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Research Article

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Plasma Surface Wear-Resistant Titanium Aircraft Alloys

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Abstract

Titanium, is known as the "aerospace material", "marine material," like an indispensable material in the modern industry. Due to its low hardness and poor thermal conductivity, the surface of titanium is prone to adhesion under a friction condition. In some special media, the passivation film on the titanium surface loses its protective ability and shows the strong chemical activity. As a consequence, proper surface modification for its physical, chemical, or mechanical property change is required for some specific applications. This chapter is to introduce Plasma Surface Metallurgy on Titanium matrix and Titanium Alloys by the double glow plasma surface alloying technology to enhance wear-, corrosion- and flame resistance.

Keywords: Plasma Surface Metallurgy, Wear-Resistant Titanium Alloys, Double Glow Plasma Alloying, Titanium Surface Modification, Tribological Properties, Corrosion Resistance, Flame-Resistant Titanium

Introduction to Titanium and Titanium Alloys

Titanium is the fourth most abundant structural metal in the crust of the earth after aluminum, iron, and magnesium. The development of its alloys and processing technology started only in the late 1940s. Titanium element was discovered in 1791. In 1908, Norway and USA started producing titanium dioxide by the Sulfate Process. In 1910, sponge titanium was first prepared by Sodium Method in the laboratory. In 1948, mass production of sponge titanium was achieved by US DuPont Company with using the Magnesium method. Afterward, titanium had begun to be wildly used as an important metallic structural material. With further studies, people realized that titanium is a major functional material as well.

Classification and Properties

There are two allotrope forms of titanium: α- Ti at 882.5 °C or lower, with a close-packed hexagonal (HCP) lattice structure and β-Ti at 882.5 °C or higher with a body-centered cubic (BCC) lattice structure. Upon the phase structure and the content of b stable element, Titanium alloys are classified into three categories: α, α+β and β. Upon the mechanical characteristics of titanium alloy, it can be further divided into: corrosion-resistant titanium alloy, heat-resistant titanium alloy, low temperature titanium alloy, structural titanium alloy, bio titanium alloy, flame-resistant titanium alloy, etc. Titanium and titanium alloy exhibit several unique properties and have been widely used in the field of chemical industry, aviation, aerospace, marine, and medical devices as regular supplies since 1950's. Main physical properties of titanium and titanium alloys include: (1) Low density and high specific strength: The specific weight / (density) of Ti is 4.51 g/cm3 with tensile strength up to 1300 MPa. The specific strength is much higher than that of aluminum and alloying steel, the highest among metal materials; (2) Good heat resistance: Some new types of titanium alloys can be used for a long time at 600 °C or higher, and is suitable for the aviation and aerospace heat-resistance components; (3) Good low temperature resistance: At temperature of (-196 to -253 °C), titanium maintains relatively good ductility and toughness. These make Ti to be an ideal material for cryogenic vessels, and tank equipment's; (4) Good corrosion resistance: Ti is very stable among many media. For example, Ti is corrosion resistant in the medium of oxidation, neutral, and weak reduction. However, as is listed below, Titanium also has some drawbacks along with its a fore mentioned advantages. (1) Low wear resistance: The low surface hardness of titanium makes the adhesive wear easy to occur; (2) Low oxidation resistance at high temperature: Titanium shows a strong tendency of oxidation at a temperature of 350 °C or higher. The higher the temperature is at; the higher degree of oxidation would occur; (3) High cost: the price of titanium is about 5–10 times higher than that of the stainless steel.

Effect of Alloying Elements

The intrinsic characteristics of titanium alloy determine its low hardness, poor thermal conductivity, and prone to adhesion in friction. Therefore, in many practical applications, the surface modification must be carried out to improve their tribological properties, when titanium parts are working under the condition of friction and wear. Pure titanium metal has good corrosion resistance and biocompatibility, but its mechanical strength is low. In order to meet the requirements for the structure application, some other elements need to be added into titanium to form titanium alloys with improved properties. Aluminum is the typical a-phase stable element and most widely used in titanium alloy. In addition, carbon, nitrogen and oxygen are also typical a-phase stable elements. In plasma surface metallurgy technology, Al, C, N, and O are often used for plasma alloying treatment to improve the strength, heat resistance, corrosion resistance, and wear resistance of titanium surface. According to the characteristics of the phase diagram, b-phase stable elements can be divided into b-eutectoid elements and b-amorphous elements. b-eutectoid elements, including Mn, Fe, Cr, Si, Cu, Co, Ni, W, and Ag, etc., have the limited solid solubility in a- and b- phase. The positions of b- amorphous elements including Mo, V, Nb, and Ta, etc. in the periodic table, are close to titanium, and the lattice type of these elements is similar to that of titanium. They have the unlimited solid solubility in b titanium. In the plasma surface metallurgy process, these elements can be used to improve the strength of the alloy while maintaining high plasticity. There is no brittle phase generated by eutectoid or peritectic reaction in the alloyed layer. The structural stability is outstanding. Hydrogen is rather a special element, falling into the gap element in the b-phase stable element group. It can reduce the allotropic transition temperature, generate eutectoid reaction, and form hydrogen composition gap solid solution. The solubility of hydrogen in b-titanium is higher than that in a-titanium. The dissolved hydrogen precipitates at room temperature and forms brittle TiH2, which makes titanium brittle. This is so-called “hydrogen embrittlement.” In plasma surface metallurgy technology, carbon vaporization is generated by solid graphite as the target material. The existence of pure carbon overcomes the reaction of hydrogen in traditional carburizing technology.

Optimal Alloying Parameters

In last ~25 years, the double glow plasma surface alloying technique has been used to prepare high- performance titanium surface-alloyed layer with high corrosion resistant, wear resistant, flame resistant, and antioxidant and gives new properties to titanium besides the original high specific strength. The superiority of the double glow discharge technology in preparation of surface-alloyed layer has been demonstrated. The substrate materials are often selected among fully annealed and solid strengthen Ti-alloy materials, such as TC4: (Ti6Al4 V), TC11: (Ti6.5Al3. 5Mo1.5Zr0.3Si) and industrial pure titanium TA1, TA2, and TA3. The high purity metals or alloys are often selected as the source material, such as high purity Pd, Nb, and Mo. High purity argon is often used as a gas source for. glow discharge plasma media. If the discharge gas is required to participate in the reaction, high purity nitrogen is added. Both the working—pieces and the source electrode are biased with negative potential by two DC power supplies. Typical process parameters are set as:

- Background Vacuity: Better Than 1 10-3 Pa,
- Gas Pressure: 20–40 Pa,
- Discharge Gas: Chemical pure argon or mixture of argon and nitrogen,
- Distance Between Work-piece and Source Electrode: 10–30 mm,
- Source Electrode Bias Voltage: 800–1200 V,
- Work-piece Electrode Bias Voltage: 600–1000 V.

The bias voltages on the working-piece and on the source, electrode affect directly the source sputtering yield for alloying element supply, as well as the operation temperature on the working-piece for the diffusion rate control of alloying elements. Therefore, in the whole process, the relationship between the voltage of the work-piece and source electrode needs to be coordinated. Through the aforementioned W-Tec process, the wear resistant of Ti–Mo, Ti– Mo–N, and Ti–C-alloyed layers, flame resistant of Ti–Cu, Ti–Cr, and Ti–Cr– V-alloyed layers, corrosion resistant of Ti–Pd and Ti–Nb- alloyed layers can be formed on the surface of titanium and titanium alloy.

Plasma Surface Metallurgy Wear-Resistant Alloys

The research activities on plasma surface alloying of titanium alloys began in 1997. Surface treatments on titanium alloys with molybdenizing, niobizing, chromizing, nitriding, carburizing, oxidizing, and composite molybdenitriding, carbonitriding have been adopted for experiments and applications for improving the surface hardness and wear resistance.

