

Full length article

Development of a Zr-based bulk metallic glass with excellent industrial producibility and high fracture toughness

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ABSTRACT

Bulk metallic glasses with superior mechanical properties represent a class of advanced engineering materials. However, most metallic glasses developed in the laboratory exhibit poor industrial producibility, as well as low fracture toughness or ductility under industrial conditions. In this study, we successfully developed a new Zr-based bulk metallic glass ((Zr₅₈Ti₂Cu₁₆Ni₁₂Nb₂Al₁₀) Y_{0.2}) combining excellent industrial producibility and high fracture toughness via the thermodynamic-guided multi-element engineering strategy. The Zr-based alloy can achieve a fully amorphous structure in 15 mm-diameter rods via high-vacuum suction casting and 3.5 mm-thick plates via industrial die casting, which outperforms the current commercial Zr-based bulk metallic glasses such as Vit-106 (an amorphous dimension of 2.5 mm thickness for industrial die casting). Meanwhile, the suction-casting glass sample exhibits a fracture toughness up to 139 MPa·m^{1/2}, together with an impact toughness of as high as 14.75 J/cm², a large compressive plasticity of 19.5%, exceeding all previously reported beryllium-free Zr-based bulk metallic glasses. Furthermore, a fracture toughness of up to 60 MPa·m^{1/2} is achieved in the industrial die-casting sample, and is about 50% higher than that of commercial Vit-106 bulk metallic glasses (~40 MPa·m^{1/2}). Finally, we demonstrated the potential of industrial applications of the bulk metallic glass by fabricating a variety of defect-free components with complex shapes, such as hinges of foldable phones and flexsplines of harmonic gear drives.

1. Introduction

Bulk metallic glasses (BMGs), characterized by their disordered atomic structure and the lack of crystalline defects, demonstrate an exceptional high strength (up to $E/50$, E is the Young's modulus), large elastic limit (~2%), and remarkable wear resistance [1–5]. These attributes have made BMGs attract numerous attentions over the past decades, establishing them as promising alternative structural materials in many critical applications. Generally, structural materials are required to have outstanding mechanical properties while remaining amenable to industrial-scale manufacturing [6–8]. Among various BMG systems, Zr-based BMGs distinguish themselves by combining the

relatively low cost with the high glass forming ability (GFA), offering the greater potential for industrial applications as compared to other BMGs [9–11]. Nevertheless, scaling up from laboratory development and optimization to industrial utilization remains fraught with challenges. Central among these are developing alloy systems that simultaneously fulfill critical industrial viability factors, including cost-effectiveness, substantial amorphous dimensions, and the balance between strength and toughness.

Although numerous Zr-based BMGs have been developed so far, there is only a limited number of compositions suitable for industrial applications. Typical alloys include Be-containing and Be-free Zr-based alloys, such as Vit-105, Vit-106, and Vit-1 [12–14]. These alloys can be

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fabricated into amorphous rods with a critical diameter exceeding 10 mm under laboratory conditions. However, their amorphous dimension significantly deteriorates under industrial production conditions. For instance, the Vit-106 alloy can only form fully amorphous plates with only a 2.5 mm thickness under industrial low-vacuum conditions. Consequently, this material is solely suitable for thin-walled components. Be-containing Zr-based BMGs exhibit superior GFA, enabling a critical casting dimension even exceeding 10 mm under industrial conditions [15–17]. However, stringent regulatory controls on Be raw materials further limit the applicability of these alloys due to the possible toxicity of Be preventing the applications involving human contacts. Therefore, developing new Be-free Zr-based BMGs that can form large-dimension amorphous structures under industrial conditions is crucial for practical applications.

In addition, maintaining excellent mechanical properties under industrial conditions is also a vital factor for assessing the industrial applicability of Zr-based BMGs. In particular, fracture toughness determines the material's resistance to catastrophic failure under static stress concentration and dynamic impact. Among currently developed BMG systems, the Pd-based BMG ($\text{Pd}_{79}\text{Ag}_{3.5}\text{P}_{6.5}\text{Si}_{9.5}\text{Ge}_2$, at atomic percents (at%)) exhibits an exceptional fracture toughness ($\sim 200 \text{ MPa}\cdot\text{m}^{1/2}$), but the prohibitive cost limits it to niche uses [18–21]. The Be-containing BMGs also demonstrate high fracture toughness, i.e., $\text{Ti}_{40}\text{Zr}_{25}\text{Cu}_{12}\text{Ni}_3\text{Be}_{20}$ BMG achieve a fracture toughness of $100 \text{ MPa}\cdot\text{m}^{1/2}$ [22], yet the processing challenges and toxicity concerns associated with Be continue to restrict their industrial adoption. As a result, Be-free Zr-based BMGs remain the preferred choice for industrial applications. However, these alloys generally exhibit a relatively low fracture toughness. For example, under laboratory conditions, the Zr-Cu-Al ternary system demonstrates an average fracture toughness of approximately $60 \text{ MPa}\cdot\text{m}^{1/2}$ [23,24]. Although the ZT1 BMG ($\text{Zr}_{61}\text{Ti}_2\text{Cu}_{25}\text{Al}_{12}$) developed based on the ternary alloys exhibits the highest recorded value of $112 \text{ MPa}\cdot\text{m}^{1/2}$ [25], its fracture toughness may be further reduced when being produced under industrial environments because the mechanical properties are highly sensitive to processing conditions. Therefore, developing alloy systems that exhibit high fracture toughness under industrial conditions is of great significance.

In the present work, we developed a new Zr-based BMG ($(\text{Zr}_{58}\text{Ti}_2\text{Cu}_{16}\text{Ni}_{12}\text{Nb}_2\text{Al}_{10})\text{Y}_{0.2}$, ZN2-Y) through thermodynamic-guided multi-element engineering (TG-MEE). The ZN2-Y can form amorphous rods with a diameter of 15 mm via high-vacuum suction casting, and plates with a 3.5-mm thickness via industrial die casting, surpassing all previously reported Be-free Zr-based BMGs. More importantly, the industrial die-cast ZN2-Y achieves a fracture toughness up to $60 \text{ MPa}\cdot\text{m}^{1/2}$, which is 50% higher than that of commercial Vit-106 ($\sim 40 \text{ MPa}\cdot\text{m}^{1/2}$). In addition, the ZN2-Y also shows an impact toughness of $14.75 \text{ J}/\text{cm}^2$ and a compressive plasticity as high as $\sim 19.5\%$. The processability and mechanical properties of the ZN2-Y BMG allowed the fabrication of defect-free amorphous complex-shape components (e.g., hinge, flex spline) that are fully amorphous and defect-free even by industrial die casting, validating its readiness for industrial deployment. This work establishes a generalize paradigm for designing alloys that seamlessly integrate laboratory-level properties with industrial scalability and significantly broadens the scope for engineering applications of BMGs.

2. Experimental

2.1. Materials and processes

Industrial-grade raw metals (Zr, Cu, Ti, Al, Ni, Nb, Y purity $\geq 99.5\%$) were arc-melted within a water-cooled copper crucible under an argon atmosphere. To ensure compositional homogeneity, ingots underwent a minimum of six remelting cycles. Rod specimens with diameters of 2 mm, 3 mm, 5 mm, 7 mm, 10 mm, 12 mm, and 15 mm were fabricated via the copper-mold suction casting method. We establish 10 mm in such casting as the critical dimension for further industrial die casting. Master

alloys for die casting were initially melted under relatively high vacuum conditions (1–50 Pa) and subsequently comminuted, and each die-casting batch utilized 200 g of material. During industrial processing, raw materials underwent induction melting in a graphite crucible under 30–50 Pa vacuum for 30–40 s, with melt temperatures maintained 323–373 K above the liquidus point as monitored by infrared pyrometry. Following 10 s of superheating above the melting point, the molten alloy was tilt-cast into the runner system for die injection. Current die-casting molds employ hot-work tool steels with thermal conductivity measuring 40 W/(m·K), and copper exhibits significantly higher conductivity at 402 W/(m·K), exceeding that of tool steels by an order of magnitude. In addition, to ensure complete mold filling and minimize thermal stress in geometrically complex components, the mold temperature was maintained at 453–493 K without a waterless cooling system, specifically stabilized at 473 K for this study. Finally, solidified castings were ejected using mechanized knockout pins.

2.2. Structural characterization

The material structure was verified by X-ray diffraction using a Bruker D8 ADVANCE instrument with Cu K α radiation ($\lambda = 0.15406 \text{ nm}$). Specimen surfaces were ground flat and ultrasonically cleaned in ethanol prior to testing. Thermal stability analysis was employed using differential scanning calorimetry (DSC 404 F3) under an argon flow with samples weighing $15 \pm 0.1 \text{ mg}$ heated at 20 K/min. Casting integrity was assessed via X-ray micro-computed tomography (XRM) scanning at tube voltages of 30–160 kV and power settings of 1–25 W. Scanning electron microscopy (SEM) was used to characterize the fracture morphology of the fractured samples. High-resolution transmission electron microscopy (HRTEM) was utilized to characterize the nanoscale microstructure. Oxygen content is measured using an oxygen-nitrogen analyzer.

2.3. Mechanical properties testing

Room temperature compression testing employed 2-mm-diameter amorphous rods fabricated through copper-mold suction casting. Specimens from industrial die casting plates were sectioned into 2-mm-diameter rods using wire electrical discharge machining. All compression specimens are maintained at a 2:1 aspect ratio with mechanically polished parallel end surfaces. Uniaxial compression tests were performed on an LE5105 universal testing system at a constant strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. The room-temperature tensile test employs a flat dog-bone-shaped specimen with a 10-mm gauge length, $2.5 \text{ mm} \times 2 \text{ mm}$ cross-sectional dimensions, and a strain rate of 10^{-3} s^{-1} . Mode-I fracture toughness assessment employed notched three-point bend specimens for Vit-106, ZN2, and ZN2-Y alloys. Master plates ($100 \times 10 \times 2.2 \text{ mm}$) produced via suction/die casting were machined into $65 \times 10 \times 2 \text{ mm}$ bending specimens by wire electrical discharge machining. A standardized V-notch geometry ($W = 2 \text{ mm}$, $D = 4 \text{ mm}$, $\theta = 60^\circ$) was introduced at the specimen mid-span. Bend testing implemented displacement control on the LE5105 platform with a 25 mm support span and 0.2 mm/s cross-head velocity. Triplicate tests per alloy composition were guaranteed statistical significance. Upon yielding during stress loading, the loading process halts to examine shear bands and crack distributions at the notch tip. Charpy impact specimens measure $65 \times 8 \times 2 \text{ mm}$ with a 20-mm-span, featuring a 1-mm-wide, 3-mm-deep notch with a 1-mm root radius. Testing employed a 22 kg pendulum mass impacting at 5 m/s.

