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ORIGINAL REPORTS



Oxidation difference of microstructural bands in additive manufactured titanium alloy

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ABSTRACT

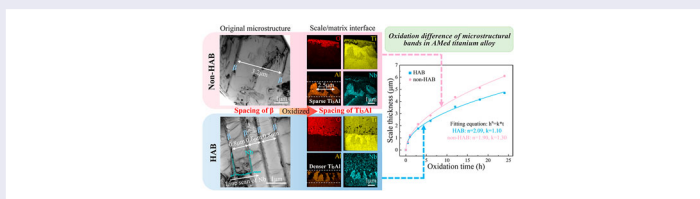
In this study, Ti6Al7Nb alloy produced by twin-wire arc additive manufacturing was oxidized at 800°C to identify the oxidation difference induced by heat-affected bands (HABs), which have been widely reported in additive manufactured titanium alloys. The oxidation kinetics proved that HABs with compact β laths have stronger oxidation resistance compared with that of the non-HAB zone. Nb element enriched in β phase promoted Ti_3Al to precipitate at the original position of β laths after oxidation, having a similar spacing to the β laths. The formation of compact Ti_3Al on HAB beneficially inhibits oxygen diffusion across the oxide scale/matrix interface.

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KEYWORDS

Additive manufacturing; titanium alloys; oxidation; heat-affected bands



IMPACT STATEMENT

Oxidation difference induced by microstructural bands in additive manufactured titanium alloy was identified, and the stronger oxidation resistance of heat-affected bands was attributed to the more compact β laths.

Introduction

Additive manufacturing (AM) is a promising method that offers many advantages over the conventional manufacturing processes, some of which include high flexibility for complex-shaped component design, reduction in cost, and savings in materials [1–3]. Significant progress has been obtained in the utilization of AM in processing titanium alloys, as their features of high raw material cost and difficulty-to-machine made them strong candidates for AM techniques [4–6]. During the layer-by-layer deposition process of AM, the repeated translation of the heat source can lead to multiple heating and cooling cycles with gradually decreasing peak temperature [7–9]. A unique microstructural variation will occur in the thermal cycle with a specific peak temperature and cooling rate, forming a heat-affected zone in the previously deposited titanium alloy [10,11]. The heat-affected zone presents a series of parallel bands known as heat-affected bands (HABs), in the etched cross-section of the

additively manufactured single-track wide walls. HABs are more noticeable in wire arc additive manufacturing (WAAM) and directed laser deposition (DLD) processes due to their thicker deposition layers [12,13]. The existence of HABs was first reported on the Ti6Al4V sample produced by the DLD process, and subsequent studies have focused on the formation mechanism of HABs [14,15]. The formation of HABs was recently determined to be by the migration of α/β phase interfaces, where the peak temperature approaches the β transition temperature [16]. The mechanical properties of HABs have been examined to include higher hardness [17] and efficient inhibition of fatigue crack propagation [18], but little is known about the oxidation behavior of HABs. In this work, Ti6Al7Nb (Ti67) alloy produced by the WAAM process was oxidized at 800°C for up to 24 h. Oxide scales grown on HAB and non-HAB zone were characterized separately and compared in detail to determine the difference in oxidation resistance. The possible mechanism of