Double Glow Plasma Molybdenizing

Molybdenum (Mo) has the same crystal lattice structure and similar atomic radius with titanium. As a b-phase stable element, Mo is an unlimited solid-dissolved element in b-phase with reduced b transition temperature, widely expanded b phase region, and good stability. Using pure Mo material as a source electrode in the W-Tec process, a Mo alloy layer can be formed on the surface of a titanium alloy substrate [1, 2]. Figure1 shows the microstructure of the Mo surface alloy on Ti6Al4V alloy substrate by the molybdenizing process at 950 °C, together with the depth distribution of Mo, Ti, V, and Al in the surface-alloyed layer. The alloyed layer on the titanium surface is composed of a deposition layer and a diffusion layer, with the total thickness of about 28 μm. From the depth profile analysis, it can be seen that the top surface layer is mainly Mo, with a thickness of about 15 μm. In the following diffusion layer, the content of Mo is gradually decreased, and the thickness is about 13 μm. It is also further found that, because the molybdenizing process is carried out under high temperature, Al and V in the original surface layer of titanium alloy have out-diffused slightly to the top Mo deposition layer and deep into the titanium alloy substrate respectively, leading to impoverishment of Al and enrichment of V. Temperature of plasma molybdenizing has a significant influence on the formation of a Mo–Ti-alloyed layer. Mo content in the alloyed layer has varied with the layer depth at different substrate temperature, shown in Fig. 2. It is seen that, with the increase of temperature, the thickness of diffuse layer increases. This is the increase of temperature, the thickness of diffuse layer increases. This is caused by the increase of the diffusion coefficient of Mo in the matrix at the elevated higher temperature. The wear resistance of molybdenized Ti6Al4 V titanium alloys was studied. The ball-disk wear tests were operated under the condition of dry friction with 30# oil lubrication and GCr15 hardened steel ball of U4.75 mm for friction pair couple. Shown in Fig. 3 is the correlation between the friction coefficient and the sliding distance under oil lubrication. It can be seen that, under the test condition, 30# oil lubrication has little anti-friction effect on Ti6Al4 V titanium alloy substrate. On the contrary, the plasma Mo-alloyed sample showed excellent friction reduction performance under oil lubrication. The friction coefficient of about 0.1 was very stable in the whole sliding distance. Figure 4 gives a SEM micrograph of wear surface topography of two samples after a sliding test for 70 min. As is seen, the grinding marks of Mo alloy samples

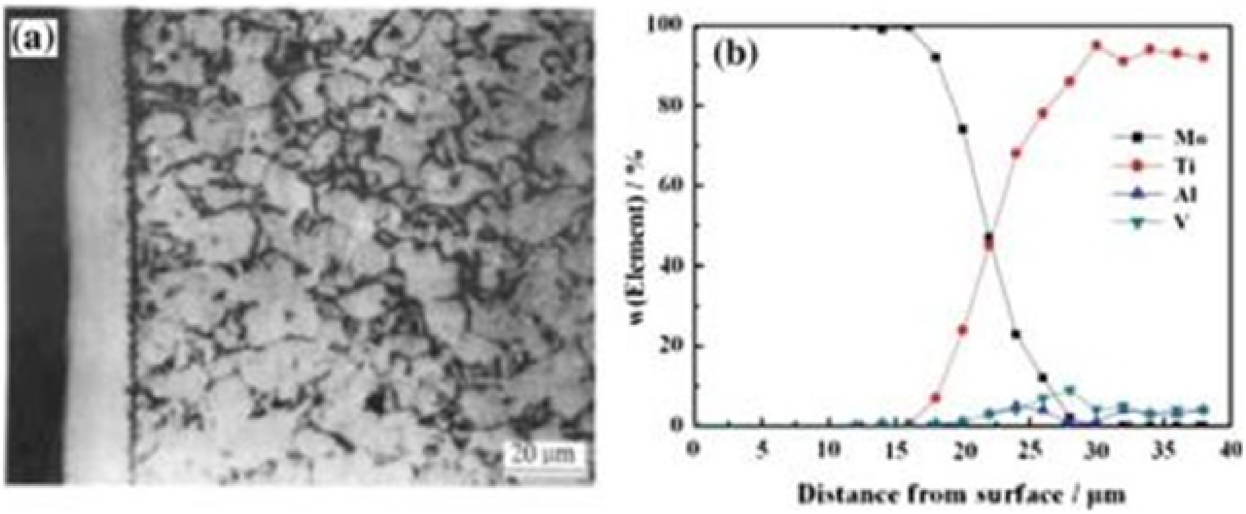
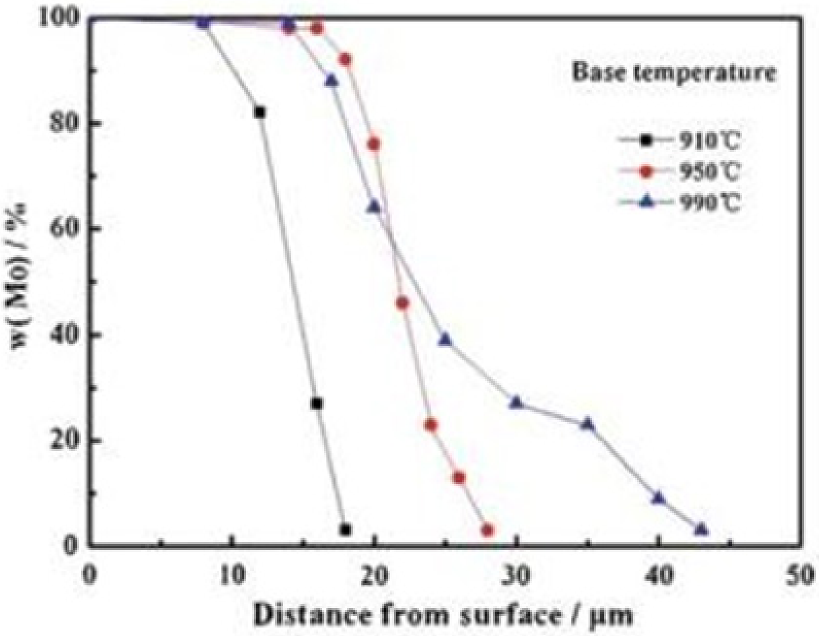


Fig. 1 a Microstructure and b composition distribution of Mo-alloyed layer on surface of Ti6Al4V

Fig. 2 Distribution of Mo element in alloyed layer at different operation temperatures



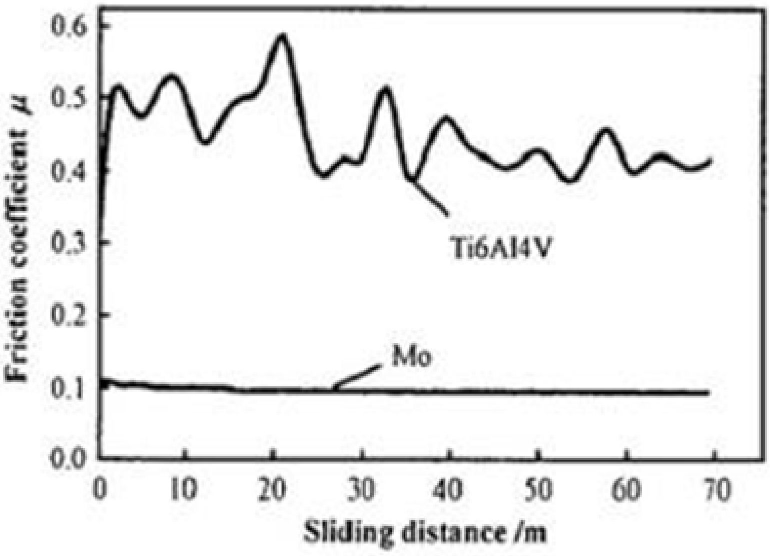


Fig. 3 Relationship between friction coefficient of Ti6Al4V substrate and Mo-alloyed sample and sliding distance in oil lubricated condition