3. Results

3.1. Alloy design development

Based on the ZT1 ($\text{Zr}_{61}\text{Ti}_2\text{Cu}_{25}\text{Al}_{12}$) alloy with the atomic percent of Al fixed at 12%, the effect of Zr/Nb ratio on GFA by varying Nb content in $\text{Zr}_{61-x}\text{Nb}_x$ alloys was studied. The results are plotted in the (Zr+Ti)-Cu-Nb pseudo-ternary eutectic phase diagram (Fig. 1(a)). It reveals that

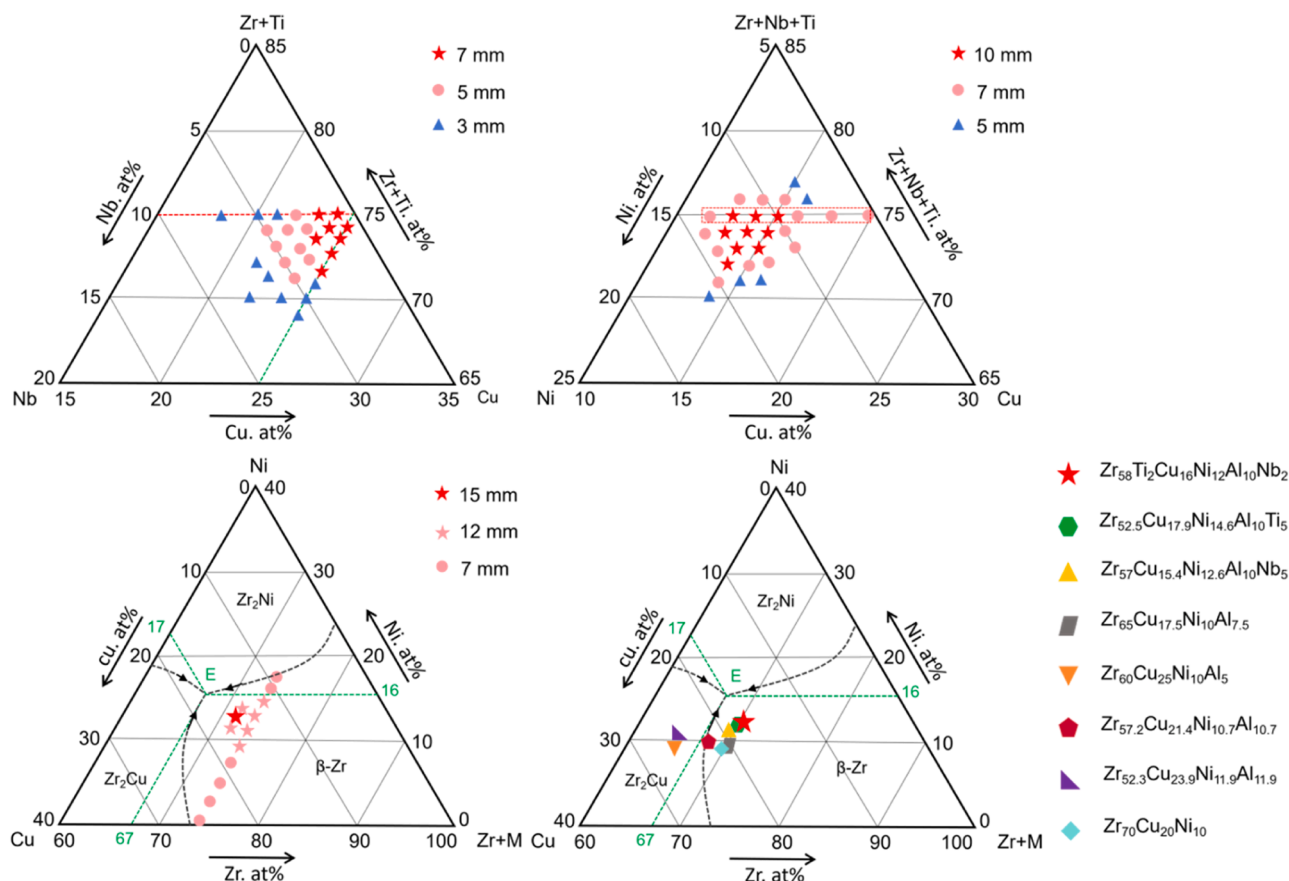


Fig. 1. Developing BMGs compositions with strong GFA via the TG-MEE method. (a) Zr/Nb, Cu/Nb compositions in the Zr-Cu-Al phase diagram. (b), (c) Cu/Ni composition in the Zr-Cu-Ni phase diagram. (d) Composition statistics of Cu/Ni-containing Zr-based BMGs.

under the condition of a constant Cu: Al atomic ratio of 25:12 (as indicated by the green line), the enhancement in GFA correlates directly with the increase of Nb content (Nb_1 , $Nb_{1.5}$, and Nb_2), resulting in a maximum critical diameter of 7 mm. The XRD patterns for different compositions are presented in Figs. S1 (a) and (b). Meanwhile, mechanical property results shown in Fig. S1(c) indicated that the Nb_2 alloy achieves the optimal yield strength (1620 MPa) and plasticity (7.5%). Furthermore, the effect of replacing Cu with Nb ($Cu_{25-x}Nb_x$) on GFA and mechanical properties was investigated at Zr: Al=61:12 (Fig. 1a, red line). Within these alloys, the Nb_1 and $Nb_{1.5}$ alloys were found to be able to maintain a GFA of 7 mm, whereas the Nb_2 and $Nb_{2.5}$ alloys exhibited a reduced GFA of 5 mm. Further increasing Nb to Nb_3 , Nb_5 , and Nb_7 resulted in even worse GFA with a critical casting diameter below 5 mm. XRD patterns and mechanical properties presented in Figs. S2 (a)-(c), revealing that the Nb_2 alloy exhibits the highest yield strength (1628 MPa) and the optimal plasticity (8.5%). In the intermediate region of the red-green trajectory (Fig. 1(a)), simultaneous substitution of Zr and Cu via the $Zr_{61-x}Cu_{25-y}Nb_{x+y}$ formula results in a GFA of 7 mm exclusively for the Nb_1 and $Nb_{1.5}$ compositions. In addition, the optimization of $Al_{12-x}Nb_x$, with XRD patterns and mechanical properties, summarized in Figs. S3 (a) and (b). These results indicate a progressive deterioration in GFA with increasing Nb content. Notably, both the strength and plasticity of these Al-substituted alloys are inferior to those of the Zr-Nb/Cu-Nb substituted systems, with the peak plasticity of the Nb_1 composition reaching only 2%.

The above results indicate that while Nb effectively enhances GFA, it fails to achieve a critical casting diameter of 10 mm, which is typically required for industrial die casting. Therefore, the effect of $Cu_{25-x}Ni_x$ substitution on GFA was subsequently investigated. The results are summarized in the (Zr+Ti+Nb)-Cu-Ni pseudo-ternary phase diagram

(Fig. 1(b)). As shown in the XRD patterns in Fig. S4(a), alloys containing 10–15 at% Ni and 12–18 at% Cu achieve a critical diameter of 10 mm. Mechanical properties as a function of Ni content are shown in Fig. S4 (b), which demonstrates that the $Zr_{58}Ti_2Cu_{16}Al_{10}Ni_{12}Nb_2$ (ZN2) exhibits the optimal performance, with a yield strength (σ_y) of 1580 MPa and 8.5% compressive plasticity (ϵ_p). Furthermore, the Cu/Ni ratio and the corresponding GFA of alloy compositions are plotted in the Zr-Cu-Ni ternary phase diagram (Fig. 1(c)). The results reveal that the increase of amorphous dimensions is accompanied by the decrease of Cu/Ni ratios, with compositional coordinates concurrently approaching the eutectic point. Additionally, statistical analysis of Cu- and Ni-containing Zr-based BMGs [12,13,26,27] possessing industrial production capacity, including Vit-105 and Vit-106, indicates that they cluster near eutectic points (Fig. 1(d)), implying that identifying eutectics is critical for developing alloys with strong GFA.

For further improvement of GFA, the rare-earth element yttrium (Y) was added to the ZN2 alloy. XRD patterns shown in Fig. S5 confirmed that all Y-doped alloys maintained a fully amorphous structure even at a diameter of 10 mm. The 10-mm-diameter samples of Vit-106 and ZN2-Y and their XRD patterns are shown in Fig. 2(a). One can see that Vit-106 and ZN2-Y exhibit the characteristic diffuse diffraction peak around $2\theta=38^\circ$ without distinct Bragg peaks, confirming their fully amorphous structure. Notably, the ZN2-Y alloy can be cast into fully amorphous rods with a diameter of 15 mm (Fig. 2(b)). In contrast, the XRD pattern for the 12-mm-diameter Vit-106 rod shows prominent crystallization peaks, primarily corresponding to the Zr_2Cu intermetallic phase. In addition, XRD characterization was conducted on the ZN2 alloy ingot at different positions along the central axis (red line) (Fig. 2c), demonstrating that the alloy ingot possesses a fully amorphous structure. These results indicate that the ZN2 and ZN2-Y may possess superior production

