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Developing nacre-inspired laminate-reticular 2024Al/B₄C composites with high damage resistance by adjusting compositional wettability

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Abstract: To address the issue that B_4C ceramics are difficult to be wetted by aluminum metals in the composites, TiB_2 was introduced via an in-situ reaction between TiH_2 and B_4C to regulate their wettability and interfacial bonding. By pressure infiltration of the molten alloy into the freeze-cast porous ceramic skeleton, the 2024Al/B₄C-TiB₂ composites with a laminate-reticular hierarchical structure were produced. Compared with 2024Al/B₄C composite, adding initial TiH₂ improved the flexural strength and valid fracture toughness from (484±27) to (665±30) MPa and (19.3±1.5) to (32.7±1.8) MPa m^{1/2}, respectively. This exceptional damage resistance ability was derived from multiple extrinsic toughening mechanisms including uncracked-ligament bridging, crack branching, crack propagation and crack blunting, and more importantly, the fracture model transition from single to multiple crack propagation. This strategy opens a pathway for improving the wettability and interfacial bonding of Al/B₄C composites, and thus produces nacre-inspired materials with optimized damage tolerance.

Key words: bio-inspired composites; freeze casting; titanium hydride; mechanical properties; damage tolerance

1 Introduction

Boron carbide (B₄C) ceramics have been widely used for industrial applications, including neutron-absorbing components, lightweight armor and wear-resistant parts due to their low density, high hardness and excellent chemical stability [1,2]. Unfortunately, intrinsically low fracture toughness and poor sinterability greatly limit their further development [3]. Introducing a ductile phase is a feasible way to improve the fracture toughness of B₄C. Particularly, Al/B₄C composites, which combine the advantages of B₄C ceramics and metallic Al, enjoy a special status in electronic devices and body armor [4–6]. However, when the mass fraction of B₄C exceeds 20%, the brittleness of the composite increases markedly, which largely limits its application [7]. Indeed, in terms of structural materials, achieving high strength and toughness is the most critical demand, yet these two characteristics are normally mutually exclusive, i.e., one part is pursued at the expense of the other [8]. To date, the development of bulk materials featuring high strength and toughness remains a major challenge.

Recently, freeze casting has provided an effective approach to constructing porous ceramic scaffolds with complex hierarchical microstructures [9–11]. Combined with the infiltration of compliant phases, various nacre-like composites with the high damage-tolerance have been fabricated [12–14]. Nevertheless, in these materials, the ceramic particles are generally sintered into

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dense layers without compliant phase inside the lamellae. This architecture differs significantly from the multi-scale hierarchical structure found in nacre. Specifically, the single-scale laminated composite provides a limited toughening effect owing to the inherent brittleness of the ceramic layers [15].

To create a hierarchical structure, it is an ingenious strategy to consciously maintain the freeze-cast ceramic scaffolds incompact with an appropriate strength, allowing the compliant phase to fill both the interlaminar channels and the remaining voids within the ceramic layers. Therefore, the wetting behavior of molten Al on B₄C during the infiltration process largely determines the feasibility of the infiltration process and the final properties [16]. However, the poor wettability between B₄C and Al makes it difficult to completely fill the interlaminar pore channels and the in-layer cavities within the ceramic lamellae, resulting in poor interfacial adhesion and thus degrading the mechanical properties of the composite [17,18].

In response to this challenge, titanium diboride (TiB₂) has become an effective means of increasing the wettability and interfacial bonding in the B_4C-Al system [19–22]. LÜ et al [20] used B_4C and TiO₂ to in situ synthesize TiB₂, which effectively improved the mechanical performance of Al/B₄C-TiB₂ composites prepared by vacuum infiltration, but the presence of extraneous elements resulted in more impurities in the composites. Moreover, titanium powder is frequently used to increase wettability in the Al-B₄C system by in situ reaction with B₄C to form TiB₂, whereas water as a freezing carrier will lead to the oxidation of titanium powder surface [22,23]. Recent studies have shown that titanium hydride (TiH₂) is a source of titanium metal through hydride decomposition. TiH₂ represents much higher sinterability and lower oxygen content compared to Ti powder, leading to finer particles created by the TiH2-B4C system and better properties of the composite [24,25]. However, to the best of our knowledge, there are few reports on improving the performance of Al/B₄C composites by introducing TiB₂ via the in situ reaction of TiH₂ and B₄C.

