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Bonding enhancement of cold rolling TA1 P-Ti/AA6061 composite plates via surface oxidation treatment

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Abstract: TA1 P-Ti/AA6061 composite plate was produced by oxidizing the surface of the titanium plate and adopting a cold roll bonding process. The results revealed that the oxide film (Ti_6O) prepared on the surface of TA1 pure titanium was easy to crack during the cold roll bonding, thereby promoting the formation of an effective mechanical interlock at the interface, which can effectively reduce the minimum reduction rate of the composite plates produced by cold rolling of titanium and aluminium plates. Moreover, the composite plate subjected to oxidation treatment exhibited high shear strength, particularly at a 43% reduction rate, achieving a commendable value of 117 MPa. Based on oxidation treatment and different reduction rates, the annealed composite plates at temperatures of 400, 450, and 500 °C displayed favorable resistance to interface delamination, highlighting their remarkable strength−plasticity compatibility as evidenced by a maximum elongation of 31.845%.

Key words: TA1 P-Ti/AA6061 composite plate; oxidation treatment; annealing treatment; cold roll bonding

1 Introduction

The TA1 pure titanium/AA6061 aluminium alloy (TA1 P-Ti/AA6061) composite plates prepared in this study are one of the representative bimetallic composite plates. TA1 P-Ti possesses commendable attributes such as corrosion resistance, heat resistance, and low-temperature resistance [1]. AA6061 is recognized for its high specific strength, lightweight nature, and cost-effectiveness [2−4]. TA1 P-Ti/AA6061 composite plates achieve the combination of the advantages of the two materials. For instance, they have practical application in the construction of ship exterior structures.

The main methods for producing Ti/Al composite plates are explosive welding [5−7] and the rolling method [8−11]. Explosive welding is a straightforward process that does not impose strict requirements on plate size or surface cleanliness. For example, WU et al [7] used AA1060 as the interlayer to prepare TA2/AA1060/AA5083 composite plates by explosive cladding. Shear tests indicated a shear strength of 110 MPa at the TA2/AA1060 interface. But the explosion creates a high level of noise, emits toxic gases and pollutants, and diminishes dimensional accuracy in the resulting composite plates. For the rolling composite method, the previous research usually used hot roll bonding and differential temperature rolling processes, but both of which suffer from drawbacks. For the hot roll bonding method, the disparity in deformation resistance between titanium and aluminium plates increases after heating [2], and the brittle intermetallic compounds (IMCs) that affect the bonding strength will easily

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be formed at the higher temperature of the interface [12−15]. The generation and type of IMCs are uncontrollable. Therefore, it is difficult to prepare composite plates with good bonding properties through hot roll bonding. For example, CAO et al [16] annealed the Ti/Al/Ti laminated composites prepared by hot pressing and hot rolling at 200−600 °C, and revealed that the interfacial bonding strength reached the peak at 400 °C, with a peeling strength of 19.8 N/mm. At the annealing temperature above 400 °C, the thickening of the $TiAl_3$ phase at the interface decreased. To address these challenges, researchers have explored different temperature rolling processes [11,17]. For example, QI et al [8] rolled Ti/Al composite plates by heating titanium plates at different temperatures separately. When the titanium layer was heated to 800 °C with a rolling reduction rate of 40%, the interfacial shear strength of composite plates was about 75 MPa. However, in theory, it is difficult to control temperature distribution during the production process due to the high thermal conductivity of aluminium plates, which often leads to temperature equalization between the titanium and aluminium plates before entering the rolls, thus increasing the difficulty of rolling production. Therefore, recent research has shifted the key process of different material composites towards cold roll bonding. However, composite plates produced by cold roll bonding (CRB) typically exhibit low bonding strength. For example, LIU et al [18] found that the critical reduction rate of Ti/Al cold rolling is 40%. The interfacial shear strength will exceed 55 MPa when the reduction rate surpasses 46.8%. Therefore, it is essential to establish favorable composite conditions for the cold-rolling process of titanium and aluminium plates. For example, by artificially creating a wavy interface similar to explosive recombination, LIU et al [9] prepared Ti/Al composite plates using a two-pass CRB process. The first pass involved a combination of corrugated roll (upper roll) + flat roll (lower roll), followed by a flat roll pass. The mechanism analysis demonstrated that the large strain change at the wave trough was conducive to the fracture of the hardened layer and the exposure of fresh metal, thereby benefiting the bonding of the interface.

The purpose of this paper is to form a mechanical occlusive morphology at the interface after rolling and subsequently produce a composite plate with high bonding strength through annealing. In the cold rolling process of dissimilar metals with large differences in properties, the composite mechanism typically involves the fracture of the hardened layer on the hard metal surface, the piercing of soft metal, the exposure of fresh metal, and subsequent squeezing contact, thus forming an effective mechanical lock to achieve the purpose of preparing composite plates. Annealing treatment further enhances the mechanical properties of composite plates. Therefore, the difficulty of the new process described in this paper is how to form a suitable hardened layer on the surface, which can form an effective mechanical lock after rolling. In this study, the thickness of the oxide film is controlled by regulating the oxidation temperature and duration, capitalizing on the titanium's inherent susceptibility to oxidation. A layer of oxide film is prefabricated on the surface of titanium plate to make it have a strong bonding property with the substrate, and this oxide film readily fractures during the rolling process, facilitating the formation of mechanical lock. Therefore, it is anticipated that the oxide film on the titanium plate surface serves as a favorable element, thus reinforcing the interface bonding.

In this study, an innovative method was proposed to prepare oxide films on the surface of titanium by heating titanium plates at a constant temperature of 500 °C. After that, TA1 P-Ti/AA6061 composite plates were prepared by the CRB process. Then, the bonding properties and interfacial morphologies after rolling were compared between the pre-rolling surface oxidation treatment process (G-500 °C/10 min) and the non-oxidation treatment process, and the mechanism by which the tensile properties of the composite plates are improved by annealing under the oxidation treatment process was investigated. This study is expected to provide new insight into the environmentally friendly and efficient preparation of Ti/Al composite plates.

2 Experimental

The TA1 P-Ti was selected for experimental cladding, and AA6061 was selected as the substrate.

Table 1 Chemical compositions of raw materials

Material	Content/wt.%												
	C	Si	Mn	O	N	H	Cu	Mg	Zn	Cr	Fe	Ti	Al
TA1 P-Ti	0.05	0.1	−	0.15	0.03	0.015	−	−	−	−	0.15	Bal.	−
AA6061	−	0.61	0.15	−	−	−	0.28	1.05	0.25	0.19	−	0.15	Bal.

The chemical compositions of the materials are listed in Table 1. Both AA6061 and TA1 P-Ti plates had a thickness of 2 mm. The stress−strain curves of the original materials are shown in Fig. 1. AA6061 exhibited an ultimate tensile strength of 337.30 MPa and an elongation of 15.94%, whereas TA1 P-Ti showcased an ultimate tensile strength of 429.24 MPa and an elongation of 42.10%.

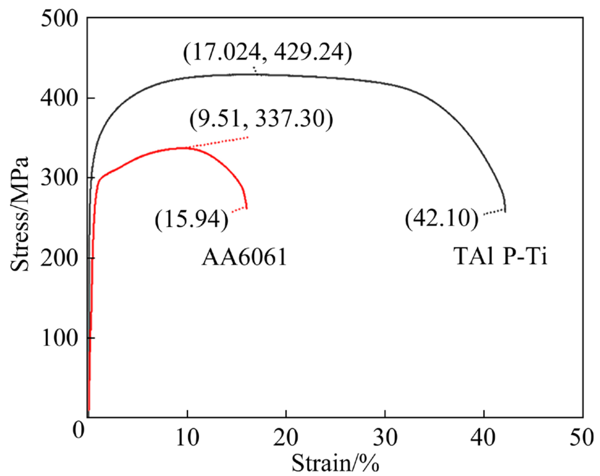

Fig. 1 Stress−strain curves of AA6061 and TA1 P-Ti

The original pollutants on the metal surface were removed by the process of water bath + manual grinding. The abrasive belt of a particle size was 80 μm. This meticulous procedure effectively controlled the temperature rise and reduced the grinding speed, mitigating the potential heating and oxidation of the titanium surface during compounding and enabling the investigation of the influence of the oxide film. The treated materials to be compounded were repeatedly scrubbed with acetone and alcohol, and dried with a cold air blower. The cleaned titanium plates were divided into two groups according to different surface treatment processes. One group was subjected to grinding process (Grinding for short), while the other group received grinding and oxidation in a heating furnace at the constant temperature of 500 °C for 10 min (G-500 °C/10 min for short). The front end of the blank was riveted and the tail end was bound with iron wire (Fig. 2). The dimensions of the assembled blank were 100 mm in length, 30 mm in width, and 4 mm in height. The CRB process was employed using upper and lower rolls with a diameter of 200 mm, a rolling speed of 50 mm/s, and actual rolling reductions of 30%, 35%, 40%, and 43%. The rolled composite plates were divided into two batches, one before annealing and the other after annealing, for further analysis. Annealing was conducted for 1 h at temperatures of 400, 450, and 500 °C respectively, followed by cooling in the furnace.