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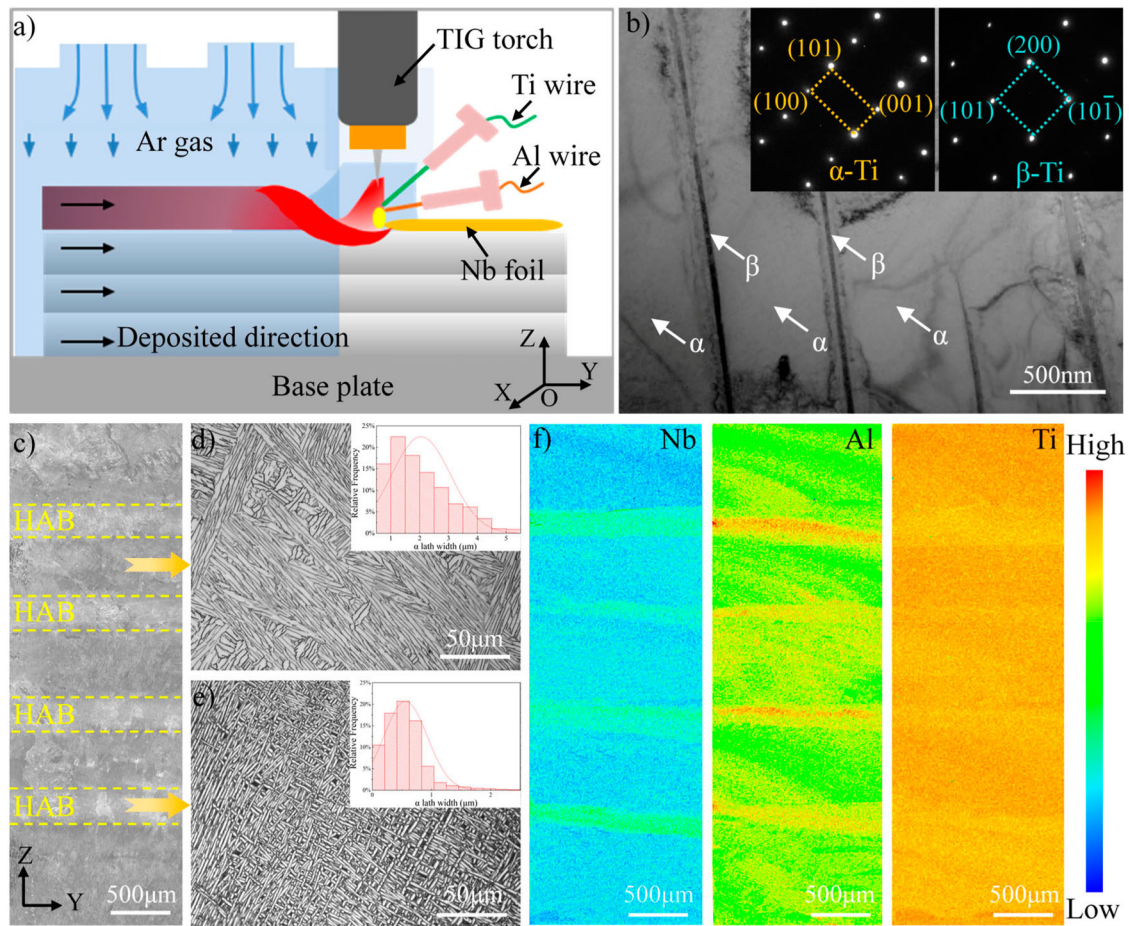


Figure 1. Description of as-deposited Ti67 alloy: (a) schematic of the deposition process, (b) phase structure, (c) etched surface of the oxidation specimen, (d) microstructure of non-HAB region, (e) microstructure of HAB, and (f) EPMA mapping of c.

oxidation difference was discussed in terms of elemental distribution and original microstructure.

Experimental

The Ti67 alloy was prepared by a twin-wire arc additive manufacturing technology combined with in-situ alloying as shown in Figure 1(a), using the same process parameters as reported in a previous study [19]. The oxidation specimens with dimensions of $30 \times 15 \times 3 \text{ mm}^3$ were cut from the deposited wall in the YOZ plane, then ground up to grit No. 7000 and ultrasonically cleaned in acetone before the oxidation tests. The elemental distribution of original oxidation specimens was revealed by the electron probe microanalyzer (EPMA, Shimadzu 1720H). Isothermal oxidation tests were carried out in a muffle furnace at 800°C in the air for 0.5, 1, 3, 6, 12, 18, and 24 h, respectively. The phase structure of the oxidation specimens was identified with X-ray diffraction (XRD, Bruker D8 Advance) using Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. Microstructural characterization of the oxide scale was performed by

scanning electron microscopy (SEM, JSM-7800F) and transmission electron microscopy (TEM, JEM-2100F) equipped with the energy dispersive spectroscope (EDS). To measure scale thickness, the cross-section of the oxidized samples was wrapped by the resin, then ground up to grit No. 7000, polished, and etched using Kroll's reagent (1 vol.% HF, 3 vol.% HNO_3 , and 94 vol.% water) to distinguish HAB and non-HAB zones. The scale thickness was measured on HAB and non-HAB zones 10 times through SEM, respectively, and the average value was taken. For high-resolution characterization of the oxide scale and the oxide scale/matrix interface, focused ion beam (FIB) technology was used to prepare the TEM sample.