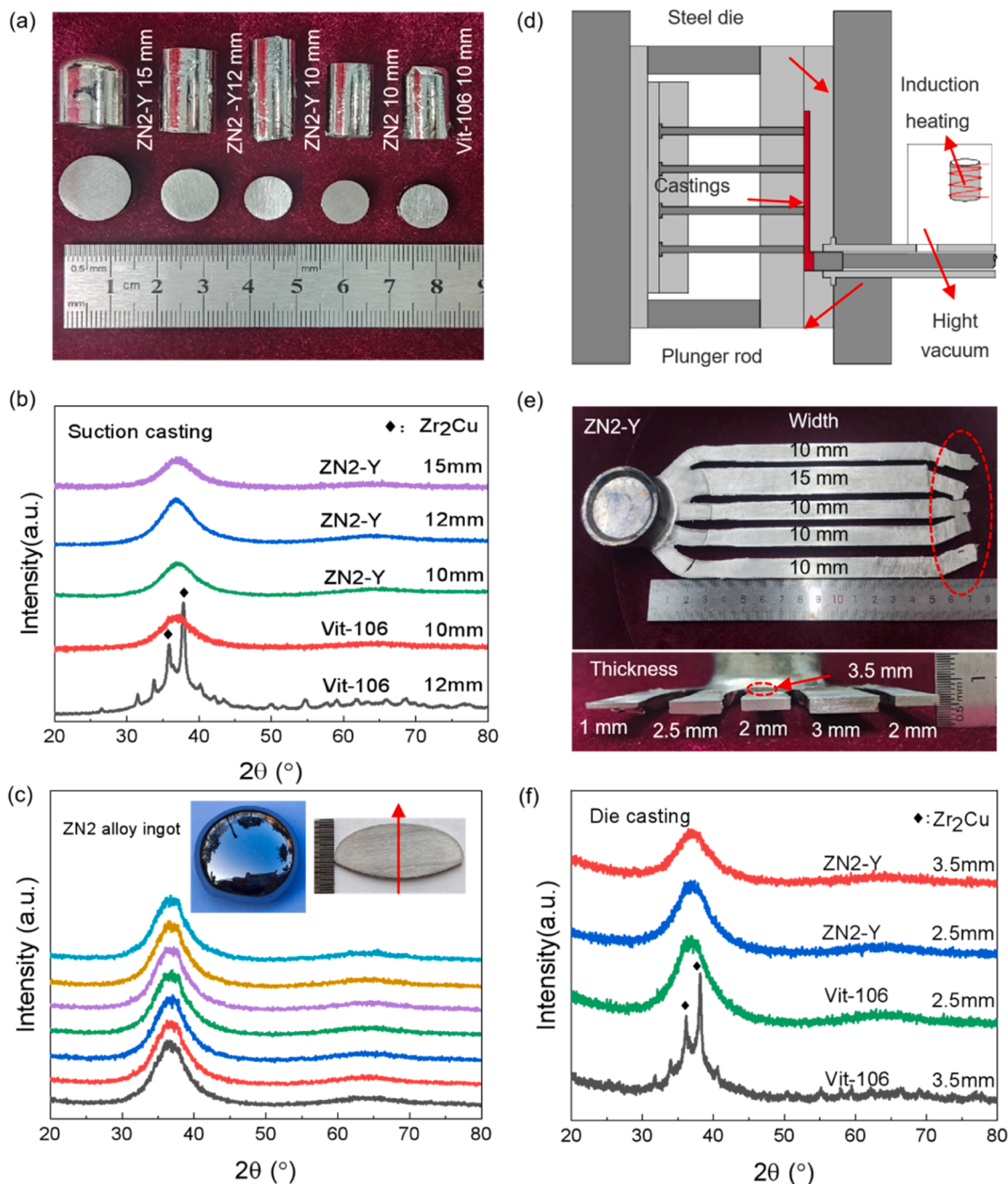


Fig. 2. GFA under laboratory and industrial conditions. (a) suction-cast samples of Vit-106, ZN2, and ZN2-Y. (b) XRD patterns of Vit-106 and ZN2-Y with different diameters. (c) XRD patterns of the ZN2 alloy ingot at different positions along the center line. (d) Schematic diagram of the industrial die casting. (e) Photos of the ZN2-Y plates with different thicknesses prepared by die casting. (f) XRD patterns of ZN2-Y and Vit-106 die-cast samples with different thicknesses.

capacity as compared to Vit-106 under industrial conditions.

To assess the production capacity of Vit-106, ZN2, and ZN2-Y alloys under industrial conditions, sheet samples of different thicknesses were fabricated by an industrial die casting machine. Fig. 2(d) schematically illustrates the die casting technique, and the details for the die casting process have been given in Section 2.1. Fig. 2(e) shows the appearance of the die-cast ZN2-Y sample. It can be seen that all sections with different dimensions are fully filled. Notably, even at the end of the spline (red zone), where the thickness is only 0.5 mm, a nearly 20-mm-long sheet can be successfully die cast. This highlights the high fluidity and the excellent castability of ZN2-Y. XRD characterizations on the sheets of different thicknesses are shown in Fig. 2(f). For the 2.5-mm-thick samples, Vit-106 and ZN2-Y exhibit the characteristic diffuse

scattering halos of amorphous structures, respectively. Notably, the 3.5-mm thick specimen of ZN2-Y still retains the amorphous structure, whereas Vit-106 shows evident crystallization (Zr_2Cu). The CT scanning of the 3.5-mm thick ZN2-Y sample (Fig. S6) indicates that no pores or shrinkage cavities form in the die-cast sheet sample. The defect-free castability of the ZN2-Y alloy with GFA stronger than Vit106 indicates that it represents a significant enhancement in its potential for industrial application.

3.2. Mechanical and thermodynamic properties

To investigate the mechanical properties of the three alloys produced under suction casting, quasi-static compression tests were

conducted using 2-mm-diameter specimens at room temperature. The engineering stress-strain curves are depicted in Fig. 3(a). The Vit-106 exhibits a yield strength, $\sigma_y=1650$ MPa, and plastic strain, $\epsilon_p=5.5\%$. ZN2 achieves σ_y of 1610 MPa with substantially enhanced plasticity ($\epsilon_p=7\%$). Notably, ZN2-Y exhibits both increased yield strength ($\sigma_y=1680$ MPa) and plasticity ($\epsilon_p=19.5\%$), such high compressive ductility is rarely observed in as-cast Zr-based BMGs. In addition, the compressive properties under die casting conditions were compared. Fig. 3(b) presents the stress-strain curves for samples prepared under the die casting. Evidently, both strength and plasticity undergo significant degradation as compared to those prepared by suction casting. Statistical comparison visualizes distinct strength-plasticity trends across processing conditions in Fig. 3(c) and (d). The yield strengths of Vit-106, ZN2, and ZN2-Y are 1580 MPa, 1520 MPa, and 1525 MPa, respectively. Specifically, the plastic strain of both Vit-106 ZN2 drops nearly zero. Interestingly, ZN2-Y can still retain a plastic strain of $\sim 6\%$, which is even higher than that of Vit-106 under suction casting conditions. This finding reveals its outstanding potential for industrial applications. The compressive fracture morphologies of the three alloys were observed. The suction-casting sample of Vit-106 only exhibits sparse, parallel shear bands, whereas ZN2 manifests an increased number of secondary shear bands (Fig. S7(a,b)). Notably, ZN2-Y displays prominent multiple

intersecting shear bands (Fig. S7(c)), and exhibits distinct branching and intersection of shear bands, indicating intense plastic deformation after Y addition. Conversely, industry die-casting specimens of Vit-106 (Fig. S7(b)) and ZN2 demonstrate a significant reduction in shear band density (Fig. 3(e)), ZN2-Y still remain to exhibit extensive multiple shear bands (Fig. 3(f)) with pronounced interactions. It also indicates that Y can remarkably improve the plastic deformation capacity even under industrial service conditions.

In addition, we also performed uniaxial tensile tests of three alloys under die casting, and the engineering stress-strain curves are presented in Fig. 4(a). The tensile strengths of Vit-106 and ZN2 are 1598 MPa and 1550 MPa, respectively, while ZN2-Y reaches 1691 MPa. The mechanical properties are listed in Table 1. Notably, all specimens exhibit merely elastic deformation, with no discernible tensile ductility. This is because that deformation is highly localized within shear bands and accompanied by flow softening, which induces the rapid unstable crack propagation [1,4,5]. Furthermore, by comparing the fracture morphologies of ZN2 and ZN2-Y (Fig. 4(b,c)), it can be observed that ZN2-Y exhibits a significant number of shear bands, whereas ZN2 shows relatively fewer shear bands, demonstrating a phenomenon similar to its compression morphology. The result indicates that despite the absence of apparent tensile plasticity, ZN2-Y undergoes a greater extent of plastic

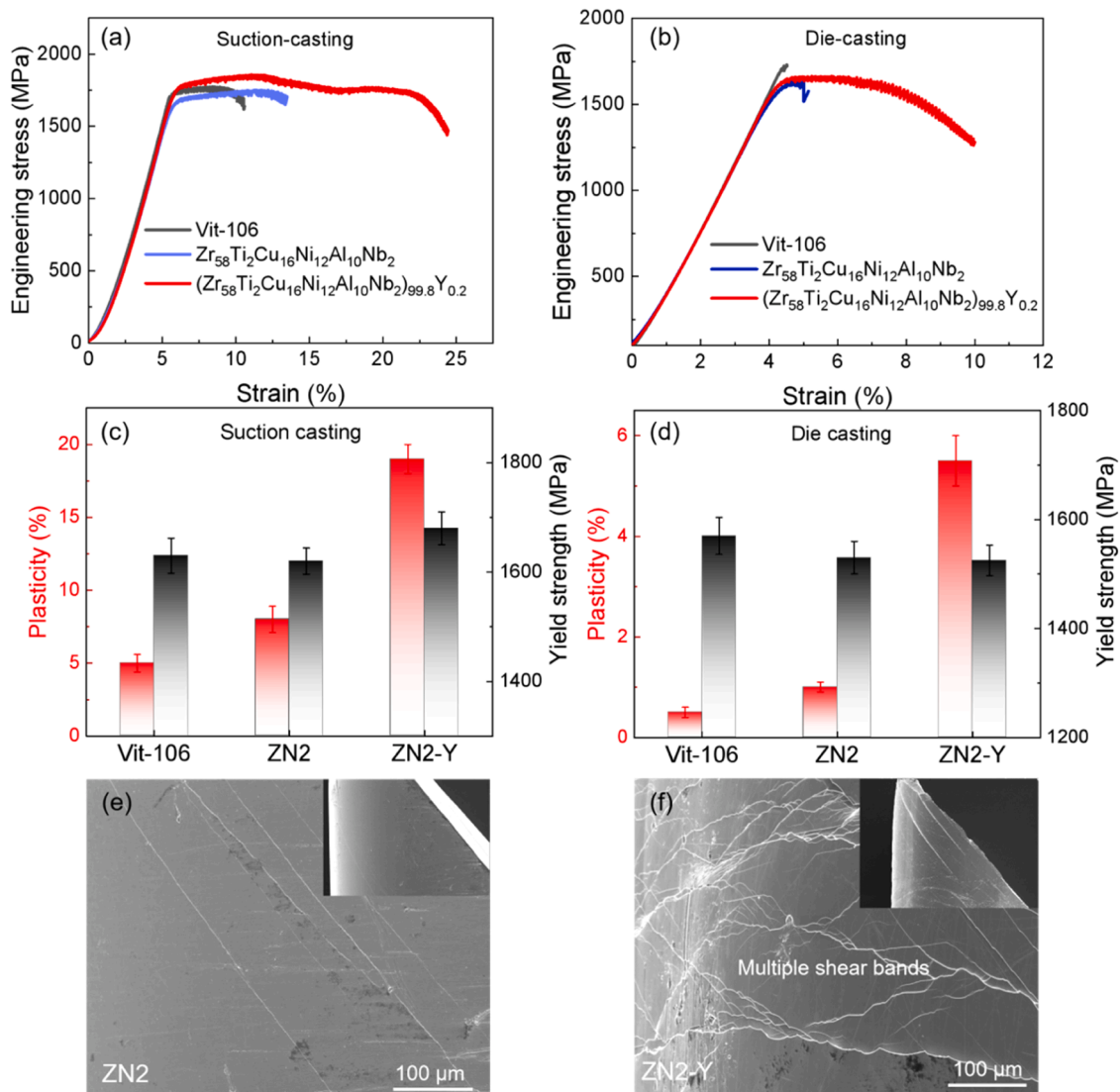


Fig. 3. Compressive mechanical properties of three alloys under suction casting and die casting. (a), (b) Engineering stress-strain curves. (c), (d) Plasticity and yield strength trends of change. (e), (f) Fracture morphology of ZN2 and ZN2-Y under die casting.