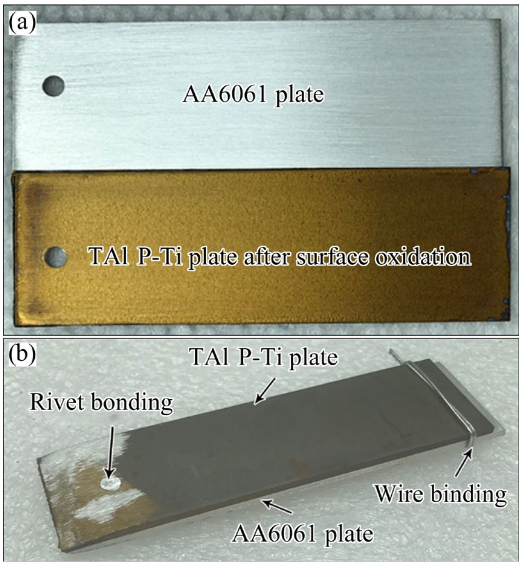

Fig. 2 Materials preparation before cold roll bonding: (a) Physical drawing of TA1 P-Ti plate surface oxidation; (b) Physical drawing of blank assembly

TA1 P-Ti/AA6061 composite plates were prepared under each process. Three shear specimens and three tensile specimens were cut along the rolling direction of each composite plate. In addition, the shear properties were tested on an Inspekt table 100 kN high-temperature universal testing machine according to Chinese Standard GB/T 6396—2008, as shown in Fig. 3(a), with a shear rate of 0.5 mm/min. The tensile properties were tested on a Zwick 100 kN electronic universal material testing machine according to Chinese Standard GB/T 228.1—2010. The size of tensile test piece is shown in Fig. 3(b), and a tensile rate of 0.01 mm/min was employed.

The oxide film on the surface of the titanium plate was preliminarily analyzed by X-ray diffraction (XRD, Bruker D8 Advance), and the metallographic specimens at the bonding interface of the composite plates were cut parallel to the rolling direction. The interface morphology was characterized and analyzed by nanoindentation (U9820A Nano Indenter G200) and electron probe micro-analyzer (EPMA, EPMA−8050G). The shear and tensile fracture morphologies were observed by scanning electron microscopy (SEM-Zeiss sigma 700), and the elemental distribution of the shear fracture was analyzed by energy dispersive spectrometer (EDS). The characterization and analysis of the characteristic interfaces of the annealed composite plates were completed by scanning transmission electron microscopy (STEM-FEI-Talos f200x).

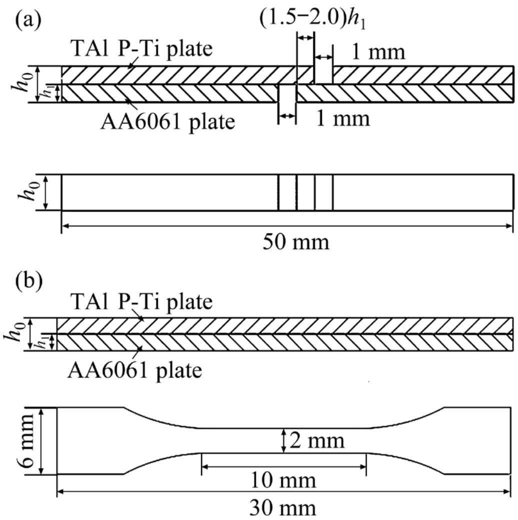

Fig. 3 Specimen dimensions for mechanical property test: (a) Shear specimen; (b) Tensile specimen

3 Results

3.1 Oxide film microstructure and shear strength

The titanium plate underwent oxidation in a heating furnace at a constant temperature of 500 °C for 10 min, followed by XRD analysis of the surface of the oxidized titanium plate. It was uncovered that a Ti_6O oxide film formed on the surface of the oxidized titanium plate, as shown in Fig. 4. In order to further accurately determine the composition and thickness of the oxide film, a high-resolution image of the oxide film position was analyzed. Moreover, according to the results of diffraction spot calibration after Fourier transform, a Ti_6O oxide film with a thickness of 26.75 nm was formed on the titanium plate surface in the oxidation process, as shown in Fig. 5.

In the two surface treatment processes, namely, Grinding and G-500/10 min, the shear strength of TA1 P-Ti/AA6061 composite plates obtained after CRB at different reduction rates is illustrated in Fig. 6. Through analysis and comparison of data

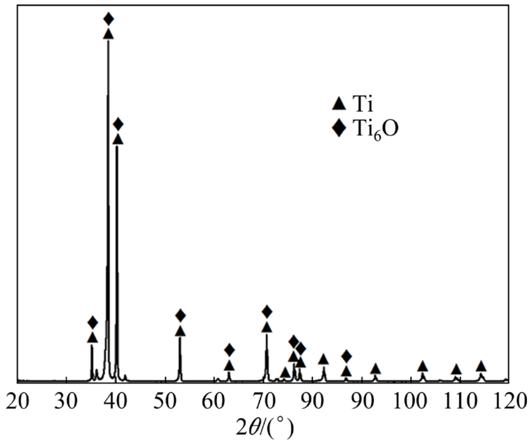

Fig. 4 XRD pattern of oxidized titanium plate surface

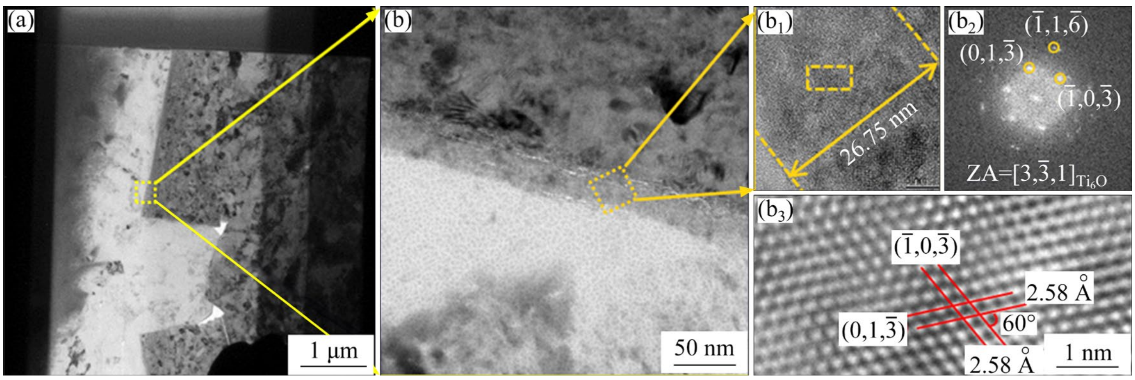

Fig. 5 TEM images of oxide film: (a) TEM bright field image; (b, b_1) Local HRTEM images; (b_2) FFT image; (b_3) Inverse FFT image

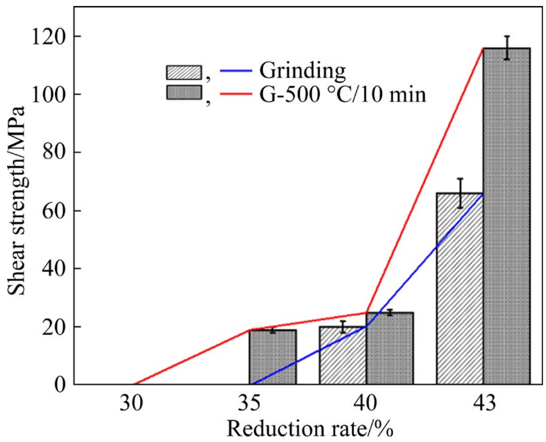

Fig. 6 Shear strength of composite plate before annealing

shown in Fig. 6, it could be concluded that the minimum reduction rate of the composite plates produced by the grinding pre-treatment process was 40%, while the G-500 °C/10 min pre-treatment process produced effective bonding at the reduction rate of 35%, achieving a 5% reduction rate lower than that of the cold rolled composite plates. With the increase of the reduction rate, the shear strength of the composite plates was enhanced under both processes. When the reduction rate was 43%, the shear strength of the Grinding and G-500 °C/10 min processes was 66 and 117 MPa, respectively. The strength comparison results also manifested that the G-500 °C/10 min process significantly enhanced the bonding strength of the composite plates. Compared with the research results reported in the introduction, the G-500 °C/10 min process could effectively reduce the reduction rate for cold rolling and obtain the highest bonding strength (117 MPa) at a reduction rate of 43%.

3.2 Bonding mechanism of TA1 P-Ti/AA6061 composite plate before annealing

As unveiled by the aforementioned shear strength analysis results, oxidation treatment of the titanium plate surface before rolling could effectively reduce the rolling reduction rate, and the shear strength at the reduction rate of 43% was significantly different from that in the Grinding process. Therefore, the research focus shifted to the investigation of the micro-morphology of the interface and the shear fracture of the composite plates at a reduction rate of 43% without annealing.