Results and discussion

The TEM analysis in Figure 1(b) proved that the Ti67 alloy was primarily composed of α matrix phase, separated by nano-scaled β laths. Periodic HABs could be observed on the etched surface of the oxidation specimen (Figure 1(c)), in which the average spacing of β laths was

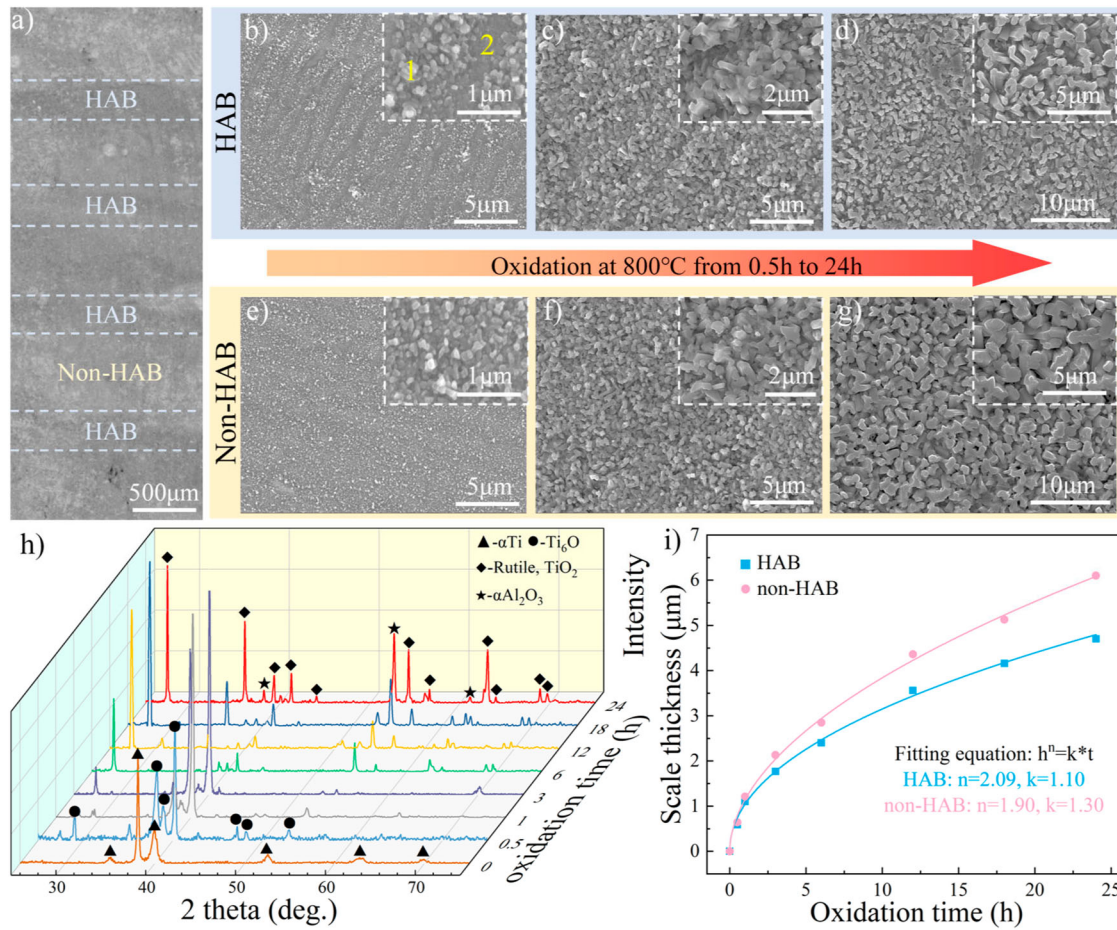


Figure 2. Characterization of oxide scales on specimens oxidized at 800°C for different times: (a) photograph of the surface shown in Figure 1c after being oxidized for 24 h, (b–d) surface morphologies of HAB oxidized for 0.5 h, 6 h and 24 h, respectively, (e–g) surface morphologies of non-HAB zone oxidized for 0.5, 6, and 24 h, respectively, (h) XRD spectra of the original Ti67 alloy and the specimens oxidized for different times, and (i) oxidation kinetics of HAB and non-HAB zone.

