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ARTICLE

High Temperature Oxidation Behavior of Pure Ti TIG Welded Joint

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Abstract: The oxidation behavior, oxidation morphology, and oxidation products of pure Ti joint welded by tungsten inert gas welding technique at 550 °C for different durations (2, 4, 6, and 8 h) and those at different temperatures (650, 750, 850, and 950 °C) for 4 h were investigated. Results show that at 550 °C, the oxidation time has a slight influence on the oxidation behavior of welded joint. The oxidation temperature has a significant impact on the oxidation behavior, and the higher the temperature, the more severe the oxidation of welded joints. The oxidation kinetics is very close to the quasi-linear law at low temperatures. With increasing the temperature, the oxidation rate is increased exponentially. Additionally, the oxidation products generated on the surface of welded joint are TiO_2 with anatase and rutile structures, and the temperature barely has effect on the TiO_2 type. The oxidation process of pure Ti welded joint can be described as follows: oxygen atoms are absorbed on the surface; oxides preferentially nucleate in the defective zone; oxides grow laterally and the oxidation film becomes thicker. At relatively higher temperatures, the cracks or voids appear in the oxidation film, which become the transmission channels of O atoms, leading to the high diffusion rate of O and Ti atoms and high oxidation rate.

Key words: welded joint; oxidation treatment; oxidation kinetics; oxidation film

Titanium (Ti) and its alloys have attracted much attention in the fields of aerospace, petroleum exploration, marine equipment, chemical industry, and bioimplant materials due to their light weight, high strength, good welding performance, and excellent biocompatibility[1–4]. However, they are prone to abrasion under high temperature or acidic corrosion condition due to their poor wear resistance and small thermal conductivity[4–8]. Besides, a thin oxidation film with thickness of 0.5–7 nm will be formed spontaneously on the Ti surface in the air, providing slight corrosion protection[7]. The poor wear resistance and corrosion resistance restrict the wide application and development of Ti and its alloys.

In order to improve the wear and corrosion resistance of Ti and its alloys at high temperatures, the modifications, such as surface oxidation, nitridation, and carbonization[9–11], are conducted. It is known that the oxidation treatment can generate a specific oxide layer on the surface to improve the corrosion resistance of Ti and its alloys, and the good protective passive film also has a significant impact on the wear performance[12–16]. Currently, the effect of oxidation treatment on the microstructure and properties of pure Ti has been widely researched, whereas the oxidation behavior of pure Ti welded joints is rarely researched. In practical applications, Ti components are usually processed by welding, and the welded Ti joints are normally used under aggressive conditions[17–19]. The high temperature oxidation properties of titanium and its alloys are usually achieved by coatings[20–21]. The oxidation behavior in the weak zone of welded components with defective coatings should be investigated. Due to the heat concentration during welding process, the temperature distributions around the welded joint, including the welded seam, heat-affected zone, and base metal, are quite

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different, therefore resulting in significant difference in the microstructure and properties. Thus, it is of great significance to study the high temperature oxidation behavior of pure Ti welded joint for the safe use of welded components.

In this research, pure Ti joints welded by tungsten inert gas (TIG) technique were prepared, and the effect of oxidation time and temperature on the oxidation behavior of welded joint was investigated. The macrostructure, oxidation morphology, and oxidation products were analyzed to clarify the oxidation mechanism. This research provided technical reference for the application of pure Ti components under the actual working conditions.

1 Experiment

The material used in the experiments was pure Ti (base metal) and TIG welded Ti joints. The raw materials were machined by wire-electrode and cut into the specimens with size of 15 mm×10 mm×5 mm. The specimens were ground by SiC paper from 300# to 2000#. Then, they were polished, cleaned in ethanol and distilled water, and finally dried in the air. Before oxidation experiments, the specimens were weighed at least three times and the average mass was used for analysis.

The oxidation experiments were conducted in the MF-1100C mini-muffle furnace. The oxidation processes were conducted at 550 °C for 2, 4, 6, and 8 h to investigate the effects of oxidation time on the welded joints, and they were conducted at 550, 650, 750, 850, and 950 °C for 4 h to investigate the effects of oxidation temperature on the welded joints. Then, the specimen was cooled to room temperature and weighed again.