EPMA results manifested that the interface of the TA1 P-Ti/AA6061 composite plates (Grinding process) presented a wavy and weak mosaic morphology. Previous studies [5,9] have illustrated that the bonding strength of the wavy bonding interface in the composite plate is higher than that of the straight interface, indicating that the process contributes to good bonding strength, as shown in Fig. 7(a). However, the interface of the TA1 P-Ti/AA6061 composite plates (G-500 °C/10 min)

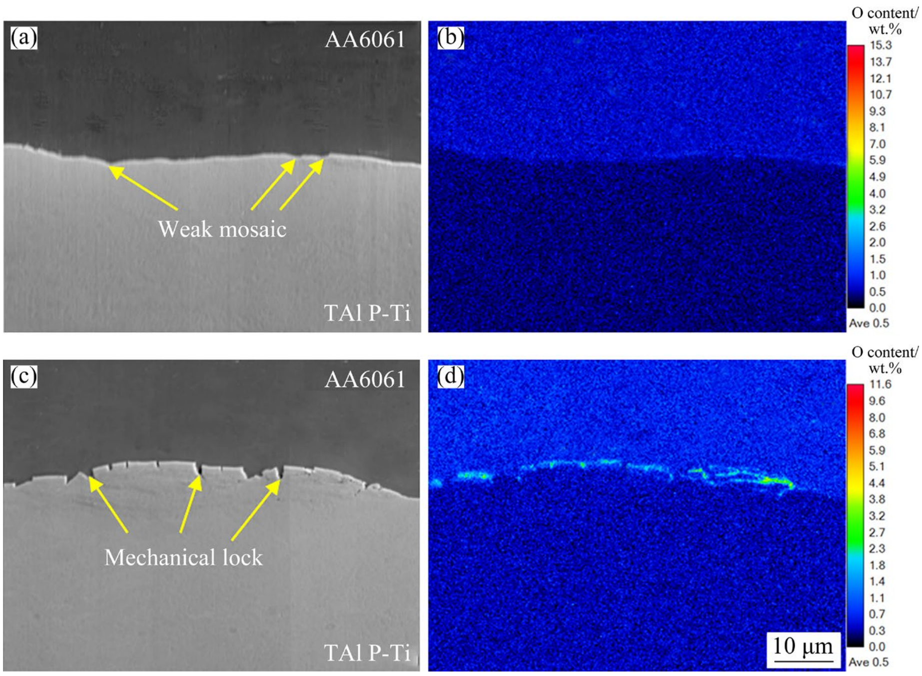

Fig. 7 EPMA analysis results: (a, b) Grinding process interface morphology and O element mapping, respectively; (c, d) G-500 °C/10 min process interface morphology and O element mapping, respectively

process displayed obvious mechanical lock and wavy characteristics, including the intermittent inlay of long blocks on the titanium side and the inlay of fine cracks on the long blocks, as shown in Fig. 7(c). Additionally, the energy spectrum analysis of O elements under both processes denoted that there was no obvious distribution of O elements at the interface under the Grinding process before rolling, as shown in Fig. 7(b). In contrast, the G-500 °C/10 min process prior to rolling exhibited intermittent distribution of O elements at the interface, with fracture bulges observed in the titanium matrix at locations of high O content. This observation indicates that the depressed region within the crack corresponds to the contact location of fresh metal exposed during the CRB process, as shown in Fig. 7(d). The above morphological analysis results combined with the shear strength comparison results confirmed that the interface showing mechanical occlusion was more conducive to improving the bonding strength of the composite plates than the corrugated interface in the preparation of the composite plates by the CRB process.

In order to further elucidate the phenomenon that mechanical locks were easily formed at the interface of the oxidized titanium plate through rolling, microscopic characterization of the hardness at characteristic locations was performed by nanoindentation under both processes, as shown in Fig. 8. The nanoindentation results under the pre-rolling Grinding process indicated hardness values of 6.282 GPa at the crest and 5.192 GPa at the trough of the wave-like interface, as shown in Figs. 8(a) and (c). The results manifested that during the rolling process, the matrix near the interface underwent significant deformation under the action of rolling force, which led to the increased hardness in the vicinity of the interface. However, due to the absence of an oxide layer, the metals on both sides only exhibited ductility, making it difficult to form mechanical locks at the interface. This observation aligns with the results of a study by YU et al [19], which highlighted the increased slip system activation at the interface during deformation of Ti/Al composite plates, leading to the enhanced interaction and dislocation storage, thereby contributing to a high work hardening rate at the interface. For the G-500 °C/10 min process before rolling, two types of characteristic areas, namely, the convex and concave areas of the titanium matrix, were selected, and the hardness was measured along the nanoindentation line perpendicular to the interface of the two metals, so

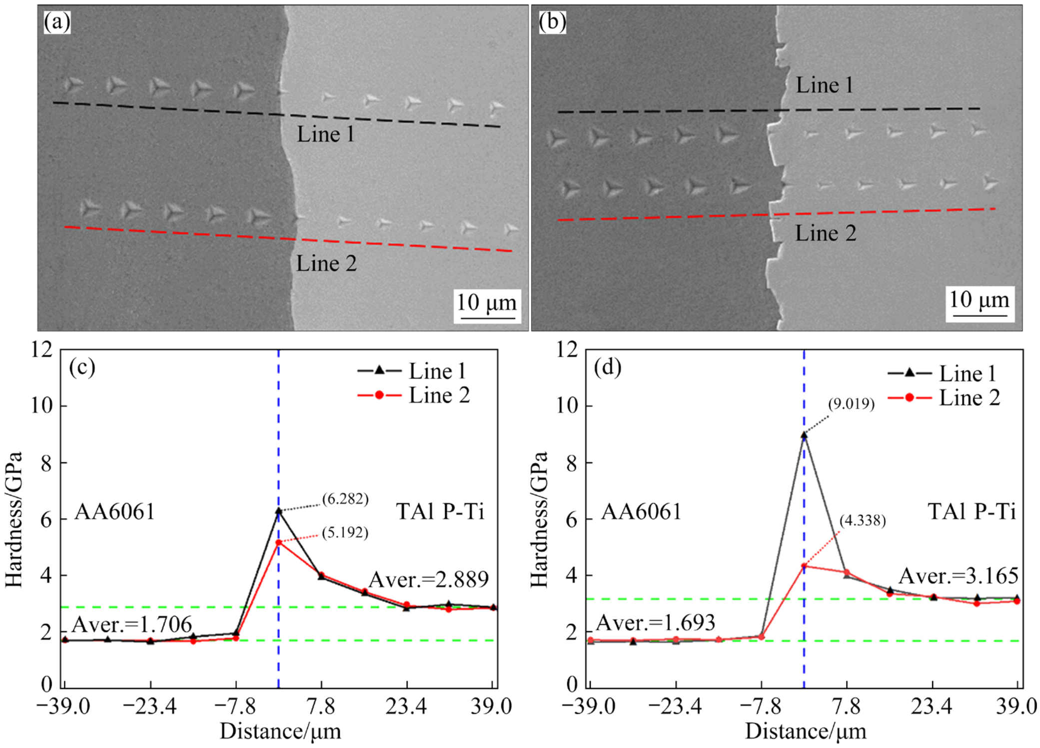

Fig. 8 Morphology (a, b) and hardness (c, d) at interface of TA1 P-Ti/AA6061 composite plates before annealing during nanoindentation: (a, c) Grinding process; (b, d) G-500 °C/10 min process

as to observe the hardness change in the interface area. The results revealed a hardness value of 9.019 GPa for the titanium matrix convex region and 4.338 GPa for the titanium matrix concave region, as shown in Figs. 8(b) and (d). These results demonstrated that oxide film was formed on the surface of the titanium plate under G-500 °C/10 min process before rolling. During rolling, the oxide film fractured, and the crack expanded with the increase of the rolling reduction rate. The aluminium matrix was squeezed into the crack, and the titanium matrix on both sides of the crack was squeezed, so that the titanium-side convex was subjected to the pressure perpendicular to and parallel to the interface. Therefore, the hardness at the bulge of the titanium matrix was relatively high.

In addition, as shown in Fig. 9, the line scan imaging results of the interface position showed that the inter-diffusion distance of Ti and Al elements under the Grinding process before rolling was 1.906 μm. However, the diffusion distance of Ti and Al elements in the non-oxidization region (fresh metal bonding region) reached 2.240 μm under the G-500 °C/10 min process before rolling. The results also proved that the fresh metal exposed due to the fracture of the oxide film could better diffuse after contact, thus improving the bonding strength of the composite plates.

