



Annealing hardening and deformation behavior of layered gradient Zr–Ti composite

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Abstract: To investigate potential strengthening approaches, multi-layered zirconium–titanium (Zr–Ti) composites were fabricated by hot-rolling bonding and annealing. The microstructures of these composites were characterized using scanning electron microscopy with energy dispersive spectroscopy (SEM–EDS) and electron backscatter diffractometry (EBSD). Their mechanical properties were evaluated by uniaxial tension and compression measurements. It was found that the fabricated Zr–Ti composites are composed of alternating Zr/diffusion/Ti layers, and chemical compositions of Zr and Ti showed a gradient distribution in the diffusion layer. Compared with as-rolled samples, annealing can strengthen the layered gradient Zr–Ti composite, and this is mainly caused by solid-solution strengthening and microstructure refinement-induced strengthening. Compared with the raw materials, a synergistic improvement of strength and ductility is achieved in the Zr–Ti composite as a result of the layered gradient microstructure. Tension–compression asymmetry is observed in the Zr–Ti composites, which may be attributed to twinning and microvoids induced by unbalanced diffusion.

Key words: Zr–Ti layered structural material; diffusion annealing strengthening; tension–compression asymmetry yielding; ductility

1 Introduction

Due to their excellent corrosion resistance and small capturing cross-section for thermal neutrons, zirconium alloys such as Zr–Sn [1,2], Zr–Nb [3–5], and Zr–Sn–Nb [6,7] are widely used as cladding materials in the nuclear power industry. For a cladding material, the most important concern is resistance to damage induced by neutron irradiation and exposure to high temperatures. However, scant attention has been given to the strength, ductility, underlying strengthening and toughening mechanisms of traditional Zr alloys used in the nuclear power industry. Investigations have

indicated that considerably high strength can be achieved in Zr and Zr-based alloys. By the refinement of grain size, for example, through accumulated rolling bonding [8], surface circulation rolling treatment [9], or heavy cold rolling [10], the ultimate tensile strength of pure Zr can reach ~650, ~850, or ~930 MPa, respectively. Alloying is an effective method for strengthening many materials, and it is also suitable for Zr. It has been reported that the tensile strength of Zr–Ti binary alloy increases with increasing Ti content due to the solid-solution strengthening effect, and a tensile strength of ~1200 MPa has been achieved with 45 at.% Ti [11,12]. Adding V and Al to a Zr–Ti binary alloy can lead to a higher tensile strength

(between 1300 and 1500 MPa) [13,14].

The high strength of Zr and its alloys indicates that these materials have wide potential for application in various fields as structural materials. However, traditional strengthening methods, such as, grain size refinement-induced strengthening and alloying strengthening, are often accompanied by a reduction in ductility. For a Zr–Ti binary alloy, when the highest tensile strength (~1200 MPa) was obtained, the tensile elongation was only ~5% [11]. Recently, it has been revealed that the strength and ductility of metallic materials can be synergistically improved by inducing inhomogeneous microstructures [15–17]. These microstructures in heterogeneous metallic materials generally comprise multiple domains with remarkably different mechanical properties [18]. The inter-domain transitions may be sharp or gradual, and compatible deformation among different domains significantly reshapes the applied strain path or/and stress state, which provides an opportunity to achieve extraordinary strengthening and strain hardening [15,19,20].

Layered materials, which feature bonded alternating layers [21,22], are typical hetero-structured materials. Additional strengthening above the rule of mixture (ROM) and a high work-hardening rate have been reported in many layered materials, for example, coarse-/ultrafine-grained copper [23], Ti–Al [24], and coarse-/ultrafine-grained Cu–Zn [25]. In previous reports, we described the fabrication of layered Zr–Ti composites by diffusion and rolling bonding and evaluated their mechanical properties using hardness and compression tests [26,27]. However, due to sample-size limitations, the ductility of these composites was not directly measured. In this work, hot-rolling bonding was used to fabricate layered Zr–Ti composites, and their mechanical properties were examined by the uniaxial tension and compression tests. Their microstructures were characterized by electron backscatter diffraction (EBSD) and scanning electron microscopy (SEM). Higher strength and better ductility can be obtained for Zr–Ti composites when compared with the raw materials (commercial purity Zr and Ti), and these materials therefore show good potential for application in the aerospace, chemical, and

biomedical industries.

2 Experimental

2.1 Materials

Commercially pure Zr (Zr702) and Ti (CP-Ti) sheets were used as raw materials to fabricate Zr–Ti composites. The raw Zr and Ti sheets, with a thickness of 0.5 mm, were manufactured by a rolling and annealing process. The main chemical compositions of the raw Zr and Ti sheets are listed in Table 1.

Table 1 Chemical compositions of Zr702 and CP-Ti sheets (wt.%)

Sheets (wt.%)					
Material	Hf	Sn	Fe+Cr		Zr
Zr702	0.95	0.16	0.15		Bal.
Material	Fe	C	N	O	Ti
CP-Ti	0.04	0.01	0.003	0.04	Bal.

To fabricate the Zr–Ti composites, small sheets, with dimensions of 80 mm (rolling direction, RD) × 30 mm (transverse direction, TD), were cut from the raw sheets. Mechanical grinding and pickling were performed to obtain an oxide-free and fresh surface. Then, the small Zr702 and CP-Ti sheets were alternately stacked, and this was followed by hot-rolling bonding. Ten Zr702 sheets and nine CP-Ti sheets were used in each Zr–Ti billet. The hot-rolling bonding was conducted at 700 °C. A total rolling reduction of 88% was achieved after multiple passes. After the hot-rolling bonding, annealing was used to relieve the residual stress that may occur during rolling deformation and cause further diffusion between Zr and Ti. Annealing was carried out at 800 °C for 30, 60, 90, or 120 min for different samples, or 900 °C for 120 min. To avoid oxidation, the Zr–Ti composite specimens were sealed in vacuum quartz tubes during annealing. For the sake of convenience, the specimens were named after their annealing temperature and holding time. For example, the 800-90 specimen was annealed at 800 °C for 90 min. Additionally, a hot-rolling-bonded specimen was examined without further annealing, and this is referred to as the as-rolled (AR) specimen.

2.2 Mechanical properties measurement and microstructure characterization

To evaluate the mechanical properties of the fabricated Zr–Ti composites, uniaxial tension and compression tests were performed. In the tension tests, a dog-bone specimen with a gauge area of $16\text{ mm} \times 4.2\text{ mm}$ was used. The tension tests were carried out on an AG-X50 kN machine at a constant speed of 0.36 mm/min . To obtain reliable data, each sample test was repeated three times. A laser extensometer was used to measure the strain. In addition, a digital image correlation (DIC) method was applied to capturing the in-plane strain. Before the tension tests, black and white speckles were carefully sprayed onto the surface of the samples, acting as markers for the DIC analysis. A charge-coupled device camera was used to record images at different strains. The two-dimensional strain distributions on the rolling plane were calculated based on the relative displacements of the aforementioned markers. For the compression tests, small specimens with dimensions of $2.5\text{ mm (RD)} \times 2\text{ mm (TD)} \times 1.8\text{ mm (normal direction, ND)}$ were cut from the Zr–Ti composites. The compression tests were also carried out on the AG-X50 kN machine, with a fixed speed of 0.12 mm/min . Each test was repeated three times. Both tension and compression were along the RD.