The surface morphology of the welded joint after oxidation was characterized by the scanning white light interferometry. The specimen microstructures were analyzed by optical microscope (OM) and scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). X-ray diffraction (XRD) was used to analyze the phase composition of the oxidation products with Cu Kα radiation and 2θ=20°–90°. Raman spectroscopy was also used to analyze the phase structures of the oxidation products from 80 cm^{-1} to 1200 cm^{-1}.

2 Results and Discussion

2.1 Effect of oxidation time on welded joint

The appearances of welded joints after high temperature oxidation at 550 °C for 0–8 h are displayed in Fig.1. It can be observed that after oxidation for 2 h, light blue products are generated on the welded joint, whereas the base metal still exhibits the metallic luster, as shown in Fig.1b. The color of welded joint becomes deeper and the covered area becomes larger with prolonging the oxidation time, as shown in Fig.1c and 1d. After oxidation for 8 h, the base metal and welded joint areas are covered by light yellow products, as shown in Fig.1e. Moreover, it can also be observed that the oxidation of base metal is slower than that of welded joint, and the difference in morphologies between base metal and welded joint becomes smaller with prolonging the oxidation time.

The grain sizes of weld zone and heat-affected zone of the welded joint are larger than those of the base metal[6]. The thickness/density of oxide film and the oxygen diffusion layer formed in the initial stage is smaller than that in the base metal. Therefore, the oxide formation rate of oxygen atoms in the weld zone and heat-affected zone of the welded joint is faster than that in the base metal. The oxidation degree of each zone becomes similar to each other. The oxide film gradually thickens, becomes brittle, and finally falls off, and cracks and voids are generated, which become the main channel for the rapid diffusion of oxygen to the inner oxide film and metal matrix.

Fig.2 shows the mass gain of welded joint after oxidation at 550 °C for different durations. It can be seen that with prolonging the oxidation time from 0 h to 8 h, the mass gain is increased, whereas the increment is gradually decreased. After oxidation for 2 h, the mass gain is 0.0178 mg/cm^2. With prolonging the oxidation time to 4, 6, and 8 h, the mass gain is 0.0266, 0.0355, and 0.0415 mg/cm^2, which increases by 49.4%, 33.5%, and 16.9%, respectively. It can also be inferred that the oxidation rate of the welded joint is decreased with prolonging the oxidation time.

SEM morphologies of base metal, heat-affected zone, and welded seam after oxidation at 550 °C for different durations

Fig.1 Appearances of welded joints after high temperature oxidation at 550 °C for 0 h (a), 2 h (b), 4 h (c), 6 h (d), and 8 h (e)

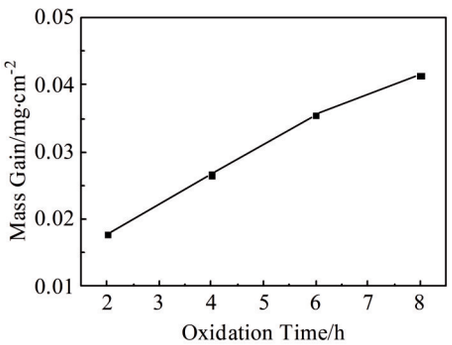

Fig.2 Mass gain of welded joint after oxidation at 550 ° C for different durations

are shown in Fig. 3. It can be seen that the surface of fresh specimen has slight scratches and small pits, as shown in Fig.3a–3c. After the specimen is oxidized for 2 h, the area of scratches and pits decreases, and the specimen surface becomes flat. This may be caused by the formation of oxidation products on the surface during oxidation treatment, which fill and cover the scratches and pits. A small number of white products appear on the welded joint, as shown in Fig.3d–3f. With prolonging the oxidation time to 4 h, the area of scratches and pits becomes smaller, and the differences in morphology among welded joint, heat-affected zone, and base metal become even less. After the specimen is oxidized for 6 and 8 h, the volume fraction of white oxidation products increases and the area of pits and scratches further decreases.