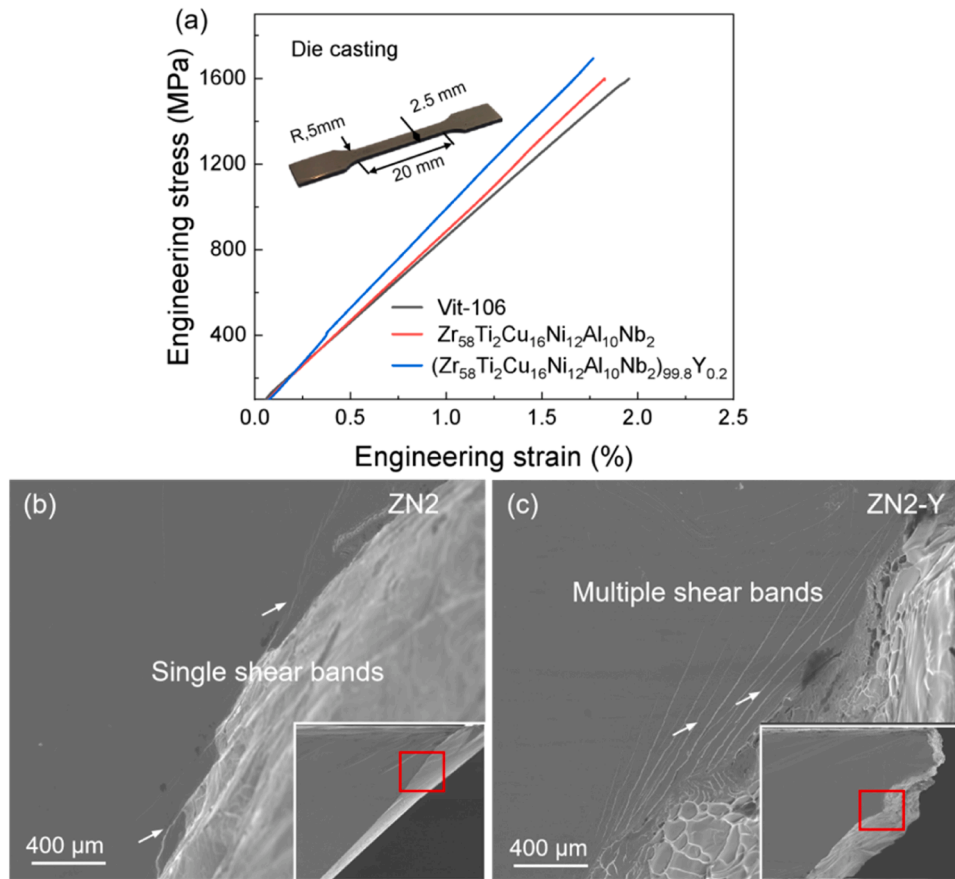


Fig. 4. Tensile mechanical properties of three alloys under die casting. (a) Engineering stress-strain curves. (b) Fracture morphology of ZN2. (c) Fracture morphology of ZN2-Y.

Table 1

Mechanical properties of the three alloys under suction casting and die casting conditions.

Performance	suction casting			die casting		
	Vit-106	ZN2	ZN2-Y	Vit-106	ZN2	ZN2-Y
σ_y (MPa)	1650 ±15	1640 ±12	1680 ±16	1580 ±17	1520 ±15	1525 ±17
σ_f (MPa)	1270 ±14	1590 ±10	1475 ±12	1600 ±12	1506 ±15	1250 ±17
ϵ_p (%)	5.5 ± 1	7.2 ± 1	19.5 ± 1.5	0.2	1 ± 0.2	6 ± 1

flow deformation under stress. Combined with the compression fracture morphology, this further proves the remarkable effect of Y on plasticity enhancement.

Differential scanning calorimetry (DSC) curves of ZN2 and ZN2-Y are presented in Fig. 5. The thermodynamic parameters for both preparation methods are summarized in Table 2. Firstly, the results reveal that the die casting sample exhibit a substantially reduced supercooled liquid region (ΔT) as compared to the suction casting, indicating reduced thermal stability. The difference in free volume content can be quantified by the relaxation enthalpy (ΔH_{rel}) before the glass transition. We estimated the ΔH_{rel} for BMGs prepared under both conditions (Fig. 5(d)). When the BMGs are prepared by suction casting, the ΔH_{rel} value is 3.8 J/g for ZN2 and 4.2 J/g for ZN2-Y, respectively. These values decreased sharply to 1.2 J/g and 2.1 J/g when being prepared by the die casting. The strong correlation between this trend and the plasticity data suggest that the reduction in ΔH_{rel} under industrial conditions leads to a decrease free content, and consequently the reduction of plasticity.

3.3. Fracture toughness

Fracture toughness was measured following the protocols utilizing standardized V-notched specimens with defined geometries (see Figs. 6 (a) and (b)). The sample dimensions strictly comply with established standards. Load-deflection curves under the two processing conditions are depicted in Figs. 6(c) and (d). The three BMGs exhibit typical linear elastic deformation stages. Notably, ZN2-Y specimens exhibit significant nonlinear elastic deformation, indicative of substantial plastic deformation capacity. Compared to suction casting, the deflection displacement of all the three die-casting samples decreased significantly. Specifically, the deflection displacement of ZN2-Y decreased from 0.82 mm by suction casting to 0.71 mm by die casting, indicating a severe reduction in its plastic deformation capability. Fracture toughness was calculated following ASTM E399-22 specifications [28]:

$$K = \frac{PS}{BW^{3/2}} f\left(\frac{a}{W}\right) \quad (1)$$

$$f\left(\frac{a}{W}\right) = 3\sqrt{\frac{a}{W}} \frac{1.99 - \left(\frac{a}{W}\right)\left(1 - \frac{a}{W}\right)\left[2.15 - 3.93\frac{a}{W} + 2.7\left(\frac{a}{W}\right)^2\right]}{2\left(1 + 2\frac{a}{W}\right)\left(1 - \frac{a}{W}\right)^{3/2}} \quad (2)$$

where P is peak load, S is span length, B is specimen thickness, and a_0 indicates the initial crack length. The resulting fracture toughness of the suction-casting samples is 107 MPa/m^{1/2} for ZN2, while Vit-106 exhibits 109 MPa/m^{1/2}. It is remarkable that the fracture toughness of ZN2-Y can be as high as 139 MPa/m^{1/2}. Under die-casting conditions, however, all three BMGs undergo substantial decreases in fracture toughness, with Vit-106 decreasing to 40 MPa/m^{1/2}, ZN2 to 35 MPa/m^{1/2}. Despite the

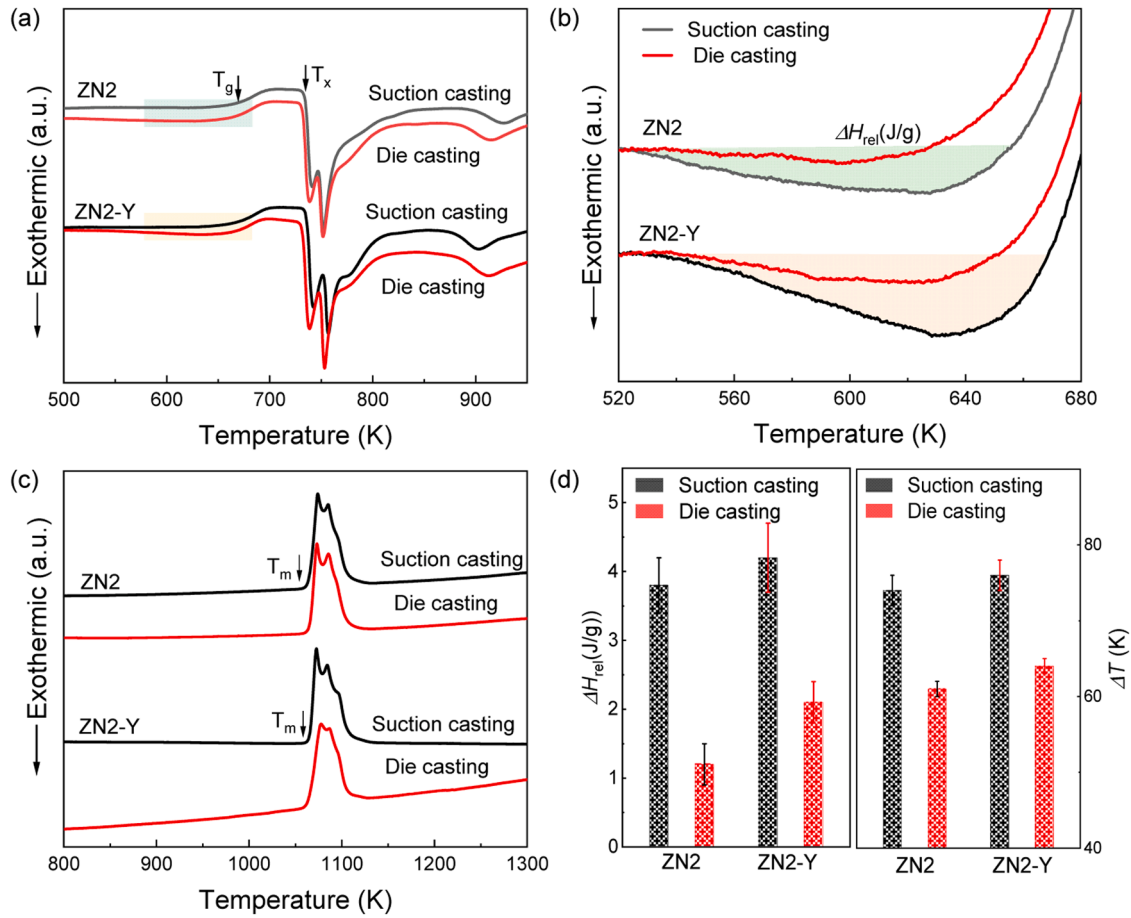


Fig. 5. Thermodynamic properties of ZN2 and ZN2-Y under two preparation conditions. (a) Glass transition temperature (T_g). Crystallization temperature (T_x). (b) Relaxation enthalpy (ΔH_{rel}). (c) Melting temperature (T_m). (d) The variation trends of ΔH_{rel} and supercooled liquid region width (ΔT) for ZN2 and ZN2-Y.

