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Enhanced strength and transformation-induced plasticity in rapidly solidified Zr–Co–(Al) alloys

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Transformation-induced plasticity and significant work-hardening capability were verified to be an effective way to enhance the performance of materials. This work reports on a Zr₄₉Co₄₉Al₂ alloy obtained by traditional water-cooled copper mold casting with high strength and large plasticity due to B2-to-B33 deformation-induced martensitic transformation. The B33 martensite with orthorhombic structure does not form spontaneously above room temperature in Zr–Co–(Al) alloys, except when it is induced by local stress concentration.

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Rapid solidification techniques for chilling metallic liquids at very high rates allow freezing of the configuration of alloy melts and obtaining bulk metallic glass (BMG) for some alloys. When the cooling rate is not sufficiently high to obtain a fully amorphous alloy, BMG composites, nanocrystalline material or ultra-fine-grained (UFG) material can be obtained, depending on the glass-forming ability (GFA) of the respective alloy [1]. The rapid solidification processing results in increased strength, as well as enhanced fracture and fatigue resistance, with concurrent improvements in mechanical, physical and chemical properties [2,3]. The deformation of BMG at room temperature is highly localized into shear bands, owing to strain softening and/or thermal softening [4]. Finally, they develop towards catastrophic failure along one dominant shear plane, thus restricting wide application of BMG [5–7]. Many desired mechanical properties, however, can be achieved from either in situ or ex situ BMG composites

by controlling the type, size, volume fraction and/or distribution of the second phase dispersions [6–10].

Transformation-induced plasticity and significant work-hardening capability have been found in Ti-based [9–11] and Zr-based [12–18] composites and are verified to be an effective way to enhance the performance of materials [2,19]. Nevertheless, most of the Ti- and Zr-based BMG and their composites often require the addition of copper, nickel or beryllium, which makes these alloys less suitable to be used as biomedical implants. Recently, the discovery of Zr–Co–Al ternary alloys with superior corrosion resistance and good bioactivity has renewed interest in this type of glass-forming alloy [20,21].

ZrCo alloys with B2 (CsCl structure) are inherently ductile, owing to the existence of a mechanically induced B2-to-B33 martensitic transformation [14]. However, monolithic crystalline phases are often soft, despite obvious strain-hardening, as observed in both compressive and tensile tests [14,18]. A possible way to obtain both high strength and high plasticity is to combine the ductile B2 phase with bulk amorphous/nanograined/UFG phase(s) through rapid solidification methods. ZrCo alloys alloyed with low-cost aluminum are good candidates to verify this conjecture. In the present study, a

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Zr₄₉Co₄₉Al₂ alloy was produced by traditional water-cooled copper mold casting, which exhibits a nominal maximum compression strength of 2260 MPa, together with an ultimate true failure strain of 69%, owing to deformation-induced martensite formation.

Zr₄₉Co₄₉Al₂, Zr₅₀Co₅₀ and Zr₅₆Co₂₈Al₁₆ (nominal composition in atomic per cent) pre-alloys were synthesized by arc-melting the proper amounts of the constituting elements (purity of 99.99% or higher) in a Ti-gettered high purity argon atmosphere. The pre-alloy ingots were remelted at least four times in order to ensure chemical homogeneity. The ingots were cut into small pieces with a mass of ~5–6 g, and then they were melted and cast into cylindrical rods with diameter 2 mm and length ~50 mm, using water-cooled copper mold suction casting. The structure and the thermal behavior were checked by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Low-temperature magnetometry was performed using a superconducting quantum interference device (SQUID). Compression tests (height-to-diameter ratio 2:1) were performed using an Instron 5869 testing machine equipped with a laser extensometer (Fiedler) at a constant strain rate of 0.0005 s⁻¹ at room temperature. Micro-indentation was carried out at at least 15 points on each of the samples, using a Vickers diamond indenter and a load of 25 g with a dwell time of 10 s. The morphology and the atomic-level structure of the sample were investigated using high-resolution scanning electron microscopy (Gemini 1530) and field emission transmission electron microscopy (JEM 2010F). The deformation behavior was also investigated by high-energy XRD ($\lambda = 0.020728$ nm, beam size 0.6×0.6 mm²) at the P02.1 beam line of PETRA III (Hamburg, Germany).