EDS results of base metal, heat-affected zone, and welded joint are listed in Table 1, suggesting that the products may be TiO_2. However, it cannot be detected by XRD due to its low content. The results also infer that prolonging the oxidation time can lead to the increase in the volume fraction of oxidation products.

The results of mass gain, oxidation rate, oxidation morphology, and oxidation products all prove that the oxidation reaction of pure Ti TIG-welded joint at 550 ° C is extremely slow, and the effect of oxidation time is relatively slight.

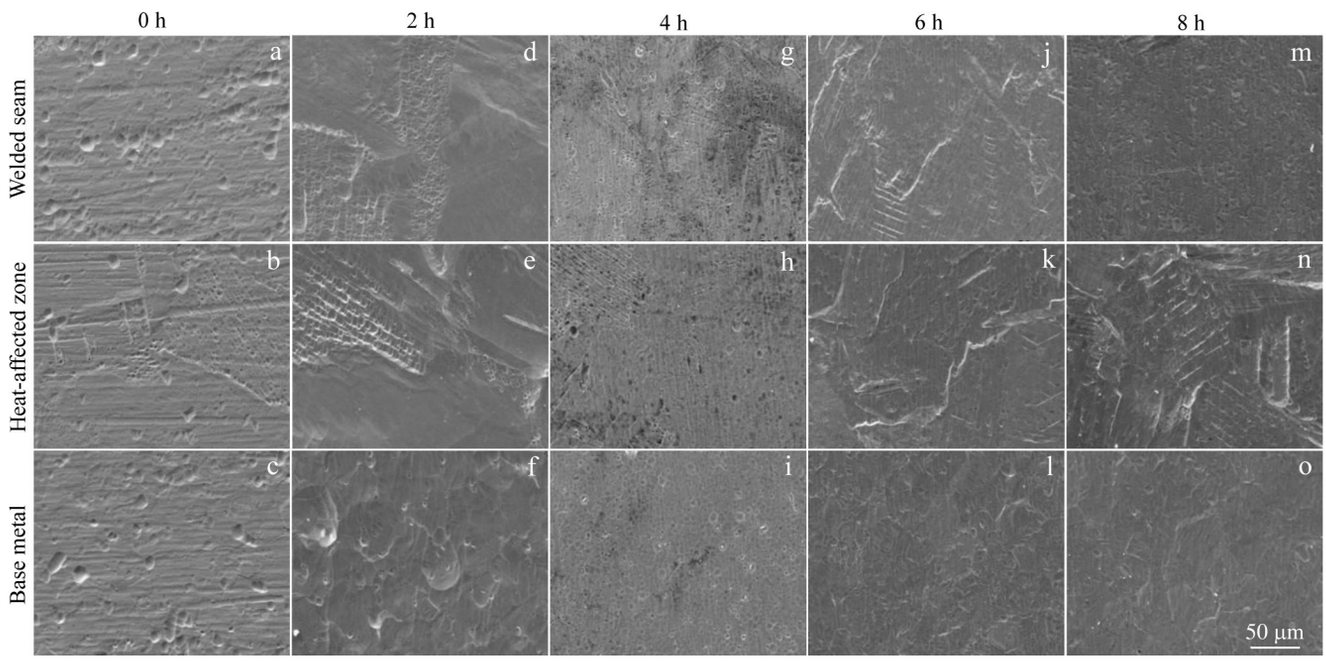

Fig.3 SEM morphologies of welded seam (a, d, g, j, m), heat-affected zone (b, e, h, k, n), and base metal (c, f, i, l, o) areas after oxidation at 550 °C for 0 h (a–c), 2 h (d–f), 4 h (g–i), 6 h (j–l), and 8 h (m–o)