In this work, 2024Al alloy was chosen as the metal matrix because of its favorable strength and acceptable ductility [26]. To improve the wettability, we introduced TiH₂ into the aqueous B_4C slurry and

deliberately sintered the ceramic skeleton to an uncompacted state yet with reasonable strength. Due to the considerable cavities and the enhanced wettability, we squeezed the molten 2024Al into both the interlayer channels and the voids within the ceramic layers to create the 2024Al/B₄C-TiB₂ composite with a laminate-reticular hierarchical structure. The damage-tolerant behavior, fracture modes and toughening mechanism were discussed.

2 Experimental

2.1 Starting materials

Commercially available B_4C powders (Purity: 96%, 3.5 µm, Mudanjiang Boron Carbide Co., Ltd., Mudanjiang, China) and TiH₂ powders (Purity: 99.9%, 1 µm, Shanghai Naiou Nanotechnology Co., Ltd., Shanghai, China) were used as starting materials. Tetramethylammonium hydroxide (TMAH, 25 wt.% in water solution, Aladdin Chemical Co., Ltd., Shanghai, China) was selected as a dispersant agent. Gelatin (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used as an organic binder. The chemical composition of 2024Al alloy is summarized in Table 1.

Table 1 Chemical composition of 2024Al alloy (wt.%)

Si	Mg	Fe	Cr	Cu	Mn	Al
< 0.5	1.2-1.8	< 0.5	< 0.1	3.8-4.9	0.3-0.9	Bal.

2.2 Sample preparation

B₄C and TiH₂ powders, distilled water and TMAH dispersant were ball-milled for 24 h to produce the slurry with 25 vol.% initial solid content. The amount of TiH₂ powder accounts for 10 vol.%, 20 vol.% and 30 vol.% of the total ceramic powders, respectively. To further illustrate the effect of TiH₂, we introduced the infiltrated composites prepared from pure B₄C scaffolds for comparison. However, pure B4C ceramics are difficult to sinter owing to strong covalent bonding and low self-diffusion coefficient, making the scaffolds so fragile and prone to collapse. Thus, $8 \text{ wt.}\% \text{ (Al}_2\text{O}_3 + \text{Y}_2\text{O}_3 \text{)}$ were added as sintering additives, as reported in our previous work [27]. Thereafter, the corresponding ceramic scaffolds and infiltrated composites were abbreviated as 10:0, 9:1, 8:2, and 7:3, respectively. Gelatin was added into the ceramic slurry preheated to 50 °C with continuous stirring to obtain well-dispersed slurries,

followed by being de-aired in a vacuum desiccator. Then, the slurry was poured into a polyethylene mold ($d60 \text{ mm} \times 20 \text{ mm}$) and kept at -50 °C for directional solidification. Subsequently, the frozen samples were freeze-dried at -50 °C under vacuum to sublimate the ice platelets. Finally, the green bodies placed in a graphite furnace were sintered at 750 °C with a dwell time of 0.5 h and then increased to 1900 °C with a dwell time of 1 h under an argon atmosphere.

We fabricated the laminated 2024Al/B₄C composites by squeezing 2024Al alloy into the B₄C ceramic scaffolds. The ceramic scaffolds placed in a heat-resistant steel mold were preheated at 550 °C. The 2024Al alloy was heated up to 800 °C, followed by pouring onto the preheated scaffolds. Subsequently, a pressure of 10 MPa was employed until the 2024Al alloy cooled and solidified. After infiltration, the composites were solid-solution treated at 495 °C for 2 h, water quenched at ambient temperature, and artificially aged at 175 °C for 7 h. More details can be seen in our previous report [13].

2.3 Characterization

Phase components of the ceramic scaffolds and composites were identified by X-ray diffraction (XRD, Empyrean, Panalytical, the Netherlands) with $\operatorname{Cu} K_{\alpha}$ radiation. The chemical states of elements characterized were using X-ray photoemission spectroscopy (XPS, Escalab 250Xi, ThermoFisher, USA). Pore size distribution was obtained using a mercury intrusion porosimeter (Auto Pore IV 9500, Micromeritics Instrument Corp., USA). The morphology observation and composition analyses were performed by scanning electron microscopy (SEM, Helios Nano-Lab 600i, FEI, USA) and transmission electron microscopy (TEM, Talos F200x, FEI, USA) equipped with energy-dispersive X-ray spectroscopy (EDS). Threepoint bending strength was applied to testing the flexural strength at a loading rate of 0.5 mm/min with a span (S) of 16 mm using a universal testing machine (Instron 5599, Instron, USA). The unnotched samples were 3 mm in thickness, 4 mm in width and 20 mm in length. Fracture toughness was determined by the single-edge notched beam (SENB) method at a cross-head speed of 0.05 mm/min with a span of 16 mm. The dimensions of the SENB samples were 2.5 mm in