0.87 μm. In comparison, the β laths were spaced far apart in the non-HAB zone with an average spacing of 2.73 μm, as seen in Figure 1(d,e). The formation of compact β laths in HAB was because the secondary α heterogeneously nucleated on the residual α phase when the reheating temperature was just below the β transition temperature [16,19]. The chemical composition difference between HAB and the non-HAB zone was detected by EPMA mapping and the result presented in Figure 1(f), which revealed that the HABs are rich in Nb and Al elements. The concentrations of Nb and Al in HABs were 7.42 wt. % and 6.37 wt. %, and it reduced to 6.51 wt. % and 6.21 wt. % in the non-HAB zone, respectively. This reduction was attributed to thermally induced diffusion during the formation process of the HABs [19]. It should be noted that the addition of Nb and Al as alloying elements has proven to be effective in improving the oxidation resistance of titanium alloy [20–22].

Figure 2 depicts the surface morphology, phase structure and the thickness of the oxide scale on the specimens

oxidized at different time intervals. The local appearance of the specimen after being repolished to remove the etched surface and oxidized for 24 h was presented in Figure 2(a). The oxidation difference between the HAB and non-HAB zone was indicated by several parallel dark bands located at the site of HABs. The morphologies of the oxide scale on HAB and non-HAB zone after oxidation for 0.5, 6, and 24 h were shown in Figure 2(b–g). As the oxidation time increased, the oxide particles increased in size with statistics presented in Table 1. The oxide particles on HAB are notably smaller than those on the non-HAB areas regardless of the oxidation time. It was reported that the formation of finer oxide particles indicated greater oxidation resistance of titanium alloy [23]. Thus, HAB covered by finer oxide particles had stronger oxidation resistance than the non-HAB zone.

The oxide particles on the HAB presented a lamellar distribution after 0.5 h oxidation (Figure 2(b)), which might be related to the lamellar α/β microstructure of the original Ti67 alloy. High magnification of the

Table 1. The average particle size of the oxide at various oxidation times (unit: nm).

	0.5h	6h	24h
HAB	67	279	421
Non-HAB zone	80	311	728

Table 2. EDS analysis of the points in Figure 2 (at. %).

	Ti	Al	Nb	O
Point 1	31.6	5.6	1.6	61.2
Point 2	34.4	3.8	2.2	59.6

lamellar characterization revealed a mixture of coarse oxide particles (point 1) and fine oxide particles (point 2). EDS analysis of these points presented in Table 2 indicated that the fine particles contained more Nb and less Al than the coarse particles. The formation of lamellar oxide distribution was attributed to the preferential oxidation nucleation of α or β phase induced by the chemical composition difference [24]. Since Nb is enriched in the β phase as a solid stabilizing element that can reduce the solid solubility of oxygen in the titanium alloy [25], the oxide is presumed to nucleate at the α phase first, forming coarse oxide particles with lower Nb content. Subsequently, the fine oxide particles grow on the initial β phase with stronger oxidation resistance. For the non-HAB region with lamellar α/β microstructure, the distribution of oxides was uniform rather than lamellar, with coarse oxide particles covering the surface. In this phenomenon, the wide α phase between sparse β laths provides more nucleation sites for the oxide formation and promotes the rapid growth of oxide particles, resulting in uniform oxide on the non-HAB zone. When the oxidation time reaches 6 h, the lamellar oxide on HAB was covered by subsequent growing oxide particles.

Figure 2(h) shows the phase structure of the deposited Ti67 alloy and the oxidized surface for different holding times. The diffraction peaks of the α phase dominated the XRD pattern of the original Ti67 alloy, while the β phase was absent due to its nano-scale dimension. Ti_6O was formed at the initial oxidation stage, while the weak peak of Rutile- TiO_2 at 27.5° was enhanced with the extension of oxidation time. When the oxidation time was extended to 6 h, the oxide was composed mainly of TiO_2 , while Ti_6O disappeared in the XRD pattern. The α - Al_2O_3 peaks were first detected at the oxidation time of 12 h and increased with increasing oxidation time. The variation of oxide thickness as a function of time was shown in Figure 2(i), where HAB was covered by thinner scales than the non-HAB zone at all the oxidation times. The thickness of the oxide scale remarkably decreased by 23% from $6.1\mu m$ on the non-HAB zone to $4.7\mu m$ on

HAB after 24 h oxidation. To identify the law of the oxidation kinetics on HAB and non-HAB zone, the following equation was used to fit the thickness of the oxide scales:

$$h^n = k \times t \quad (1)$$

where h is the thickness of the oxidation layer (μm), n is the oxidation exponent, k is the oxidation rate constant ($\mu m^n/h$) and t is the oxidation time (h). The fitting curve was plotted, and the oxidation exponents (n) of the HAB and non-HAB zone were 2.09 and 1.90, respectively. Both HAB and non-HAB zone obeyed parabolic growth kinetics ($n \approx 2$) at $800^\circ C$ exposing. The oxidation rate constant (k) of the non-HAB zone was $1.30\mu m^2/h$, and it decreased to $1.10\mu m^2/h$ on HAB, indicating a stronger oxidation resistance of HAB, which is consistent with the finer oxide particles developed on HAB.