2.2 Effect of oxidation temperature on welded joint

Fig. 4 shows the appearances of the welded joints after oxidation at 650, 750, 850, and 950 °C for 4 h. It can be seen that the surface color of welded joint is continuously lightened with increasing the oxidation temperature. The substrate can still be observed at 650 °C (Fig.4a), whereas the welded joint becomes gray with the appearance of a small number of white spots at 750 °C (Fig.4b). With further increasing the oxidation temperature to 850 °C, the color of welded joint turns to light yellow, the surface is fully covered by oxidation products, and the surface becomes smooth (Fig. 4c). When the oxidation temperature increases to 950 ℃, the surface becomes

Table 1 EDS results of base metal, heat-affected zone, and welded joint (at%)

Oxidation time/h	Welded joint		Heat-affected zone		Base metal	
	O	Ti	O	Ti	O	Ti
0	0.00	100.00	0.00	100.00	0.00	100.00
2	2.18	97.82	1.57	98.43	1.92	98.08
4	3.36	96.64	3.01	96.99	3.14	96.86
6	3.70	96.30	3.39	96.61	2.98	97.02
8	6.01	93.99	4.07	95.93	5.63	94.37

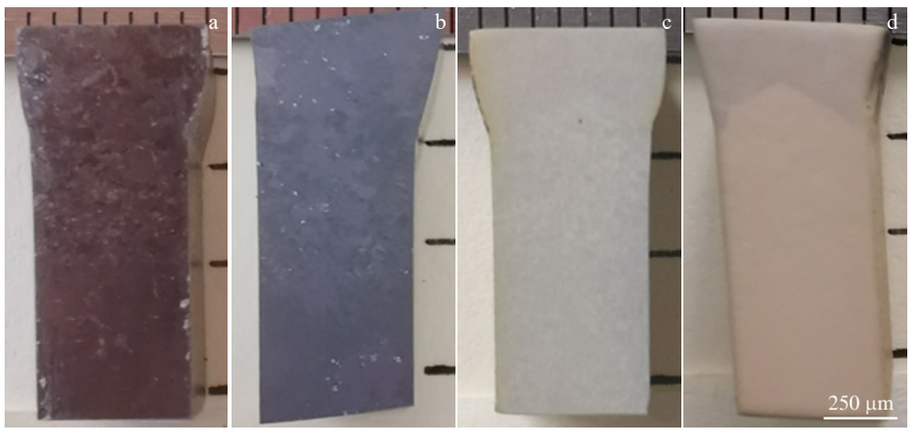

Fig.4 Appearances of welded joints after oxidation at 650 °C (a), 750 °C (b), 850 °C (c), and 950 °C (d) for 4 h

smoother. These phenomena suggest that the oxidation of welded joint is intensified with increasing the oxidation temperature.

The mass gain of welded joints after oxidation at different temperatures for 4 h is shown in Fig.5a. It can be seen that the average mass gain is slowly increased at first and then rapidly increased with increasing the oxidation temperature. The mass gain of welded joint is 0.0226 mg/cm^2 after oxidation at 550 °C for 4 h. With increasing the oxidation temperature to 650, 750, 850, and 950 °C, the mass gain is 0.1377, 0.6573, 2.457, and 4.501 mg/cm^2, which is 3.18, 22.71, 90.37, and 167.18 times higher than that at 550 °C, respectively. These results indicate that the higher the oxidation temperature, the more severe the oxidation degree of welded joints. Fig. 5b displays the oxidation rate of welded joints after oxidation at different temperatures for 4 h. The oxidation rate is increased with increasing the oxidation temperature, indicating that the oxidation reaction becomes more intense. Moreover, it can be found that the oxidation kinetics is very close to the quasi-linear law at lower temperatures, and the oxidation kinetics shows exponential growth with increasing the oxidation temperature.

Fig. 6 displays SEM morphologies of welded joints after oxidation at different temperatures for 4 h. Small scratches and pits can be observed on the surface of welded joint after oxidation at 550 °C. With increasing the oxidation temperature to 650 °C, all parts of the welded joint, including the welded seam, heat-effected zone, and base metal, show a large number of pits with large sizes. When the temperature increases to 750 °C, the scratches and pits on the surface of welded joint become smaller and the surface becomes flat. When the temperature increases to 850 and 950 °C, all parts of the welded joint become flatter, and the scratches as well as pits disappear. Besides, some white products appear on the surface of welded joints.