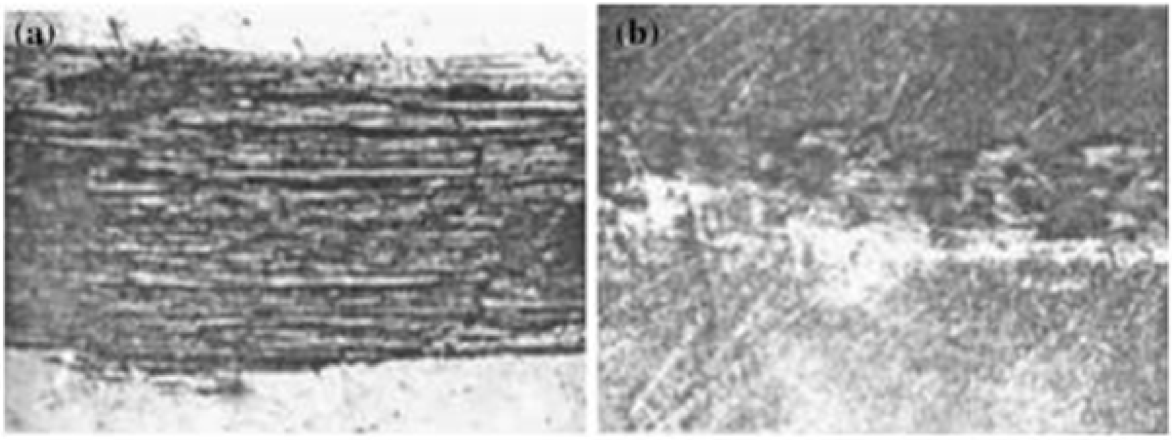


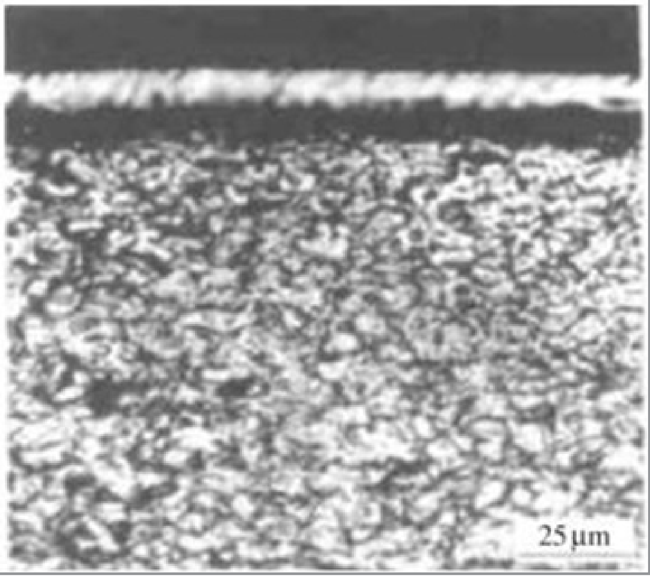
Fig. 4 SEM micrographs of surface morphology of a Ti6Al4V substrate and b Mo-alloyed sample under a dry friction test

are smaller than that of the substrate Ti6Al4 V. Its adhesion and abrasion performance were effectively improved. The wear mark zone was full of the transfer material of GCr15 and is caused by the high hardness and elastic modulus of molybdenum-alloyed layer and the high bonding strength between the alloyed layer and the substrate. Under the condition of oil lubrication, the variation of friction coefficient is very different from that of the above-mentioned materials. The fluctuation of friction coefficient curve of Ti6Al4 V alloy is attributed to the constant formation and rupture of boundary lubrication films in the process of friction. In contrast, the hardness of the plasma Mo-alloyed layer is 8.6 times higher than that of the Ti6Al4 V substrate. When the load capacity is enhanced, the boundary lubrication has shown some improvement with a small and stable friction coefficient. Through the above analysis, it is concluded that after going through a plasma molybdenzing process, the friction state of titanium alloy to GCr15 is much improved, as well as its wear resistance and anti- friction property.

Double Glow Plasma Molybden “ Nitriding”

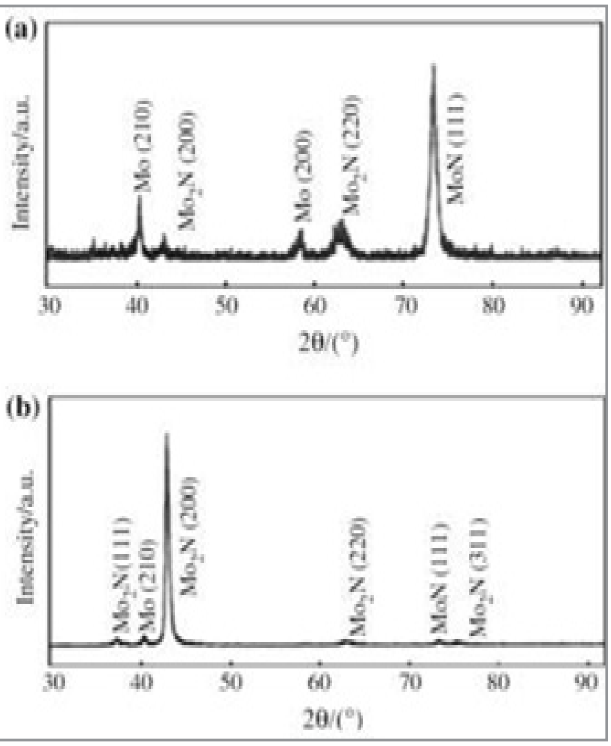
In the plasma molybdenizing, the mixed plasma with argon, nitrogen and metal ions can be generated through the gas mixture of argon and nitrogen in the vacuum. Under this plasma condition, a Mo-N-alloyed layer can be produced on the surface of a titanium alloy substrate. This alloyed layer has better tribological performance and corrosion resistance than a pure molybdenum layer [3-6]. Normally, there are two processes to form a Mo-N-alloyed layer. The typical processing is: first molybdenizing at 830 °C for 3 h, then cooling to 810 °C,

Fig. 5 Microstructure after molybdenum nitriding of Ti6Al4V [3]



followed with plasma nitriding for 3 h with Ar: N2 ratio about 2:1. Figure 5 is an optical microstructure picture of a moly-nitriding alloy layer on the surface of Ti6Al4 V substrate. Two uniform-alloyed layers (one in white bright and another in black) at the surface are formed by double glow plasma surface alloying technology in a thickness of about 10 µm. The X-ray diffraction diagram of the sample, in Fig. 6, shows that both the white alloy layer and black alloy layer have included three phases: Mo-N, Mo2N, and Mo. The white alloy layer on the surface of Ti6Al4 V consists more Mo-N and some Mo2N and Mo. The black alloy layer was mainly formed by Mo2N with a small amount of Mo-N. Both the layers have no matrix elements, which means no out-diffusion of Ti from matrix and all of the outmost- alloyed layers are molybdenum and Nitrogen. The hardness of the Mo–N-alloyed layer by nitriding after molybdenizing is 1804 HV, the surface hardness of sample by molybdenizing is 1681 HV, comparing with the hardness of original sample at 360 HV. The hardness of both layers is substantially increased. Figure 7 shows the wear rate of two plasma treated samples and the original Ti6Al4V sample (a), with the running-in distance of 200 m. It can be seen that the wear rate (b) of modified sample by molybdenizing decreased by 405 times, and the wear rate (c) of nitriding after molybdenizing modified sample decreased by 1081 times. Although the friction coefficient of TC4 sample with double glow plasma Mo +N alloying is increased, the wear rate has decreased by 2–3 orders of magnitude, showing excellent wear resistance. The test also shows that the width of the wear trace of Ti6Al4V sample for 100 m is much larger than that of the Mo-N modified sample for 200 m, as shown in Fig. 8.