thickness (*b*), 4 mm in width (*w*), and 20 mm in length. The notch was 0.25 mm in width and approximately 2 mm in depth (*a*). We calculated crack-initiation toughness (K_{Ic}) and crack-growth toughness (K_{Jc}) based on the following formulae [11,28]:

$$f(a/w) = \{3(a/w)^{1/2}[1.99 - (a/w)(1 - a/w) \cdot (2.15 - 3.93(a/w) + 2.7(a/w)^2)] / [2(1 + 2a/w)(1 - a/w)^{3/2}]\}$$
(1)

$$K_{\rm Ic} = \frac{f(a/w)FS}{bw^{3/2}} \tag{2}$$

where F is the load.

The elastic contribution (J_{el}) and plastic contribution (J_{pl}) related to *J*-integral calculation were used to calculate K_{Je} :

$$J_{\rm el} = \frac{K_{\rm lc}^2}{E'} \tag{3}$$

$$J_{\rm pl} = \frac{1.9A_{\rm pl}}{b(w-a)}$$
(4)

$$K_{\rm Jc} = \sqrt{(J_{\rm el} + J_{\rm pl})E'} \tag{5}$$

$$E' = E/(1-v^2)$$
 (6)

where $A_{\rm pl}$ is the plastic areas underneath the fracture surface, *E* is the elastic modulus and *v* is the Poisson's ratio. Crack extension, Δa , was calculated using the following formula [29,30]:

$$C_n = u_n / f_n \tag{7}$$

$$a_n = a_{n-1} + \frac{w - a_{n-1}}{2} \frac{C_n - C_{n-1}}{C_n}$$
(8)

$$\Delta a = a_n - a \tag{9}$$

where u_n , f_n , a_n and C_n are the displacement, force, crack length and complaisance calculated at each point after crack departure, respectively. The elastic modulus *E* was estimated using the rule of mixtures described in the previous study [11], taking the midpoint between the lower and upper bounds. To calculate the *E* of the composite, we used *E* values for 2024Al of 70 GPa [31], B₄C of 460 GPa [32] and TiB₂ of 500 GPa [33], and the Poisson's ratio *v* was 0.3.

3 Results and discussion

3.1 In situ reaction behavior of ceramic scaffolds

The DSC curve of the B₄C-TiH₂ system is

displayed in Fig. 1(a), where the endothermic peak at approximately 555 °C belongs to the dissociation of TiH₂. Research has found that TiH₂ typically decomposes at 500–800 °C and releases liberate chemically active Ti, according to the following reaction [34]:

$$TiH_2 \rightarrow Ti+H_2 \uparrow$$
(10)

Hence, to ensure complete dissociation of hydride and removal of hydrogen from dense solids with open pores, the scaffolds in this work were held at 750 °C for 30 min. Furthermore, an exothermic reaction initiated at 1307 °C can be observed, which is consistent with the two reactions of B₄C and Ti beginning at 1300 °C proposed by ZHAO and CHENG [35]:

$$5Ti+B_4C \rightarrow 4TiB+TiC$$
 (11)

$$3Ti+B_4C \rightarrow 2TiB_2+TiC$$
 (12)

Borides are more thermodynamically stable above 1800 °C, leading to the disappearance of the TiC phase and the conversion towards TiB_2 and carbon, as expressed in Reaction (13) [36]:

$$2\text{TiC}+B_4\text{C} \rightarrow 2\text{TiB}_2+3\text{C} \tag{13}$$

Therefore, for each composite, no other phases can be identified apart from the diffraction peaks of B_4C , TiB_2 and C (Fig. 1(b)).

To further identify the elemental composition of the in situ reaction between TiH_2 and B_4C , XPS analysis was performed, and the spectra of B 1s, C 1s, Ti 2p and O 1s in the 7:3 scaffold are shown in Fig. 2. In the high-resolution B 1s spectrum, the highlighted peaks of 187.75 and 190.73 eV are assigned to the B—C bonding of B₄C and high bonding energy of B state in B₄C, respectively. The small signal at 192.82 eV can be designated as B—O bonding in B₂O₃ [37]. The C 1s peak exhibits an asymmetric shape consisting of three distinct chemical environments. The observed peak at 284.85 eV is attributed to free carbon on the surface. The peak at 282.15 eV is relevant to B-C of B_4C , while a minor peak at 286.24 eV is ascribed to C—O—C, probably caused by carbon oxide in air or oxidized free carbon [38,39]. From the Ti 2p spectrum, the peaks of 454.82 and 459.87 eV correspond to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of TiB₂, respectively [40]. It is worth noting that no peaks correlated with TiC can be detected, further demonstrating the absence of TiC in the final scaffold. In addition, the peak of O 1s centerd at 532.3 eV is associated with B-O. These results indicate that the regulated B₄C-TiH₂ system can be almost completely transformed into a B₄C-TiB₂ composite by in situ synthesis.

