
| Zr$_{46.5}$Co$_{46.5}$Al$_7$ | 390 ± 20  | 3.28    |
| Zr$_{46}$Co$_{46}$Al$_8$ | 363 ± 20  | 3.06    |

The max room temperature tensile strain of the Zr$_{50}$Co$_{50}$ alloy prepared by rapid cooling was 6.99%, which is slightly higher than the 6% strain obtained by Matsuda et al. in their study of the Zr-Co-Ni alloy [6,33]. A 4% addition of Al increased the UTS of the alloy from 240 ± 20 MPa to 304 ± 20 Mpa during room-temperature tensile, but the UFS was decreased to 3.75%. Compared with compression, the initiation and expansion of cracks during the tensile process are more sensitive to shrinkage cavities caused by rapid cooling, and are more likely to generate stress concentration at shrinkage cavities that can cause specimen fracture and reduce its elongation. The UTS of the Zr$_{47.5}$Co$_{47.5}$Al$_5$ alloy reached a maximum of 464 Mpa when the Al content was 5 at.%, while maintaining a UFS of 3.39%. Further addition of Al led to a degradation in both the UTS and the UFS of the alloys. The Zr$_{47.5}$Co$_{47.5}$Al$_5$ alloy showed enhanced strength due to a combination of fine grain strengthening, solid solution strengthening, secondary phase strengthening and possibly stress-induced phase transformation and phase transformation-induced plasticity. In the field of structural materials, several traditional common materials are selected to compare with the tensile properties of the materials in this study, such as composite materials, which are currently the most popular to research. Guan et al. prepared Fe-based metallic glass particles that carry carbon nanotubes to reinforce Al matrix composites with a tensile strength of 284 Mpa and elongation of 6%. Liu et al. prepared a carbon nanotube-reinforced Cu matrix nanolaminated composite with 392.3 Mpa tensile strength. Carbon
nanotube-reinforced copper matrix composites with 307.4 Mpa strength were prepared by Deng et al. [34–36]. The addition of low content Al significantly enhanced the mechanical properties of ZrCo alloy.

Although fine grain size enhances the strength of an alloy, excessive Al content (more than 5 at.%) increases the size and number of shrinkage cavities at the second phase. The microdefects cause stress concentration and induce crack initiation, leading to a decrease in both the strength and the plasticity of the alloy. It is worth noting that although the increase in Al content decreases the plasticity of the alloys, the UTS of Zr_{48}Co_{48}Al_{4}, Zr_{47.5}Co_{47.5}Al_{5}, Zr_{47}Co_{47}Al_{6}, Zr_{46.5}Co_{46.5}Al_{7}, and Zr_{46}Co_{46}Al_{8} alloys is still higher than that of Zr_{50}Co_{50} alloy, which can be attributed to the synergistic effects of secondary phase strengthening, fine-grain strengthening, and solid solution strengthening.

SEM images of the fractured surface after tensile testing are shown in Figure 6. There were no obvious plastic fracture characteristics on the fractography. On the contrary, a large number of cleavage fracture surfaces (red arrows) and holes after grain pullout (yellow arrows) with different sizes were observed, showing a typical brittle intergranular fracture. With the increase in Al content, the cleavage planes gradually decreased and more holes remained after grain pullout, indicating that the plasticity of the alloy gradually deteriorated, which is consistent with the previous characterization results of tensile mechanical properties.