Table 2

Thermodynamic characteristic parameters under two preparation conditions.

Method	Composition	T_g (K)	T_x (K)	T_m (K)	ΔT (K)	ΔH_{rel} (J/ g)
suction	ZN2	670	738	1061	74	3.8
casting	ZN2-Y	667	738	1060	76	4.2
die casting	ZN2	664	731	1060	61	1.6
	ZN2-Y	662	733	1058	64	2.1

decrease, ZN2-Y retains a fracture toughness of 60 MPa/m^{1/2}, which is much higher than that of many BMGs fabricated in laboratory conditions. Fig. 7(a) compares the fracture toughness for the developed Zr-based BMG and previously reported ones [24,29]. It can be seen that the fracture toughness of ZN2 is nearly identical to that of previously developed ZT1 (112 MPa/m^{1/2}) [25] and the fracture toughness of ZN2-Y is much higher than ZT1. As shown in Fig. 7(b), under die-casting conditions, ZN2-Y outperforms the commercial Vit-106 and Vit-105 BMGs in fracture toughness. The Ashby plot shown in Fig. 8 demonstrates that the ZN2-Y BMG developed in the present study is outstanding both in fracture toughness and yield strength compared to common alloys, including titanium (Ti) alloys, steel, and even tungsten alloys [30–32].

3.4. Impact toughness

We further evaluate the impact toughness of Vit-106, ZN2, and ZN2-Y alloys prepared by suction casting and die casting. The impact toughness was derived from following reference [33]:

$$K_v = \frac{KV}{A} \quad (3)$$

where, KV denotes impact energy obtained from the Charpy impact test, and A represents the cross-sectional area. The values of impact energy for the three alloys obtained from the Charpy impact test are given in Table 3. Calculations based on Eq. (3) indicates that the impact toughness under suction casting is 7.37 J/cm² for Vit-106 and 5.88 J/cm² for ZN2, respectively. ZN2-Y exhibits a value of 14.75 J/cm², which is approximately two times higher than Vit-106. The samples prepared by die casting show significantly reduced values, consistent with the trend of compression plasticity and the fracture toughness. For example, the impact toughness is 2.87 J/cm² for Vit-106 and 1.38 J/cm² for ZN2. In contrast, ZN2-Y can maintain an impact toughness of 3.88 J/cm². It is clear that the impact toughness of ZN2-Y is under both processing conditions than the performance benchmark of Be-containing Zr-based BMGs.

4. Discussion

4.1. Thermodynamics of micro-alloying

The mechanism of GFA variation induced by Nb and Ni doping can be explained from the perspective of thermodynamics. Studies have demonstrated that intense exothermic interactions between different elements can strengthen atomic bonding, which further promotes the formation of amorphous structures [38]. Such exothermic effect is generally evaluated by the mixing enthalpy (ΔH_{mix}), mixing entropy (ΔS_{mix}), and atomic size mismatch [39,40]. The mixing enthalpies of

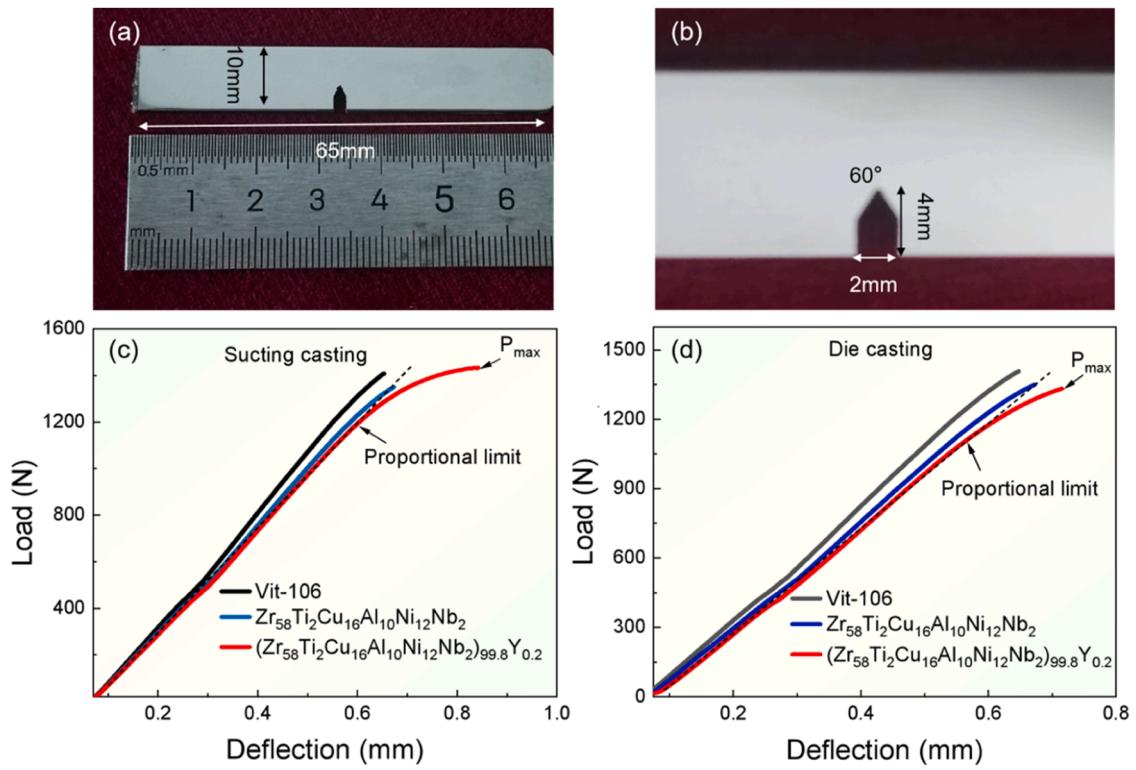


Fig. 6. Notch fracture toughness testing and results. (a) V-shaped specimen dimensions. (b) Enlarged view of the notch specimen. Load-displacement curves of three alloys under (c) Suction casting, and (d) Die casting.

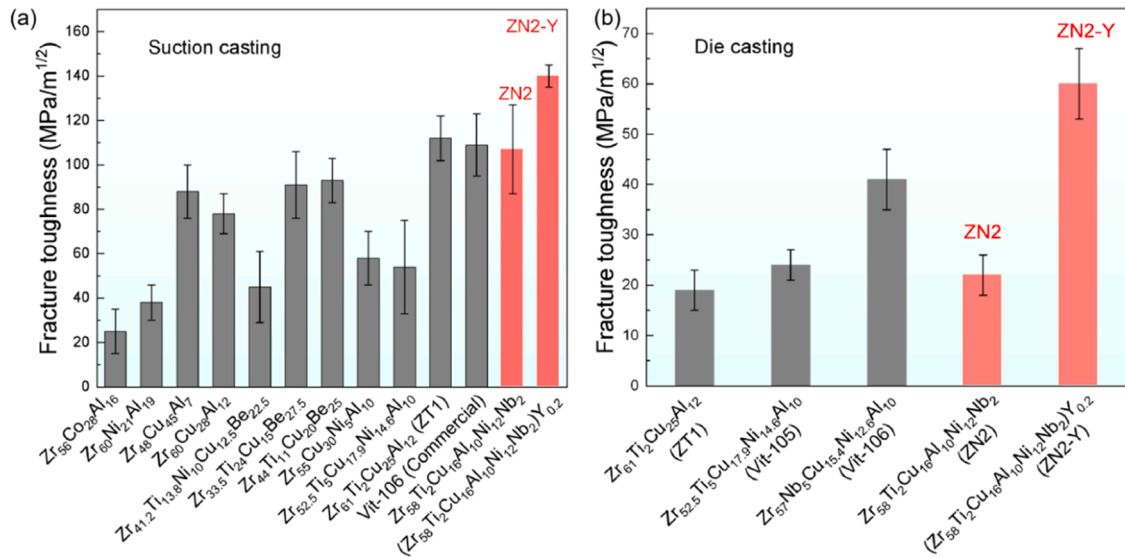


Fig. 7. Statistics of fracture toughness. (a) Comparison of fracture toughness between suction-cast samples of the three alloys in this work and conventional Zr-based BMGs. (b) Fracture toughness of die-cast samples of the three alloys and typical Zr-based BMGs, including ZT1, Vit-105 and Vit-106.

alloys with various compositions are systematically calculated using the following formula [41]:

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^n c_i c_j \Omega_{ij} \quad (4)$$

$$\Omega_{ij} = 4\Delta H_{mix}^{AB} \quad (5)$$

where Ω_{ij} is binary interaction parameters, ΔH_{mix}^{AB} is the mixing enthalpy of equiatomic binary liquid alloys (kJ·mol⁻¹). The calculated results

based on equation above are summarized in Tables S2-S4 of the supplementary materials. Among the involved elements, Ni exhibits strongly negative mixing enthalpies with the main constituent components, including Ni-Zr (−49 kJ/mol) and Ni-Al (−22 kJ/mol). Experimental results demonstrate that moderate Ni addition effectively enhances the GFA, thereby verifying the enthalpy-dominated stabilization mechanism of amorphous structures. Notably, the ΔH_{mix} rises gradually with increasing Nb content. This phenomenon originates from the positive ΔH_{mix} of Nb-Zr (4 kJ/mol), Nb-Cu (3 kJ/mol), and Nb-Ti (2 kJ/mol). It is noteworthy that such positive enthalpy promotes liquid

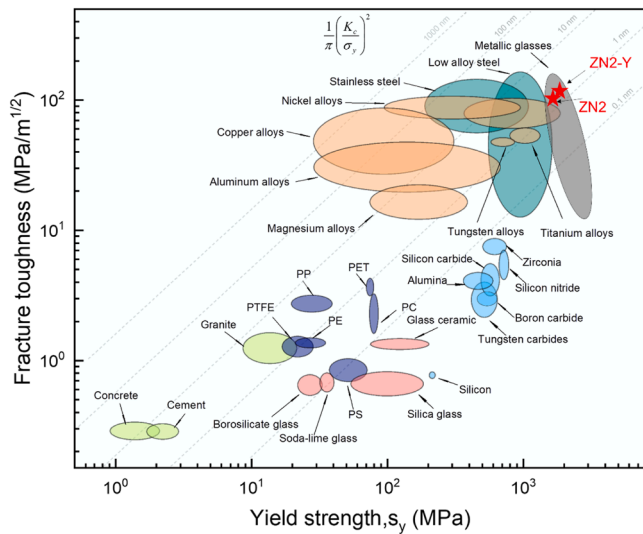


Fig. 8. Statistical comparison of yield strength and fracture toughness between ZN2, ZN2-Y, and common engineering materials.

phase separation and generates unique topological features, rather than deteriorating the GFA directly [42–45]. These mutually restricted liquid phases suppress the nucleation and growth of crystalline ordered phases, and further stabilize the disordered atomic configuration [46–48]. Meanwhile, the continuous addition of Ni and Nb elevates the configurational mixing entropy of the alloy system. The increased entropy lowers the total free energy of the undercooled liquid, which acts as a favorable driving force for the formation and stabilization of amorphous phases.