To obtain a comprehensive understanding of the composite mechanism in the two processes, further analysis of the shear fracture morphology was conducted in this study. The shear fracture morphologies of the TA1 P-Ti/ AA6061 composite plates (Grinding process) after CRB before rolling are shown in Fig. 10. It was observed that the aluminium matrix was embedded perpendicularly to the rolling direction, due to the large plastic deformation of the metal on the titanium side along the rolling direction in the rolling process, resulting in cracks perpendicular to the rolling direction. The aluminium matrix with high fluidity filled the cracks on the titanium side through the effect of the rolling force, thus forming a mechanical lock, which reflected the weak mosaic morphology of the interface. In addition, in the shearing process, the aluminium matrix was stretched and then ductile fracture occurred, as shown in Fig. 10(a). This was accompanied by the formation of a ridge-shaped morphology formed by the fracture parallel to the rolling direction on the aluminium-side fracture, as shown in Fig. 10(e).

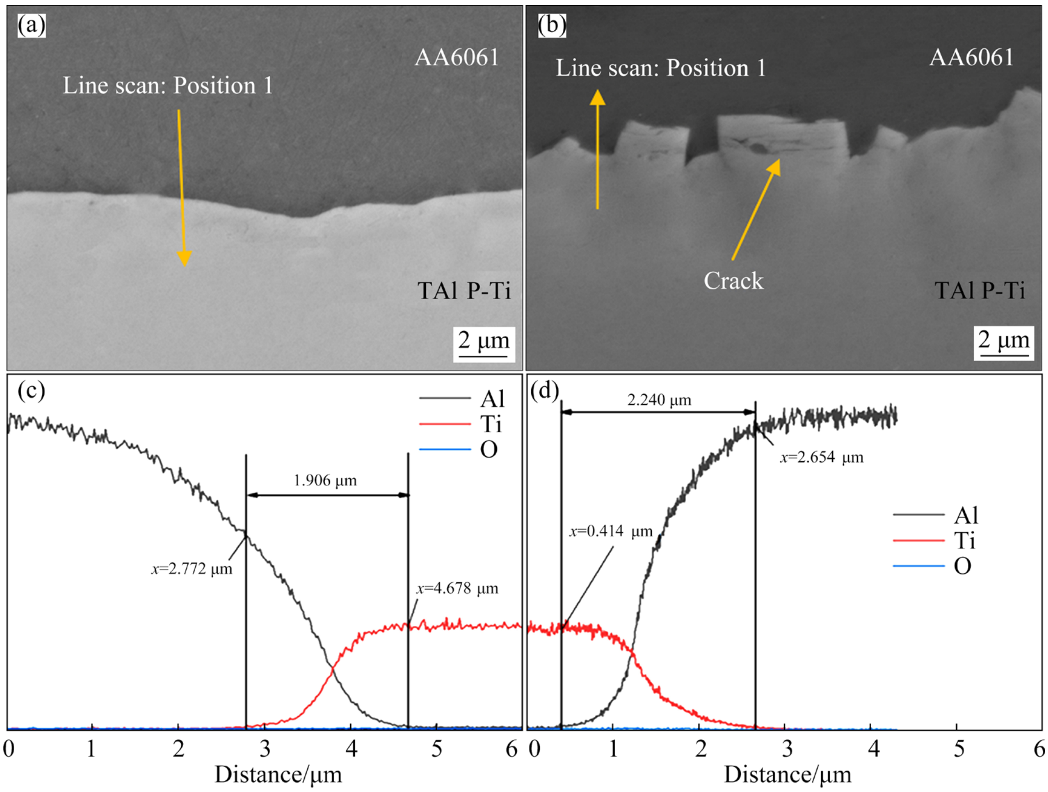

Fig. 9 Morphological images (a, b) and line scan data (c, d) at interface of TA1 P-Ti/AA6061 composite plates before annealing: (a, c) Grinding process; (b, d) G-500 °C/10 min process

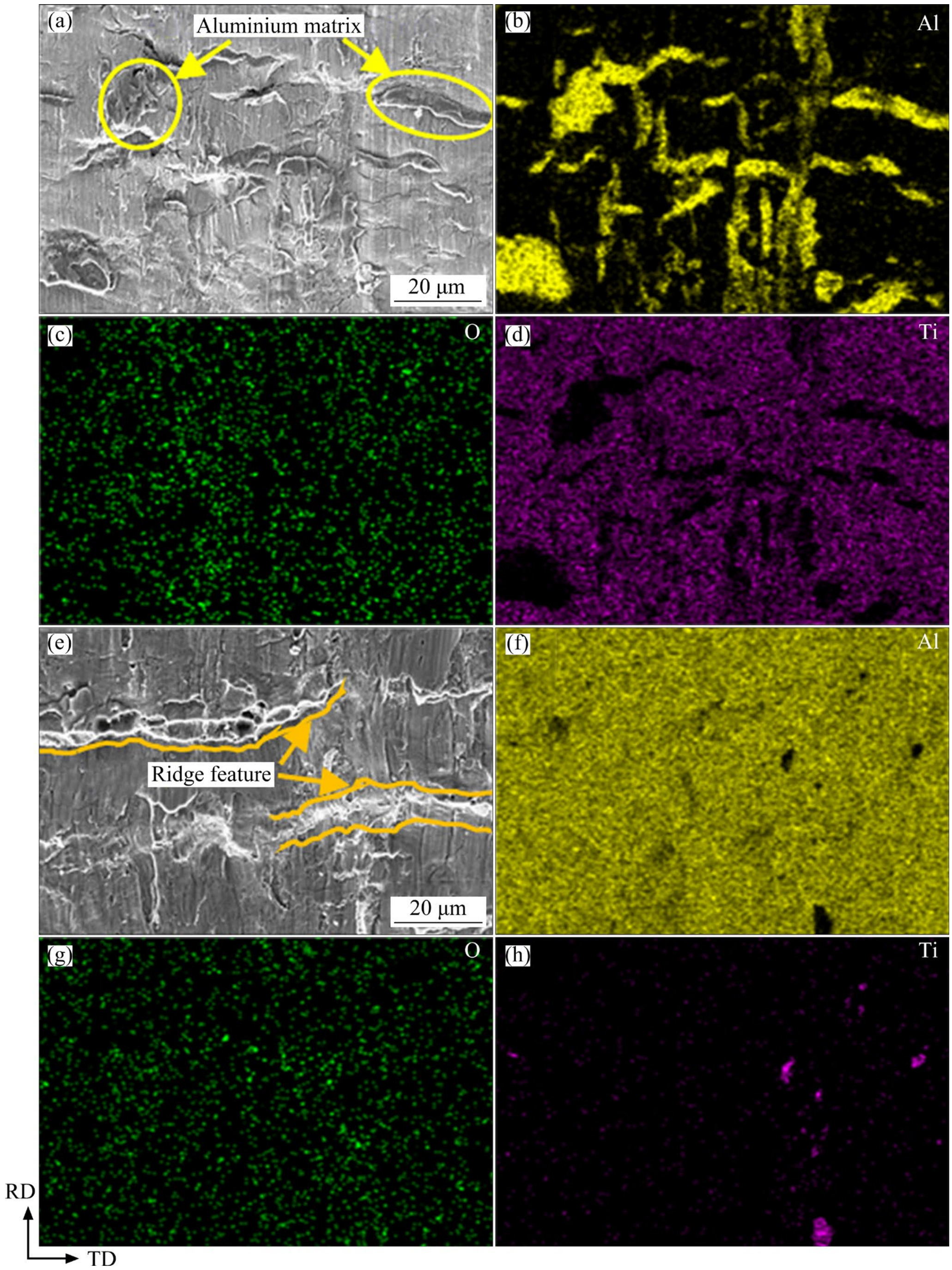

Fig. 10 Shear fracture morphologies of TA1 P-Ti/AA6061 composite plate under Grinding process: (a−d) Shear section and EDS mappings on TA1 P-Ti side; (e−h) Shear section and EDS mappings on Al side

The shear fracture morphologies of the TA1 P-Ti/AA6061 composite plates under G-500 °C/ 10 min process after CRB are shown in Fig. 11. It was found that the titanium side displayed a more obvious fracture and had a large area of mechanical lock. These mosaic aluminium matrixes were perpendicular to the rolling direction or at an angle of 45° to the rolling direction. Moreover, an edge deconstruction fracture and a central ductile fracture were observed on the sheared aluminium matrix, indicating a high bonding strength of the composite plates produced by this process. In addition, dense and numerous cracks perpendicular to the rolling direction were found in the area complementary to the inlaid aluminium matrix (titanium matrix). This phenomenon can be attributed to the oxidation treatment involved in this process, where high-temperature reaction between titanium and oxygen