Fig. 6 XRD spectra of **a** a white alloy layer and **b** a black alloy layer [4]



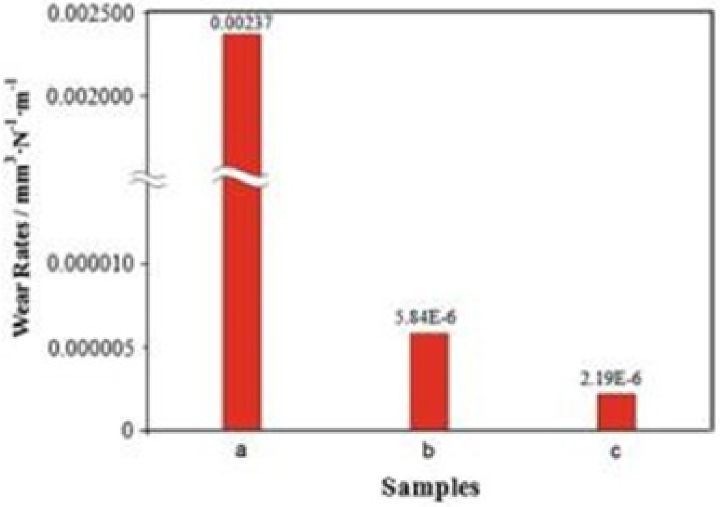


Fig. 7 Wear rate of **a** Ti6Al4V, **b** molybdenizing and **c** nitriding after molybdenizing

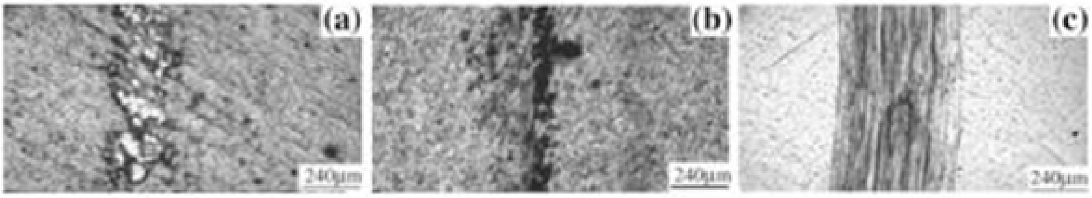
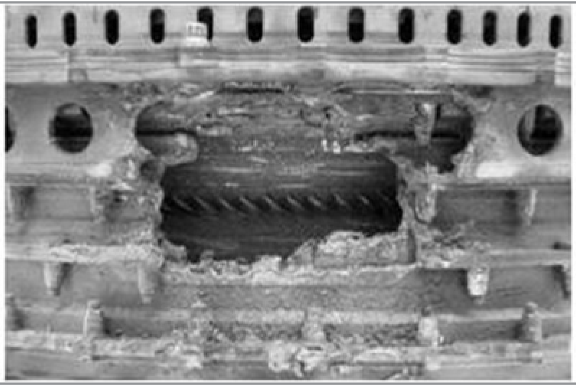


Fig. 8 Wear surface morphology of **a** Nitriding after molybdenizing and **b** molybdenizing for 200 m and **c** Ti6Al4V for 100 m

Plasma Surface Metallurgy Flame-Resistant Alloys Method for Protecting Titanium Alloy

“Titanium ars (burn)” is a kind of combustion on titanium or titanium alloy parts, caused by some actions, such as severe impact and friction, resulting in a certain level of damage or destruction to the part. In essence, titanium alloy combustion or “ars” is caused by uncontrolled oxidation at elevated temperature. SEM micrograph in Fig. 9 shows such damage on titanium alloy engine parts caused by “titanium-ars.”. In the past, to prevent “titanium ars” from happening, a great effort of developing flame- resistant titanium alloy was carried out world-widely. Flame-resistant titanium alloy mainly consists of Ti–Cr–V series, Ti–Cu–Al series, Ti–Nb series, and TiAl intermetallic compounds. These four kinds of titanium alloys have certain flame-resistant properties, but they also have the following limitations: (1) The increase of the density of the titanium caused by adding large amount of heavy alloy elements makes the titanium alloy no longer has the advantage of high specific strength [7, 8]. (2) The addition of alloying elements increases the difficulty of smelting and processing, as well as the processing cost. (3) The high content of valuable elements, such as Nb, Cr, and V, increases the cost of flame-resistant Ti alloys. Facing the above problems, it was proposed to prepare the surface- alloyed layer with flame-resistant properties by using the double glow plasma surface alloying technology. At present, a series of surface flame-resistant alloyed layers including Ti–Cu, Ti–Mo, Ti– Cr, Ti–Nb, etc., have been prepared on the surface of titanium alloys by the W-Tec process. Compared with the flame-resistant titanium alloy, these surface-alloyed layers have the following characteristics: (1) The flame-resistant performance is assumed by the surface flame-resistant alloyed layer, while its mechanical properties are assumed by the substrate material. Hence the advantage of high specific strength of titanium alloy is maintained. (2) Surface alloying is carried out on the common titanium alloy parts. This overcomes the complicity and poor performance of the integral manufacturing process for flame-resistant titanium alloy. (3) The thickness of the surface flame-resistant titanium alloy can be in the range of 50–300 lm, with a small consumption of alloy element materials, leading to a significant cost saving of the flame-resistant titanium alloy.

Fig. 9 Titanium alloy parts destroyed by "titanium fire" [1]



Plasma Surface Metallurgy Ti–Mo Flame-Resistant Alloy

Molybdenum (Mo) is one of the most important alloying elements for Ti alloy. Mo, in a body- centered cubic lattice structure, can form a continuous solid solution with β-phase Ti, which has the same crystal lattice and a limited solid solution with a phase Ti in close-packing hexagonal lattice structure. The solubility of Mo in a phase Ti is very low, no more than 0.8%. The formation of Ti–Mo alloy is a substitution solid solution, with a small lattice distortion. The Ti–Mo substitution solid solution with high content of Mo not only has high mechanical strength, but also maintains high plasticity [9, 10]. Figures 10 and 11, show the microstructure images of surface alloys on TC4 and TC11, formed by plasma surface alloying with Mo element. The composition distribution of surface-alloyed layer on TC4 alloyed with Mo after 850 °C for 3 h detected by GDS test is shown in Fig. 12. The outmost surface is a 3 µm deposition layer, with Mo content of 100%. In the layer 3–30 µm from surface, Mo element content shows a gradient distribution. Outward diffused Al is concentrated at a distance of 15 µm from the surface due to the blocking by the deposition layer. There exists aluminum deficit at the depth of 10 µm from the surface and the interface between the substrate and the alloyed layer.

