TC4 titanium alloy oxygen diffusion strengthening with surface cladding

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Abstract: To improve the wear resistance of titanium alloy surfaces and adapt to a richer service environment. In this paper, a surface antioxidant protective coating is used to clad TC4 titanium alloy, followed by oxygen diffusion treatment at different temperatures and times. The metallographic organization, hardness and friction curves of the specimens after the oxygen diffusion treatment were also characterized. The results show that the clad protective coating can effectively mitigate the high temperature oxidation behavior of TC4 and inhibit the formation of sparse and brittle oxides on the surface. The microhardness of TC4 alloy surface layer was increased from 320 $HV_{0.3}$ to 737 $HV_{0.3}$ after oxygen diffusion treatment at 950°C×10 h. The hardening depth reached more than 100 μm, and the wear resistance was improved by 48%.

1. Introduction

Titanium alloy has high specific strength and good corrosion resistance. It has a wide range of applications in medical treatment [1], aerospace and other fields, nevertheless, they have the disadvantages of low hardness and high friction factor [2], resulting in its poor wear resistance. Surface strengthening processes, such as nitriding, oxygen diffusion, physical vapor deposition (PVD) and thermal spraying, can generate coatings with high hardness and improve the wear resistance of titanium alloys. Among them, the oxygen diffusion strengthening [3] technology of titanium alloy has the advantages of simple equipment, no pollution and large thickness of the hardened layer. Oxygen has small atomic radius and high solubility, the ultimate solid solution of oxygen in titanium is up to 13%. Oxygen diffuses into the matrix at high temperatures, allowing oxygen to form a supersaturated solid solution in titanium through a solid solution strengthening mechanism. Jia, Y. F et al. [4] used TA2 at 700℃ thermal oxidation for 20 min, and then carried out vacuum diffusion at 700℃ for 15h, and obtained the hardness. Zabler [5] used Ti6Al4V for 80 min (700℃) + 120 min (850℃) to obtain a 36 μm oxygenated layer with a hardness of 434 HV. Zhen [6] et al. performed oxygen diffusion of Ti6Al4V alloy at 850°C for 20 h. The hardness of the modified layer was improved to 651$HV_{0.05}$.

The oxygenation process generates TiO, TiO_2 and other oxides. Because of the large difference in thermal expansion coefficient between TiO_2 and titanium alloy matrix, the hardening layer will be peeled off during the cooling process [7], which will seriously reduce the surface quality. Therefore, the ideal oxygen diffusion strengthening is to form a dense α-Ti (O) solid solution on the surface of titanium alloy while avoiding the generation of oxides, so controlling the oxidation and oxygen diffusion process is the key. The most commonly used oxygen diffusion technique is the two-step oxygen diffusion proposed by H. DONG [8], in which the sample is first thermally oxidized in air, and then the pre-oxidized sample is further diffused in vacuum for treatment. Considering the high oxygen partial pressure requirement in the vacuum oxygen diffusion process, which leads to high process cost, it is difficult to be used in actual production. In this paper, we propose to construct a vacuum-like environment by using a coating of antioxidant coatings to reduce the production cost. Using TC4 titanium alloy as the research object, the process of thermal oxidation and coating cladding with oxygenation is carried out to prepare a high hardness oxygenated reinforced layer on the surface of titanium alloys. To study the effect of time, temperature and coating on the oxygenation of titanium alloys. Which is important to improve the reliability of the operation of mechanical components as well as to extend the service life.

2. Test material and method

A square TC4 titanium alloy plate specimen of 30mm×30mm×2.5mm was selected for the experiment and its surface was polished with glossy surface. The specimens were thermally oxidized at 750°C for 40 min, and after cooling to room temperature, the surface of the titanium alloy was coated with Ti-1 mixed silicate antioxidant coating with particle size ≤ 5 μm and solute ratio 1:1. The coated TC4 alloy was subjected to oxygen diffusion strengthening treatment in air atmosphere at 850°C, 900°C and 950°C for 8, 10 and 12 h. Under the same conditions, the same treatment was carried out on the uncoated TC4 alloy for control. After the oxygen diffusion process, the specimen sections were taken, ground and polished, and the metallographic organization of the specimen sections was observed using an optical microscope. The micro hardness of the specimen section was measured using a Vickers hardness tester with a load weight of 300 g. The wear resistance of the material surface was characterized using a comprehensive material property tester with a load of 10 N, a speed of 500 r/min, and a test time of 20 min with an indenter material GCr15.

