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Microstructure and mechanical properties of novel ZrB_2-reinforced zirconium alloys

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ABSTRACT

Novel ZrB_2-reinforced zirconium (Zr) alloys with different boron (B) and aluminum (Al) contents were produced by arc-melting technique. Microstructural observation indicated that both the α-lath and the prior-β grain size were significantly refined with increased B content. The thickness of α lath gradually increased with increased solute atom Al content. Compressive test results showed that the modulus and strengths of the alloys improved with increased ZrB_2 and Al contents. The presence of abundant ZrB_2 whiskers and solid solution atom Al were responsible for the increased Young's modulus. The strengthening mechanisms can be attributed to strengthening through load transfer between the ZrB_2 whiskers and Zr matrix, morphological changes in alloys resulting from the formation of ZrB_2 whiskers, and solid-solution strengthening caused by Al addition. Fractography confirmed that ZrB_2 whiskers undertook the load transferred from Zr matrix and that crack sources were primarily generated at ZrB_2 whiskers.

1. Introduction

Zirconium (Zr) and Zr-based alloys are attracting considerable interest because of their excellent physical and chemical properties, such as small thermal neutron absorption cross-section, good corrosion resistance, low creep under high temperature, and low coefficient of thermal expansion [1–5]. Studies on ultrahigh-strength ZrTiAlV series alloys have shown that Zr alloys have potential applications as structure materials [6,7]. To meet the requirements of structure materials, new Zr-based alloys with excellent mechanical properties need to be developed.

Microstructure significantly affects mechanical properties. Finer grain size, homogeneous microstructure, and excellent phase composition can effectively improve the mechanical properties of alloy. Grain refinement is a common and effective method of altering the mechanical properties of alloys. Many mechanical properties such as elongation-to-failure, strength, machinability, and damage tolerance can be improved by refining grain size [8]. Grain refinement can be achieved by rapid solidification, solute addition, violent agitation, equal-channel angular processing, and differential speed rolling, among others [9–12]. Among these techniques, solute addition is the most convenient and economic way to obtain fine grain structure. For example, Bermingham et al. [13] investigated beryllium as grain refining solute in titanium alloys. Their results showed that only small additions of Be can cause dramatic refinement through solute mechanisms. The key factors affecting the significant refinement are enhanced nucleation rate and growth restriction factor values of Ti alloys resulting from Be addition. Jin et al. [14] used carbon addition to refine magnesium alloys. Carbon elements are prone to segregation in Mg alloys, thereby restricting grain growth during solidification. Lee et al. [15] studied the effect of silicon content on grain size in hypoeutectic Al–Si alloys. Grain size decreases with increased silicon content. Constitutional effects during growth and the competitive process of nucleation contributed to the grain refinement of Al alloys. Thus, solute addition is a very effective way to refine grain structure. However, studies on the grain refinement of Zr alloys through solute addition are limited.

Boron (B) was selected as the alloying element in this work. The research on the use of B as an alloying element in Ti alloys is extensive, which share similarities to Zr alloys [16–18]. Zhu et al. [19] refined dental cast titanium alloys by adding a small amount (< 0.5 wt%) of B. They found significant refinement of the as-cast structure and improvement of mechanical properties. Dargusch et al. [20] studied the effects of B on the microstructure of cast Zr alloys. Their earlier work showed grain refinement of Zr alloys by adding a small amount of B (< 1.25 at%). However, details such as microstructure evolution with higher B content, the influence of B

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addition on the mechanical properties of alloys, and validation of the existence of compound were inadequately addressed. The solubility of B in pure Zr is low. The intermetallic compound ZrB_2 is segregated at prior-β grain boundaries after B addition. ZrB_2 whiskers have many excellent physical properties, including low work function, excellent thermal and electrical conductivity, high melting point and hardness, and good oxidation stability [21,22]. Thus, it can be used in various extreme environments, such as that in aerospace [23–25].

Solid-solution strengthening is also considered an important method of improving the mechanical properties of Zr alloys [26]. In general, the influence of solid-solution strengthening on Zr alloys has been investigated using many kinds of solute element [27]. Aluminum (Al) element is an important solute atom that is used to effectively improve strength because of the large difference in atomic radius between Al and Zr and the wide solubility range [28].

In this work, B and Al were selected as alloying element, and the microstructure and phases of ZrB_2-reinforced Zr alloys were examined. Compressive properties at room temperature were investigated. Strengthening and fracture mechanism were discussed from a microstructure viewpoint. Effects of Al atom as solute atom on change in ultimate compressive strength of alloys were studied.

2. Experimental procedure

In Zr alloys, the raw materials were sponge Zr (> 99.5 wt%), Al (> 99 wt%), and B powder (> 99 wt%). These materials were melted in a nonconsumable vacuum arc-melting furnace. All ingots were turned and remelted six times to ensure compositional homogeneity. Nominal chemical compositions of the ingots are listed in Table 1.