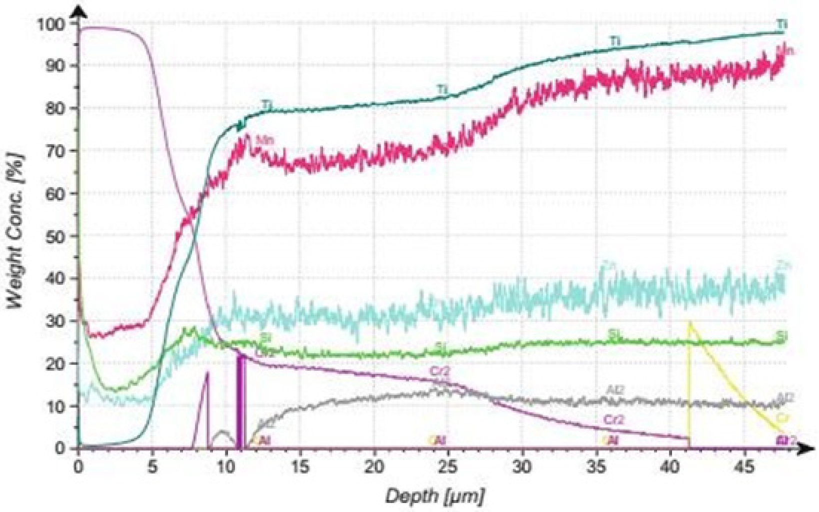


Fig. Composition depth distribution of a Cr-alloyed layer on TC11 substrate

Fig. -- Sectional microstructure of Mo-alloyed layer on TC4 substrate

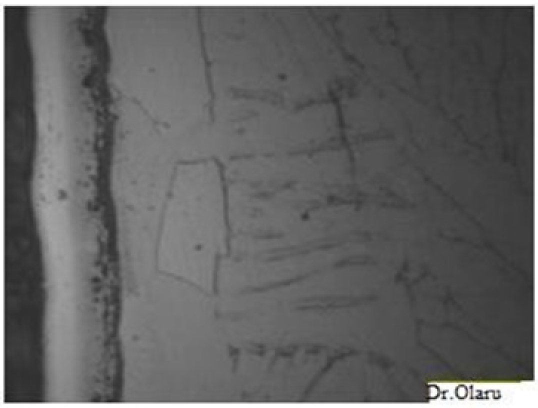


Figure 13, shows the composition distribution of surface-alloyed layer on TC11 after plasma surface alloying at 900 °C for 3 h measured by the GDS test. The Mo content at the outmost surface is 15%, and remains above 7% at the position 40 lm from the surface, with a low gradient concentration. The content of other elements is basically constant, which indicates that a uniform-alloyed layer is formed on the surface. Mo is a strong β stable element to Ti. It can drastically decrease the α-β phase transition temperature of titanium. For titanium alloy with Mo content less than 11–12%, the martensite transformation occurs during the quenching of the β region. The thickness of the layer is over 40 lm. According to XRD analysis, Mo element completely dissolved into β-phase, and formed a substitution solid solution. In addition to single element diffusion, the W-Tec process can also be used to prepare Cr–Mo diffusion layer to forma surface flame-resistant alloy. The composition distribution of such an alloyed layer on TC11 after Cr + Mo diffusion treatment at 900 °C for 3 h is shown in Fig. 14. The content of Cr and Mo elements is a gradient distribution. The Mo content at the outmost surface is 3 and 13% for Cr. The concentration gradients of Cr and Mo are both small fig.15a; Figure 15b, shows the microstructure of Cr + Mo alloying on TC11

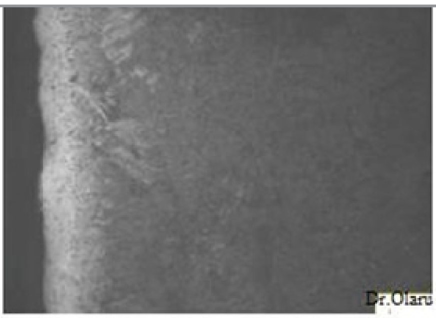


Fig. . Sectional microstructure of Mo-alloyed layer on TC11 substrate

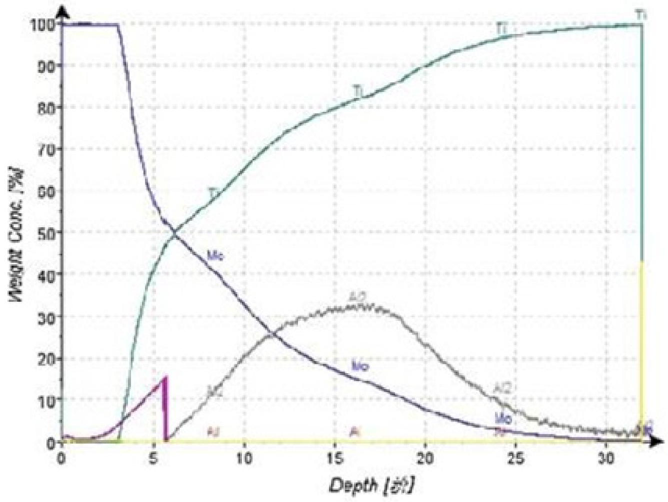


Fig. Distribution of Mo in alloyed layer on TC4 substrate

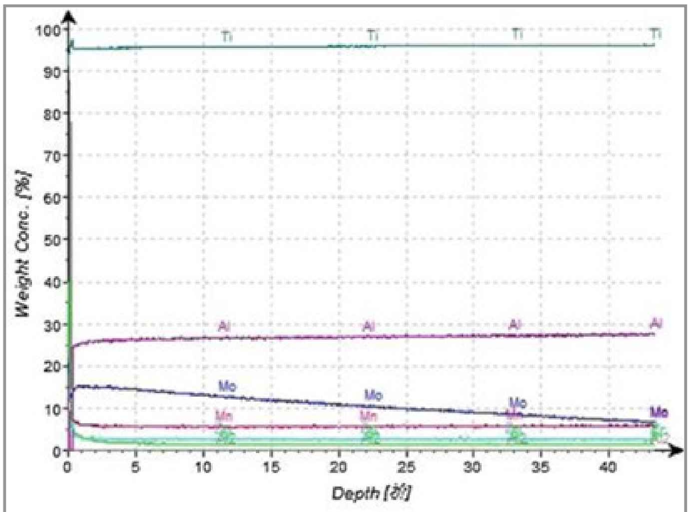


Fig. Distribution of Mo in alloyed layer on substrate

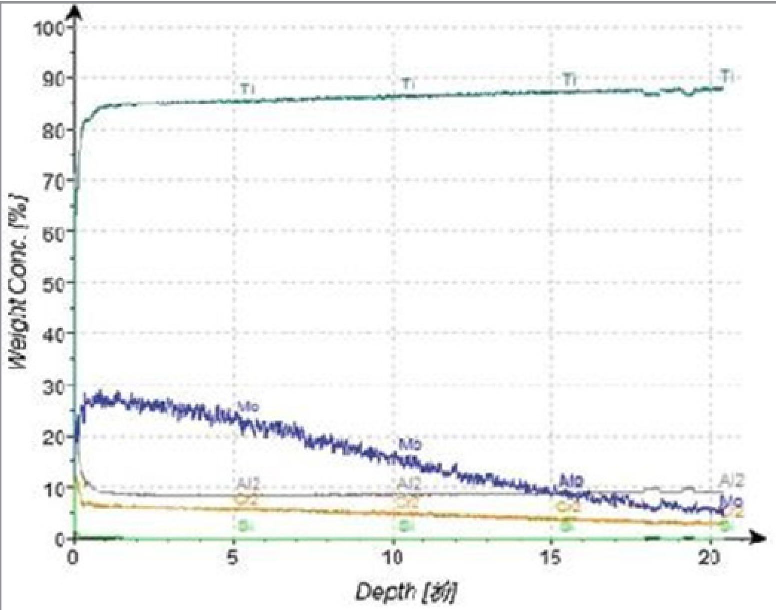
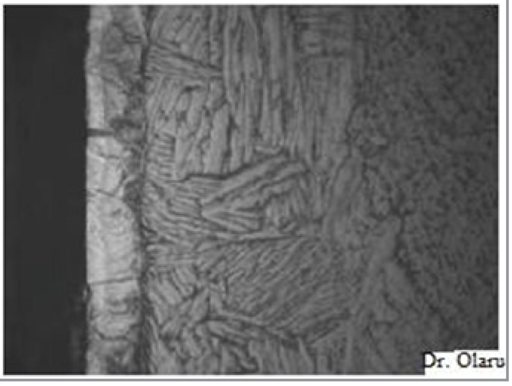


Fig. Component distribution of Cr–Mo-alloyed layer on substrate

Fig. Sectional microstructure of Cr–Mo-alloyed layer on substrate



Plasma Surface Metallurgy Ti–Pd Corrosion-Resistant Alloy

Overview of Corrosion-Resistant Titanium Alloys

In order to improve the corrosion resistance of titanium in a reduction medium, it was added alloy elements into titanium to form corrosion-resistant titanium alloy. In 1949, W. L. FiFlay found that the Ti–Mo alloy has excellent corrosion resistance to strong reducing acid like sulfuric acid and hydrochloric acid. In 1956, US developed Ti–(20–25)Mo–20Nb, Ti–25Mo–15V, Ti–27Mo–17V and other acid-resistant titanium alloy. In 1958, Ti15Mo5Zr alloy was developed in Japan. In 1962, the Soviet Union developed Ti32Mo2.5Nb and used for mass production. Together with the study of the Ti–Mo alloy, rapid progress has also been made in the study of Ti–Pd alloy. Both Ti–0.2Nb and Ti–0.15Nb not only have good corrosion resistance in oxidation acids, but also have certain corrosion resistance of the reduction acid, especially with excellent resistance to crevice corrosion. However, due to the high price of Pd, it makes the price of Ti–Pd alloy higher than that of pure titanium, Ti–Ru– Ni, and Ti–Ru–W(Mo) and other cheaper titanium alloys. At present, Ti–Pd and Ti–Mo–Ni are two major types of titanium alloys that are largely used [11]. Because of the high price of those two types of corrosion-resistant alloys when adding with high price elements, like Pd, Ni, and Mo, it restricts the application usage of titanium material. Therefore, preparing corrosion-resistant Ti–Pd alloy on the surface of Ti substrate by the W-Tec process becomes significant in the cost reduction of Ti alloy as it not only solves the problem of corrosion resistance, but also can reduce the consumption of Pd through surface treatment.

