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Advancements in Boriding Techniques for Enhancing Titanium Alloy Performance

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Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

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Short Communication

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ABSTRACT

As an important structural material in the 21st century, titanium and its alloy have the advantages of corrosion resistance, high melting point, small density, high specific strength, no magnetism and biocompatibility, but low surface hardness, poor wear resistance, large friction coefficient, poor high temperature oxidation resistance and other defects seriously limit its application scope. Boride-titanium intermetal compounds can effectively improve the surface hardness and wear resistance of titanium and its alloys. This paper summarizes the research status of titanium alloy embedding permeability, surface molten salt electrolysis boron permeability and plasma boron permeability, and discusses the process parameters and mechanism in the process of boron permeability.

Keywords: Titanium alloy; surface treatment; boronization; hardness; wear resistance.

1. INTRODUCTION

Titanium and its alloy are widely used in aerospace, building materials, shipping, biomedicine and other fields due to their high specific strength, small density, strong heat and corrosion resistance, and excellent biological compatibility [1-6]. However, titanium and its alloy still have the disadvantages of low surface hardness, high friction coefficient, poor wear

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resistance, easy adhesion and wear. [7]. As a result, titanium alloy parts are prone to serious wear under sliding conditions and shorten the service life. In order to make titanium and its alloy more widely used in various fields, it is urgent to use surface modification technology to improve its surface hardness and wear resistance, enhance heat and corrosion resistance and other properties. In the process of titanium alloy surface boron permeability, Ti and B reaction compound TiB2 both ceramic materials of high melting point, high hardness, high strength, and metal material high conductivity, high thermal conductivity, can significantly improve the wear resistance and other surface properties of titanium alloy. In order to better study titanium alloy boron permeability technology, this paper introduces the titanium alloy boron permeability several different methods and new progress, summarizes the recent technology in the titanium alloy boron permeability heat corrosion resistance, wear resistance [8-10].

2. EMBEDDING PENETRATION

The embedding penetration method is generally divided into: solid powder method and paste method, both of which are solid boron infiltration method [11-14].

(1) Solid powder method of boron infiltration

Solid embedded boron is a process in which the sample and powder agent are sealed in corundum crucible, and a series of reactions at high temperature produce a large number of active boron atoms to diffuse Inside the sample. Including boron donor, activator, and filler [15]. The boron agent provides active boron atoms. At present, the boron supply agents used at home and abroad mainly include iron boron, boron carbide, borax, boron anhydride and amorphous boron, among which boron carbide is a good boron supply agent. The action of the activator is the reaction involved in the boron permeability process, prompting the production of active boron atoms, which is the decisive factor of the speed of boron permeability. Domestic Fluorosilicon sodium instead of sodium fluorororate as activating agent, the effect is remarkable. The role of filler is to regulate, prevent leachate sintering, and keep the loose nature of leachate. The most widely used silicon carbide in China, which in addition to the role of activation but also reducing, can well improve the speed of boron permeability [16].

(2) Paste boron

The paste boronizing method is similar to the solid method. In paste boronizing, a paste-like boronizing agent is applied to the surface of the workpiece. In addition to boronizing agents, activators, and fillers, the boronizing agent also includes a binder. Activators in the paste method are generally a mixture of one or more substances, with commonly used activators including fluorides, chlorides, and potassium fluoroborate.The paste boronizing method can be divided into box-paste boronizing, self-protective paste boronizing, and partial paste boronizing according to the process. The disadvantages of the paste method include its high cost of boronizing agents, large wastage, poor thermal conductivity of the boronizing agent, long heating time, high energy consumption, low efficiency, inconvenience in handling large components, difficulty in removing samples, and challenging cleanup 17].

2.1 Research Status of Embedded Boron Infiltration

At present, the study of embedded boron infiltration mainly focuses on the influence of rare earth elements on the boron infiltration process. Han et al. [18]. conducted experiments to accelerate the growth of boride layers on the surface of TC4 (Ti-6Al-4V) titanium alloy during solid powder pack boronizing. They added Y_2O_3 to the boronizing agent in the solid powder pack process to carry out boronizing of TC4 substrate at 1050℃/8h. The experiments included control experiments where Y_2O_3 was not added to the boronizing agent, as well as experiments where Y_2O_3 was added at mass fractions of 1%, 3%, 5%, and 7% in the boronizing agent for comparison. The results proved that the effect of Y_2O_3 in promoting permeability growth is closely related to the amount of its addition. The addition of 1%~3% Y_2O_3 to the infiltration agent can promote the growth of the boron layer, and the addition of 3% Y_2O_3, the infiltration effect is the best, and the addition of 5%~7% Y_2O_3 will inhibit the growth of the boron layer.