The microstructures of the Zr–Ti composites were characterized by SEM, energy dispersive spectroscopy (EDS), and EBSD. The observed areas were on the RD–ND plane. Mechanical grinding and electrochemical polishing were applied before EBSD characterization. The volume ratio of perchloric acid/*n*-butanol/methanol of the electrochemical polishing liquid was 3:17:30. The electrochemical polishing was performed at temperatures of $0\text{--}10\text{ }^{\circ}\text{C}$ with a DC voltage of 15 V for $\sim 45\text{ s}$. Except for the RD–ND plane, the fracture surface of the tensile specimen was observed by SEM.

3 Results and discussion

3.1 Layered gradient structure in fabricated Zr–Ti composites

Figure 1 shows the macroscopic structures of the AR and annealed samples. Chemical element distributions based on the EDS tests are also

presented in Fig. 1. In the AR sample, alternating light and dark layers can be observed. Based on the EDS results, it can be determined that the bright and dark layers consist of Zr and Ti, respectively. Sharp and clear interfaces exist between the Ti and Zr layers. No obvious pores or oxides are observed near the interface, indicating good bonding. After annealing, the Zr and Ti elements diffuse across the original interfaces, resulting in a gradient distribution. After this mutual diffusion, the Zr–Ti interfaces are no longer clear due to the emergence of diffusion zones. Since a diffusion zone is always between a Zr layer and a Ti layer, it is hereafter referred to as an interface layer. With increasing annealing temperature or time, the widths of the interface layers increase. After annealing at $900\text{ }^{\circ}\text{C}$ for 120 min , both the Zr and Ti layers are completely consumed by the interface layers. However, the chemical elements still show a gradient distribution in the 900-120 sample. Therefore, a unique heterostructure, i.e. a layered gradient structure, is formed in the fabricated Zr–Ti composites.

The average thicknesses of the Zr, Ti, and interface layers were quantitatively established based on the EDS results. The layer thicknesses at different annealing temperatures and time are shown in Fig. 2. The results indicate that the Ti layers are slightly thinner than the Zr layers in the AR sample, despite the sheets having the same initial thicknesses. This may be attributed to the flow strength of CP-Ti being lower than that of Zr702, and CP-Ti may therefore accommodate more deformation during rolling bonding. With increasing annealing time or temperature, the thickness difference between the Ti and Zr layers firstly increases and then decreases. The increasing thickness difference is caused by the faster diffusion of Ti atoms in the Zr layer and slower diffusion of Zr atoms in the Ti layer. With increasing interface layer thickness, the diffusion distance for Ti atoms to reach the Zr layer increases and vice versa, thus leading to the subsequent decreasing thickness difference. After annealing at $800\text{ }^{\circ}\text{C}$ for 120 min , the Ti layer is almost completely consumed. However, the full consumption of the Zr layer requires a longer annealing time or a higher annealing temperature, for example, annealing at $900\text{ }^{\circ}\text{C}$ for 120 min .

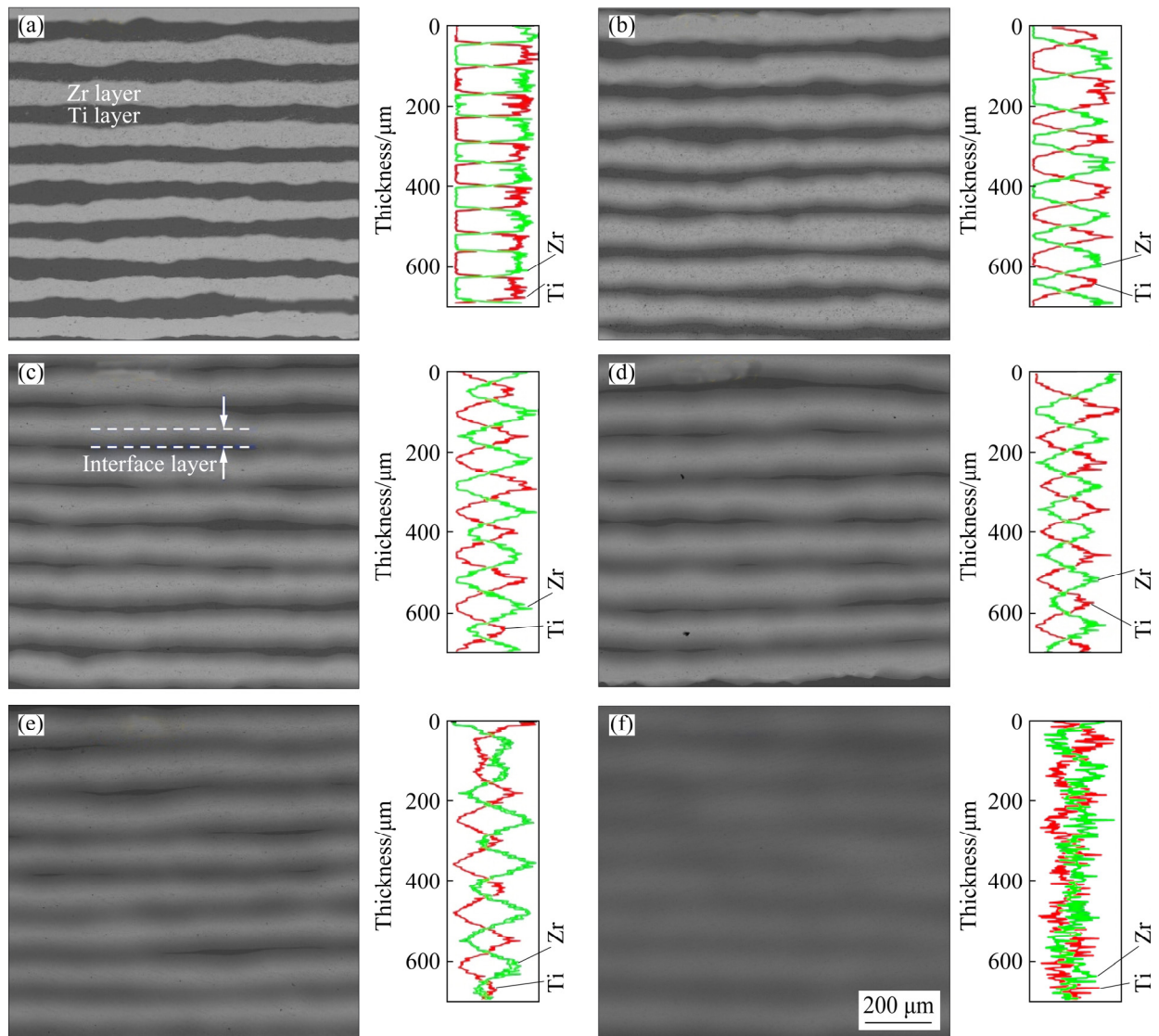


Fig. 1 Macroscopic structures and chemical element distributions in Zr–Ti composites as-rolled (AR) and annealed at different temperatures for different time: (a) AR sample; (b) 800-30; (c) 800-60; (d) 800-90; (e) 800-120; (f) 900-120