Compared with laboratory conditions, the reduced critical size of amorphous alloys under industrial conditions is mainly attributed to the low cooling rate and high oxygen content during die casting. Owing to the dimensional requirements of castings, the mold temperature cannot be excessively low in order to ensure complete mold filling. Therefore, reducing the oxygen content via Y has become the primary approach to improve the critical forming size of amorphous alloys. On the one hand, Y exhibits a negative ΔH_{mix} with major matrix elements, and its large atomic radius increases the δ of the alloy system. These factors jointly stabilize the disordered atomic arrangement and inhibit crystallization.

In addition, Y possesses an extremely high oxygen affinity, which is much stronger than that of Zr, Cu, and other matrix elements. During melting and solidification after Y addition, the corresponding deoxidation reaction occurs as follows [49]:



Table 3

Vaules of impact toughness for BMGs reported previously and in this work.

Composition	Type and depth of notch	Sample size (mm)	Impact energy (J)	Impact toughness (J·cm ⁻²)
La ₅₅ Al ₂₅ Cu ₁₀ Ni ₅ Co ₅	U, 3 mm	2.5 × 10 × 55	—	6.3 [25]
La ₆₂ Al ₁₄ Cu ₂₄ Ni ₂₄	\, 0.5 mm	d5 × 60	—	1.77 [34]
Mg ₆₆ Zn ₃₀ Ca ₄	\	d2.4 × 40	—	0.16 [35]
Ti _{32.8} Zr _{30.2} Ni _{5.3} Cu ₉ Be _{22.7}	U, 3 mm	10 × 10 × 55	—	5 [36]
Zr ₅₀ Cu ₄₀ Al ₁₀	U, 2 mm	5 × 10 × 55	—	8.0 [37]
Vit-1 (Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5})	V, 1 mm	3 × 3 × 30	0.68	7.6 [27]
Vit-1 (Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5})	\, 2.5 mm	3 × 5 × 30	1.0	13.3 [27]
Vit-106 suction casting	U, 4 mm	2 × 8 × 55	0.59	7.37
ZN2			0.47	5.88
ZN2-Y			1.18	14.75
Vit-106 die casting	U, 4 mm	2 × 8 × 55	0.23	2.87
ZN2			0.11	1.38
ZN2-Y			0.31	3.88

This work

$$K^{\ominus} = \frac{a_{(M_xO_y)}^{1/y}}{a_{[O]} a_{[M]}^{x/y}} \quad (7)$$

where $K^{\ominus}$ is the deoxidation equilibrium constant, $a_{[O]}$ is the activity of oxygen, and $a_{[M]}$ is the activity of the deoxidizing element. For the formation of pure oxide, $a_{(M_xO_y)}^{1/y} = 1$. According to thermodynamic laws, the relationship between the equilibrium constant and Gibbs free energy is given as follows [49]:

$$\Delta_r G_m^{\ominus} = -RT \ln K^{\ominus} = \Delta H_f - T \Delta S_f \quad (8)$$

where ΔH_f and ΔS_f are the enthalpy and entropy of formation of the oxide, respectively. Thus, the following expression can be obtained [50]:

$$[O] \propto \frac{1}{K} \exp\left(\frac{\Delta H_f}{RT} - \frac{\Delta S_f}{R}\right) \quad (9)$$

Within the current alloy system and temperature range, the contribution of ΔS_f is negligible, so the oxygen concentration is dominated by the enthalpy of oxide formation. In this study, the enthalpy of formation for Y_2O_3 , Cu_2O , CuO , ZrO_2 , and Al_2O_3 are -1906.67 kJ/mol, -167.47 kJ/mol, -155.33 kJ/mol, -1101.55 kJ/mol, and -1678.49 kJ/mol, respectively [50]. From these data, it can be concluded that Y exhibits a superior deoxidation effect. We conducted precise measurements of the oxygen content in the ZN2 alloy under both laboratory and industrial preparation conditions. The results show that the oxygen content is 800 ppm under laboratory conditions, but increases to 2600 ppm under industrial conditions, representing a more than threefold increase. A high oxygen content leads to a higher density of heterogeneous nucleation sites for crystallization, thereby suppressing the formation of the amorphous phase [51–53]. After the addition of Y, the oxygen content is reduced from 2600 ppm to 420 ppm, which is even lower than the level under laboratory conditions.

Y doping can effectively reduce oxygen content and thereby significantly improve the GFA under die-casting conditions. Meanwhile, variations in oxygen content also induce changes in atomic arrangement. Previous studies have demonstrated that 3500 ppm oxygen content acts as the critical value for the brittle-ductile transition, while a reduction in oxygen content promotes the proliferation of short-range ordered (SRO) structures and consequently deteriorates mechanical properties [54–56]. To reveal the effect of Y addition on the microstructural change, high-resolution transmission electron microscopy (HRTEM) characterization was performed on ZN2 and ZN2-Y specimens prepared by the die casting, respectively. Figs. 9 (a, b) show the HRTEM morphologies of two alloys, with the corresponding selected area electron diffraction (SAED) patterns presented in the insets. No distinct lattice diffraction spots are observed in the SAED patterns of either specimen, confirming their fully amorphous structure. To visually present the evolution of structural order, the two-dimensional

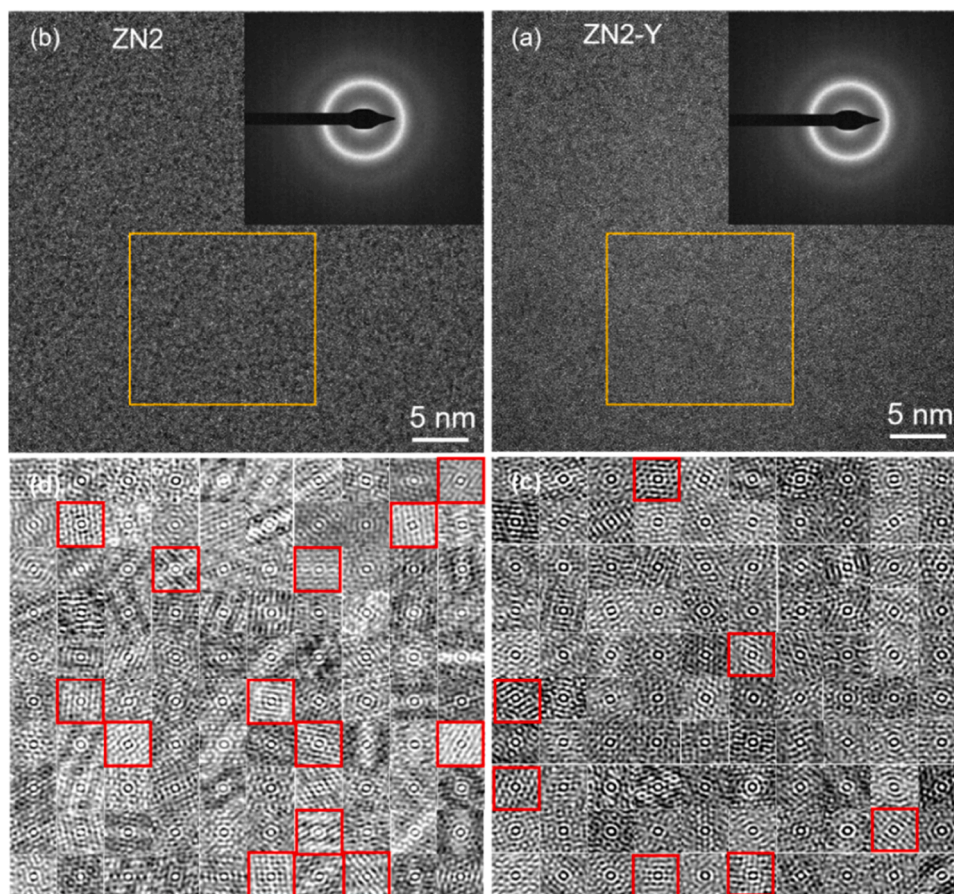


Fig. 9. (a), (b) HRTEM images of ZN2 and ZN2-Y BMGs under die casting, with the insets showing the corresponding SAED patterns. (c), (d) Representative two-dimensional autocorrelation function (ACF) maps of ZN2 and ZN2-Y, respectively (scale bar: 2 nm).

autocorrelation function (ACF) was employed to calculate the proportion of fringe-featured crystal-like ordered (CLO) structures for the two alloys, and at least three HRTEM images analyzed for each specimen to guarantee statistical accuracy. The results show that the CLO fraction is 7% for ZN2-Y and increases to 13% for ZN2, indicating that the addition of Y can largely reduce the content of oxygen and thus suppress the formation of CLO structures. Previous investigations have proved that moderate CLO structures are conducive to enhance GFA, whereas excessive CLO structures weaken the crystallization inhibition effect of icosahedral-like clusters and thus degrade the GFA [57–60]. This explains the microstructural origin for the GFA improvement through Y doping.

In terms of mechanical properties, the increased proportion of CLO structures exacerbates local stress concentration and degrades mechanical performance. This underlies experimental observations that both strength and plasticity of ZN2 are inferior to those of ZN2-Y. Previous studies on the mechanism of rare earth elements reveals that an optimal combination of GFA and mechanical properties can be achieved at a Y: O molar ratio of 2:3 [56]. In fact, the practical industrial die casting environment is remarkably different from the laboratory condition. The vacuum degree differs by four orders of magnitude between the two environments, resulting in a large difference in oxygen content, and poor sealing during industrial die casting allows air ingress, which raises the actual oxygen content during the solidification and makes it difficult to achieve accurate quantification. In this case, shortening the melting time is usually adopted to avoid severe oxidation, and prevent excessive consumption of yttrium that would impair the deoxidation effect. Moreover, the melting temperature, heating rate, and superheating time during die casting can all alter the oxygen content, thereby affecting the GFA, mechanical properties, and casting quality of BMGs.