Plasma Surface Metallurgy Ti–Pd Alloy

Shown in Fig. 16, is a typical microstructure of Ti–Pd-alloyed layer produced by plasma surface alloying with Pd source on the titanium surface. The thickness of Ti–Pd-alloyed layer is generally greater than 50 µm, and the layer is dense and forms a "canina"-shaped interface with a Ti substrate [12, 13]. The Ti–Pd layer is made up of four sub-layers. The layer A is the outmost layer, with a high content of Pd and uniform thickness; the layer B is continuous, in which the Pd content is lower that of the layer A; the layer C is very thin, and not continuous; the layer D forms "canina" shaped interface, connecting with the Ti substrate. Scanning electron microscopy was used to analyze the energy spectrum (relative content of alloy elements in the layer), which is shown in Fig. 17a. It can be seen that, the content of Pd varies greatly in different layers. The curve of the content of Pd in alloyed layers is shown in Fig. 17b. It can be seen that in each layer the content of Pd is linearly decreasing, with a significant reduction jump at the interface. According to the phase diagram, there will be several layers with different intermediate phase structures. However, in each layer, there is only one single phase structure. On the interface of the two phases, the element content has a distinct mutation. It can be seen that the Ti–Pd-alloyed layer formed by the W-Tec process is a typical reaction diffusion layer. According to the phase structure analysis, the surface-alloyed layer formed by diffusion of Pd concludes many different layers as shown in Fig. 18. From the surface of the substrate there are followed layer as Pd, TiPd2, TiPd3, Ti2Pd, and substrate α-Ti.

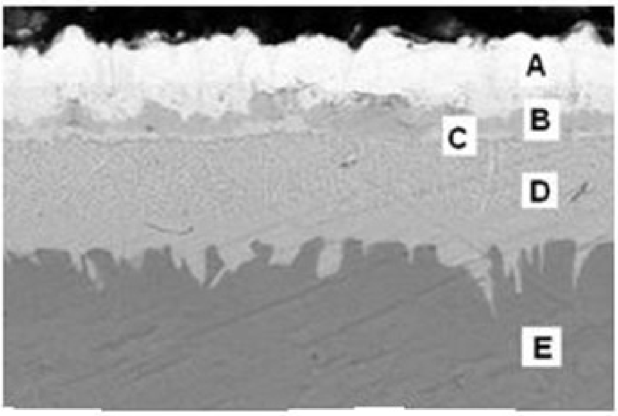


Fig. Back scattered electron microscopy of a section of the Ti–Pd layer

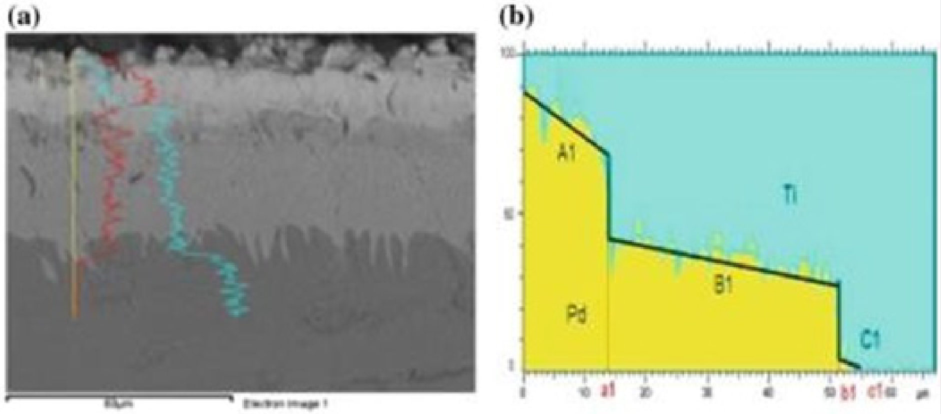
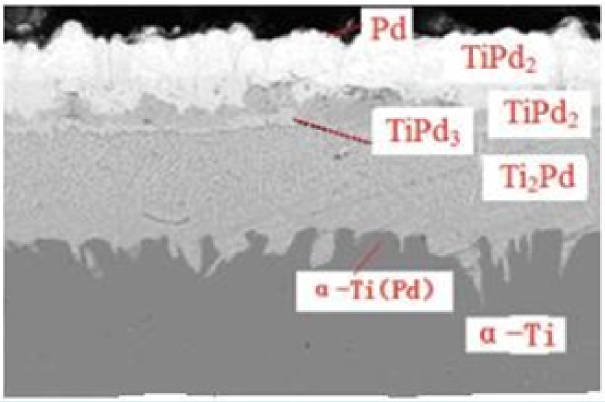


Fig. a Scanning photo of sectional energy line and the scanning position of energy line b Linear scanning energy spectrum

Fig. Phase composition of Ti–Pd-alloyed layers created by plasma surface alloying process



Corrosion Resistance of Plasma Surface Ti–Pd Alloy

The corrosion resistance of surface Ti–Pd alloy, the crevice corrosion resistance and erosion corrosion resistance of industrial pure titanium and Ti–0.2Pd alloy were studied. According to the analysis, the immersion test in the 100 °C NaCl saturated and HCl solution shows that the crevice corrosion resistance of Ti–Pd alloy is not only superior to that of TA1 industrial pure titanium, but also better than that of Ti– 0.2Pd alloy. In another analysis, at room temperature of 25 °C, industrial pure titanium, Ti– 0.2Pd alloy and titanium surface Ti–Pd alloy are immersed in 80% H2SO4 solution and 30% HCl solution. After the immersion test for 145 h, the calculated corrosion rates are listed in Table 1, The corrosion rate of Ti–Pd-alloyed layer on the titanium surface is only 0.682 mm/a in the 25 °C water solution of 80% H2SO4, 1/6 of that of Ti–0.2Pd alloy and 1/20 of that of industrial pure Ti. In the 25 °C water solution of 30% HCl, the corrosion rate of the Ti–Pd-alloyed layer is only 0.004 mm/a, equivalent to 1/8 of that of Ti–0.2Pd alloy, and 1/215 of that of industrial pure Ti. The corrosion resistance of titanium alloy was greatly improved after the double glow Pd treatment.

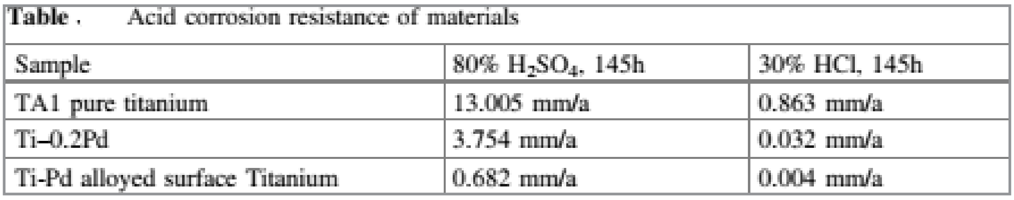


Table . Acid corrosion resistance of materials

Sample	80% H_2SO_4, 145h	30% HCl, 145h
TA1 pure titanium	13.005 mm/a	0.863 mm/a
Ti–0.2Pd	3.754 mm/a	0.032 mm/a
Ti-Pd alloyed surface Titanium	0.682 mm/a	0.004 mm/a

Plasma Surface Metallurgy Ti–Nb Corrosion-Resistant Alloy

The Ti–Nb-alloyed layer on titanium surface, prepared by the W-Tec process, not only improves the flame resistant and tribological properties, but also improves its corrosion resistance. The Ti–Nb alloy is especially favor to the service performance of titanium under corrosion and friction situation. Figure 19a shows the weight losing versus time curve of the Ti–Nb alloy on TC4 surface in 10% H2SO4 solution. It can be seen that passivation of Ti–Nb-alloyed layer occurred after 144 h of immersion. The passive film can effectively protect the substrate, and improve the corrosion resistance in 10% H2SO4 solution. This phenomenon also occurs in 10% HCl solution, as shown in Fig. 19b [14]. Electrochemical test indicates that, since a Ti–Nb-alloyed layer is formed through the diffusion of Nb into TC4 substrate, the self-corrosion potential of TC4 is increased. Ti–Nb layer is more prone to passivation than TC4. Therefore, the Ti– Nb-alloyed layer prepared by plasma surface metallurgy on the surface of titanium has excellent corrosion resistance.