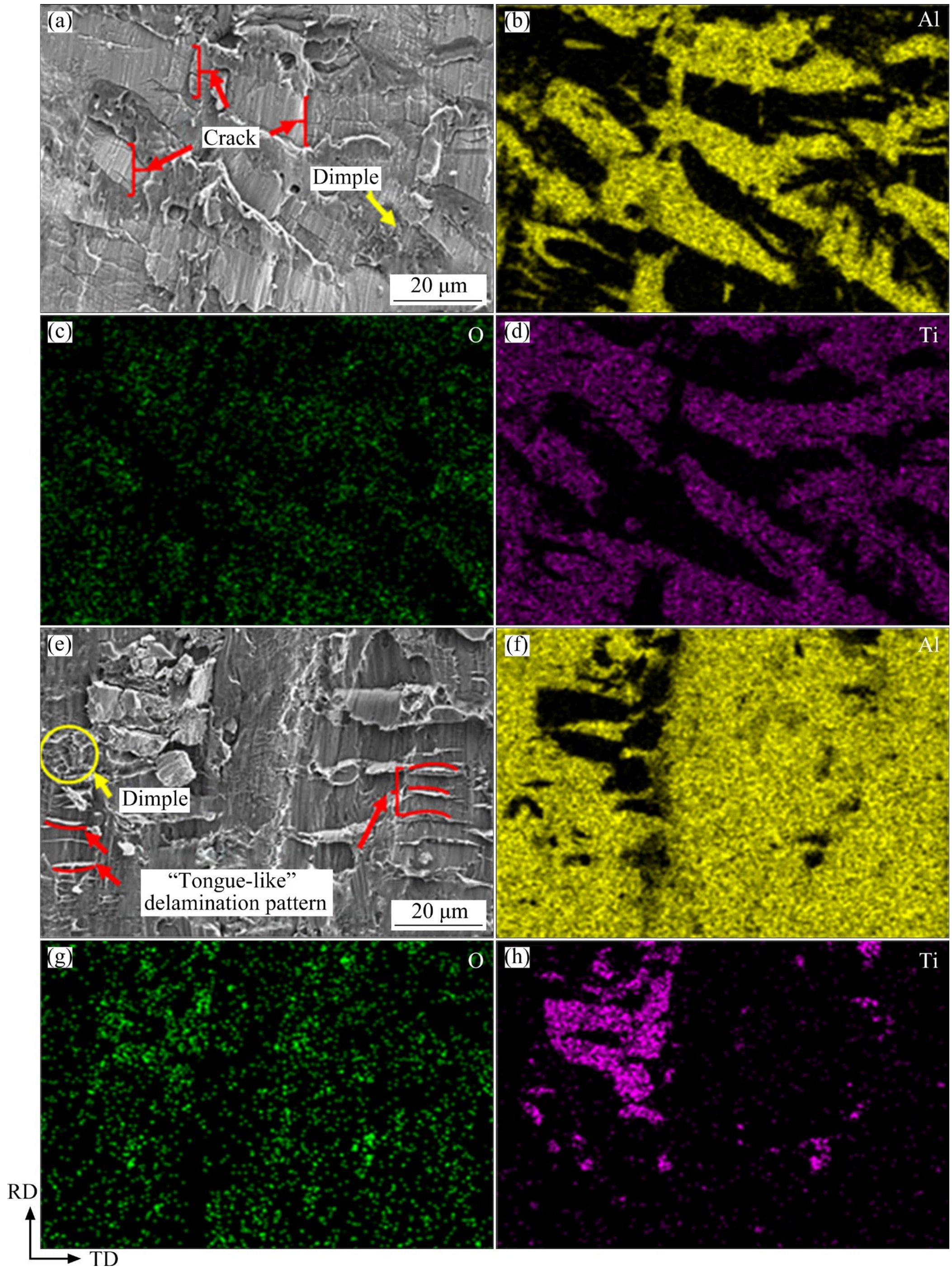

Fig. 11 Shear fracture morphologies of TA1 P-Ti/AA6061 composite plate under G-500 °C/10 min process: (a−d) Shear section and EDS mappings on TA1 P-Ti side; (e−h) Shear section and EDS mappings on Al side

results in surface hardening, rendering the titanium plate susceptible to cracks perpendicular to the rolling direction under the influence of rolling forces, as shown in Fig. 11(a). Furthermore, the Ti and O elemental surface scans also revealed a one-to-one correspondence between Ti and O elements, which also confirmed the occurrence of cracks in the oxidized area on the surface of the titanium plate. On the other hand, the bonding strength between the oxide and the aluminium matrix was low, allowing the shear fracture surface to occur at a position coplanar with the oxide on the titanium side, as shown in Figs. 11(a, c, d). On the aluminium side, the fracture analysis revealed a "tongue-like" delamination pattern corresponding to the aluminium matrix fracture edge on the titanium side, as well as a tough nest feature corresponding to the ductile fracture in the middle of the aluminium matrix fracture. In addition, a spaced distribution of strong occlusions was observed between the titanium-side matrix and the aluminium-side matrix. These findings, in combination with the interface morphology analysis results, confirmed that the aluminium matrix was squeezed into the crack, exerting pressure on the titanium matrix on both sides of the crack. Moreover, in the shearing process of the composite plates, the aluminium matrix penetrated more deeply, and cracks appeared in a few blocks on the titanium side, so that a small number of blocks on the titanium side were sheared and separated from the titanium matrix, and blocks remained in the aluminium-side fracture morphology, as shown in Fig. 9(b) and Figs. 11(a, e).

As revealed by the results of the above fracture analysis, the TA1 P-Ti/AA6061 composite plates (Grinding process) after CRB were observed to form in a direction perpendicular to the rolling. However, these cracks were not dense and could hardly expand along the rolling direction, and the extrusion into the aluminium matrix was limited. For the TA1 P-Ti/AA6061 composite plates (G-500 °C/10 min process) after CRB, the presence of the hardened oxide layer reduced the strain required for crack formation in the direction perpendicular to the rolling. These cracks exhibited higher density and readily expanded under the same compression conditions. The extrusion into the aluminium matrix also increased, leading to the creation of a concave contact area between the fresh matrix metal at the post-rolling interface. This expansion of the matrix contact area ensured the achievement of high bonding strength in the composite plates (G-500 °C/10 min process).

4 Discussion

4.1 Microstructure of annealed TA1 P-Ti/AA6061 composite plates

In order to investigate the effect of annealing on the mechanical properties and microscopic morphology of the TA1 P-Ti/AA6061 composite plates prepared under the G-500 °C/10 min process at a reduction rate of 43%, annealing treatments at temperatures of 400, 450, and 500 °C were conducted. Based on the G-500 °C/10 min pre-treatment process before rolling, the interface micro-morphology of the annealed composite plates was further tested and characterized to gain insights into the fracture behavior of the aluminium matrix in the shearing process. TEM was adopted for the microscopic analysis of the characteristic interface position of the TA1 P-Ti/AA6061 composite plates annealed at 400 °C with a reduction rate of 43%, as shown in Fig. 12.

According to the bright-field images observed at the thin area position and a low magnification, the titanium matrix showed cracks with the depth of 1 μm and the width of 1.5 μm. The aluminium matrix was squeezed into these cracks during rolling. Influenced by factors such as the reduction rate, the aluminium matrix was unable to fill the entire crack, resulting in the presence of about 100 nm-sized voids under higher magnification conditions, as shown in Fig. 12(a). Upon extrusion into the fractures, three contact surfaces of the titanium were in direct contact with the aluminium matrix, enabling element diffusion throughout the annealing process. Additionally, during the shear testing of numerous samples of the titanium−aluminium composite plate under the conditions of a 43% reduction rate and 400 °C annealing temperature, a fracture angle of 55° was observed at the interface between the aluminium matrix and the composite plate, as shown in Fig. 13. At this time, the strength near the interface was higher than that of the aluminium matrix, and the shear fracture occurred at the aluminium matrix, indicating that the existence of voids will not compromise the bonding strength of the interface.

The energy spectra of the non-cracked area (Position 1), the bottom area of cracks (Position 2) and the side area of cracks (Position 3) were analyzed by surface and line scans, as shown in Fig. 12 and Fig. 14, respectively. It could be observed that HAADF images at high magnification and the surface scan results at Position 1 illustrated that Position 1 is the contact area of the oxide film (Ti_6O) on the surface between aluminium matrix and titanium matrix, and the diffusion of Al element in the oxide film, imparts a certain level of bonding strength to the oxidation area, as shown in Figs. 12(c, c_1−c_4). As shown in Fig. 14(a), the line scan results (Line 1) illustrated that the Al element