The elemental distributions of the cross-sectional oxide scales on HAB and non-HAB zone evaluated by FIB-TEM were shown in Figure 3. The oxide scale and the titanium matrix on HAB were collected by FIB milling, but only part of the oxide scale was obtained from the non-HAB zone. The oxide scales primarily contained TiO_2 as well as some Al_2O_3 particles, as confirmed by the elemental distribution and selected area electron diffraction (SAED) patterns. A similar multilayer structure was observed in the oxide scales on both HAB and non-HAB zone, consisting of three layers: a porous TiO_2 outermost layer, a thin Al_2O_3/Ti_2O mixture layer and a TiO_2 innermost layer. TiO_2 and Al_2O_3 were the most thermodynamically stable phases in the Ti-Al-O system [26], but the TiO_2 grew faster at $800^\circ C$ [27], thus, TiO_2 occupied the largest volume in the oxide scale. TiO_2 grew by consuming Ti in the matrix, leading to the formation of a Ti-poor and Al-rich zone under the TiO_2 layer, which promoted the diffusion of Al through the TiO_2 and reacting with oxygen to form Al_2O_3 . The enrichment of Al also resulted in precipitation of the Ti_3Al phase due to the limited solid solubility of Al in αTi (approximately 10 at. % [28]). Therefore, the oxide scale/matrix interface on HAB was composed of Ti_3Al with high Nb content and αTi .

It is worth noting that Nb could be soluble in TiO_2 , which was beneficial to inhibit the oxygen diffusion across the already formed TiO_2 layer by reducing the oxygen vacancy concentration, thereby decreasing the growth rate of TiO_2 [29,30]. The Nb content in HAB was slightly higher than that in the non-HAB zone, which promoted the dissolving of Nb into the TiO_2 and enhanced the oxidation resistance of HAB. In consequence, the average Nb content in TiO_2 was 2.1 wt. % on HAB which is slightly higher than that on the non-HAB zone (1.5wt. %) through TEM-EDS. In addition to elemental content, the unique original microstructure of