3. Results and discussion

3.1 Effect of coating cladding on surface oxygen diffusion behavior

After thermal oxidation of TC4 alloy, Ti(O) solid solution is formed on the surface of the alloy as oxygen atoms in the air penetrate into the matrix of TC4 alloy, followed by a gradual increase in the concentration of solid solution oxygen and the gradual formation of TiO_2 oxide, while oxygen atoms continue to diffuse into the internal matrix tissue and continue to form a solid solution oxygen diffusion layer under the oxide layer. Fig. 1 shows the organization of the specimen after heat treatment. The microstructure of the surface layer of the alloy after oxygen diffusion at 900°C × 8 h consists of equiaxed α-phase and β-phase matrix.

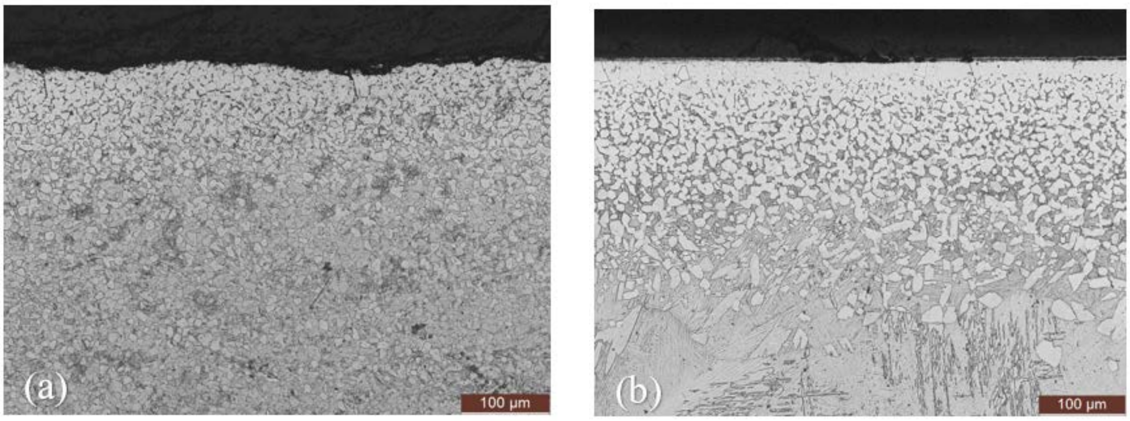


Fig 1. Microstructure after oxygen diffusion at 900°C and 8h under air atmosphere.

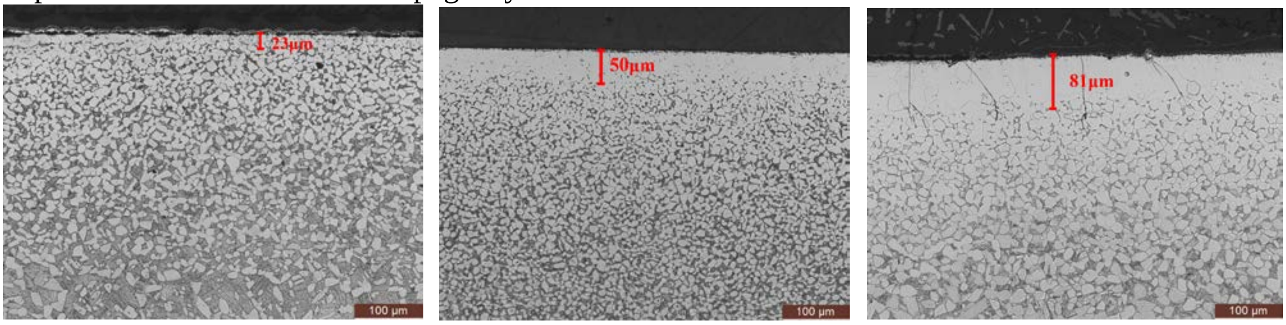
Among them, Fig. 1(a) shows the microstructure of the specimen without antioxidant coating after heat treatment at 900°C and 8h under air atmosphere. Due to the fast oxidation rate of Ti at high temperature, the oxide film formed is more brittle and the bonding force with the substrate is weaker, and the oxide flaking occurs on the surface after oxygen diffusion treatment, leading to the rise of surface roughness. And due to the fast oxygen diffusion rate and high concentration of solid-soluble oxygen, the surface of the specimen is more likely to generate an oxide layer rather than an oxygen-permeated layer, and the change of α-phase size is not obvious. Fig. 1(b) shows the microstructure of the specimen coated with an antioxidant coating after oxygen diffusion. The surface remained flat after oxygen diffusion treatment and the oxide film did not flake off. There is an obvious α-phase enrichment on the surface of the specimen, and there is a certain increase in the size of isometric α-phase, and the content of α-phase shows a gradual decrease from the surface to the interior.