3.2 Microstructure of ceramic scaffolds

Figures 3(a-c) show the SEM images of the porous ceramic scaffolds with various compositions. In all cases, the porous materials possess well-developed lamellae with long-range order. Through tip-splitting and healing, ceramic powders entrapped in the ice crystals develop ceramic bridges between adjacent walls. This microscopic characteristic can enhance mechanical properties of the composites when the pore channels are filled by molten metal [10,41]. The initial content of TiH₂ plays a remarkable effect on the lamellar structure of the B₄C architecture. With the initial TiH₂ content increasing from 10 vol.% to 30 vol.%, the ceramic thickness reduces from (28.4±1.6) to $(19.9\pm1.8) \mu m$; correspondingly, the structure wavelength (λ), namely the total of ceramic layer thickness and pore channel width, decreases from



Fig. 1 DSC curve of B₄C-TiH₂ system (a) and XRD patterns of 9:1, 8:2 and 7:3 scaffolds (b)



Fig. 2 XPS spectra of B 1s (a), C 1s (b), Ti 2p (c) and O 1s (d) peaks in 7:3 scaffold



Fig. 3 SEM images of ceramic scaffolds with various compositions of 9:1 (a), 8:2 (b), 7:3 (c) and EDS mapping analysis (d) of 7:3 scaffold

 (47.9 ± 3.2) to (33.5 ± 2.4) µm. The main reason is that the volume shrinkage of the ceramic lamellae and the consumption of the reactants greatly reduce

the thickness of the ceramic layers after the reactive sintering. The EDS mapping of the C, Ti and B elements in the 7:3 scaffold is displayed in Fig. 3(d),

where TiB_2 is uniformly distributed within the ceramic walls, contributing to the penetration of molten metal into the interlaminar pore channels and interstices of ceramic lamellae.

3.3 Microstructure of composites

Figure 4 shows the XRD patterns of the 2024Al/B₄C–TiB₂ composites with different initial B₄C:TiH₂ proportions. As expected, the phase components in each case include B₄C, Al, TiB₂ and Al₂Cu. Notably, there exist no reaction products between B₄C and Al such as Al₃BC, AlB₂ and Al₄C₃ [42], which is probably ascribed to the low temperature and short time in the squeeze casting process, making the products below the minimum



Fig. 4 XRD patterns of $2024Al/B_4C$ -TiB₂ composites with varying initial B₄C:TiH₂ proportions

value identified by XRD analysis. Moreover, the intermetallic Al₂Cu phase, mainly derived from the precipitation of 2024Al, can inhibit the interfacial reactions associated with Al₃BC formation, while diminishing the erosion of B_4C particles by the molten alloy [43].

Figures 5(b–e) show the BSE images and elemental mapping of the $2024Al/B_4C-TiB_2$ composites. Combined with the XRD and EDS results, the light gray and dark gray layers correspond to Al and B₄C phases, respectively, and the bright white phase adhered to the surface of the B₄C lamellae represents the TiB₂ phase. The interlaminar pore channels are entirely filled by the molten alloy with the ceramic lamellae remaining intact, allowing the infiltrated composite to inherit the laminar structure of the ceramic scaffolds. In addition to the interspaces between the lamellae, the molten alloy also infiltrates into the voids between the ceramic particles due to the loose structure of the ceramic lamellae.