Samples for microstructural observation and mechanical test were cut by electric discharging machining from as-cast ingots. Phases of the produced samples were determined by X-ray diffraction (XRD) with copper Kα X-radiation (D/max-2500/PC) and identified by matching each characteristic peak with JCPDS files. Optical microscopy and Hitachi S-3400 scanning electron microscopy (SEM) were used to observe microstructures. For light microscopy, surfaces were mechanically polished through a standard metallographic procedure to a final level of 0.5 μm using diamond paste. The polished samples were etched in a mixture of water, nitric acid, and hydrofluoric acid (85:10:5 by volume). Microstructural parameters were characterized by image analysis software. Compression properties were characterized on 12 mm-long rods (aspect ratio = 2) using an Instron 5892 testing machine at an initial strain rate of $5 \times 10^{-4}\ s^{-1}$. An extensometer with 12.5 mm gauge length was mounted to measure compressive strain during testing. At least three tests were performed on each condition, and average values were reported. Fracture morphologies of specimens were characterized by SEM.

Table 1
Nominal chemical compositions (and analyzed chemistry) of the current alloys (at %).

Alloy no.	B	Al	Zr
Zr	–	–	Bal.
Zr–3.5B	3.50 (3.41)	–	Bal.
Zr–7B	7.00 (6.87)	–	Bal.
Zr–3.5B–2.5Al	3.50 (3.44)	2.50 (2.47)	Bal.
Zr–3.5B–5Al	3.50 (3.42)	5.00 (4.92)	Bal.

3. Results and discussion

3.1. Phase and microstructure

XRD patterns of as-cast ZrB alloys with different contents of B are shown in Fig. 1a. The phase component of alloys contains two phases (i.e., α-Zr and ZrB_2). No other metastable boride is detected. Fig. 1a shows that the intensity of ZrB_2 phase gradually increases with increased B content. Fig. 1b shows the XRD patterns of ZrB alloys after Al addition, and two phases (i.e., α-Zr and ZrB_2) are also found. This result means that Al addition (< 5 at%) does not lead to the formation of a new phase in Zr alloys. The peaks of α-Zr move toward the direction of large diffraction angles, indicating that Al atoms are dissolved into its lattices.

Fig. 2 shows microstructural morphologies observed in as-cast Zr alloys with different B and Al contents. Fig. 2a–c shows two major microstructural features, namely, the prior-β grain structure and the lath-like α-phase. Prior-β grains are the remnants of grain structure formed during solidification. The site of α-phase nucleates and grows near these prior-β boundaries [29,30]. A dramatic change is observed in the prior-β and α grain size produced by B addition. In the case of no B addition, prior-β morphology exhibits large angular grain boundary structure. The microstructure changes to dendritic equiaxed structure after 7 at% B addition. Internal α laths become more refined with increased B content, and the aggregates of parallel α laths give way to a more random basketweave structure. This result is consistent with Dargusch's study on as-cast pure Zr after trace B addition [20].

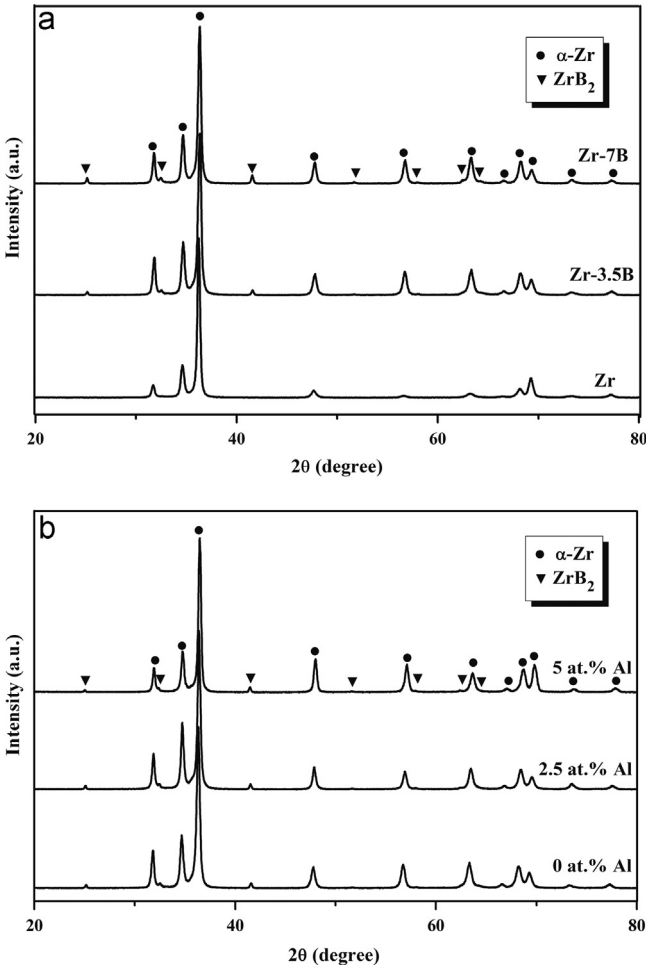

Fig. 1. XRD patterns of (a) as-cast Zr–*x*B alloys with varied B contents and (b) as-cast Zr–3.5B–*x*Al alloys with varied Al contents.