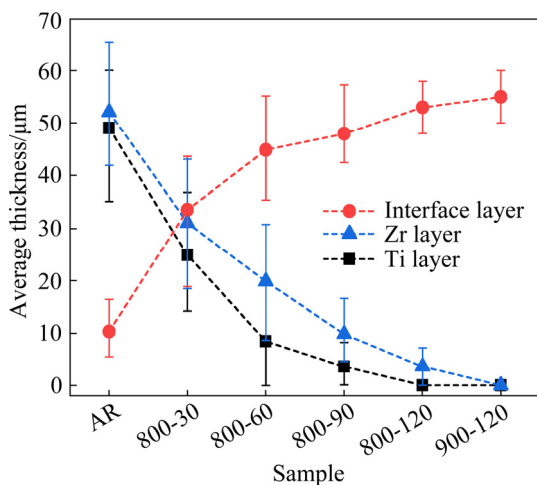


Fig. 2 Average thicknesses of Ti, Zr, and interface layers after annealing at different temperatures for different time

3.2 Microstructure based on EBSD

The microstructures of the AR and annealed Zr–Ti composites as obtained by EBSD are presented in Fig. 3. Grains are colored according to their crystal orientations (Euler angles). Un-indexed regions are colored black. For the AR sample (Fig. 3(a)), the grains in the Ti and Zr layers are elongated and the indexing ratio is low, indicating a deformed microstructure. High residual stress may exist between different layers as a result of their different flow stresses and elastic moduli. Some twin lamellae can be observed in the Ti layer. The indexing ratio in the Ti layer is higher than that in the Zr layer, which implies that the degrees of dynamic recovery and recrystallization in the Ti layer are higher than those in the Zr layer during the

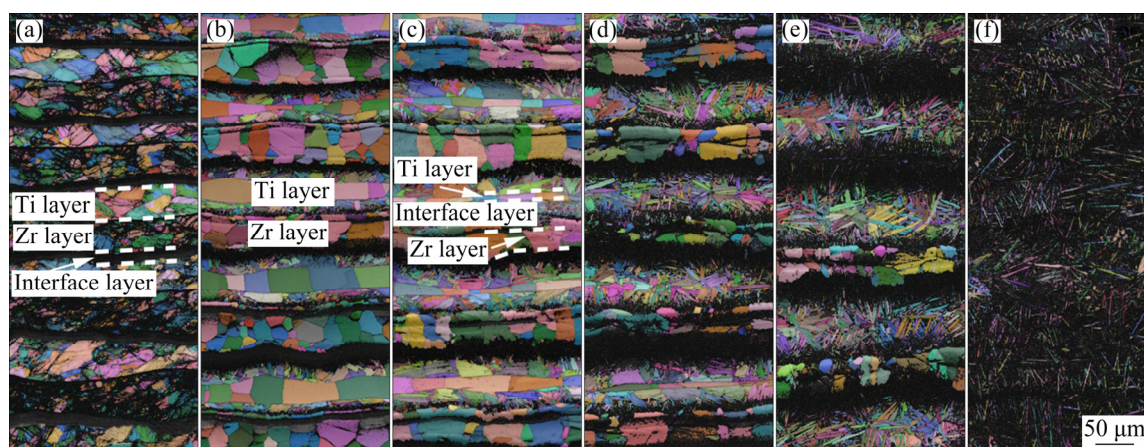


Fig. 3 Microstructures in Zr–Ti composites as-rolled and annealed at different temperatures for different time: (a) AR; (b) 800-30; (c) 800-60; (d) 800-90; (e) 800-120; (f) 900-120

hot-rolling bonding process. Based on the EDS results (Fig. 2), the interface layers are relatively thin ($\sim 10\ \mu\text{m}$). However, the microstructures in the interface layer are not clearly characterized by EBSD due to the low indexing ratio.

After annealing at $800\ ^\circ\text{C}$ for 30 min, the grains in the Ti and Zr layers are clean and free from twin lamellae, indicating a recrystallization state, as shown in Fig. 3(b). This is reasonable, since the annealing temperature of $800\ ^\circ\text{C}$ is obviously higher than the general recrystallization annealing temperature for commercially pure Zr and Ti [28–30]. Most of the grains in the Ti layer have a brick-like profile, which may be caused by the fast grain growth and the limitation of the layer boundary. In contrast, the grains in the Zr layer have equiaxed profiles. The microstructures in the interface layers show a lamellar profile, which becomes more obvious when the samples are annealed for longer time, for example, in the 800-90 and 800-120 samples. Lamellar microstructures should be formed by $\beta \rightarrow \alpha$ phase transition during the cooling stage of annealing treatment. It is worth noting that the $\beta \rightarrow \alpha$ phase transition temperature decreases with increasing alloying in the Zr–Ti system [31]. The lowest phase transition temperature is $\sim 605\ ^\circ\text{C}$ when the composition is $\text{Zr}_{50}\text{Ti}_{50}$, which is lower than the annealing temperature used [31]. Therefore, the central part of the interface layer during annealing is actually β phase, and this will be transformed to α phase during the cooling stage, thus leading to a lamellar microstructure.

Many areas in the interface layers of the

samples annealed at $800\ ^\circ\text{C}$ are un-indexed, although recrystallization has occurred in the Ti and Zr layers. There are two possible reasons for this un-indexing. The electrode potentials of the Ti, Zr, and interface layers are different due to their different chemical compositions. During electrochemical polishing, different degrees of electrochemical corrosion may occur, leading to the formation of grooves in the interface layers. During EBSD characterization, the feedback signal is weak when the electron beam scans over these grooves, and this may lead to the un-indexing. The second possible reason is that the phase transition induces residual stress. The β phase has a BCC crystal structure and α phase has an HCP crystal structure. The volume change that accompanies the $\beta \rightarrow \alpha$ phase transition will induce residual stress, and this may also lead to the un-indexing in the interface layer. After annealing at $900\ ^\circ\text{C}$, as shown in Fig. 3(f), all layers have a lamellar microstructure since the annealing temperature is higher than the phase transitions of pure Ti and Zr [31]. In addition, the thicknesses of the lamella in the 900-120 sample are smaller than those in the samples annealed at $800\ ^\circ\text{C}$, which may be caused by the higher undercooling when annealing at a higher temperature.