Figure 6. The fracture surface morphology of Zr_{50−x/2}Co_{50−x/2}Al_{x} alloys after tension at ambient temperature: (a) Zr_{50}Co_{50}; (b) Zr_{48}Co_{48}Al_{4}; (c) Zr_{47.5}Co_{47.5}Al_{5}; (d) Zr_{47}Co_{47}Al_{6}; (e) Zr_{46.5}Co_{46.5}Al_{7}; (f) Zr_{46}Co_{46}Al_{8}. Holes formed by grain pull-out indicated by yellow arrows, and cleavage planes indicated by red arrows.
Figures 7 and 8 show the TEM images of Zr$_{50}$Co$_{50}$ and Zr$_{46.5}$Co$_{46.5}$Al$_{7}$ alloys, respectively. The Zr$_{50}$Co$_{50}$ alloy has no third group of alloying elements, and therefore, no solid solution strengthening. However, many precipitated particles of about 30–40 µm are uniformly distributed at the grain boundaries, and these particles were determined to be hard and brittle ZrO$_2$ by EDS, as shown in Figure 7c. During the tensile process, stress concentration was easily generated near the ZrO$_2$ particles, and a large number of microcracks were generated at the interface between the B2 phase and ZrO$_2$ particles, which generated large plasticity through the “microcrack toughening mechanism”. In Figure 8a, the Zr$_{46.5}$Co$_{46.5}$Al$_{7}$ alloy matrix contains many continuous precipitated phases, the EDS results showed that the composition of the precipitated phases was Zr:Co:Al = 38.3%:44.38%:17.3%, and the composition of the matrix was Zr:Co:Al = 51.96%:46.5%:1.52%. Li et al. analyzed the precipitated phase and matrix by energy spectroscopy and SAED and found that the precipitated phase was Zr$_5$Co$_7$Al$_3$ and the matrix was Zr$_{50}$Co$_{50}$ [10]. The addition of Al caused the Zr$_5$Co$_7$Al$_3$ intermetallic compound precipitated at grain boundaries or inside the grains of the Zr-Co-Al alloy, and its content was inversely proportional to the elongation of the Zr-Co-Al alloy. The XRD results showed that the content of the brittle phase Zr$_5$Co$_7$Al$_3$ increased with the increase in Al content. The addition of Al element led to precipitate a large amount of brittle phases in the alloy, and the rupture of the brittle phase during the tensile process led to the fracture of the alloy.

![TEM images of Zr$_{50}$Co$_{50}$ alloys](image1.png)

**Figure 7.** TEM images of Zr$_{50}$Co$_{50}$ alloys: (a) microstructure of the as-cast alloy; (b) second phase particles along the GBs; (c) EDS pattern.

![TEM images of Zr$_{46.5}$Co$_{46.5}$Al$_{7}$ alloys](image2.png)

**Figure 8.** TEM images of Zr$_{46.5}$Co$_{46.5}$Al$_{7}$ alloys: (a) microstructure of the as-cast alloy; (b) EDS pattern of point A; (c) EDS pattern of point B.

4. Conclusions

In this work, the following conclusions were obtained by investigating the effect of Al addition on the phase composition and mechanical properties of Zr-Co alloys.

The Zr-Co alloy, fabricated by copper mold suction casting, consists of a single B2 phase matrix with many ZrO$_2$ particles uniformly distributed at the grain boundaries as observed in TEM image. After the addition of Al, the grain size decreased from 60 µm to 4 µm with the Al content increased from 0 at.% to 8 at.%. The best combination of mechanical proper-
ties (464 MPa of UTS and 3.4% of UFS, respectively) was achieved with 5 at. % addition of Al. The excessive addition of Al element results in the precipitation of a brittle $Zr_{5}Co_{7}Al_{3}$ phase at the grain boundaries or inside the grains of the Zr-Co-Al alloy. Al atoms exceeded the solid solubility of Zr-Co phase accumulate at the solid–liquid interface, forming constitutional undercooling and leading to the formation of dendrites and shrinkage cavities. The strengthening mechanism of Zr-Co-Al alloy mainly included fine grain strengthening, solid solution strengthening of Al elements and secondary phase precipitation strengthening.

Author Contributions: Z.W. investigated the relationship between microstructure and mechanical properties and wrote the manuscript. W.L. measured the mechanical properties. C.L. analyzed the strengthening mechanisms. P.G. and X.Y. prepared the samples. J.T. revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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