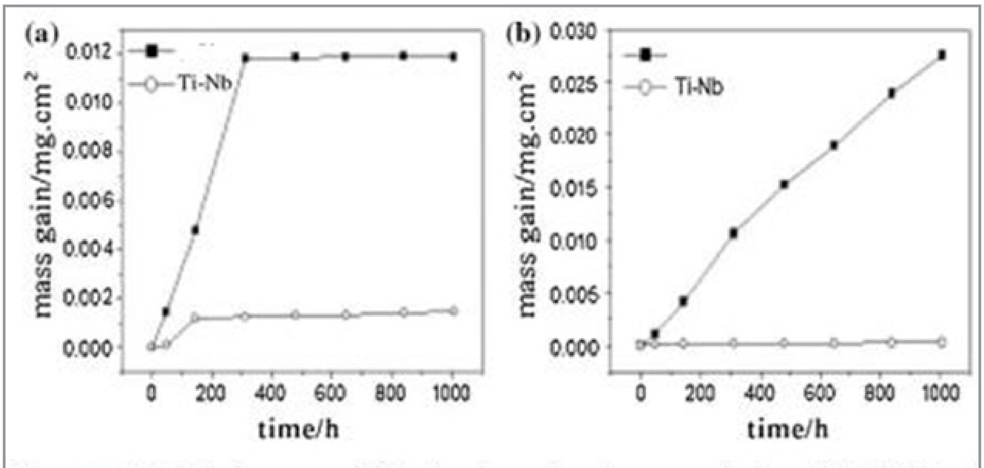


Fig. a-·Weight losing curves of Nb-alloyed sample and sample in a 10% H2SO4 and b- 10% HCl

Tribological Properties

The friction coefficient of a non-hydrogen carburizing layer on titanium surface was studied by a ball-disk wear test, and the wear resistance of the material was characterized by specific wear rate test [15]. Figure 20 (a, b), shows the relationship curve of friction distance and friction coefficient of the TC4 substrate and carburized TC4 grinding with GCr15 under the dry friction condition. Due to the existence of a large amount of high hardness phase TiC and other carbides, the friction coefficient with an average value of 0.23 and 30% is lower than that of the untreated sample. The test results indicate that carburizing can greatly improve the wear resistance of titanium. To determine the weight loss rate, it is required to weight the sample before and after the friction test. The wear rates of three samples are shown in Fig. 21; It can be seen that, the wear rate of original TC4 samples is 0.0934 g/h; after carburizing, the wear rates are 0.0032, 0.0064, 0.0026 and 0.0019 g/h. The wear rates of

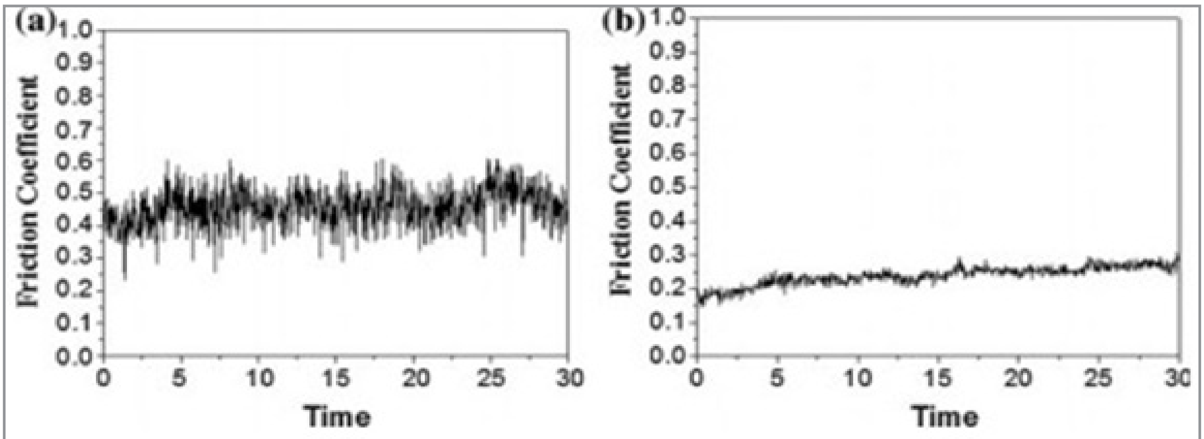
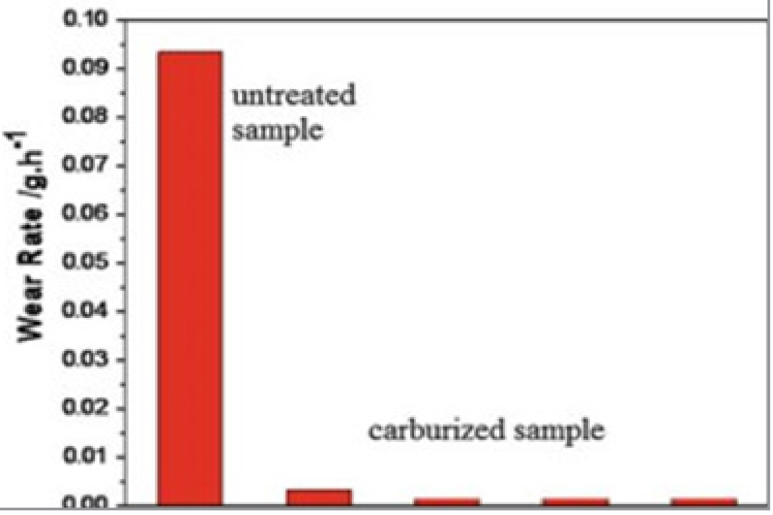


Fig. 8.36 Curves of friction coefficient of **a** TC4 and **b** carburized TC4 [26]

Fig. 8.37 Wear rate of different carburized samples [26]



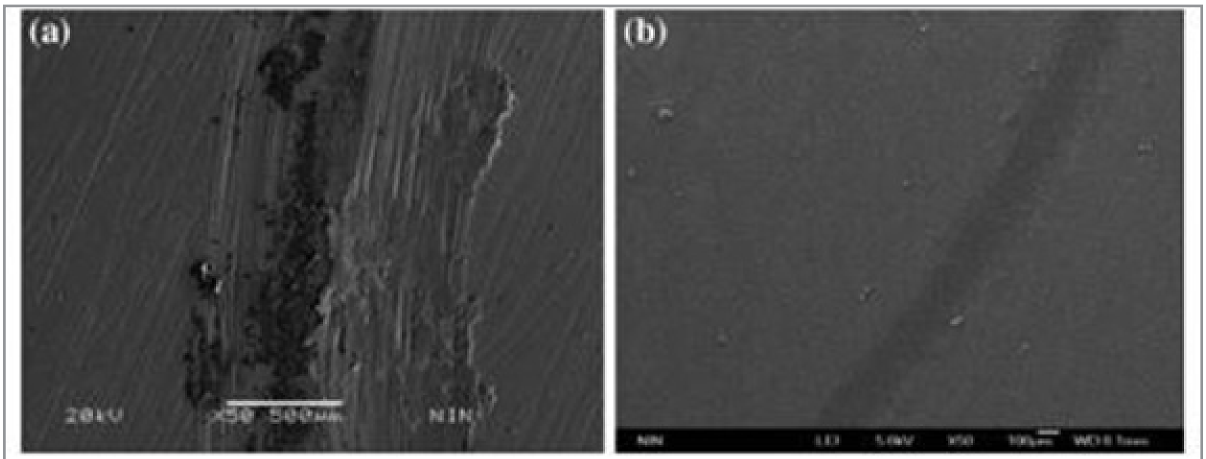


Fig. 8.38 SEM images of **a** TC4 alloys wear friction surface and **b** carburized TC4 alloys wear friction surface [26]