3.3 Mechanical properties

3.3.1 Tensile properties

The tensile engineering stress–strain curves of the raw materials are shown in Fig. 4. The yield strengths ($\sigma_{0.2}$) of the raw Zr702 and CP-Ti are 406 and 248 MPa, respectively. This means that the

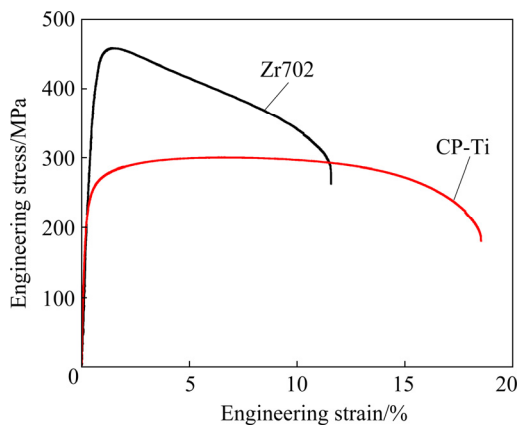


Fig. 4 Tensile curves of raw materials

Zr702 is stronger than the CP-Ti. The tensile elongations of the raw Zr702 and CP-Ti are 10.5% and 17.9%, respectively. The tensile engineering stress–strain curves of the Zr–Ti composites are displayed in Fig. 5(a). The yield strengths ($\sigma_{0.2}$) and

ultimate tensile strengths are presented in Fig. 5(b). The uniform elongation and the fracture elongation are shown in Fig. 5(c). For comparison, the strengths and elongations of Zr–Ti composites calculated according to the ROM are also provided in Figs. 5(b) and (c). For the AR sample, the tested yield strength is almost the same as the value calculated using the ROM. However, the tested ultimate tensile strength is higher than the calculated value, indicating a stronger work-hardening capability. Higher uniform elongation and fracture elongation are obtained compared with the calculated values, which may be also related to the stronger work-hardening capability of the layered Zr–Ti composites. A higher work-hardening capability in the layered material has been reported to be caused by the accumulation of geometrically necessary dislocations due to the compatible deformation between different layers [30,32].

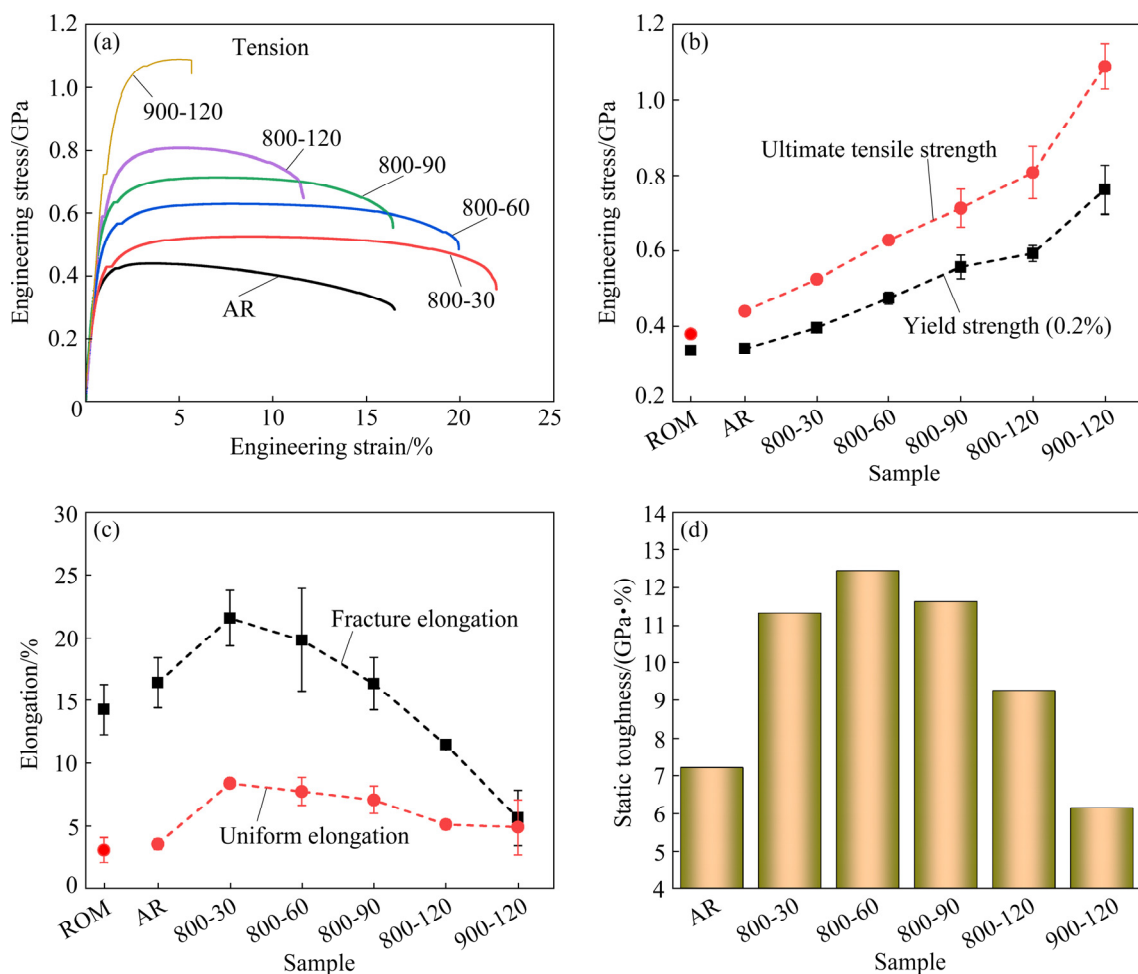


Fig. 5 Tensile properties of Zr–Ti composites as-rolled and annealed at different temperatures for different time: (a) Engineering stress–strain curves; (b) Yield strength and ultimate tensile strength; (c) Elongations; (d) Static toughness (product of tensile strength and fracture elongation)

After annealing at 800 °C for 30 min, the strength and elongation increase compared with the AR sample. The increase in strength may be caused by solid-solution strengthening and microstructure refinement-induced strengthening. As indicated in Fig. 2, the width of the interface layer increases from ~10 to ~35 μm after annealing at 800 °C for 30 min, which makes the area fraction of the interface layer account for more than 35%. In the interface layer, the solid solution of Ti atoms in a Zr matrix will cause obvious strengthening, and this has been reported in the literature as well as in our previous study [11,26,27]. In addition, the $\beta \rightarrow \alpha$ phase transition in the central part of the interface layer refines the microstructure, which may also contribute to the strengthening. The enhanced ductility may be related to the recrystallization that happens in the Ti and Zr layers and the relief of residual stress between different layers.