It can be seen that the antioxidant coating has a significant effect on the high-temperature oxidation behavior of TC4 alloy, and the coating can inhibit the surface oxidation to a certain extent.

According to Fick's second law $C(x) = C_s + (C_0 - C_s)erf\left[\frac{x}{2(D_s t)^{1/2}}\right]$ antioxidant coating causes the actual oxygen concentration on the alloy surface to be lower than that of air to reduce the oxygen concentration gradient on the alloy surface, i.e., $(C_0 - C_s)$ decreases; the temperature remains constant and the diffusion coefficient D of oxygen in TC4 alloy remains constant. Therefore, the antioxidant coating reduces the infiltration rate of oxygen atoms, resulting in the formation of saturated solid solution in the α-phase oxygen permeation layer on the alloy surface.

3.2 Effect of oxygen diffusion temperature on the surface strengthening effect

Fig. 2 shows the microstructure of the specimens coated with antioxidant coating after 10h treatment at different oxygen diffusion temperatures, where the white bright layer is the oxygen diffusion modified layer with saturated solid solution, which is dominated by single-phase α after oxygen diffusion treatment, and the grain growth is obvious, which plays a strengthening role and thus improves the hardness of the seepage layer.



(a) 850℃ (b) 900℃ (c) 950℃

Fig 2. Microstructure after 10h treatment at different oxygen diffusion temperatures.

Under the air atmosphere, the thickness of the oxygenated layer on the surface was 23 μm at the oxygen diffusion temperature of 850°C; at the oxygen diffusion temperature of 900°C, the thickness of the oxygenated layer increased significantly and reached 50 μm; at the oxygen diffusion temperature of 950°C, the thickness of the oxygenated layer reached a maximum of 81 μm. The reason for the increase in the thickness of the oxygenated layer with the increase in temperature is that the higher the temperature, the greater the solid solution of the solute elements, the faster the diffusion of O atoms, and the greater the depth of diffusion. The higher the temperature, the greater the solid solution of the solute element, the faster the O atoms diffuse, and the greater the depth of diffusion, thus obtaining a higher thickness of the oxygenated layer.

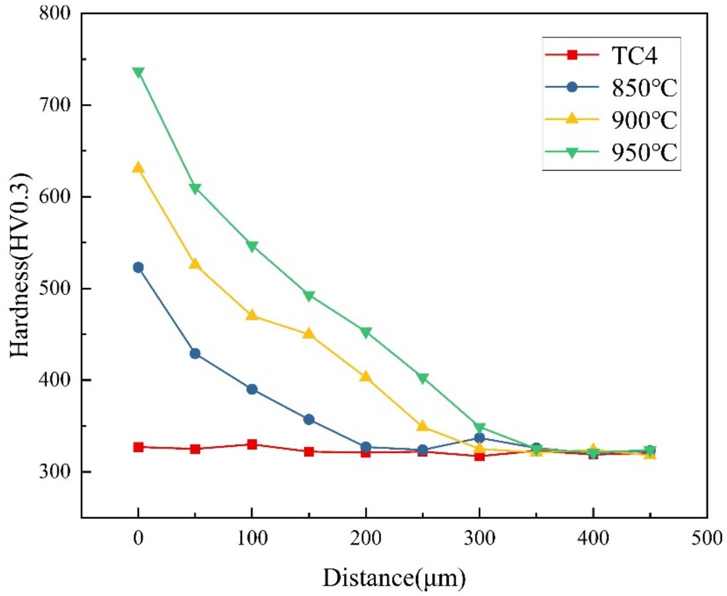
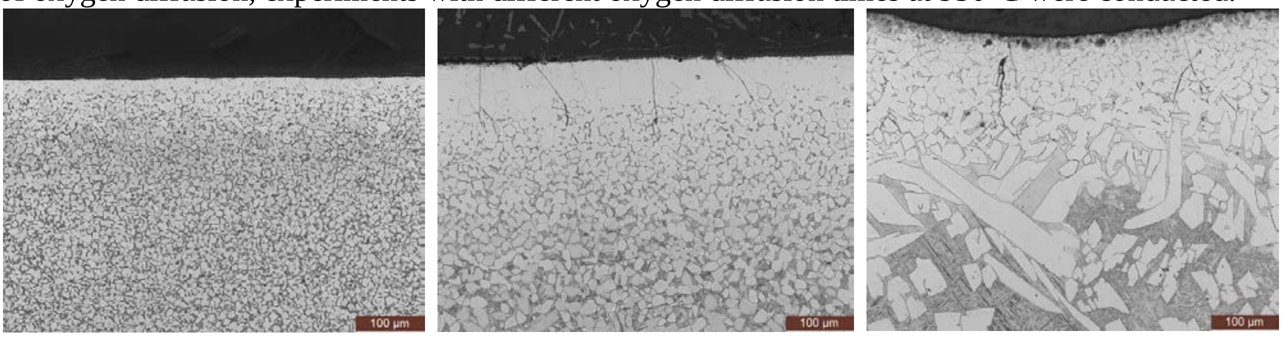