When filling the in-layer cavities with 2024Al melt, the capillary force (P_0) to be overcome can be evaluated based on the capillary equation of the porous medium system, namely

$$P_0 = 6\sigma\lambda_1 \cos\theta \frac{f_p}{(1 - f_p)r}$$
(14)

where σ is the surface tension of the molten Al (σ_{Al} =865 mN/m at 800 °C) [44]; λ_1 is a geometrical



Fig. 5 BSE images of $2024Al/B_4C$ -TiB₂ composites with various initial B₄C:TiH₂ proportions of 10:0 (a), 9:1 (b), 8:2 (c) and 7:3 (d), and EDS elemental mapping of 7:3 composite (e)

factor that typically varies between 2 and 4, and is mainly related to the surface roughness of the particles and the assumed pore geometry (here, assuming λ_1 =4) [45]; f_p and r are the volume fraction of the particle in the ceramic layers and the average particle diameter, respectively, which are evaluated from SEM images via the ImageJ software [15]; θ is the equivalent contact angle of the B₄C ceramic scaffold with 2024Al. Given that the ceramic scaffold is composed of two different components, the equivalent wettability of the 2024Al melt is evaluated following the Cassie equation [46]:

$$\cos\theta = f_1 \cos\theta_1 + (1 - f_1) \cos\theta_2 \tag{15}$$

where f_1 is the volume fraction of B₄C in the ceramic scaffold; θ_1 and θ_2 represent the contact angles of the alloy on the B₄C and TiB₂ substrates, respectively (θ_1 =131° [47] and θ_2 =55° [48]). Table 2 displays some required parameters and corresponding results. The capillary force in the 10:0 composite is 10.9 MPa, which is greater than the pressure we utilized in our squeeze casting process. Thus, the in-layer cavities of the 10:0 composite are hardly filled completely by the molten alloy and pores can be observed (Fig. 5(a)). By contrast, the capillary forces are lowered to 5.5, 2.9 and 2.0 MPa for the 9:1, 8:2 and 7:3 composites, respectively. This indicates that the introduced TiB₂ significantly facilitates the penetration of molten 2024Al into the cavities within the layer, which largely diminishes or even eliminates the cavities,

creating the lamellar-interpenetrated structure (Figs. 5(b-e)). This architecture decreases the strength difference between ceramic and metal layers, leading to the improved toughness of the composite by enhancing the plastic strain and hindering the crack propagation [49]. In addition, we estimated the interfacial bonding strength between the 2024Al melt and ceramic phase by calculating the work of adhesion *W*, as expressed in Eq. (16) [50]:

$$W = \sigma(1 + \cos \theta) \tag{16}$$

The obtained W values of the 10:0, 9:1, 8:2 and 7:3 composites are 0.29, 0.41, 0.57 and 0.67 N/m, respectively, demonstrating that the in situ formation of TiB₂ improves the adhesion work of the ceramic layer to the alloy.

The TEM images, inverse FFT pattern and the corresponding interfacial configurations of the 7:3 composite are shown in Fig. 6. According to the elemental mapping image (Fig. 6(a)) and the

Table 2 Equivalent contact angle (θ), volume fraction of particle in ceramic lamellae (f_p), average particle diameter (r), calculated capillary force (P_0) and work of adhesion (W) of 2024Al/B₄C–TiB₂ composites

Composite	$\theta/(^{\circ})$	$f_{\rm p}$	r/µm	P ₀ /MPa	$W/(N \cdot m^{-1})$
10:0	131	0.68	~2	10.9	0.29
9:1	122	0.57	~2	5.5	0.41
8:2	110	0.52	~2	2.9	0.57
7:3	103	0.54	~2	2.0	0.67



Fig. 6 TEM micrograph of 7:3 composite and corresponding elemental mappings (a), SAED patterns of corresponding phases of red areas (b–d), inverse FFT pattern (e) from area labelled "e" in (a), and HRTEM images taken from yellow areas (f, g)

corresponding SAED patterns (Figs. 6(b-d)), the white irregular-shaped particle, gray rod-shaped phase and the black continuous area correspond to B_4C , TiB_2 and Al, respectively. Apparently, there are no voids along with the interface between the 2024Al and ceramic particles. No visible reaction layer can be observed at the 2024Al/B₄C interface, which is consistent with the XRD findings. Additionally, because of the great difference in the thermal expansion coefficient between 2024Al and B₄C, geometrically necessary dislocations (GNDs) accumulate in the Al matrix near the interface, emphasized by the " \perp " symbol (Fig. 6(e)). These dislocations can pin the grain boundaries preventing the grain growth. On the other hand, there exists an incoherent interface between the B₄C particles and the 2024Al matrix (Fig. 6(f)), which is in line with the results of JIANG et al [51], who observed a random orientation relationship between them. In contrast, the TiB_2/Al interface features a clear crystallographic orientation relationship, i.e., (102)TiB₂//(220)Al (Fig. 6(g)), with a small lattice mismatch of 3.93%, indicating that the interface is basically coherent and the adhesion is strong. This conjecture is further supported by the good wettability of the molten alloy to TiB₂. Hence, the incorporation of initial TiH₂ indeed improves the crystallographic match and interfacial bonding strength between the ceramic skeleton and alloy matrix, which helps to enhance the mechanical performance of the infiltrated composites [52].