In order to improve the surface properties of TB2 alloy, Qu deyi et al. [19]. used 4%La2O3 (mass fraction) at 1100℃, for 20h, to study the composition and thickness, corrosion and wear properties of TB2 titanium alloy. The results show that La_2O_3 promotes the growth of the boride layer and increased its continuity and density, increasing the TiB whisker length from

16.80 to 21.84 μ m. This is because La_2O_3 can react with B to generate La-B active groups, which further promotes the growth of the boride layer. La_2O_3 Embedded boron infiltration can improve the wear resistance and corrosion resistance of TB2 alloy. The wear mechanism of boron and boron TB2 alloy is adhesive wear (During sliding friction, metal adhesion occurs locally on the contact surface of the friction pair) and grinding wear respectively, and the corrosion mechanism changes from local corrosion (boron TB2 alloy) to uniform corrosion (boron TB2 alloy).

Li Haibin et al. [20] obtained a uniform and dense surface infiltration layer on the surface of Ti-6Al-4V alloy. The surface permeability layer is composed of TiB2, TiB compound layer and α -Ti (B) diffusion layer, and it has a very high microhardness and is combined with the matrix metallurgy. After the boron infiltration treatment, the Ti-6Al-4V alloy sample was significantly improved in the deionized water, which may be related to its surface permeability layer with high microhardness. In the process of boron infiltration, the rare earth element La is added, which improves the boron infiltration efficiency, increases the thickness of the boron-titanium compound, promotes the growth of the TiB whisker, and further improves the cavitation resistance of the material.

Xu Zhenyuan et al. [21]. used the permeability agent adding rare earth oxide to perform 900~1050℃ high temperature solid permeability in titanium alloy, and analyzed the role of rare earth oxide in the permeability agent. The results show that rare earth produces rare borate with low melting point by chemical reaction with boron source and oxygen, and by increasing the effective contact between the substrate and the boron agent Area and curing oxygen, to achieve a higher concentration of boron infiltration reaction. By using the boron permeability agent supplemented with rare earth, the TiB / TiB2 duplex permeability layer is formed on the surface of the titanium alloy, and the thickness of the dense duplex permeability layer at 1050℃ reaches 2~3 microns, and the depth of the boron permeability area reaches 50 microns. The friction coefficient of the seepage layer surface is about 0.15. The microtissue observation and friction and wear performance test verify that the permeability layer binds firmly to the matrix, and the binding force is greater than 300N under static friction conditions. The permeability has no effect on Young's modulus and tensile strength of titanium alloy substrate, but reduces plasticity. The permeability layer shows good high temperature hardness ranging from room temperature to 900℃, indicating that the permeability layer helps to improve the mechanical properties at high temperature of titanium alloy.

Li Ping [22]. chose TA2 industrial pure titanium as the substrate and used solid boron infiltration method to modificate surface. The phase transition temperature of pure titanium α β is 882℃, so the boron permeability temperature is 860℃ ~950℃, and the boron permeability time is 1~20h. The scanning electron microscope, X-ray diffraction instrument, electron probe, electrochemical workstation, friction and wear test machine were used to analyze and test the samples after the boron infiltration, and explore the composition and comprehensive performance of the permeability layer of boron. The results show that the TA2(industrial pure titanium) permeable boron layer is a bilayer structure, and the surface layer is a continuous dense TiB_2 Layer, subsurface is TiB whiskers. The thickness of the permeable boron layer is between 4 μ m and 30 μ m. When the boron temperature is below the phase transition temperature, the thickness of the boron layer increases slowly with the increase of the boron temperature and accelerates near the α β phase transition temperature. At 920℃ – 20h. The TA2 boron layer can enhance the corrosion resistance of the matrix in acidic and saline solutions. In addition, the surface friction coefficient of the TA2 boron layer is 0.28 to 0.41, which is less than 0.43 of the TA2 matrix. Two diffusion models of d 2 = Dt and d = kt 0.5 were used to analyze the growth dynamics of the permeable boron layer, and the correlation coefficient R, mean absolute relative error MARE and root mean square error RMSE were selected to analyze the accuracy of the two diffusion models. The comparison shows that the diffusion model d2=Dt predicts the thickness of the permeable boron layer with high accuracy. Using the Arrhenius equation, the diffusion activation energy of boron in TiB2 layer and TiB layer is 207.85 kJmol-1 and 278.49kJmol-1 respectively. First principles calculations were used to investigate the gap diffusion behavior and mechanism of B atoms in α -Ti and β -Ti. The results show that the octahedral gap in α -Ti and the tetrahedral gap in β -Ti are preferentially occupied by B atoms. The preferential diffusion path of B atoms in α -Ti is O-O(oxygen atom to oxygen atom), with a diffusion energy barrier of 0.8403 eV. The preferential diffusion path for B atoms in β -Ti is T-T(Ti-Ti) with a diffusion energy barrier of 0.7751 eV. The electronic structure indicates that the B atom obtains electrons from the Ti atom during diffusion to form the B-Ti covalent bond. With increasing temperature, the diffusion coefficient of α -atoms in Ti and β -Ti increases. Meanwhile, the diffusion coefficient of B atoms in α -Ti is always smaller than β -Ti, indicating that β -Ti is the main channel for the migration and diffusion of B atoms.The lattice structure of the β phase is more open than the α phase, with larger gaps between atoms, which makes atomic diffusion in the β phase more likely to occur. In contrast, the alpha phase has a tighter lattice structure with smaller gaps between atoms, making it more difficult for atoms to diffuse [23].