With further increase of the annealing time, the strength increases while the elongation gradually decreases, which shows a traditional trade-off relationship between the strength and ductility. However, it is worth noting that the strength and elongation of the 800-60 sample are higher than those of both component materials, i.e., Zr702 and CP-Ti, indicating synergistic improvement of strength and ductility. In addition, the 800-60 sample shows the best static toughness (the product of the ultimate tensile strength and the fracture elongation), as shown in Fig. 5(d). The underlying mechanism for the excellent tensile properties of the 800-60 sample may be attributed to the special layered gradient microstructure. The high strength of the 800-60 sample is obtained as a result of the increased thickness of the interface layers, thus increasing the contribution from solid-solution strengthening and microstructure refinement strengthening. In addition, it has been reported that the best mechanical properties of a layered material will be achieved when the layer thickness is double the width of the interface-affected zone [30]. The interface-affected zone is formed as a result of the compatible deformation of a “hard” layer and a “soft” layer [30]. In the current study, interface layers with strong solid-solution strengthening and microstructure refinement strengthening are the “hard” layers, while the Ti and Zr layers act as the “soft” layers. In the 800-60 sample, the layer thickness (width) may be double the width of the

interface-affected zone, and it thus has excellent strength and ductility.

However, in the current study, the samples have a layered gradient microstructure in which the interfaces between layers are not sharp. Therefore, the underlying mechanism for obtaining the best mechanical properties may be different from that in a traditional layered material with sharp interfaces. Much work, for example, in-situ observations of microstructure evolution during tensile loading, needs to be carried out in the future to reveal the detailed strengthening and toughening mechanisms of layered gradient Zr–Ti composites. Moreover, after hot-rolling bonding, the microstructures in the Ti and Zr layers are actually different from those in the raw materials. In future studies, homogeneous Ti and Zr sheets subjected to the same thermal-mechanical processing as the layers in the Zr–Ti composite need to be fabricated to evaluate the extra strengthening and toughening effects of the layered gradient microstructure.

3.3.2 Tension–compression asymmetry

The compressive engineering stress–strain curves and the compressive yield strength are presented in Fig. 6. The compressive yield strength in the present study is defined as the flow stress at 0.2% strain. The results show that the compressive strength gradually increases with annealing temperature and holding time, and this shows a similar evolution tendency as the tensile strength. However, the detailed compressive yield strength value is different from the tensile yield strength. The ratios of the tensile yield strength to the compressive yield strength are calculated and displayed in Fig. 6(b). This plot indicates that the yield strength ratio is less than 1 (the tensile yield strength is lower than the compressive yield strength), which shows asymmetric tension–compression yielding. In addition, the yield strength ratio first increases and then decreases with increasing annealing temperature and holding time. Since no extensometer was used in the compression tests, the compressive yield strength defined at larger strain (0.4%) was also checked. As shown in Fig. 6(b), the yield strength ratio with compressive yield strength defined at 0.4% strain demonstrates a similar evolution tendency as the compressive yield strength defined at 0.2% strain, which implies that the yield strength ratio is not sensitive to the definition of compressive yield strength.

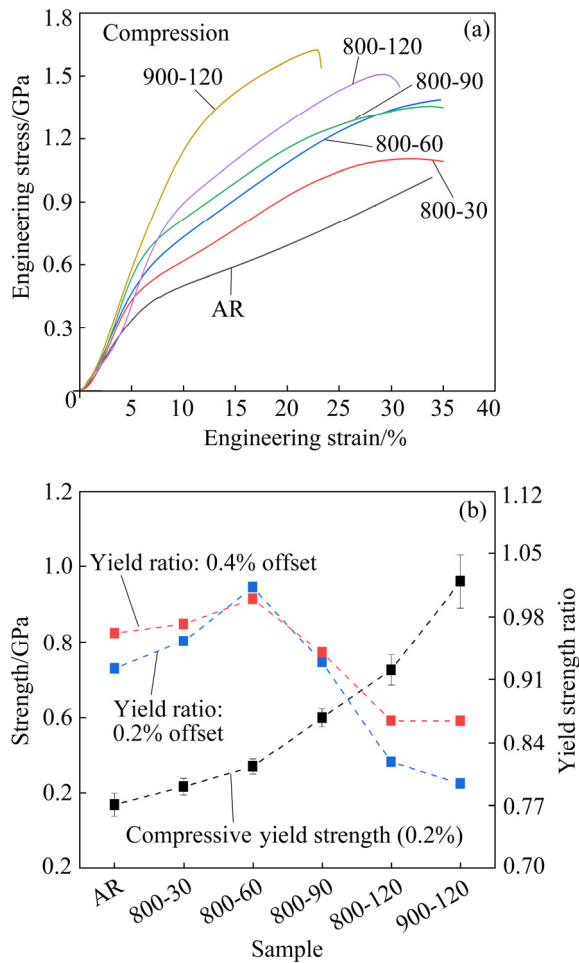


Fig. 6 Compressive engineering stress–strain curves (a), and strength and yield strength ratio (b) of Zr–Ti composites annealed at different temperatures for different time

Asymmetric tension–compression yielding has been reported in many materials, for example, in Mg alloys [33,34]. The activation of twinning is one of the key mechanisms understood to cause asymmetric yielding [35]. Residual stress and microvoids are also believed to be important factors causing asymmetric yielding [36]. For a single CP-Ti or Zr702 rolled sheet with strong basal texture, the tensile yield strength has been reported to be higher than the compressive yield strength when loading along the RD as a result of the activation of tensile twinning in compression [37]. The relatively low critical resolved shear stress and the high Schmid factor for the tensile twinning during the RD compression cause the relatively low compressive strength.

However, in the present study, the tensile yield strength is lower than the compressive yield

strength in all except the 800-60 sample. In the compression of Zr–Ti composites, the activation of the twinning-induced softening effect and the microvoid-induced strengthening effect may compete with each other. The result of this competition determines the tensile–compressive strength ratio. For the AR sample, many sub-grain boundaries and twin lamellae (Fig. 3(a)) exist, which equivalently refine the grain size and are thus not beneficial to the activation of twinning in subsequent compression along the RD [38–40]. The un-balanced mutual diffusion between the Ti and Zr layers (Fig. 2) may lead to some microvoids. The microvoid-closure effect may lead to a higher compressive yield strength compared with the tensile yield strength. In this regard, the tensile–compressive strength ratio is smaller than 1. After annealing at 800 °C for 30 min or 60 min, recrystallization and grain growth occur in the Ti and Zr layers, which is beneficial to the activation of $\{10\bar{1}2\}$ tensile twinning. Many twin lamellae are observed in the 800-30 sample after 10% compression along the RD, as shown in Fig. 7. This demonstrates the activation of twinning during the compression of Zr–Ti composites along the RD.