The white products formed on the surface of welded joints after high temperature oxidation are analyzed by XRD, and the results are displayed in Fig. 7. It can be seen that TiO_2 is formed on the surface of welded joint after oxidation at 650 °C for 4 h, but its content is relatively low. When the oxidation temperature increases, the intensity of TiO_2 peaks increases, and the intensity of Ti peaks decreases. When the temperature rises to 850 and 950 °C, the Ti peaks disappear. These results suggest that TiO_2 is formed during the high temperature oxidation of the welded joints. With increasing the temperature, the oxidation is intensified and the generation amount of TiO_2 is increased.

The oxidation products formed on the welded joint after oxidation at different temperatures are further characterized by Raman spectra, and the results are displayed in Fig. 8. It can be seen that all specimens have similar characteristic peaks: their absorption peaks are at 144, 238, 448, and 610

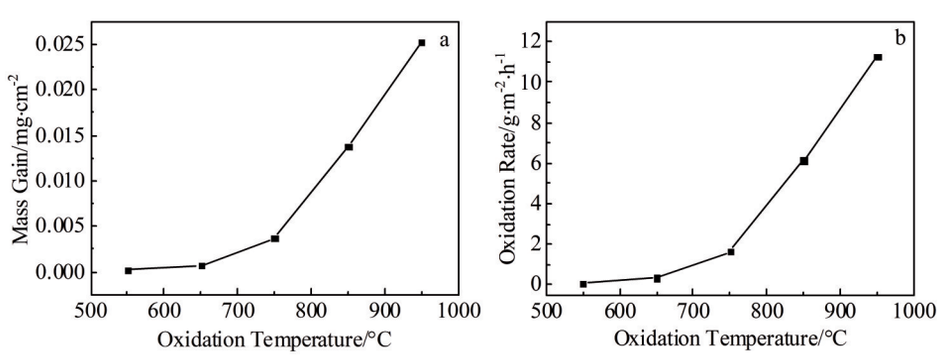

Fig.5 Mass gain (a) and oxidation rate (b) of welded joints after oxidation at different temperatures for 4 h