carburized samples are about 2–7% of that of the original one, which shows that wear rate can be reduced by carburizing. Due to the TiC wear-resistant phase formed and solid solution strengthen effect, the wear resistance of TC4 can be much improved, and the wear rate is much reduced. The wear surface morphology after 30 min of friction test on the raw substrate and carburized sample are compared. Figure 22a shows the SEM morphology of wear surface of untreated TC4 after friction. Figure 22b gives the SEM morphology of wear surface of carburized TC4 after friction. It can be seen that, with the same friction distance, there were wide wear scars, furrows, grinding particles and adhesion zone appeared on the untreated TC4 sample, and the adhesion zone went beyond the wear scars at some locations; the wear scars on the carburized sample were mild. No furrow or tear trace is observed, except for some slight traces. The wear rate and friction coefficient of the carburized sample is 2–7% while 50–60%, for a sample without carburizing. The wear rate is reduced, and the wear resistance is improved. After the high-speed ball-disk wear test, the wear of TC4 titanium alloy was serious. On the surface, it was mainly adhesion wear; no wear or tear on the surface of carburized samples, except for some scratches [16].

Applications

With the development of aviation, aerospace, marine, petroleum chemical industry and field of daily use, titanium and titanium alloys will have a good opportunity for a wide range of applications. However, the inherent performance defects of titanium alloys will impede the study of applications and products development of titanium alloys. By surface engineering treatment, especially the double glow plasma surface metallurgy, the performance can be improved in the area of the flame-resistant property under the environment of high temperature friction, the crevice corrosion resistance and corrosion resistance in reducing acid, and the wear resistance and erosion resistance under the friction of titanium alloy. The application of titanium alloy mainly includes the following aspects:

1. Plasma surface wears-resistant titanium alloy: Using the W-Tec process, the corrosion and wear-resistant TiC-alloyed layers are formed on the surface of titanium alloy. This process has been successfully applied in many engineering fields, such as titanium alloy valves, fasteners, hydraulic cylinders, gears, and bearings. These components play a key role in improving the performance of devices. From the current application results, the application of titanium alloy formed by the W-Tec process has just begun, with a very bright future.
2. Plasma surface corrosion-resistant titanium alloy: surface Ti–Pd alloy in the future will mainly be used to prevent crevice corrosion on the calcium chloride reaction kettle in the chemical industry and seawater desalination equipment. Surface Ti–Mo-based alloy is mainly used on the reaction equipment with sulfuric and hydrochloric acid in chemical industry.
3. Plasma surface flame-resistant titanium alloy: the main application will be on the titanium alloy compressor blade and casing of the airplane turbine with a high bypass ration and high thrust weight ratio.

Discussions

Specific gravity of titanium is only 1/2 of iron. Titanium and titanium alloys have a high specific strength and good corrosion resistance in seawater, so it has a very important and broad application prospects in the field of aerospace and marine engineering.

Example: Ti has a strong corrosion resistance and the test shows no corrosion after immersion in seawater for 5 years. Using a titanium alloy for manufacturing ships and marine engineering would greatly extend its service life. In the aerospace industry, using titanium in aircraft, spacecraft and space station will greatly reduce the weight. The development work introduced in this chapter has demonstrated that a great number of high hardness, wear- resisting, anti-corrosion and flame-retardant alloys can be formed by the W-Tec process on the surface of titanium and titanium alloy. This provides a new method for titanium and titanium alloy broader industrial applications. The W-Tec process has given a huge improvement and innovation to the traditional surface alloying technology and opens up a new door for plasma surface alloying technology. We found that in the future, the following studies need to be carried out: Based on the successful preparation of Ti–Pd surface-alloyed layer, the further study of the W-Tec process for reducing the Pd content in Ti–Pd-alloyed layer should continue to carry out, together with the application engineering development of corrosion-resistant equipment materials for chemical industry. The flame-resistant performance evaluation method and test for the prepared surface flame-resistant titanium alloy need to be explored and developed. In order to meet the high precision requirement of titanium alloy casing for aero-engine, the process coordination of surface metallurgy process and structure of titanium alloy casing for the aero-engine need to be studied. The study of the manufacturing technique of titanium alloy compressor casing with surface flame-resistant titanium-alloyed layer need to be performed to provide the technical support for the manufacturing of titanium alloy compressor casing with flame-resistant property. The W-Tec process may also be used to form functional alloys of electric, magnetic, acoustic, wave and other aspects on the surface of titanium alloy, and develop new types of titanium alloy.

References

1. Okamoto, H. (2002). Phase Diagrams of Dilute Binary Alloys. Materials Park, Ohio, ASM International, 308 p.
2. Li, X. Y. (2003). Tribological behavior of molybdenum alloying layer on Ti6Al4V by double glow discharge technology. Tribology, 23(2), 108-111.
3. Li, X. Y., Tang, B., & Xu, Z. (2003). Preparation of molybdenum nitride hard coating by double glow discharge technique. Chinese Journal of Nonferrous Metals, 13(4), 984-987.
4. Qin, L., Tang, B., Liu, D., & Xu, Z. (2005). Friction and Wear Behavior of Mo-N Diffusion Layer on Ti 6 Al 4 V Alloy Surface. Xiyou Jinshu Cailiao yu Gongcheng(Rare Metal Materials and Engineering), 34(9), 1465-1468.
5. Qin, Y. M., Fan, A., & Qin, L. (2005). Study on corrosion behavior of plasma Mo–N modified titanium in artificial blood solution. Physical Testing and Chemical Analysis Part A: Physical Testing, 41(3), 117.
6. Hu, H. J. (2005). Electrochemical behavior of Mo–N modified layer on pure titanium with plasma surface alloying technique. Rare Metal Letters, 24(11), 21.
7. Wang, J. Y. (1995). Development of flame-retardant titanium in Russia. Aeronautical Science and Technology, 3, 38-40.
8. Appel, F., & Brossmann, U. (2000). Recent progress in the development of gamma titanium aluminide alloys. Advanced Engineering Materials, 2(11), 699-720.
9. Zhang, P. Z. (2004). Double glow plasma surface alloying burn-resistant titanium alloy [Doctoral dissertation, Taiyuan University of Technology].

10. Zhang, P. Z., Xu, Z., & Zhang, G. H. (2005). Double glow plasma surface molybdenizing of pure Ti and Ti-6Al-4V. Journal of Nanjing University of Aeronautics and Astronautics, 37(5), 582-586.
11. He, Z. Y., & Wang, Z. X. (2007). Surface modification of titanium alloy Ti6Al4V by plasma niobium alloying process. Surface and Coatings Technology, 201, 5705-5709.
12. Wang, W. B., Xu, Z., & He, Z. Y. (2007). Study on double-glow plasma niobium surface alloying of pure titanium. Vacuum, 81, 937-942.
13. Zhang, P. Z., Xu, Z., & Zhang, G. H. (2005). Preparation of double glow plasma surface metallurgy treated Ti–Cu flame-resistant alloy. Chinese Journal of Nonferrous Metals, 15(1), 110-115.
14. Zhang, P. Z., Xu, Z., & Zhang, G. H. (2005). Study of surface flame-resistant Ti–Cu titanium alloy. Rare Metal Materials and Engineering, 34(1), 162-165.
15. Zhang, P. Z., Li, Z. H., & He, Z. Y. (2005). Surface chromizing of Ti-6Al-4V by double glow plasma surface alloying technology. Ordnance Material Science and Engineering, 28(1), 18-25.
16. Zhang, P. Z., Xu, Z., & Zhang, G. H. (2007). Surface plasma chromized flame-resistant titanium alloy. Surface and Coatings Technology, 201, 4884-4887.