3.4 Mechanical properties of composites

The flexural strength is found to be remarkably affected by the initial TiH_2 addition (Figs. 7(a) and (b)). To facilitate comparative analysis, the corresponding mechanical properties are listed in Table 3. The 10:0 composite exhibits a low flexural strength (σ_f) of (484±27) MPa. As the initial TiH₂ content increases, the strength of the 9:1, 8:2 and 7:3 composite can reach (642 ± 24) , (665 ± 30) and (633 ± 28) MPa, respectively, which are 23.5%-27.2% higher than that without initial TiH₂ additions, together with enhanced fracture strain. In addition, the crack initiation toughness (K_{Ic}) firstly increases and then decreases with the increase of TiH₂ ratio, achieving a maximum value of (12.5 \pm 0.5) MPa·m^{1/2} in the 9:1 composite. The improved flexural strength and crack initiation toughness are probably due to different flaw



Fig. 7 Stress-strain responses of 2024Al/B₄C-TiB₂ composites (a), comparison of flexural strength (b), crack-resistance curves (*R*-curves) showing toughness versus crack extension obtained from SENB tests (c), and summary of crack initiation toughness (K_{Ic}) and crack propagation toughness (K_{Jc}) (d)

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Composite	Ceramic thickness/µm	Metal thickness/µm	E/GPa	$\sigma_{\rm f}/{ m MPa}$	$K_{\rm Ic}/({\rm MPa}\cdot{\rm m}^{1/2})$	$K_{\rm Jc}/({\rm MPa}\cdot{\rm m}^{1/2})$
10:0	16.7±2.6	18.7±2.9	179	484±27	$8.9{\pm}0.7$	19.3±1.5
9:1	23.2±3.2	27.5±3.8	181	642±24	12.5±0.5	28.9±1.7
8:2	20.5±3.4	22.7±3.1	183	665±30	12.1±0.3	30.6±1.8
7:3	16.3±2.8	19.4±3.5	187	633±28	11.4 ± 0.7	32.7±1.8

Table 3 Mechanical properties of 2024Al/B₄C-TiB₂ composites

densities within the ceramic lamellae. The cavities are more likely to exist in the $2024Al/B_4C-TiB_2$ composite than in the $2024Al/B_4C$ composite (Fig. 5).

Since most of the fracture resistance in these nacre-inspired composites is achieved during crack propagation, crack-growth toughness (K_{Jc}) is extensively used to evaluate the resistance to crack propagation [53-56]. All composites display a rising resistance (*R*-curves) behavior, which suggests that the crack-growth toughness increases with the increase of crack extension (Fig. 7(c)). Such a stable crack propagation is quite different from the catastrophic failure that occurs in monolithic boron carbide. The composite with initial TiH₂ addition displays higher crack-growth toughness in a steeper R-curve form, as compared to that in the 10:0 composite. Based on the ASTM E1820 standards [57], the maximum crack extension capacity is limited by $\Delta a_{\text{max}}=0.25b_0=$ 0.5 mm (b₀ represents the initial uncracked ligament, $b_0=2$ mm). Hence, in this work, we discussed $K_{\rm Jc}$ in terms of the maximum ASTM effective toughness at $\Delta a_{\text{max}}=0.5$ mm, although the crack propagation remains stable after this limit. Under such criteria, the critical valid $K_{\rm Jc}$ reaches (19.3±1.5), (28.9±1.7), (30.6 ± 1.8) and (32.7 ± 1.8) MPa·m^{1/2} for the 10:0, 9:1, 8:2 and 7:3 composite, respectively, increasing approximately by 116%, 131%, 152% and 186% compared with their K_{Ic} (Fig. 7(d)). The K_{Jc} of 9:1, 8:2 and 7:3 composites increases by 50%-60% compared with that of the 10:0 composite. The significant enhancement in $K_{\rm Jc}$ may arise from the increased interfacial bonding caused by the initial TiH₂ incorporation. On the other hand, the thickness of ceramic lamellae decreases as the initial TiH₂ content increases from 10 vol.% to 30 vol.% (Fig. 3), which increases the amount of interface between the alloy and ceramic phases. This benefits fracture toughness by providing more microdelamination, crack deflection and pull-out, resulting in more energy dissipation.