Figure 1 depicts the mechanical properties of the Zr₄₉Co₄₉Al₂ alloy at room temperature, revealing high nominal compression strength, which is as high as that of Zr₅₆Co₂₈Al₁₆ BMG obtained under the same condi-

tions by water-cooled copper mold casting [21–24], as shown in Figure 1a. The nominal compression strength of Zr₄₉Co₄₉Al₂ is ~2260 MPa combined with >50% ultimate failure strain. For comparison, Zr₅₀Co₅₀ alloy rods were prepared. For these rods, an engineering strain as large as ~80% was achieved. As a result of such intense deformation, the rods were compressed into thin pellets without fracturing. Such results agree well with previous research in that the B2 ZrCo alloy is inherently ductile [14]. The inset in Figure 1a shows an enlarged part of the stress–strain curves. The 0.2% offset yield strength (σ_y) and the Young's modulus (E) of the different alloys are listed in Table 1. The results reveal that the yield strength (σ_y) apparently increases upon minor addition of Al. Addition of 2 at.% Al improves σ_y almost three times compared with Zr₅₀Co₅₀ rods, i.e., σ_y increases from 122 to 378 MPa. The Young's modulus (E) increases significantly from 18 ± 2 GPa to 64 ± 2 GPa. For fully amorphous Zr₅₆Co₂₈Al₁₆ BMG, the Young's modulus (E) is 92 ± 2 GPa. Hence, the minor addition of Al inevitably affects the topological and/or chemical structure of the alloys. Actually, an attractive force originates from the difference in electronegativity between the elements and is reflected in the heat of mixing, as shown in Table 2. Elements with stronger attractive force exhibit a larger enthalpy of mixing, which favors the formation of a highly dense random packed structure in which the diffusivity of the constituent elements is suppressed [1,25]. Thus, good GFA and/or high thermal stability can be more easily synthesized for Al-containing amorphous alloys [26].

The Vickers hardness (H_v) increases from 270HV25 to 406HV25, owing to the minor addition of Al element, indicating that the atomic bonding strength improves and thus leads to improvements in the elastic modulus and yield strength. The highly dense random packed structure of fully amorphous Zr₅₆Co₂₈Al₁₆ BMG shows higher Vickers hardness, elastic modulus and yield strength, as shown in Figure 1b.

The pronounced significant work-hardening behavior of the Zr₄₉Co₄₉Al₂ and Zr₅₀Co₅₀ alloys is illustrated in Figure 1c and d. However, no strain-hardening behavior was observed for Zr₅₆Co₂₈Al₁₆ BMG [21]. The work-hardening behavior of these samples was analyzed by means of the work-hardening index n , defined as [27]: $\sigma = k\varepsilon^n$, where σ represents the applied stress on the material, ε is the strain, and k is the strength coefficient. The value of the work-hardening index n lies between 0 and 1. A value of 0 means that a material is a perfectly plastic solid; while an n value of 1 represents a 100% elastic solid [27]. Most metals have an n value between 0.10 and 0.50, as shown in Table 3. The Zr₄₉Co₄₉Al₂ alloy has a larger n value, exceeding most metals, including annealed low-carbon steel, aluminum alloys and magnesium alloys, while Zr₅₀Co₅₀ has an n value of 0.509, which is higher than that of annealed 304 stainless steel [27]. The martensitic transformation in 304 stainless steel can be induced by plastic deformation at room temperature, and thus leads to obvious work-hardening behavior [28]. Therefore, it is possible to assume that the present Zr–Co-based alloys also undergo a deformation-induced transformation, leading to the large work-hardening index (n). Investigating the structural evolution

Figure 1. (Color online) Mechanical properties of the Zr–Co–Al alloys at room temperature. (a) Typical compressive engineering stress–strain curves of alloy rods with diameter 2 mm. The inset shows an enlarged part of the stress–strain curves. (b) Vickers hardness (H_v) of alloys. (c) Typical compressive true stress–true strain curves of the alloy rods revealing pronounced work-hardening behavior for Zr₄₉Co₄₉Al₂ and Zr₅₀Co₅₀ alloys. (d) The natural logarithm curves of the true stress–true strain indicate the change in working-hardening rate.

Table 1. Mechanical properties including the yield stress (σ_y), Young's modulus (E), ultimate compressive strength (UCS), strength coefficient (k) and work-hardening index (n) of Zr–Co–Al BMG and/or their composites obtained by monotonic compression test.

Alloys	σ_y (MPa)	E (GPa)	UCS (GPa)	K (MPa)	n	Adj. R^2
Zr ₄₉ Co ₄₉ Al ₂	378 ± 20	64 ± 2	2.26 ± 0.02	458	0.223	97.7%
Zr ₅₀ Co ₅₀	122 ± 20	18 ± 2	–	113	0.509	99.8%
Zr ₅₆ Co ₂₈ Al ₁₆	1897 ± 20	92 ± 2	2.1 ± 0.1	–	–	–

Table 2. Enthalpy of mixing and the atomic radius in the Zr–Co–Al system.