Fig 3. Micro hardness after 10h treatment at different oxygen diffusion temperatures.

The matrix hardness of TC4 titanium alloy is 320 $HV_{0.3}$. The interstitial solid solution formed by O diffusion leads to an increase in hardness, and the number of interstitial solid solutions is related to the O diffusion rate, so the hardness is maximum near the surface layer, and then gradually decreases with the increase of distance from the surface. It can be seen that there is a significant increase in micro hardness with the increase of oxygen diffusion temperature. When the oxygen diffusion temperature is 850°C, the surface hardness of the specimen is somewhat increased compared with the substrate, reaching 523 $HV_{0.3}$; when the oxygen diffusion temperature is increased to 900°C, the surface hardness of the specimen rapidly increases to 631 $HV_{0.3}$ and still retains a good strengthening effect at 50 μm from the surface; the surface hardness reaches a maximum of 737 $HV_{0.3}$ at an oxygen diffusion temperature of 950°C, while the hardening depth reaches 100μm or more. The results show that oxygen diffusion at 950 ℃ has the most significant effect on the surface hardening of the alloy, and the oxygen diffusion strengthening effect is positively correlated with the thickness of the oxygen diffusion layer. The interstitial solid solution of oxygen elements increases the ratio of lattice constant c/a in the α-phase, which leads to an increase in the hardness of the α-phase. Therefore, the hardness of the surface area increases with the increase of α-phase content, which is consistent with the microstructure change pattern of the alloy surface after oxygen diffusion treatment.

3.3 Effect of oxygen diffusion time on the surface strengthening effect

The optimum temperature for oxygen diffusion strengthening of TC4 specimens coated with antioxidant coatings was obtained in the previous paper as 950°C. To investigate the optimum process of oxygen diffusion, experiments with different oxygen diffusion times at 950°C were conducted.



(a) 8h (b) 10h (c) 12h

Fig 4. Microstructure after oxygen diffusion at 950°C for different times.

Fig. 4 shows the microstructure of the specimens covered with antioxidant coating treated with oxygen diffusion temperature of 950°C for different times. Fig. 4 (a) The surface layer of the specimen oxygenated for 8h showed α-phase enrichment, but the thickness was small and no effective hardening layer could be formed. Fig. 4 (c) Although the α-phase enriched layer formed by oxygen diffusion 12h is thicker, the surface shows larger deformation, part size failure, and coarse organization, which will lead to serious strong plasticity decay. Combined with the results of the micro hardness in Fig. 5, the hardness of the specimens covered with antioxidant coating was increased to 560 $HV_{0.3}$ by oxygen diffusion for 8h at 950°C, and the hardening effect of the specimens by oxygen diffusion for 10h and 12h was close, both reaching about 720 $HV_{0.3}$.