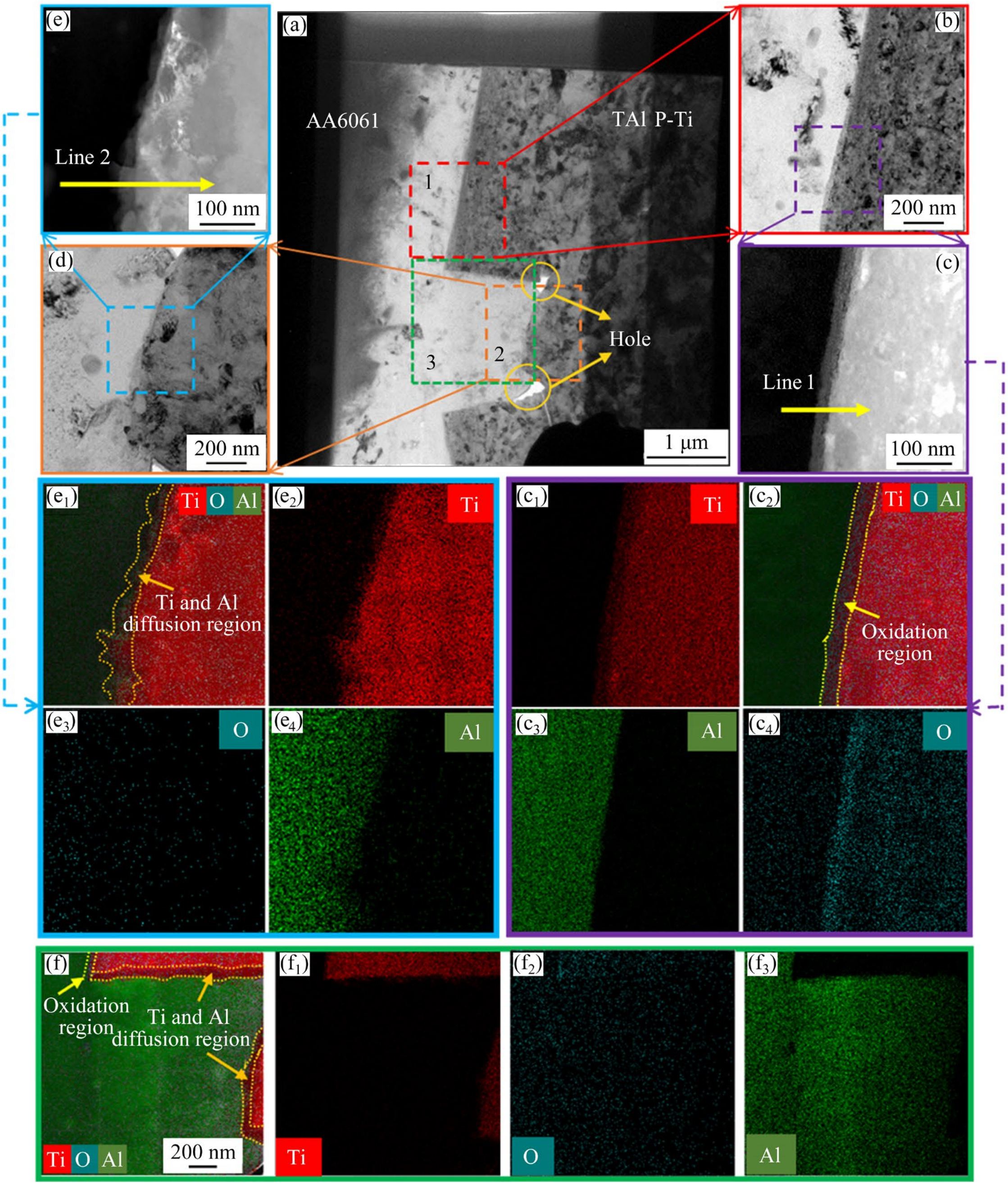

Fig. 12 TEM images of characteristic interface position: (a) TEM bright-field image; (b) Local TEM bright-field image (oxidation diffusion region); (c) Local HAADF image of (b); (c_1−c_4) Element distribution maps; (d) Local TEM bright-field image (fresh metal bonding region); (e) Local HADDF image of (d); (e_1−e_4) Element distribution maps; (f, f_1−f_3) Element distribution maps of Position 3 in (a)

presented a diffusion of approximately 16.5 nm in the oxide film with approximately 30 nm, indicating that the Al element can diffuse in the oxide film by annealing, which can accelerate the phenomenon of shear fracture on the oxide surface prior to annealing. The high magnification HAADF images and surface scan results at Position 2 and Position 3 illustrated that in the rolling process, the generation of cracks on the titanium side exposed the titanium matrix; at the same time, the aluminium matrix was squeezed into the cracks, by which the cracks expanded into a certain area, leading to the formation of fresh metal contact areas at the bottom and on the side of the cracks, as well as an inter-diffusion zone of Ti and Al elements in the annealing process. Limited by the temperature and time in the annealing process, no Ti−Al brittle phase affecting the bonding strength was formed in

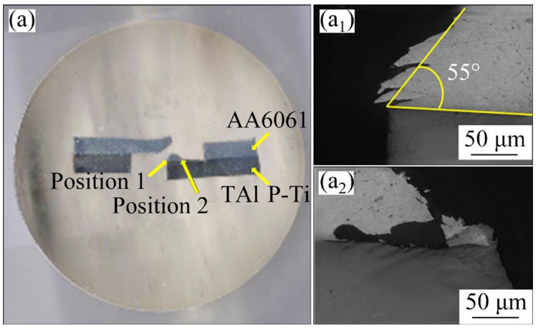

Fig. 13 Interface shear fracture morphology of TA1 P-Ti/AA6061 composite plate after annealing: (a) Overall morphology of shear fracture; (a_1) Morphology of Position 1; (a_2) Morphology of Position 2

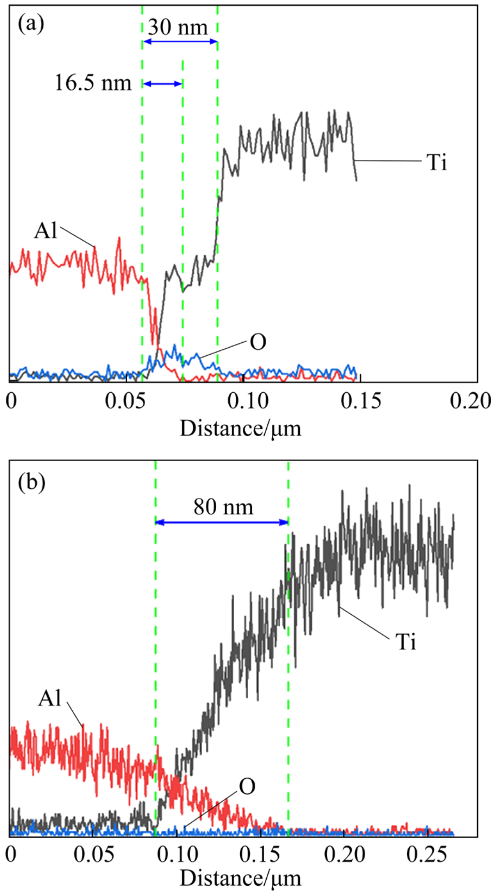

Fig. 14 EDS scanning results of lines in Figs. 12(c, e): (a) Line 1; (b) Line 2

the contact region of the fresh metal, greatly improving the overall performance of the composite plates, as shown in Figs. 12(e, e_1−e_4, f, f_1−f_3). The results of the line scan (Line 2) in Fig. 14(b) illustrated that the inter-diffusion distance between the Ti and Al elements in the fresh metal contact region was 80 nm. The results of the interface morphology characterization at three annealing temperatures of 400, 450, and 500 °C uncovered that as the annealing temperature rose, no Ti−Al brittle phase was formed at the interface, as shown in Fig. 15.

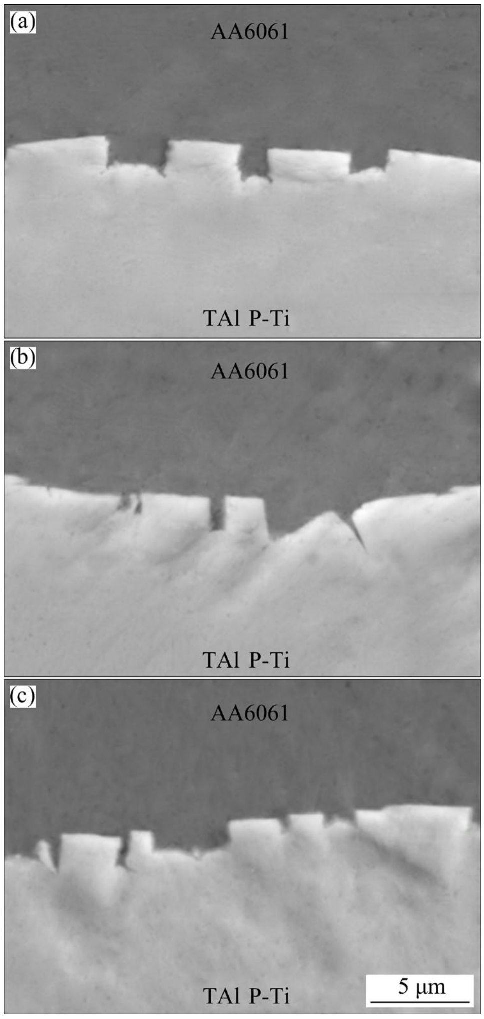

Fig. 15 Interface morphologies of composite plates at reduction rate of 43% and different annealing temperatures: (a) 400 °C; (b) 450 °C; (c) 500 °C

The dark-field morphology of the composite interface was characterized. The results showed that the heterogeneous metal structure of gradient nanocrystals with a fine-grained layer and a coarse-grained layer was formed at the convex of the interface, as shown in Figs. 16(b) and (d). This structure formation could be attributed to the cracking of the oxide film on the surface of the titanium plate in the rolling deformation region. As the rolling force increased, the cracks gradually extended towards the titanium matrix, with simultaneous extension of the titanium matrix along the rolling direction and extrusion of the aluminium matrix into the cracks. Consequently, the cracks