4.2. Fracture mechanism

To understand the mechanisms leading to the variations in fracture toughness, we analyzed the shear bands and fracture morphologies of the three alloys. Fig. 10 displays the evolution of crack formation and evolution in the ZN2-Y alloy. One can see that at the onset of yielding, the initiation site for crack formation has emerged (Figs. 10(a) and (b)). It is noteworthy that this site does not locate in the zone where more obvious shear band propagation occurs. Instead, crack formation happens at a location with a relatively low density of shear bands. This is because a higher density of shear bands leads to a more distributed stress state, thus reducing the load on individual bands, whereas fewer bands result in higher localized stress which is closer to the critical level for microcrack formation. During the deformation of BMGs, accumulated strain energy is primarily released through the initiation and propagation of shear bands [61–63]. Hence, the formation of numerous shear bands results in distributed strain, thereby enhancing the tolerance to crack. This observation aligns with the findings of Devaraj et al., showing that multiple shear bands at the notch tip promote crack tip blunting and effectively hinder crack propagation [64]. As stress increases further, the crack continues to propagate along the path defined by the shear bands. Interestingly, a noticeable angular deflection occurs during this propagation (Fig. 10(d)). This phenomenon originates from the stress concentration, which drives an advancing crack to instinctively seek the path of least resistance, a process governed by alterations in the local stress concentration and gradient around the crack tip. In addition, multiple shear band formation is intrinsically linked to plastic zone dimensions during initial fracture. Tan et al. demonstrated that the enveloped region of shear bands coincides with the plastic zone at the notch tip in ductile BMGs [65]. Consequently, for geometrically

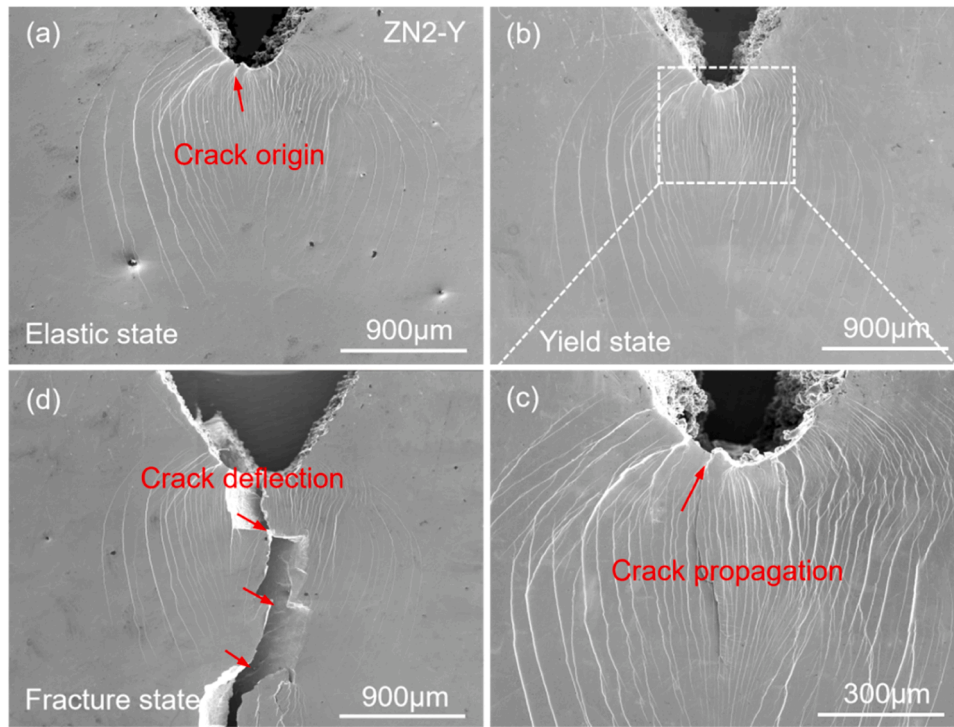


Fig. 10. Evolution process of cracks in different stages of ZN2-Y under suction casting. (a) Elastic state: The notch tip is blunted, and numerous shear bands nucleate. (b, c) Yield state: The local primary shear band attains critical bearing stress, then transforms into a crack and grows. (c) Fracture state: Shear band blunting repeatedly takes place at the crack tip, and the crack propagates with multiple deflections.

identical specimens, relative fracture toughness can be quantitatively evaluated based on crack tip plastic zone dimensions, with the calculation formula expressed as [66]:

$$r_p = \frac{K_c}{\pi \sigma_y^2} \quad (10)$$

where, K_c represents the notch fracture toughness, σ_y is the yield strength. Quantitative analysis of plastic zone shows that r_p is 1.27 mm for Vit-106, 1.25 mm for ZN2, and 1.55 mm for ZN2-Y, respectively. Combined with the fracture toughness values, this result is consistent with the strong positive correlation between the size of the plastic zone at the crack tip and fracture toughness [67–69]. This is further corroborated by the impact energy data of the three alloys. Under both laboratory and industrial processing conditions, ZN2-Y consistently exhibit the higher impact energy, indicating superior energy absorption under identical loading. The majority of this energy is consumed by plastic deformation, given that the portion required for crack propagation is comparatively small. This also implies the greater resistance to crack formation in ZN2-Y during straining, a phenomenon primarily attributed to crack tip blunting induced by multiple shear bands. Furthermore, based on the relationship between strength-plasticity and free volume, it can be demonstrated that a higher free volume content facilitates the formation of a larger plastic zone.

We also investigated the fracture morphology of the ZN2-Y alloy under suction casting and die casting conditions, as shown in Fig. 11. Fig. 11(a) presents the surface morphology of the suction-cast specimen, where it can be observed numerous shear bands form around the notch. Internal morphology is shown in Fig. 11(b), where three distinct regions are clearly visible. Region I is the notch blunting zone, in which, as the load increases, the notch tip is primarily subjected to tensile stress, leading to the initial formation of stress concentration and generating nano-scale shear bands. To alleviate sustained stress concentration, the notch front releases stress through the formation and plastic shear of multiple shear bands, ultimately causing the notch tip to blunt,

exhibiting a vein-like pattern formed by plastic shear and strain softening within shear bands (Fig. 11(c)).

With stress escalation, localized plastic strains accumulate within a single shear band until reaching a critical value, subsequently initiating a crack. During crack propagation, the shear bands ahead of the crack tip continue to undergo plastic deformation, with strain being accommodated by a limited number of shear bands and manifesting as discontinuous plastic deformation, causing the fracture surface to enter the meniscus instability region (MIR) [69], manifested as shear ridges or step-like morphology (Fig. 11(d)). With the propagation of crack, the tensile stress is converted into compressive stress, causing the strain to rapidly reach a critical threshold and triggering the rapid crack propagation. Under the combined action of tensile and compressive stresses, nano-scale free volumes evolve into nano-voids, progressively forming a highly localized plastic zone [70,71]. Meanwhile, adjacent micro-voids undergo mutual tearing and plastic necking during deformation (red zone), ultimately developing a dimple-like morphology as shown in Fig. 11(e). Compared with the ZN2-Y, Vit-106 exhibits distinct differences fracture morphology, as shown in Fig. S8. Firstly, the notch indicates a relatively low number of shear bands (Fig. S8(a)). Secondly, the intrinsic morphology lacks a discernible plastic zone, with the MIR being more prominent, suggesting that the strain release process did not involve substantial shear band participation in plastic deformation (Fig. S8(b)). Additionally, no obvious dimple structures were observed, indicating rapid fracture under subsequent compressive stress (Fig. S8(c)). These features clearly explain why its fracture toughness is lower than that of ZN2-Y.

The fracture surface morphology of ZN2-Y under die casting is shown in Fig. 11(f). First, compared with the suction-casting specimen, no apparent shear bands are observed on its surface, and no obvious deflection is observed in the crack propagation direction. This is mainly attributed to the low free volume content. The internal morphology (Fig. 11(g)) reveals no distinct regional characteristics. In addition, the absence of a notch-blunting zone formation indicates minimal plastic deformation at the notch tip. Instead, limited shear bands accommodate