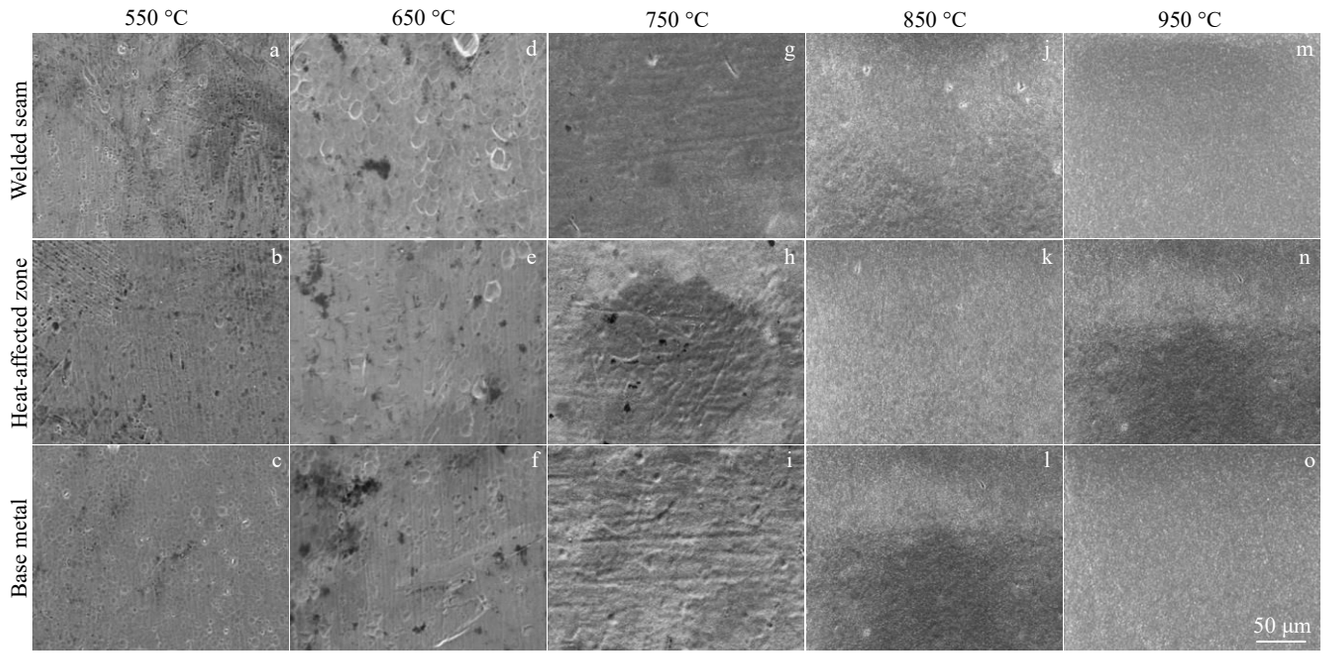

Fig.6 SEM morphologies of welded seam (a, d, g, j, m), heat-affected zone (b, e, h, k, n), and base metal (c, f, i, l, o) areas after oxidation at 550 °C (a–c), 650 °C (d–f), 750 °C (g–i), 850 °C (j–l), and 950 °C (m–o) for 4 h

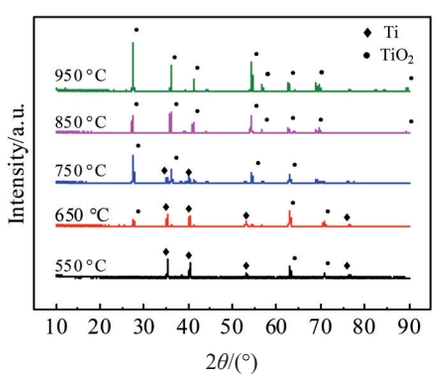

Fig.7 XRD patterns of white products on welded joint after oxidation at different temperatures for 4 h

cm^{-1}. This result suggests that the oxidation products generated on the surface of different welded joints are the same. According to the results in Ref.[22–25], the absorption peak at 144 cm^{-1} indicates the TiO_2 with anatase structure and the ones at 238, 448, and 610 cm^{-1} indicate the TiO_2 with rutile structure.

Therefore, the oxidation products generated on the surface of welded joints are TiO_2 with both anatase and rutile structures, and the temperature has no effect on the type of TiO_2. The TiO_2 content is increased with increasing the oxidation temperature.

The microstructures of welded joints after oxidation at different temperatures for 4 h are displayed in Fig.9. It can be observed that the welded seam and heat-affected zone are composed of coarse columnar structures, and the base metal consists of equiaxed crystals after oxidation at 650 °C. The oxidation can hardly be observed in Fig. 9a – 9c. The microstructures of welded joint after oxidation at 750 °C are quite similar to those at 650 °C. When the temperature rises to 850 °C, the grains in welded seam, heat-affected zone, and base metal become coarser, and the oxidation film is generated on the surface. It should be noted that the cracks appear in the oxidation film, as shown in Fig. 9g – 9i. The oxidation film is thickened with increasing the oxidation temperature to 950 °C (Fig.9j–9l).

Based on the results of oxidation rate, oxidation morphologies, and microstructures of welded joints, the oxidation kinetics can be illustrated in Fig.10 and described as the following steps. Oxygen atoms are absorbed on the surface of welded joint, and O reacts with Ti, thereby generating the TiO_2[26]. TiO_2 preferentially nucleates in the defective zone, such as the scratches and pits. TiO_2 gradually grows, the surface of welded joint becomes flat, and then the protrusions are formed. The nuclei grow laterally and get into contact with each other[27–28], resulting in the fact that the surface is covered by oxidation film. With the oxidation reaction proceeding, the oxide film grows towards atmosphere and becomes thick. At low oxidation temperatures, the oxidation film is dense and it isolates O from the welded joint. In this case, O must pass through the film and then reacts with Ti. Thus, the oxidation rate is relatively small. However, at high oxidation temperatures, the cracks or voids appear in the oxidation film, as shown in Fig.9g–9i. These micro- or macro-cracks and viods become the transmission channels of O. Therefore, the diffusion rates of O and Ti increase, leading to the high oxidation rate.