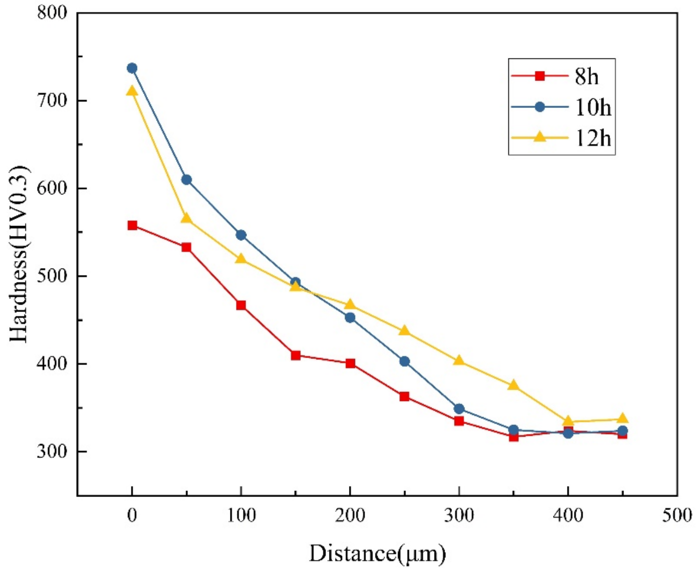


Fig 5. Micro hardness after oxygen diffusion at 950℃ for different time.

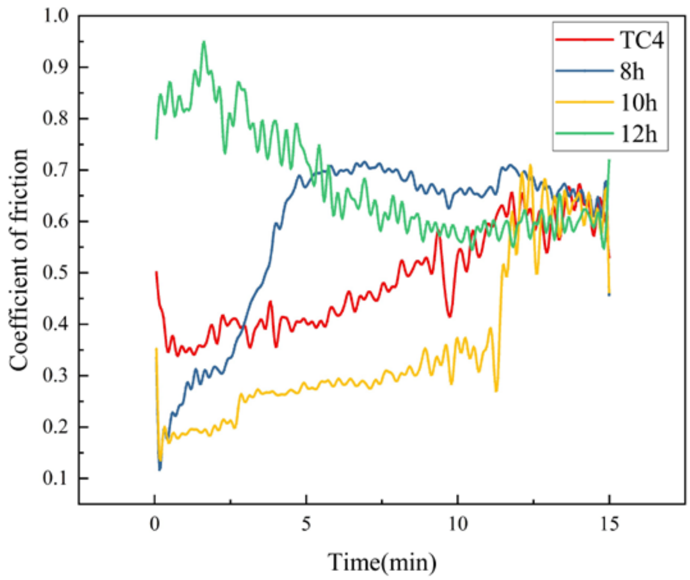


Fig 6. Friction curve after oxygen diffusion at 950℃ for different time.

The coefficient of friction is related to the surface roughness and shows the wear reduction property of the material, the lower the coefficient of friction the better the wear reduction property of the material and the corresponding better the wear resistance. Fig. 6 shows the curve of friction coefficient with time for the specimens covered with antioxidant coating under the condition of oxygen diffusion temperature of 950℃ and treated for different times. The test results show that the average friction coefficient of TC4 titanium alloy substrate is 0.48, while the friction coefficients of the specimens treated with oxygen diffusion are 0.54 \ 0.25 \ 0.71. The specimens with 12h oxygen diffusion have a large friction coefficient due to the large dimensional deformation of the surface, the failure of oxygen diffusion layer protection, and the increase of roughness. Oxygen diffusion 8h specimens at 4min friction factor increased abruptly, because the oxygen diffusion layer is thin, quickly worn through, the abrasive particles and the substrate hardness gap is large, increasing the friction. For the specimen with 10h oxygen diffusion time, the friction coefficient was much lower than that of the substrate before the oxygen diffusion layer was worn through, reaching 0.25, and rose to the same level as that of the substrate after the wear through occurred. The results showed that the surface of the specimen coated with antioxidant coating and oxygenated at 950℃ for 10h produced a flat and uniform oxygenated layer with high hardness and certain thickness, and the hardening effect of the oxygenated layer could effectively reduce the friction coefficient and improve the wear resistance.

4. Conclusions

(1) The surface oxygen diffusion strengthening of TC4 titanium alloy is achieved by the combination of surface cladding and high-temperature oxygen diffusion process. The cladding antioxidant coating can effectively prevent the generation of surface oxides and form a dense oxygen diffusion layer.

(2) After oxygenation strengthening, the micro hardness of the specimen surface was significantly increased. The hardening effect increases with increasing temperature and decreases with increasing depth from the surface. The hardness of the specimens treated with oxygenation at 950°C for 10h reached 737 $HV_{0.3}$.

(3) Oxygen diffusion treatment can effectively improve the wear resistance of TC4 titanium alloy; the friction coefficient of specimens treated with oxygen at 950°C for 10h is 0.25, and the wear rate decreases by 48%.

Acknowledgments

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