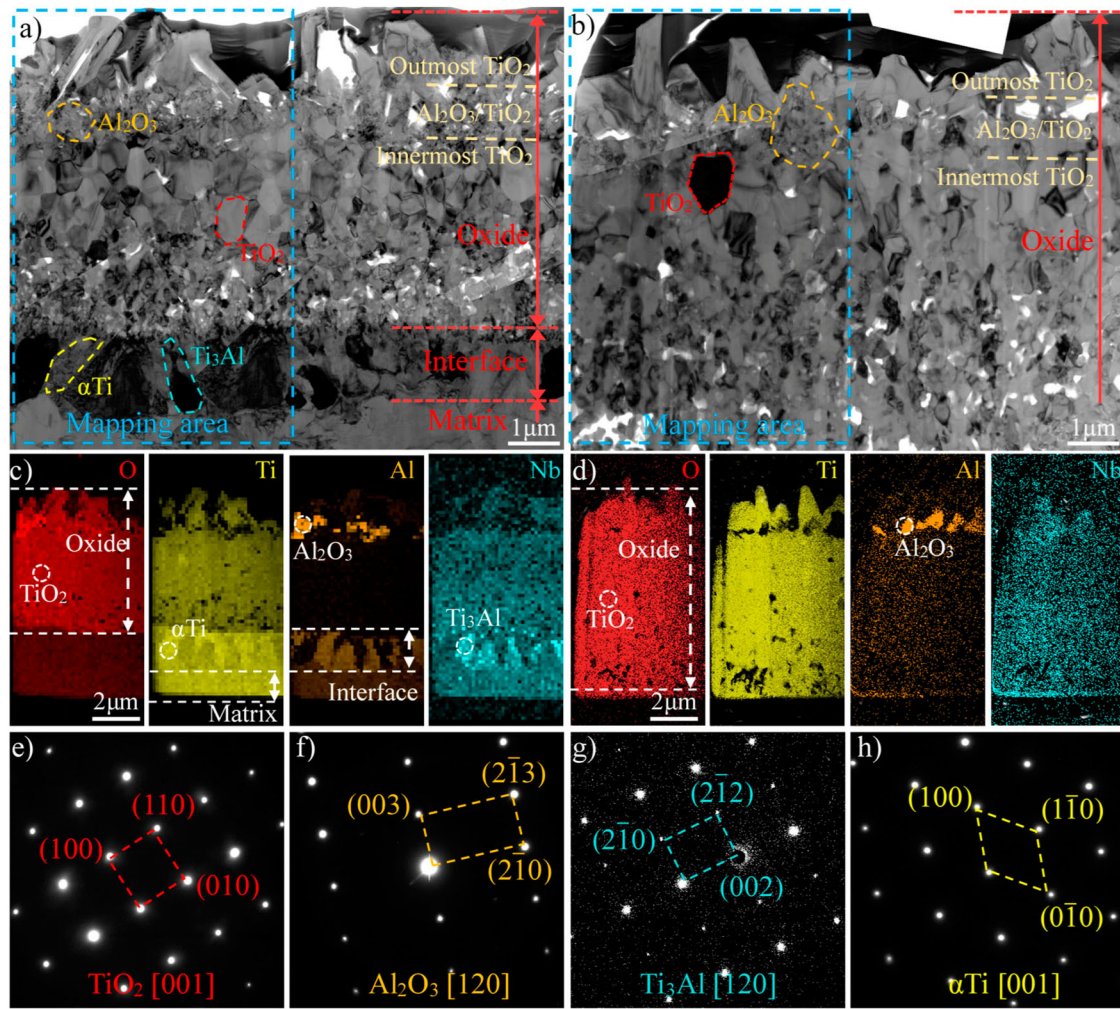


Figure 3. TEM analysis of Ti67 alloy after oxidation for 24h: (a) TEM image of the oxide scale and matrix on HAB; (b) TEM image of the oxide scale on non-HAB zone; (c,d) EDS elemental mappings for the selected area in a and b and (e-h) SAED patterns of different phases.

the HAB also contributed to the oxidation differences. To identify the effect of the original microstructure on the oxidation resistance, the oxide scale/matrix interface on non-HAB was additionally observed by FIB-TEM and presented in Figure 4(a), showing a complete contrast with HAB. Ti_3Al with high Nb content was also found to precipitate from the αTi under the oxide scale. It has been reported that Ti_3Al alloy has stronger oxidation resistance than titanium alloy [31,32], and increasing the volume fraction of the Ti_3Al phase can also improve the oxidation resistance of the Ti- Ti_3Al composite [33]. Thus, the precipitation of Ti_3Al phase in the scale/matrix interface was beneficial to the oxidation resistance of Ti67 alloy. The elemental content provided in Table 3 confirmed a lower oxygen content in Ti_3Al than that in αTi , indicating a stronger diffusion of oxygen in αTi . Hence, the boundary of oxides was convex to αTi . Previous investigations have concluded that more compact Ti_3Al precipitation and less αTi in contact with the oxide

scale were conducive to the antioxidant properties by inhibiting oxygen diffusion. The spacing of Ti_3Al precipitation was about $2.7\mu\text{m}$ on the non-HAB zone while it was less than $0.9\mu\text{m}$ on HAB, so the denser Ti_3Al precipitation is another factor contributing to the stronger oxidation resistance of HAB.

The denser Ti_3Al precipitation was considered to be related to the compact β laths in the original microstructure of HAB. The spacing of β laths in the original microstructure was about $0.7\mu\text{m}$ in Figure 4(c), which was close to the spacing of Ti_3Al precipitation on HAB. Similarly, the spacing of the β laths ($3.2\mu\text{m}$) was close to that of Ti_3Al in the non-HAB zone. A possible mechanism illustrating the approximate equivalent relationship between the spacing of β laths and Ti_3Al precipitation was shown schematically in Figure 4(e). As confirmed by the XRD analysis, titanium firstly reacts with oxygen to form oxide in the early oxidation stages, resulting in the enrichment of Al under the oxidation layer. Meanwhile,