3.5 Toughening mechanism of composites

The exceptional combination of strength and toughness can be ascribed to the activation of multiple intrinsic and extrinsic toughening mechanisms [58]. To identify the toughening mechanisms, the crack-propagation path and the corresponding fracture morphology, as depicted in Fig. 8, were examined. Debonding occurs at the ceramic/alloy interface in the 10:0 composite (Figs. 8(a, b, d)), which results from the weak interfacial bonding between B₄C and 2024Al. Although this makes the crack extension path longer, the accelerated crack propagation and connection lead to a decreased strength and crack-initiation toughness. Besides, the visible cracks inside the ceramic layers caused by in-layer voids further weaken the toughness (Fig. 8(c)). In contrast, the addition of initial TiH₂ largely alters the crack propagation mode and greatly prolongs the crack-propagation path (Fig. 8(e)). It is noteworthy that no interfacial debonding occurs at the metal-ceramic interface after fracture, which suggests a strong adhesion (Fig. 8(h)). As the advancing crack contacts the alloy layer, the layer begins to absorb and dissipate fracture energy through plastic deformation. Subsequently, the crack propagates along new cracks in the adjacent ceramic layer rather than at the metal/ceramic interface due to the well-bonded interface, enabling the adjacent ceramic layer to fracture and the alloy to deform violently [59]. After substantial inelastic deformation, the ligament alloy lamellae fail by the coalescence and nucleation of micro-pores. The crack arresting and re-nucleation processes markedly enhance the energy required for crack propagation. Accordingly, the ductile-ligament bridging in the alloy layers makes the composite reveal a stepped crack-propagation mode with several microcracks, which blunts the crack tip and prevents catastrophic damage. On the other hand, external mechanisms such as crack deflection and branching induce stable crack propagation,



Fig. 8 BSE images showing crack-growth path (a-c) and fracture surface (d) in 10:0 composite, and crack-growth path (e-g) and fracture surface (h) in 7:3 composite

undoubtedly further improving the fracture toughness. Furthermore, since the transgranular fracture appears in some ceramic grains (Fig. 8(f)), the local stress has attained the failure strength of B₄C (σ_c =1.16 GPa) calculated according to the Griffith criterion [60]:

$$\sigma_{\rm c} = \alpha (\gamma E_{\rm c}/t)^{1/2} \tag{17}$$

where parameter α is roughly equal to $\pi^{1/2}$, E_c is the elastic modulus (460 MPa), γ is the surface energy (3.27 J/m²) [61], and *t* is the thickness of B₄C ceramic crystal (3.5 µm). It is worth noting that the crack propagation in the 10:0 composite is characterized by single-cracking mode; in contrast, diffusion zones of multiple microcracks appear in the 7:3 composite, with many cracks re-nucleating in the ceramic layers on the side of the main crack (Figs. 8(e, g)).

In fact, the fracture toughness of the nacre-mimetic composite is strongly correlated with the fracture mode, including single and multiple crack propagations [62,63]. The multiple crack propagation is preferable as it can yield superior toughness via absorbing more fracture energy. Multiple cracking prevails if the maximum wake stress in the ceramic layer ($\sigma_{(wake)max}$) exceeds the stress in the adjacent unfractured ceramic layers (σ_c) before the stress in the adjacent unfractured ceramic

layers (σ_0) surpasses this value, i.e., $\sigma_{(wake)max} = \sigma_c > \sigma_0$; single cracking dominates. otherwise, It is established that this model transformation is dominated by the ratio of the constrained metal yield stress to the ceramic fracture strength (σ_m/σ_c) and the ratio of the metal lamellae to the ceramic lamellae thickness (t_m/t_c) [64]. There exists a critical thickness ratio $(t_m/t_c)_{crit}$, which is inversely proportional to the strength ratio $\sigma_{\rm m}/\sigma_{\rm c}$. If the thickness ratio $t_{\rm m}/t_{\rm c}$ exceeds the critical value, multiple cracking will occur. In our 2024Al/ B₄C-TiB₂ composites, the loose ceramic skeleton filled with more molten alloys weakens the strength of the ceramic lamellae, thereby increasing the ratio of $\sigma_{\rm m}/\sigma_{\rm c}$ and lowering the $(t_{\rm m}/t_{\rm c})_{\rm crit}$. Additionally, the tiny reticulated alloy phase in the ceramic layer dramatically relieves the interlayer mechanical mismatch, which contributes to strain delocalization and stress redistribution. This allows larger size materials to engage in deformation and cracks to nucleate from larger regions [15]. On the other hand, the improved metal/ceramic interfacial strength also reduces the critical thickness ratio, as previously reported in Ref. [65]. Therefore, the fracture mode transforms from single-crack to multiple-crack propagation via the addition of TiH2, which dissipates more fracture energy. This is the main reason for many coarse tearing ridges and wrinkled stripes in the fracture surface of alloy layers, and cleavage fracture in the ceramic particles (Fig. 8(h)).