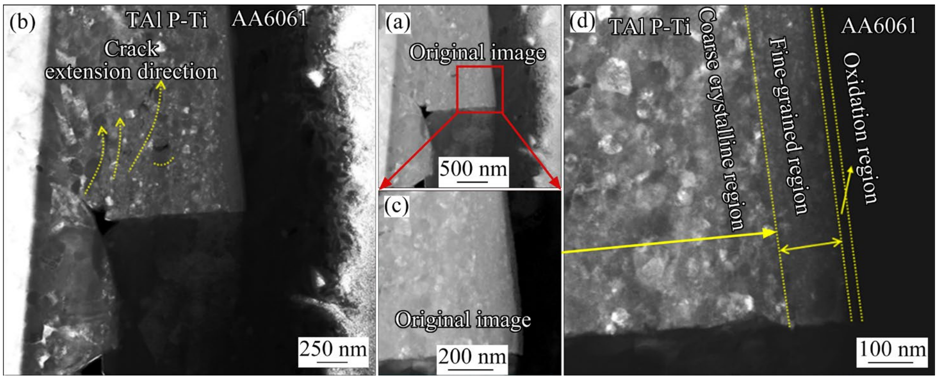

Fig. 16 Overall (a, b) and local (c, d) dark-field images of composite interface

expanded into rectangular grooves, and the aluminium matrix effectively filled the grooves, forming a mechanical lock. However, the bulge of the titanium matrix was compressed in the deformation zone along the direction perpendicular to the rolling direction, resulting in a larger strain than that at the groove position, thus leading to the formation of a gradient crystal structure at the bulge position. Some studies [20−22] have shown that the nanocrystalline gradient heterostructure can enhance the strength and toughness of materials by reducing grain size and introducing numerous grain boundaries into the materials. These grain boundaries hinder the dislocation movement, thus increasing the material strength. In addition, fine-grained regions greatly delay the expansion of the cracks. In the analyzed specimen, the annealing temperature was 400 °C, which was far below the recrystallization temperature of the titanium matrix. Therefore, the grain distribution in Fig. 16 supported the analytical nanoindentation results in Fig. 8(b), confirming that the hardness at the convex position was higher than that at the concave position.

4.2 Tensile properties of composite plates at different annealing temperatures

The analysis in Section 3.2 manifested that the G-500 °C/10 min pre-rolling treatment process facilitated the formation of a more effective mechanical lock at the interface of the composite plates, thereby enhancing the shear properties of the TA1 P-Ti/AA6061 composite plates. Further insight into the mechanical properties of the composite plates was provided by the tensile property test. The results of the stress−strain curves at different reduction rates, as shown in Fig. 17(a), uncovered that the interface started to delaminate with an elongation of 6.2% at a reduction rate of 35%, followed by the successive fracture of the aluminium matrix and titanium matrix. At a reduction rate of 40%, the tensile properties of the composite plates were improved. When the elongation was 7.84%, the interface began to delaminate. At a reduction rate of 43%, when the elongation was 10.80%, the interface began to delaminate, which became the turning point of the failure of the composite plates. Due to different strengths of titanium and aluminium, the deformation of the two matrixes was not synchronous, resulting in a lower elongation of the aluminium plate compared to that of the titanium plate. As elongation increased, the aluminium matrix experienced fracture first, followed by fracture of the titanium substrate, resulting in a step-like decline in the tensile curve. At this time, the ultimate tensile strength of the composite plates reached 490.58 MPa. Figures 17(b) and (c) show the microscopic morphologies of the tensile specimen at a reduction rate of 43%. After tensile fracture, obvious cracks appeared at the interface, the titanium-side matrix shrunk, and the aluminium-side matrix exhibited brittle fracture, which was consistent with the illustration in Fig. 17(a).

Before annealing, TA1 P-Ti/AA6061 composite plates exhibited higher ultimate tensile strength but were susceptible to the interface delamination at lower elongation. Therefore, the tensile properties of the TA1 P-Ti/AA6061 composite plate under G-500 °C/10 min process treated at different annealing temperatures were evaluated. The tensile stress−strain curves of the composite plate after annealing at different reduction rates and temperatures are shown in Fig. 18. It was uncovered that no

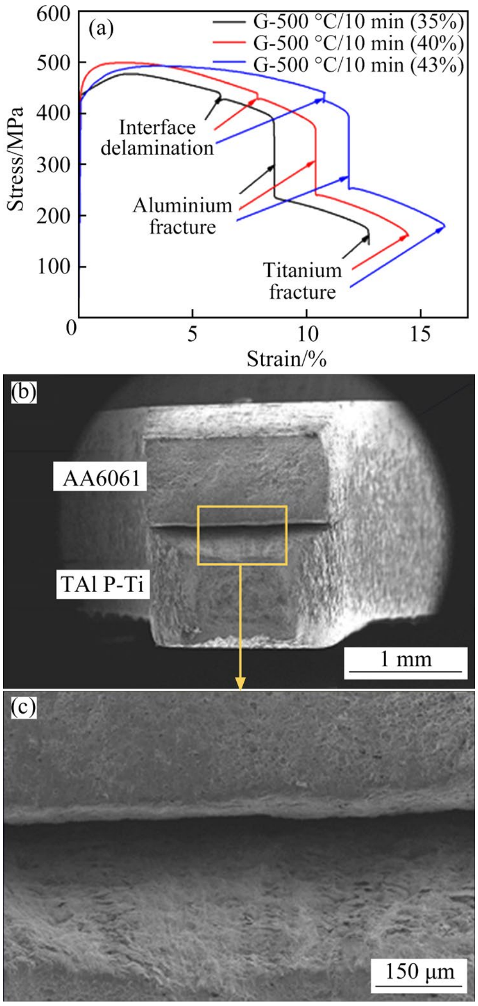

Fig. 17 Tensile properties of composite plates under G-500 °C/10 min process with different reduction rates before annealing: (a) Tensile stress−strain curves of composite plates at reduction rates of 35%, 40% and 43%; (b, c) Tensile fracture morphologies of composite plate at reduction rate of 43%

delamination occurred before fracture for the annealed composite plates at different reduction rates, and all the annealed composite plates displayed excellent synchronous deformation and interface delamination resistance, as shown in Fig. 18. At the same time, the results also demonstrated that with the increase of the annealing temperature, the overall ultimate tensile strength of the TA1 P-Ti/AA6061 composite plates under G-500 °C/10 min process showed a downtrend, and the maximum elongation displayed an uptrend. In addition, the elongation after annealing was higher than that before annealing. The fracture surface at a reduction rate of 43% was selected for microscopic morphology analysis. The results shown in Figs. 19(b, d, f) were similar, which revealed obvious adhesion of the aluminium matrix and titanium matrix at the interface and the appearance of serrated penetration, reflecting good anti-interface delamination ability of the composite plates.

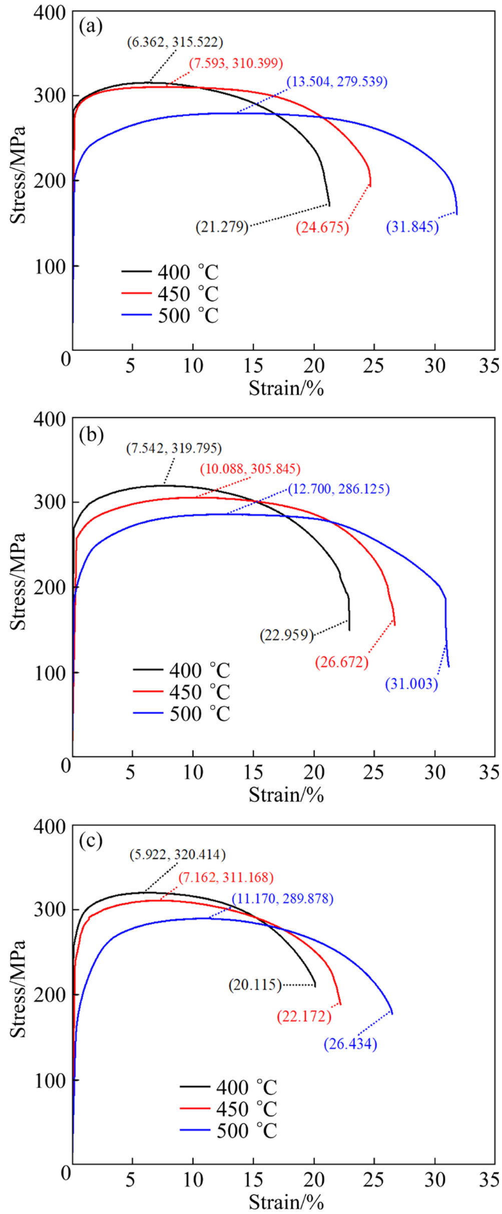

Fig. 18 Tensile properties of composite plates under G-500 °C/10 min process tested at different annealing temperatures and reduction rates: (a) 35%; (b) 40%; (c) 43%

The above analysis confirmed that the annealing treatment at different temperatures improved the ability of the composite plates to resist interface delamination during the tensile deformation. In the actual preparation processes, the appropriate annealing process could be selected according to different requirements, with elongation of the tensile specimen as the reference condition.