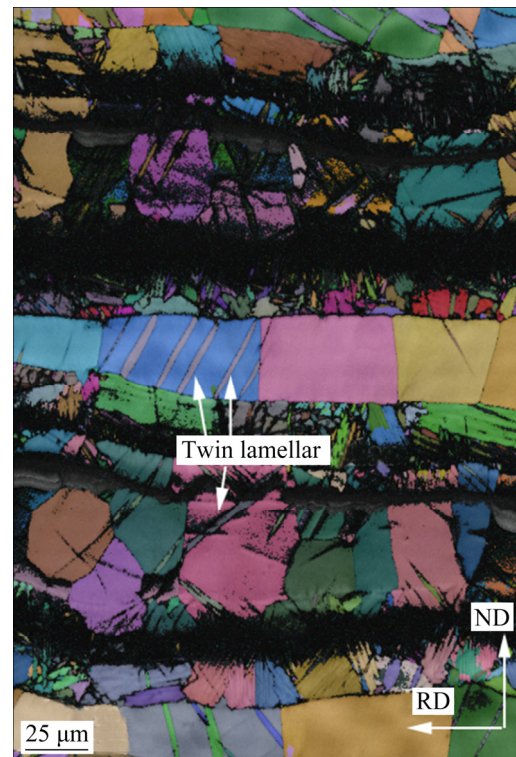


Fig. 7 Microstructures of 800-30 sample after 10% compression along RD

The twinning-induced softening and microvoid-closure-induced hardening in compression may balance each other, thus leading to almost the symmetric yielding between the tension and compression, as shown in Fig. 6(b). With further increase of annealing time or temperature, a higher fraction of the microstructure in the interface layer is refined due to $\beta \rightarrow \alpha$ phase transition, which is not beneficial to the activation of twinning. The microvoid-closure-induced hardening may cause a higher compressive yield strength, thus leading to a smaller tensile–compressive yield strength ratio.

3.4 Deformation behavior

The distributions of the strain (the strain component along the loading direction calculated using DIC) on the RD–TD plane of Zr–Ti composites at different loading stages are presented in Fig. 8. The yielding stage, the ultimate tensile stage, and the fracture stage are determined according to the tensile engineering stress–strain curves (Fig. 5). The results in Fig. 8 show that the strain is relatively homogeneous on the RD–TD plane at the yielding stage. The strain starts to concentrate at the ultimate tensile stage in many samples. Except for the 900-120 sample, strong strain localization (necking) is observed in the fracture stage. The strain localization before fracture in the 900-120 sample is not obvious, indicating a brittle fracture. Since two-dimensional strain was captured using DIC, the strain anisotropy (r), defined as the ratio of the strain rates along the

width and thickness directions of the tensile sample [41], can be calculated. This is often calculated using $r = \varepsilon_W / \varepsilon_T$, where ε_W and ε_T are the accumulated strain values along the width and thickness directions, respectively. The average r values for the AR, 800-30, 800-60, and 800-90 samples are 2.70, 1.44, 1.38, and 1.03, respectively. Average r values for the 800-120 and 900-120 samples are not presented here since their uniform deformation is too small to get a reliable value. The r value is one of the factors indicating the anisotropy of a material; the farther it deviates from 1, the larger the anisotropy is. The decrease in r with increasing annealing time demonstrates a reduction in the degree of anisotropy. This implies that the solid solution of Ti in the Zr matrix or vice versa can reduce the anisotropy.

To evaluate the contributions of different layers to the deformation during tension test, the thicknesses of the Ti, Zr, and interface layers at different distances from the fracture surface were examined for the 800-30, 800-60, and 800-90 samples based on the EDS results. In the present study, a periodic layer thickness is defined as the width from the center of a Ti layer to the center of the nearest Zr layer. The periodic layer thicknesses at different distances from the fracture for different samples are presented in Fig. 9(a). It can be seen that, as a result of tensile deformation and necking, the periodic layers are thinner when they are closer to the fracture surface. The area fractions of the Ti, Zr, and interface layers in the three different

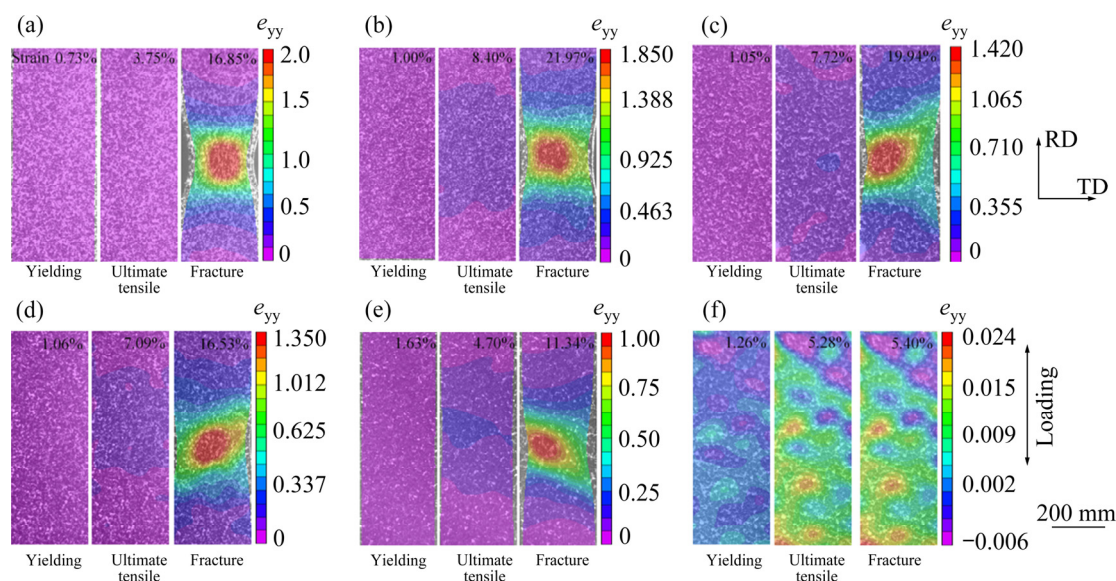


Fig. 8 Distributions of strain on RD–TD plane of Zr–Ti composites at different loading stages (e_{yy} is strain component along RD): (a) AR; (b) 800-30; (c) 800-60; (d) 800-90; (e) 800-120; (f) 900-120