Our nacre-like composites are distinguished by an exceptional combination of strength and fracture. Density is a principal concern regarding the selection of materials for structural applications. The Ashby diagram for the specific strength versus specific toughness compared with traditional engineering materials is shown in Fig. 9(a). The 2024Al/B₄C-TiB₂ composites are situated in the upper right corner, demonstrating their characteristics of low-density and high damageresistance. Interestingly, the specific strength and toughness make our composites comparable to engineering magnesium and aluminum alloys, just smaller than those of metallic glass, which is one of toughest engineered materials the currently produced, but its use is limited by its density [66].



Fig. 9 Ashby diagram for specific strength versus specific toughness compared with traditional engineering materials (a), and comparison of strength and toughness of nacre-like composite in this work with its competitors [1,31,42,52,67,68] (b)

The comparison of strength and toughness of our nacre-like composite with its competitors is shown in Fig. 9(b). We selected K_{Ic} as its toughness in this study because the validity of K_{Jc} values was not mentioned in the work of YANG et al [52]. While our nacre-mimetic 2024Al/B₄C–TiB₂ composites feature a lower strength than certain values published in the literature because of its lower B₄C content, they remain higher than most composites (Fig. 9(b)). Interestingly, the toughness obtained is outstanding compared to other reported B₄C/Al composites. Thus, tuning the compositional wettability allows our composites to fill a blank region in regard to the strength and toughness of Al/B₄C composites.

4 Conclusions

(1) By infiltrating molten alloy into the loose B_4C-TiB_2 ceramic skeleton, we created 2024Al/ B₄C-TiB₂ composites with a laminate-reticular hierarchical structure. TiB₂, synthesized by the in situ reaction of TiH₂ and B₄C, promoted the wettability and interfacial bonding of the ceramic scaffold with the alloy.

(2) The infiltrated 2024Al/B₄C–TiB₂ composites exhibited a remarkable improvement in damage resistance ability, as compared to 2024Al/B₄C composites. The introduction of TiB₂ allowed for an increase in flexural strength and valid fracture toughness (K_{Jc}) from (484±27) to (665±30) MPa and from (19.3±1.5) to (32.7±1.8) MPa·m^{1/2}, respectively.

(3) This unique combination of strength and toughness could be ascribed to multiple extrinsic toughening mechanisms, including the crack propagation, branching and blunting, specifically uncracked-ligament bridging and multiple crack extension, yielding enhanced fracture resistance with crack propagation, in the form of a rising *R*-curve behavior. We believe that this strategy can provide new insight into the design and assembly of nacre-inspired Al/B₄C composites.

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通过调整润湿性开发具有高抗损伤性能的 仿珍珠贝壳层状 2024AI/B₄C 复合材料

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摘 要:为了解决复合材料中 B4C 陶瓷相难以被金属铝润湿的问题,利用 TiH2 和 B4C 的原位反应引入 TiB2,进 而调节其润湿性和界面结合。通过将熔融合金压力浸渗到冷冻铸造法制备的多孔陶瓷支架中,制备具有层状结构 的 2024Al/B4C-TiB2 复合材料。与 2024Al/B4C 复合材料相比,加入 TiH2 后复合材料的抗弯强度和裂纹扩展韧性 分别由(484±27) MPa 提高到(665±30) MPa 和由(19.3±1.5) MPa·m^{1/2}提高到(32.7±1.8) MPa·m^{1/2}。这种优异的抗损伤 能力来自于多重外在增韧机制,包括未开裂韧带的桥接、裂纹分叉、裂纹扩展和裂纹钝化,更重要的是,断裂模 式从单一裂纹扩展转变为多裂纹扩展。这一策略为改善 Al/B4C 复合材料的润湿性和界面黏结性开辟了一条道路, 从而生产出具有优良耐损伤性能的仿珍珠贝壳状材料。

关键词: 生物启发复合材料; 冷冻铸造; 氢化钛; 力学性能; 耐损伤性

(Edited by Wei-ping CHEN)

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