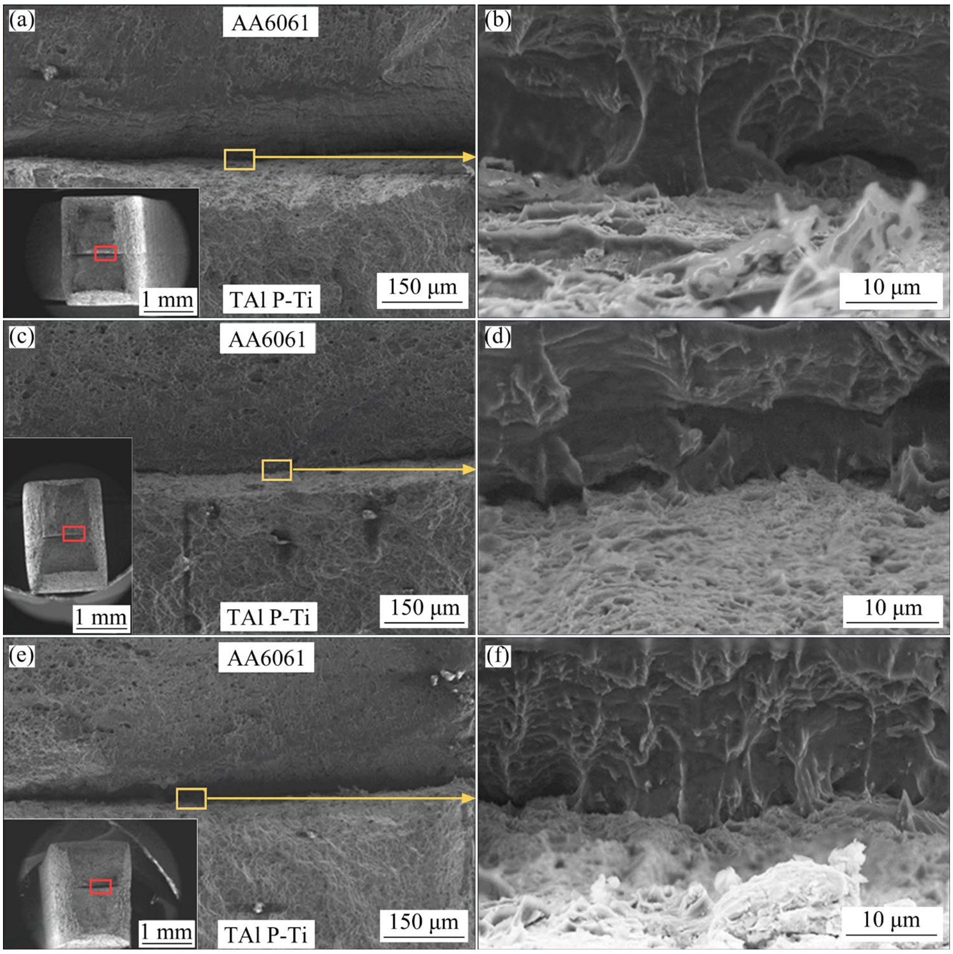

Fig. 19 Microstructures of tensile fracture surface of composite plate under G-500 °C/10 min process at reduction rate of 43% and different annealing temperatures: (a, b) 400 °C; (c, d) 450 °C; (e, f) 500 °C

4.3 Composite mechanism

According to the above analysis results, the composition mechanism of the cold rolled TA1 P-Ti/AA6061 composite plates under G-500 °C/10 min process and the element diffusion behavior during annealing are shown in Fig. 20. After oxidation treatment, an oxide film (Ti_6O) with a thickness of about 30 nm was formed on the titanium plate surface, as shown in Fig. 20(a). In the rolling process, the oxide film was first fractured. As the rolling force increased, the titanium plate and aluminium plate were compressively deformed in the direction perpendicular to the rolling direction and extended backwards. The cracks on the titanium side expanded and were squeezed into the aluminium matrix. After rolling, the interface formed a concave−convex mechanical lock with a fresh metal contact interface and an oxidation contact interface. The fresh metal contact interface included the bottom and both sides, so the oxidation treatment process was additionally used to increase

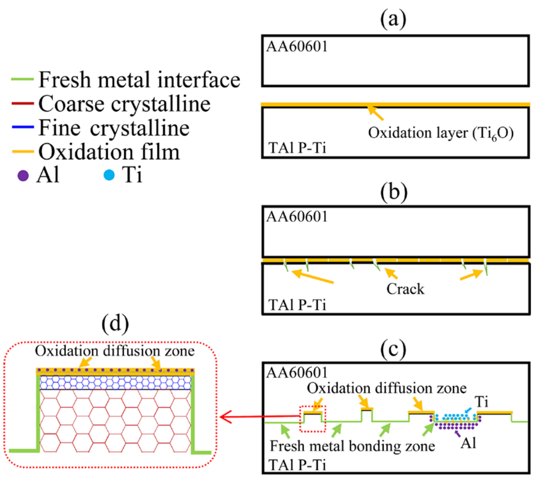

Fig. 20 Schematic diagrams showing composite mechanism: (a) Original state; (b) Broken oxide film; (c) Crack expansion and fresh metal bonding; (d) Schematic diagram of local diffusion and gradient grain morphology

the fresh metal contact area and the bonding strength of the composite plates at the same reduction rate. At the oxidation contact interface, the oxide layer and the matrix were well bonded, and the Al element could diffuse in the oxide layer, which would not have a negative impact on the bonding strength, as shown in Figs. 20(b) and (c). In addition, the titanium matrix bulges showed gradient nano-grain distribution after CRB, which increased the mechanical locking strength and the interface strength, as shown in Fig. 20(d).

5 Conclusions

(1) The Grinding pre-treatment process yielded composite plates with a minimum reduction rate of 40%, while the G-500 °C/10 min pre-treatment process produced effective bonding at a reduction rate of 35%. With the increase of the reduction rate, the shear strength of the composite plates was enhanced under both processes. At a reduction rate of 43%, the shear strengths were measured at 66 and 117 MPa for the Grinding and G-500 °C/10 min processes, respectively.

(2) The microscopic analysis manifested that the oxide layer on the surface of TA1 P-Ti prepared by the G-500 °C/10 min process before rolling showed better brittleness and hardness, which facilitated the formation of a more obvious and effective mechanical lock during the CRB. Owing to the fracture of the oxide layer and the expansion of the crack under the rolling force, a concave fresh matrix metal contact area was formed, which also expanded the contact area of the metal on both sides and improved the bonding strength of the composite plates.

(3) The TA1 P-Ti/AA6061 composite plates under G-500 °C/10 min process obtained by CRB with a reduction rate of 43% exhibited excellent bonding properties and without the formation of brittle IMCs at the interface after annealing at 400, 450 and 500 °C for 1 h. In detail, during the tensile test, these composite plates exhibited enhanced resistance to delamination and increased overall elongation, indicating that the annealed composite has excellent strength−plasticity compatibility.

(4) As revealed by TEM results, the convex morphology on the titanium side exhibited a gradient nano-grain phenomenon, which enhanced the strength of the titanium matrix at the interface, and delayed or hindered the expansion of a few cracks. After annealing, the oxide film (Ti_6O) on the titanium side did not prevent the diffusion of Al elements, allowing for the inter-diffusion of Ti and Al elements in the fresh metal contact area (non-oxidation region) in the annealing process.

CRediT authorship contribution statement

Lun FU: Formal analysis, Investigation, Data curation, Visualization, Writing − Original draft; **Bin YANG:** Investigation, Resources, Validation; **Yun-chang GUO:** Investigation, Resources; **Chao YU:** Conceptualization, Formal analysis, Writing − Review & editing, Validation, Funding acquisition; **Hong XIAO:** Methodology, Project administration, Funding acquisition, Supervision.

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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表面氧化处理提高冷轧 TA1 P-Ti/AA6061 复合板的结合性能

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摘 要：通过对钛板表面进行氧化处理，采用冷轧复合工艺制备 TA1 P-Ti/AA6061 复合板。结果表明：在 TA1 纯钛板表面制备的氧化膜(Ti_6O)在冷轧过程中容易开裂，从而促进界面处形成有效的机械互锁，可有效地降低钛、铝板经冷轧后产生复合的最小压下率；此外，经氧化处理的复合板材的剪切强度得到提高，特别是在 43%的压下率下，其剪切强度达到 117 MPa。基于氧化处理和不同的冷轧压下率，经 400、450 和 500 ℃退火后的复合板材均具有良好的界面抗分层能力，最大伸长率为 31.845%，表现出优异的强度−塑性相容性。

关键词：TA1 P-Ti/AA6061 复合板；氧化处理；退火处理；冷轧复合

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