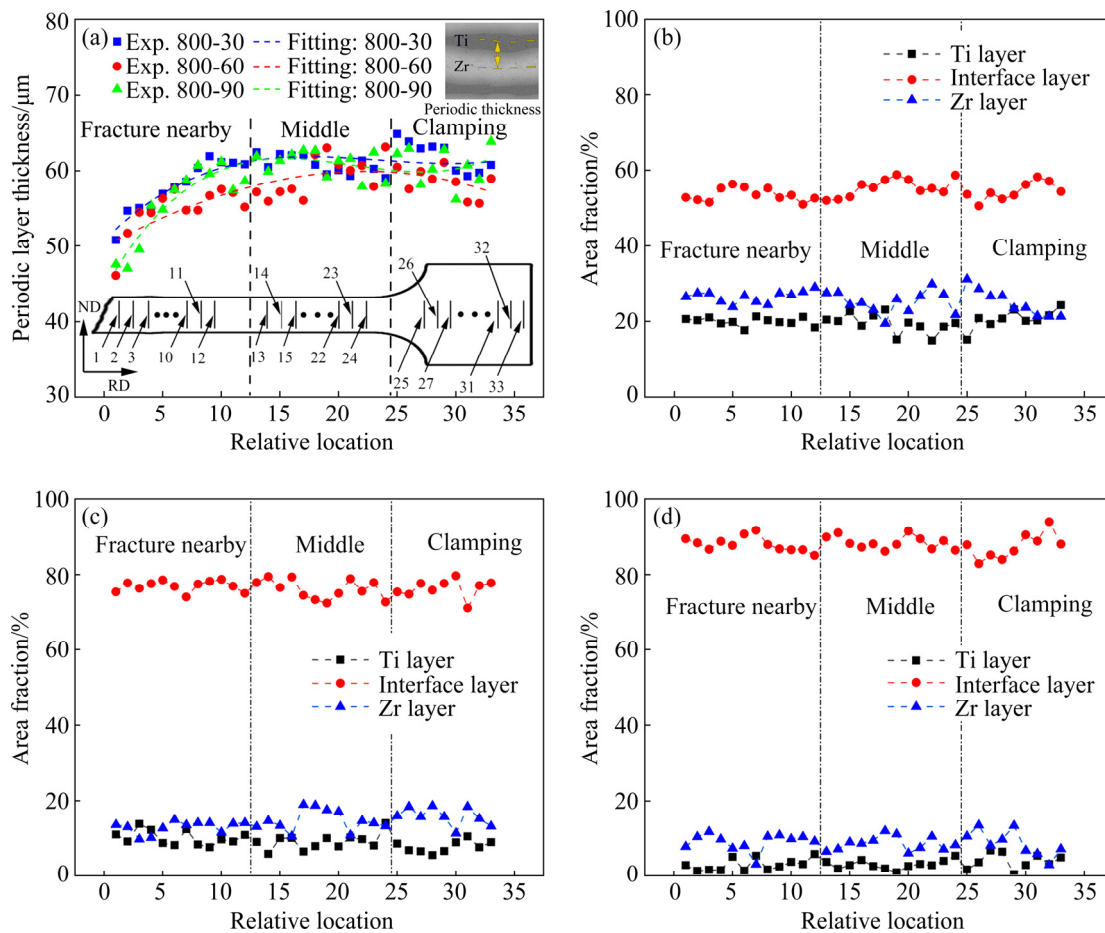


Fig. 9 Periodic layer thickness at different locations with respect to fracture (a), and area fractions of Ti, Zr, and interface layers in 800-30 (b), 800-60 (c), and 800-90 (d) samples

samples are displayed in Figs. 9(b–d). It can be seen that area fraction of the interface layers gradually increases with increasing annealing time. However, the area fraction of each layer does not obviously change with the relative location from the fracture surface. This implies that the macroscopic deformations among the Ti, Zr, and interface layers are almost identical during tension along the RD.

In the 900-120 sample, all Zr and Ti layers are consumed by the interface layer. In other words, the 900-120 sample is completely composed of interface layer. The tensile elongation of the 900-120 sample (interface layer) is $\sim 4\%$, which implies that interface layers (a solid solution of Ti and Zr) are intrinsically brittle. However, it is interesting to note that the interface layers in the 800-30, 800-60, and 800-90 samples exhibit almost the same deformation as the overall deformation. The nominal deformations (tensile elongation) of the 800-30, 800-60, and 800-90 samples are $\sim 20\%$, $\sim 19\%$, and $\sim 16\%$, respectively. This implies that the

Zr–Ti composites composed of alternating Zr/interface/Ti layers can bear much higher deformation than a composite consisting of only interface layers (900-120 sample). This may be attributed to the constraint effect in the layered materials. It has been reported that brittle intermetallic Ti–Al and martensite can bear obvious plastic deformation under the constraint of ductile layers [42,43].

3.5 Fracture behavior

Figure 10 shows the tensile fracture surface morphologies of Zr–Ti composites. The layered gradient Zr–Ti composites show periodic fracture characteristics except for the 900-120 sample. The fracture morphology of the 900-120 sample is relatively homogeneous, and the image looks like that obtained from the fracture of a homogeneous material. In addition, many dimples are observed on the fracture surface of Zr–Ti composites except for the 900-120 sample, indicating ductile fracture in

these samples. The fracture morphology of the 900-120 sample is a typical cleavage fracture, indicating a brittle fracture. The microscopic characteristics of the tensile fracture surface agree well with the elongation and strain distributions measured using DIC (Figs. 5 and 8).

Longitudinal sections near the fracture of Zr–Ti composites are shown in Fig. 11. Through comparative analysis between Figs. 10 and 11, it can be seen that cracks near the layer interface cause the periodic fracture morphology in the AR

sample. Cracks mainly occur at the interface between the Ti and Zr layers during tension along the RD, which may be related to the residual stress formed in the hot-rolling bonding and subsequent cooling process. High residual stress may cause earlier cracking during tension. After annealing at 800 °C, cracks mainly occur at the central part of the Zr layers during tension along the RD, as shown in Figs. 11(b–e). The interface layers are assumed to be less ductile than the Zr layers, as evidenced from the elongations measured for the raw Zr702