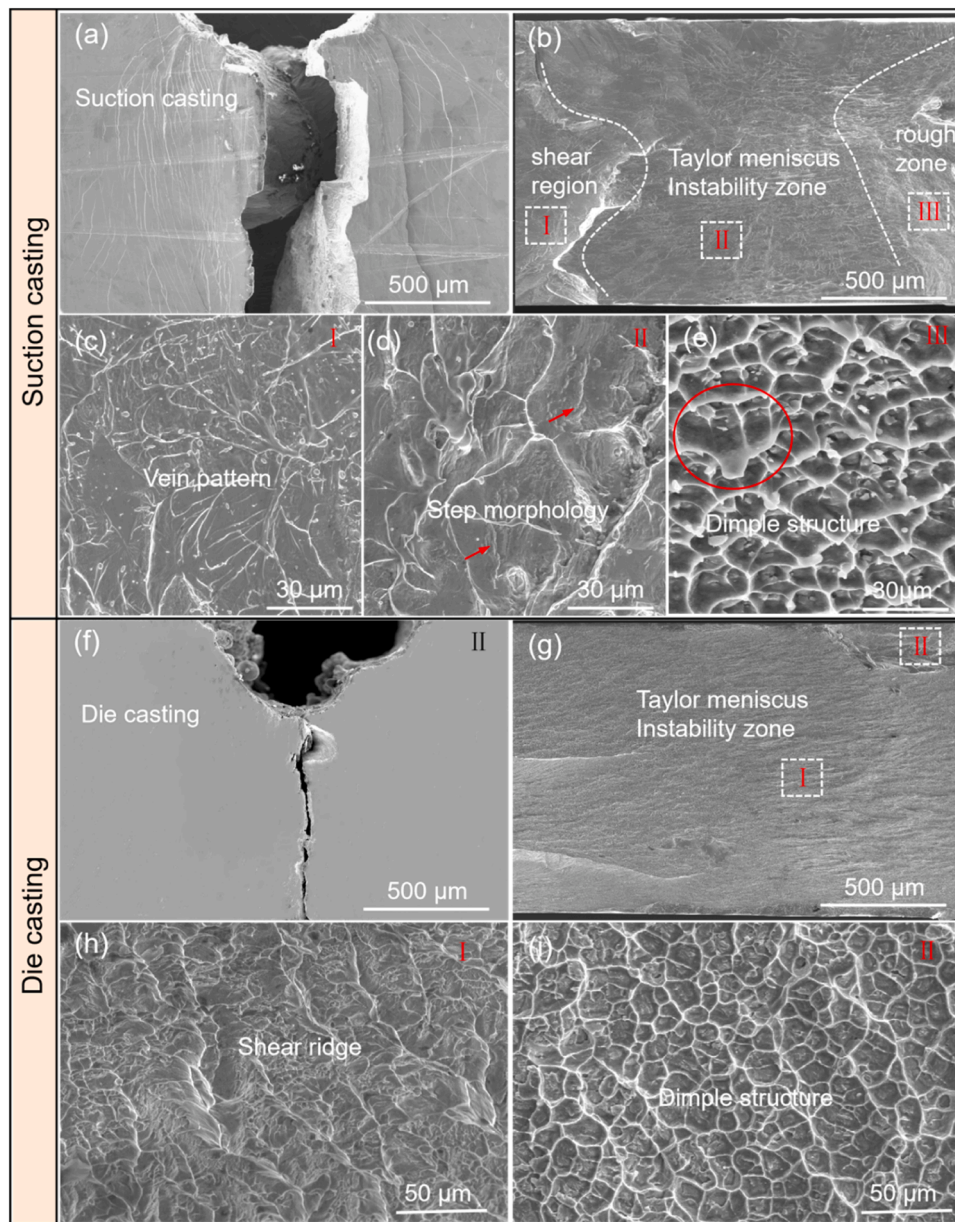


Fig. 11. Fracture morphology of ZN2-Y alloy under suction casting and die casting conditions. (a) Distribution and morphology of shear bands near the notch tip in a suction-cast specimen. (b) Internal fracture morphology of the suction-cast specimen. (c) Shear-induced microscopic morphology. (d) Step-like shear deformation morphology. (e) Rough dimple morphology under combined tensile-compressive stress fields. (f) Morphology of shear bands near the notch tip in a die-cast specimen. (g) Internal fracture morphology of the suction-cast specimen. (h) Shear ridge morphology. (i) Dimple morphology under multiaxial stress conditions.

strain to alleviate stress concentration, followed by rapid microcrack propagation. During this process, the shear bands generate heat through the plastic work, causing the material to attain a quasi-fluid state. Under the tensile stress gradient, cylindrical ridge-like structures form, as illustrated in Fig. 11(h). Eventually, when crack propagation exceeds a critical threshold, a combined tensile-compressive stress field develops, and free volumes evolve into dimple-like features (Fig. 11(i)). Notably, the die-cast specimens dimples lack obvious tearing traces, also attributable to its lower free-volume content and limited deformation during tensile-compressive loading.

4.3. Fabrication of complex components under industrial conditions

Practical implementation scenarios for ZN2-Y die casting components are diverse, ranging from precision electronic devices (connectors and structural frames) to advanced artificial intelligence products

(robotic joints and sensor housings). This characteristic is essential for functional precision in mechanical assemblies. We evaluate the potential of engineering application of the ZN2-Y BMG by fabricating complex components by industrial die casting. As shown in Figs. 12(a-c), pivot hinges and flexible gears can be successfully fabricated. They exhibit complete mold filling even at sharp corners. CT scanning confirms that the fabricated components are free of defects and pores, demonstrating the structural reliability and integrity of the components. In addition, the CT scanning indicates that there are no gas porosity, shrinkage cavities, or other casting-related imperfections. The high structural quality of the die-cast components suggests that the BMG has great potential for high-performance engineering applications. Beyond processability, a comprehensive evaluation of ZN2-Y's cost highlights its economic advantages. Unlike conventional crystalline materials, which often require multi-stage processing to achieve complex geometries, ZN2-Y enables single-step forming via industrial die casting. This

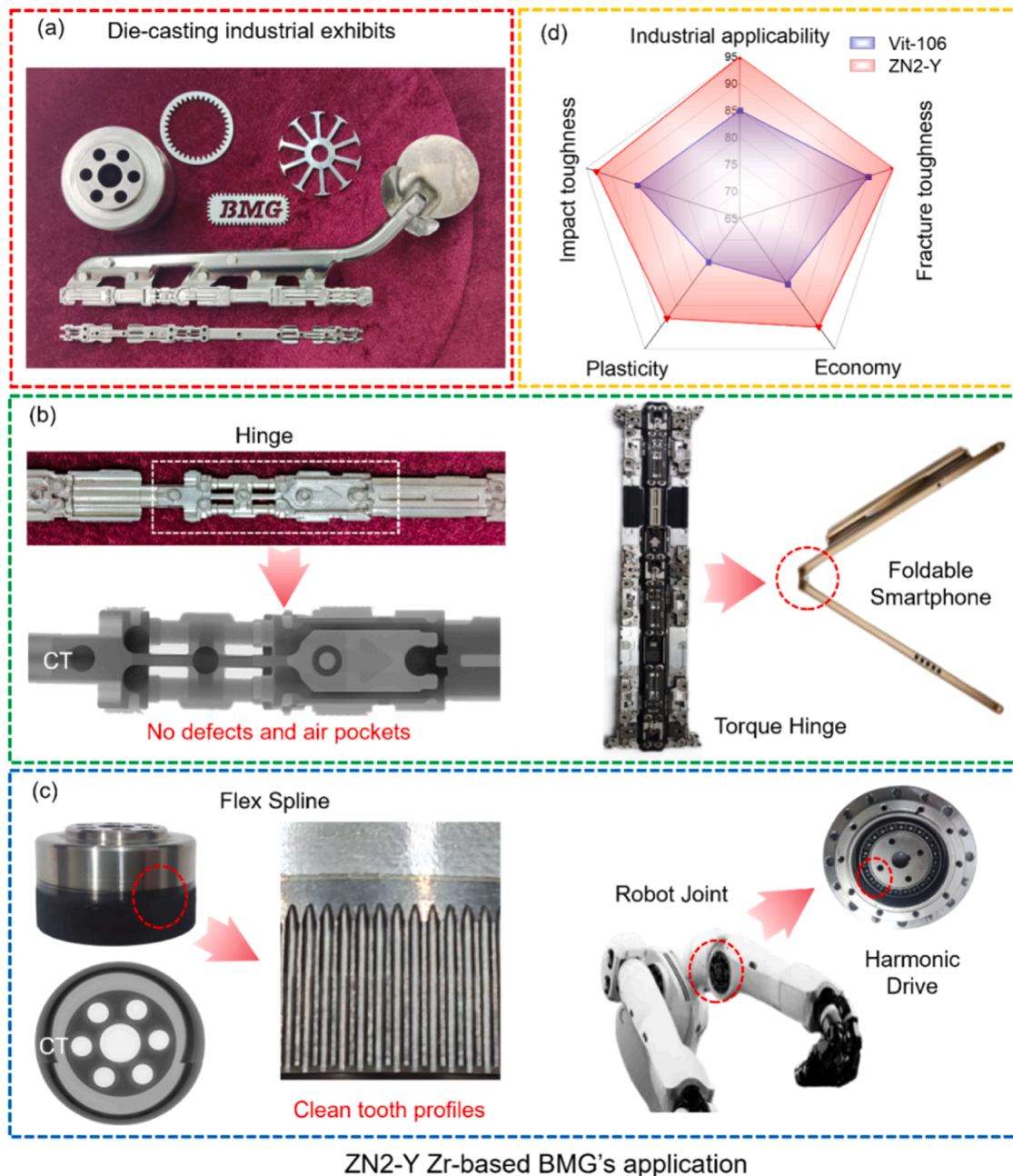


Fig. 12. Quality evaluation of ZN2-Y industrial die-cast components and application scenarios. (a) Actual images of the casting and structural diagrams. (b) Physical images, CT scan images, and application scenarios of torque hinges, and (c) Images flex spline. (d) Overall performance level of ZN2-Y.

streamlined process not only ensures high dimensional precision but also substantially reduces manufacturing lead times and labor costs. In terms of raw material expenses, ZN2-Y is priced at CNY 137.3k per ton, compared to the commercial Vit-106's CNY 146.7k per ton, effectively lowering material expenditures. To quantify its industrial competitiveness, ZN2-Y's multi-performance-cost ratio was systematically assessed across five key parameters: industrial production capacity, compressive plasticity, fracture toughness, impact toughness, and economy, as shown in Fig. 12(d). The evaluation revealed that ZN2-Y outperforms benchmark BMG Vit-106 in industrial-scale fabrication and fracture toughness under industrial processing conditions, while maintaining favorable mechanical properties and offering distinct cost advantages. To summarize, the ZN2-Y BMG demonstrates significant potential in bridging the gap between laboratory innovation and industrial application. Its well-balanced properties make it a highly promising candidate for

demanding engineering scenarios.

5. Conclusion

In this study, a novel BMG, $(\text{Zr}_{58}\text{Ti}_2\text{Cu}_{16}\text{Ni}_{12}\text{Nb}_2\text{Al}_{10})\text{Y}_{0.2}$ (designated ZN2-Y), was successfully developed via the TG-MEE approach, featuring industrial production capacity and low material cost. Under suction casting, ZN2-Y achieves a critical diameter of 15 mm while exhibiting exceptional fracture toughness of $139 \text{ MPa}\cdot\text{m}^{1/2}$. Notably, it can produce fully amorphous components with a thickness of 3.5 mm, while retaining a fracture toughness of $60 \text{ MPa}\cdot\text{m}^{1/2}$ under industrial die casting conditions, outperforming the commercial Vit-106, which only achieves 2-mm critical thickness with $40 \text{ MPa}\cdot\text{m}^{1/2}$ fracture toughness. Additionally, ZN2-Y demonstrates a 14.75 J/cm^2 impact toughness, a compressive plasticity of 19.5%, and generates multiple shear bands

during the initial fracture stage and develops an extensive plastic zone. Significantly, industrial die casting of ZN2-Y successfully produced structurally complex pivot hinges with no defects, highlighting its exceptional application potential. These achievements bridge the critical gap between alloy composition design and industrial production, thereby significantly expanding the industrial applicability of BMGs.

Data availability

Data will be made available on request from the corresponding author.

CRediT authorship contribution statement

Xiaoqiang Fu: Investigation, Validation, Methodology. **Chaoqun Pei:** Formal analysis, Investigation. **Chao Wang:** Methodology, Validation. **Chunyan Li:** Validation, Writing – review & editing. **Kuan Gao:** Methodology, Writing – review & editing. **Xi Xu:** Investigation. **Shengzhong Kou:** Formal analysis, Validation. **Yanhui Liu:** Resources, Writing – review & editing. **Weihua Wang:** Funding acquisition, Writing – review & editing. **Baoan Sun:** Conceptualization, Investigation, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.actamat.2026.122744](https://doi.org/10.1016/j.actamat.2026.122744).

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