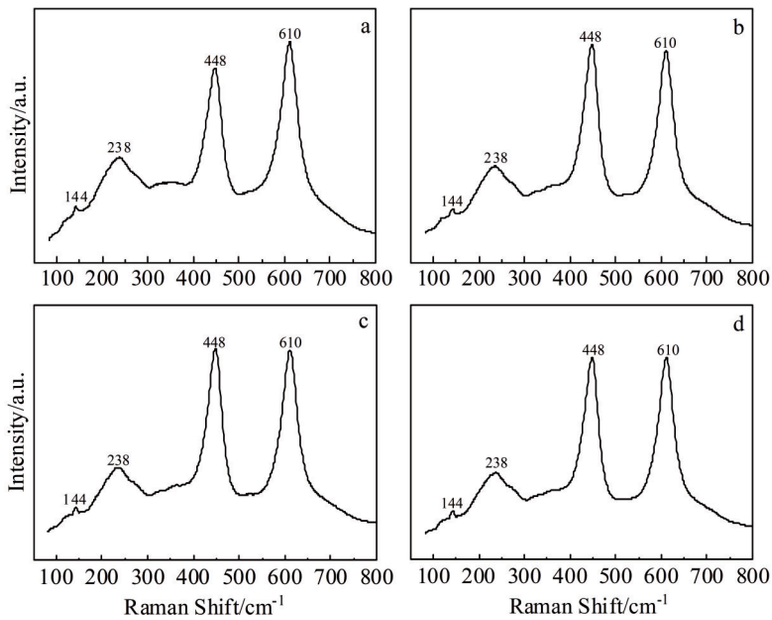

Fig.8 Raman spectra of welded joints after oxidation at different temperatures for 4 h: (a) 650 °C, (b) 750 °C, (c) 850 °C, and (d) 950 °C