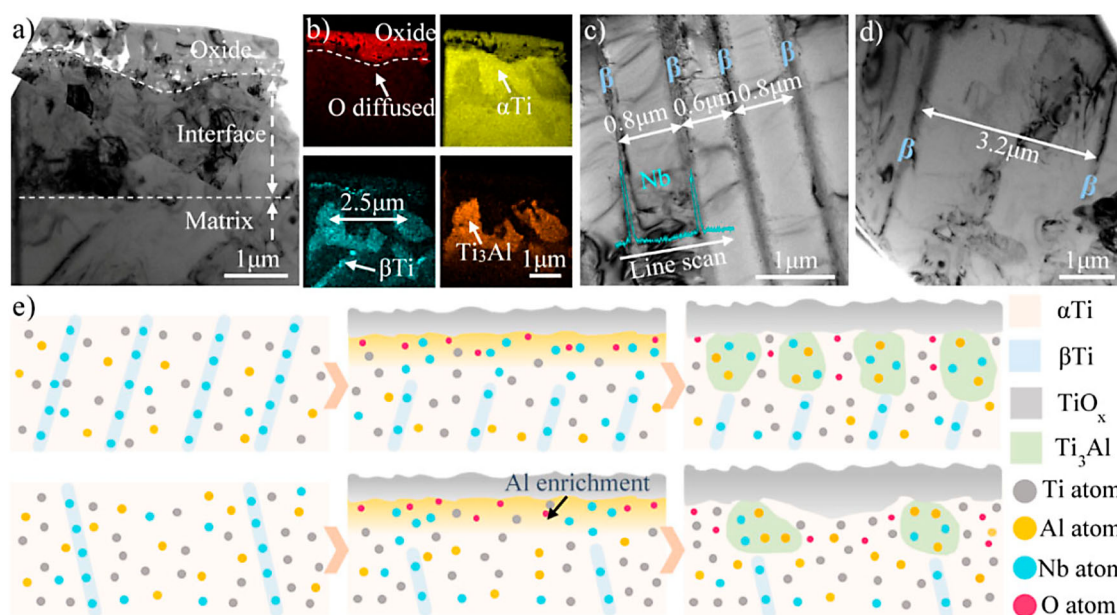


Figure 4. The influencing mechanism of original microstructure on oxidation resistance: (a) TEM image of the oxide scale/matrix interface on non-HAB zone after oxidation at 800°C for 24h6, (b) EDS elemental mappings for a, (c) original microstructure of HAB, (d) original microstructure of non-HAB zone and (e) schematic diagrams illustrating the Ti₃Al precipitation process on HAB and non-HAB zone.

Table 3. Elemental content of Ti₃Al and αTi adjacent with oxide scale in Figure 4 (at. %).

	Ti	Al	Nb	O
Ti ₃ Al	70.8	21.8	2.9	4.5
αTi	85.0	5.9	0.9	8.2

oxygen atoms diffuse through the oxide scale into the matrix. With increasing contents of O and Al, which are α-stabilizing elements, the β→α transformation occurs in the oxide scale/matrix interface, while the Nb element rich in β remains near the original β laths due to its low diffusion coefficient. The lattice distortion caused by the Nb solution can induce Ti₃Al precipitation [34,35]. Therefore, Ti₃Al forms near the positions of original β laths and contain high Nb content, owning a similar spacing to the β laths.

Conclusion

In summary, the oxidation behavior of HAB, a region with unique microstructural variation during the multiple thermal cycles in the additive manufacturing process of titanium alloy, was firstly revealed in this study. After oxidation at 800°C for up to 24 h, finer oxide particles and thinner scales were formed on HAB, indicating stronger oxidation resistance of HAB than the non-HAB area. TiO₂ was found to be the main component of the oxide scale, with a small amount of Al₂O₃ located under the surface of the oxide scale after 24 h oxidation. With the depletion of Ti in the matrix by TiO₂, the

oxide/matrix interface was enriched with Al, promoting Ti₃Al to precipitate on either HAB or non-HAB zone. The stronger oxidation resistance of HAB was attributed to the slightly higher Nb content and the compact β laths in the original microstructure by promoting the denser Ti₃Al precipitation, which was beneficial for inhibiting oxygen diffusion. This work provided a simple approach to improve the oxidation resistance of titanium alloy by controlling β laths spacing.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Declaration of interest statement

No potential competing interest was reported by the authors.

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