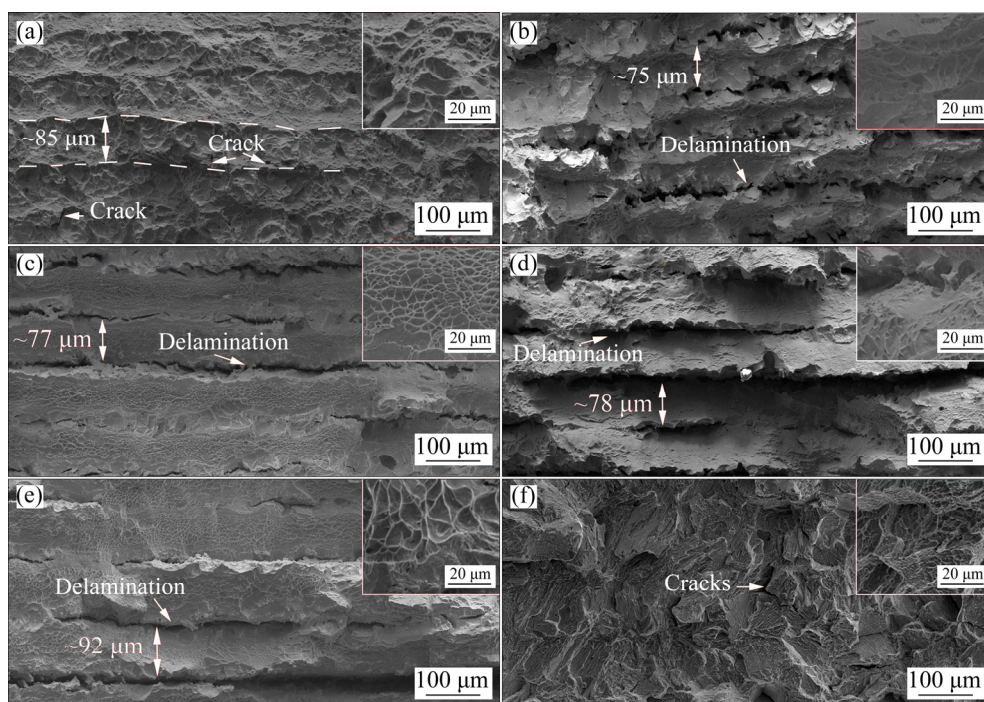


Fig. 10 Tensile fracture surface morphologies of Zr–Ti composites after annealing at different temperatures for different time: (a) AR; (b) 800-30; (c) 800-60; (d) 800-90; (e) 800-120; (f) 900-120

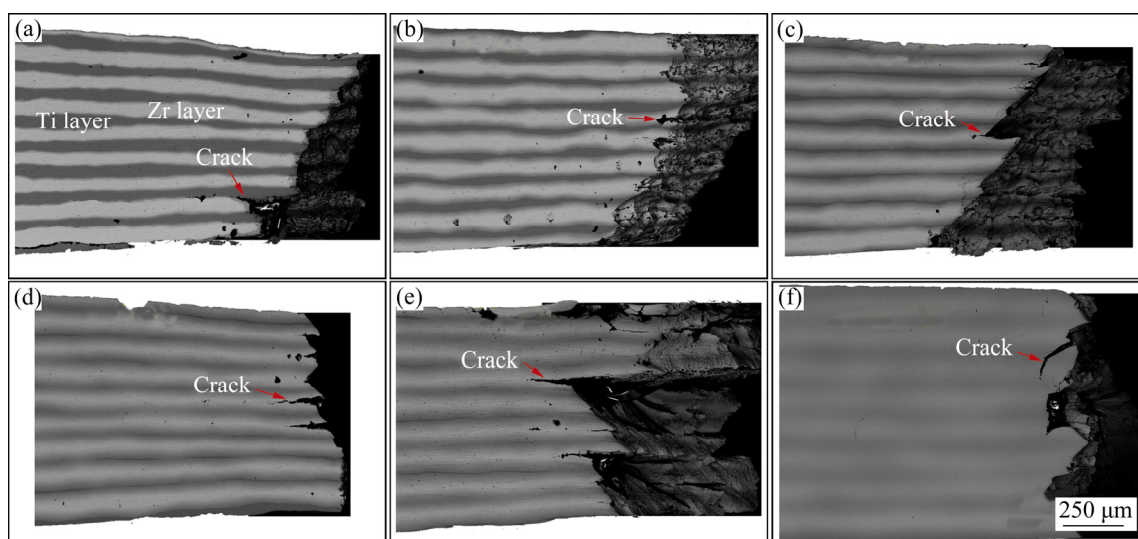


Fig. 11 Side sections of different Zr–Ti composites after tension: (a) AR; (b) 800-30; (c) 800-60; (d) 800-90; (e) 800-120; (f) 900-120

sheet and the 900-120 sample. The cracks mainly propagate in the Zr layers rather than the interface layers, which may be attributed to the relatively high impurity content in the raw Zr702 sheets used, for example, Hf and Fe. Further work needs to be undertaken to reveal the detailed mechanism.

Here, we propose a periodic width parameter, which is defined as the distance between two nearby delaminations (or interfaces with high crack concentrations). The periodic width in the AR sample is $\sim 85\ \mu\text{m}$, as indicated in Fig. 10. After annealing at $800\ ^\circ\text{C}$ for 30 min, the periodic width parameter decreases, which should be caused by larger deformation before fracture, as evidenced by the higher tensile elongation shown in Fig. 5. With the further increase of annealing time and temperature, the periodic width gradually increases due to the decreasing deformation before fracture.

4 Conclusions

(1) Annealing at $800\ ^\circ\text{C}$ can cause obvious mutual diffusion between the Ti and Zr layers, which leads to the formation of interface layers. After annealing at $900\ ^\circ\text{C}$ for 120 min, the interface layers consume all of the Zr and Ti layers.

(2) Compared with the AR sample, annealing will strengthen the Zr–Ti composites as a result of solid-solution strengthening and microstructure refinement through $\beta \rightarrow \alpha$ phase transition-induced strengthening in the interface layers.

(3) Annealing at $800\ ^\circ\text{C}$ for 60 min makes the best static toughness among all annealing conditions used in the current study, which may be attributed to the production of an optimized layer thickness.

(4) In isolation, the solid solution (the interface layer) between Zr and Ti is brittle. However, it can bear large plastic deformation under the constraint of ductile Ti and Zr layers.

(5) The tension–compression asymmetry is observed in the Zr–Ti composites, which may be related to twinning and microvoids.

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Zr–Ti 层状梯度复合材料的退火硬化和变形行为

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摘 要: 为了探寻潜在的强化途径, 采用热轧及退火复合法制备 Zr–Ti 层状梯度复合材料。利用 SEM–EDS 和 EBSD 对复合材料的显微组织进行表征, 并通过单轴拉伸和压缩试验对其力学性能进行测试。研究表明, Zr–Ti 复合材料由交替的 Zr 层/扩散层/Ti 层组成, 扩散层中 Zr、Ti 元素成分呈梯度分布。与轧制态复合板相比, 退火可显著提高 Zr–Ti 复合材料的强度, 其主要机制是扩散层的固溶强化和组织细化诱导强化; 与原始材料相比, Zr–Ti 复合材料的强度和延性得到协同提高, 这可能与特殊层状梯度结构有关。对比拉伸与压缩性能发现, Zr–Ti 复合材料中存在拉、压不对称现象, 这可能与孪生变形和非对称扩散引起的微孔有关。

关键词: Zr–Ti 层状结构材料; 扩散退火强化; 拉–压非对称屈服; 塑性

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