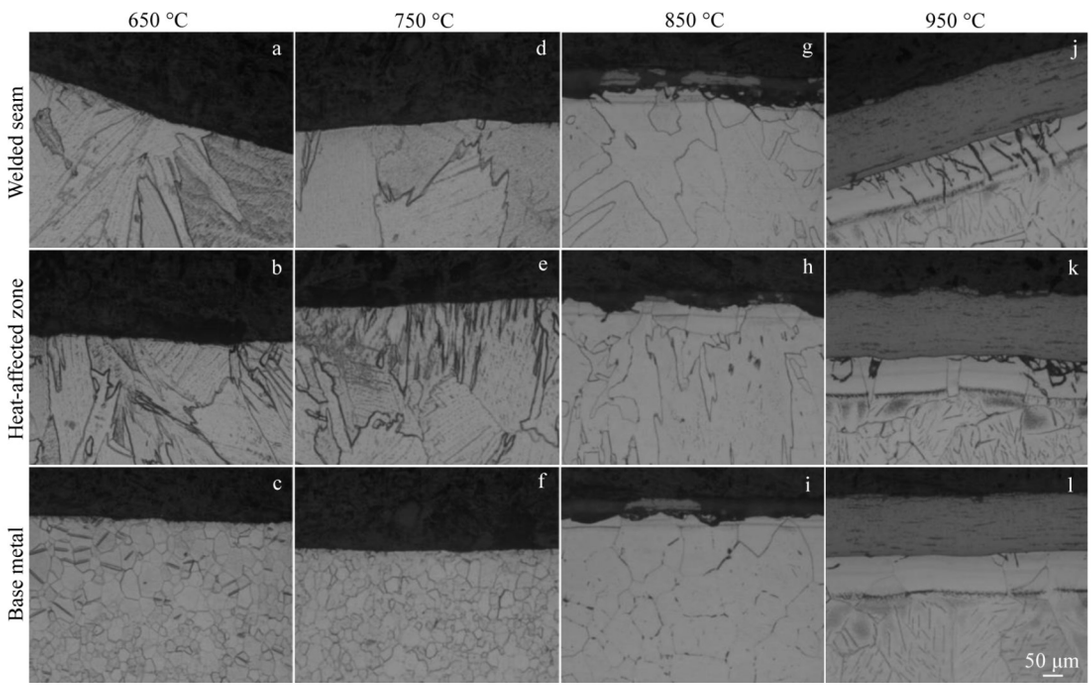

Fig.9 Microstructures of welded seam (a, d, g, j), heat-affected zone (b, e, h, k), and base metal (c, f, i, l) areas after oxidation at 650 °C (a–c), 750 °C (d–f), 850 °C (g–i), and 950 °C (j–l) for 4 h

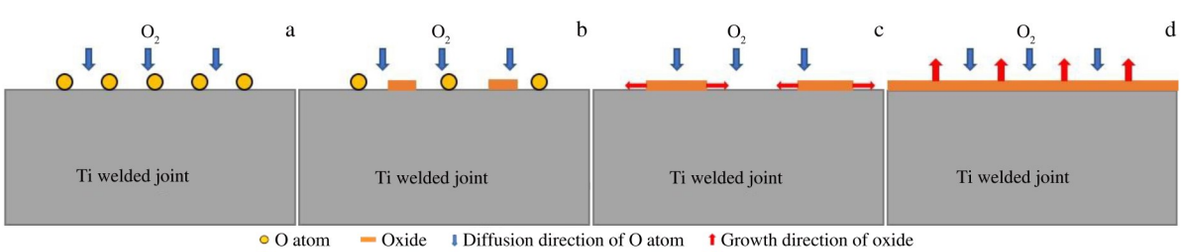

Fig.10 Schematic diagrams of oxidation film formation on surface of welded joint: (a) O absorption on surface; (b) preferential nucleation in defective zone; (c) lateral oxide growth; (d) oxidation film growth and thickening

3 Conclusions

1) The effect of oxidation time on the oxidation behavior of the TIG welded joint of pure Ti after oxidation at 550 °C is slight, whereas the oxidation temperature has a significant impact on the oxidation behavior.

2) The oxidation rate shows exponential growth with increasing the oxidation temperature above 650 °C.

3) The oxidation products generated on the surface of welded joints are TiO_2 with anatase and rutile structures, and the oxidation temperate does not affect the type of oxidation products.

4) The oxidation process can be described as follows: O atoms are absorbed on the surface and then react with Ti; oxides preferentially nucleate in the defective zone; oxides grow laterally to form the oxidation film, and the film becomes thick. At high temperatures, cracks or voids appear in the oxidation film, becoming the transmission channels of O and Ti atoms, leading to the high diffusion rates of O and Ti atoms and high oxidation rate.

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纯钛TIG焊接接头的高温氧化行为

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摘　要：对纯钛氩弧焊焊接接头在550 ℃下氧化不同时间（2，4，6，8 h）以及在不同温度（650，750，850，950 ℃）下氧化4 h的氧化动力学、氧化形态和氧化产物进行了研究。结果表明，在550 ℃下，氧化时间对焊接接头氧化行为的影响有限，而氧化温度对纯钛焊接接头的氧化行为有显著影响，且温度越高，氧化越严重。在低温下，纯钛焊接接头的氧化动力学接近准线性定律，随着温度升高，氧化速率呈指数增长。此外，焊接接头表面产生的氧化产物是具有锐钛矿和金红石结构的TiO_2，温度对TiO_2的类型没有明显影响。纯钛焊接接头的氧化过程可描述为：氧气在表面被吸收；氧化物优先在缺陷区形核；氧化物横向生长、增厚。在较高温度下，氧化膜中出现裂纹或空隙，成为O原子传输通道，导致O和Ti原子的高扩散速率和氧化速率。

关键词：焊接接头；氧化处理；氧化动力学；氧化膜

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