Elements	Enthalpy of mixing (kJ mol ^{−1})			Atomic radius (pm)
	Zr	Co	Al	
Zr	0	–	–	155
Co	−41	0	–	135
Al	−44	−19	0	125

Table 3. Tabulation of n and k values for several alloys.

Alloys	n	k (MPa)	References
Zr ₅₀ Co ₅₀	0.509	113	This work
Zr ₄₉ Co ₄₉ Al ₂	0.223	458	This work
Low-carbon steel (annealed)	0.21	600	[27]
4340 steel (tempered at 315 °C)	0.12	2650	[27]
304 stainless steel (annealed)	0.44	1400	[27]
Copper (annealed)	0.44	530	[27]
Naval brass (annealed)	0.21	585	[27]
2024 aluminum alloy (heat treated-T3)	0.17	780	[27]
AZ31B magnesium alloy (annealed)	0.16	450	[27]

upon compressive testing may provide direct evidence for this assumption.

The cross-sectional surfaces of the as-cast Zr₅₀Co₅₀ and Zr₄₉Co₄₉Al₂ alloy rods were further checked by XRD, indicating that the rapidly solidified alloys are mainly composed of the B2 ZrCo phase within the resolution limits of XRD. However, a small amount of B33 ZrCo phase, marked with the symbol “-” in Figure 2, was detected on the cross-sectional surfaces of the deformed Zr₅₀Co₅₀ alloy rod. The XRD patterns shown in Figure 2a and b reveal a B2-to-B33 martensitic transformation under compression. However, there is no remarkable transformation on both the upper and lower surfaces of the specimens compared with the as-cast specimen shown in Figure 2c. This indicates that the Zr₅₀Co₅₀ alloy

contains a distribution of a second phase with an orthorhombic (B33) structure whose composition is identical to that of the matrix, which stems from a martensitic transformation induced by local stress concentration. It is proposed that this transformation contributes to the unusually good ductility of the alloy. The results are consistent with the investigations on Zr₅₀Co₄₀Ni₁₀ [29]. The cross-sectional surface of the as-cast Zr₄₉Co₄₉Al₂ alloy rod is composed mainly of B2 ZrCo phase, shown in Figure 2d. A small volume fraction of B33 ZrCo phase and the remaining B2 ZrCo phase, shown in Figure 2e, were also detected on the cross-sectional surfaces of the deformed Zr₄₉Co₄₉Al₂ alloy rod. The result from high-energy XRD, shown in Figure 3, further confirmed the fact. It is suggested that the production of a small quantity of martensite in the vicinity of a crack tip may help to ductilize Zr₅₀Co₅₀ and Zr₄₉Co₄₉Al₂ [30,31].

Figure 4 shows the temperature dependence of the magnetic moment of the as-cast Zr₄₉Co₄₉Al₂ alloy measured by SQUID magnetometry. The intensity of magnetization is very low, so the sample remains in the

Figure 2. (Color online) The existence of martensitic transformation in Zr–Co-based alloys, owing to stress concentration. The structure evolution of the as-cast and deformed alloys indicates a B2-to-B33 martensitic transformation upon compression testing. **Figure 3.** (Color online) Comparison of the two-dimensional high energy XRD patterns of (a) as-cast and (b) deformed Zr₄₉Co₄₉Al₂ alloy. The red arrows indicate the weak structural changes after deformation.

Figure 4. Temperature dependence of the magnetic moment of the as-cast $\text{Zr}_{49}\text{Co}_{49}\text{Al}_2$ alloy measured by SQUID magnetometry, revealing a small thermal hysteresis due to martensitic transformation ~ 200 K.

paramagnetic state during the domain of temperature investigated. However, the intensity in the low-temperature regime is slightly higher. This may be because of low temperature thermal fluctuations of the magnetic moment rotation. At ~ 200 K, the existence of a small thermal hysteresis may be attributed to the martensitic transformation. These findings are similar to previous work on Zr–Co–Ni alloys, where the B33 (orthorhombic) and B2 (CsCl) structures are stable < 240 K and > 390 K, respectively, with a domain of coexistence of the two phases in-between [30,31]. The shift in the temperature might be attributed to the addition of Al to the alloys.

In conclusion, a $\text{Zr}_{49}\text{Co}_{49}\text{Al}_2$ alloy with high compression strength and plasticity was obtained by water-cooled copper mold casting. B33 martensite (orthorhombic structure) does not form spontaneously above room temperature in the investigated Zr–Co–(Al) alloys except when it is induced by local stress concentration. The alloy contains a distribution of a second phase with an orthorhombic (B33) structure whose composition is identical to that of the matrix, which stems from a martensitic transformation induced by local stress concentration. It is proposed that this transformation contributes to the good ductility of the alloy.

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