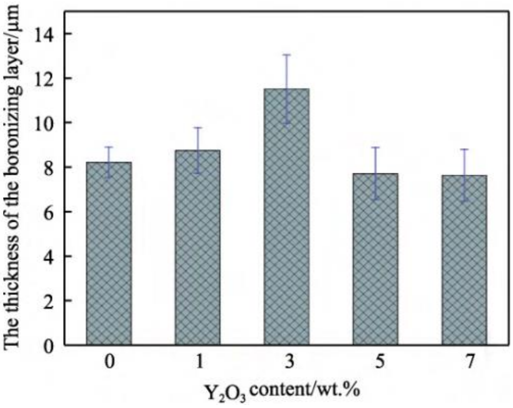

Fig. 1. Thickness of boronizing layer prepared in pack mixtures with different Y_2O_3content

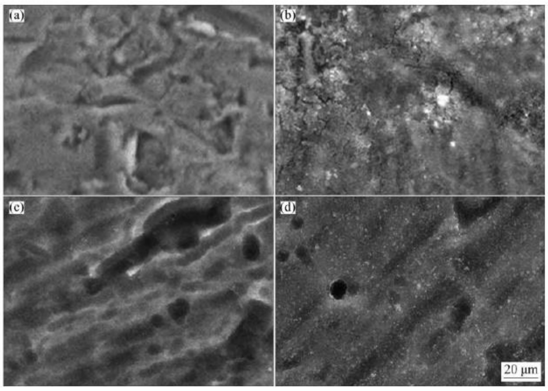

Fig. 2. Surface morphologies of sample after corrosion in 3.5 wt.% NaCl (a, b) and 5.0 wt.% $H2SO_4$ solutions (c, d): (a, c) TB2 alloy; (b, d) Borided TB2 alloy

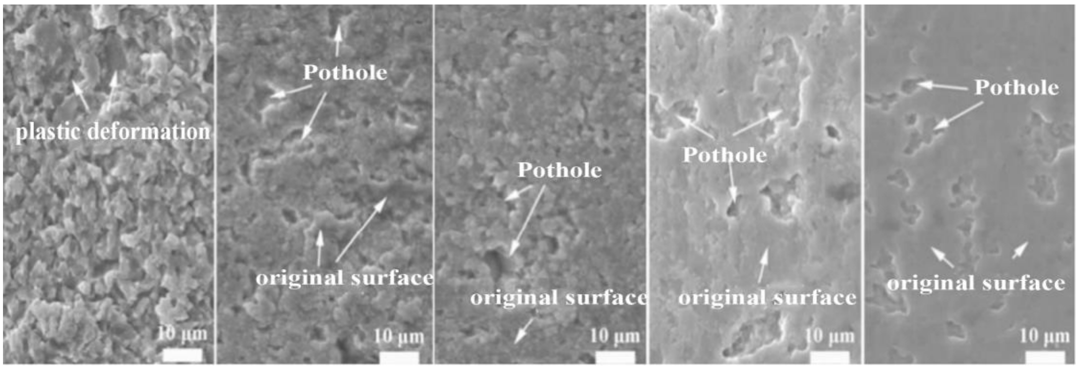

Fig. 3. Surface morphology of the Ti－6Al-4V alloy specimens after 12 h of cavitation testing

3. SURFACE-BASED MOLTEN SALT ELECTROLYSIS

Molten salt electrolysis technology using anhydrous borax ($B_4Na_2O_7$) as boronizing agent is a new technology developed in recent years. It has the advantages of simple penetrating agent, low cost, convenient operation, considerable thickness, low pollution and reusable penetrating agent. Series advantages. Generally speaking, the molten salt electrolysis process includes several important process parameters, namely electrolysis time, current density and electrolysis temperature. Any factor will have a huge impact on the permeable layer [24].

The advantages of the molten salt electrolysis method can be summarized as the following points:

(a) In the molten state of the agent, the stability and decomposition pressure are high, and the solubility in the molten salt is low, and the side reactions in the electrolysis process are less.
(b) Molten salt electrolysis because of the high current density of the method and the strong reaction capacity of electrolysis, the electrolysis efficiency is high, and the time used by boron infiltration is greatly reduced.
(c) The biggest difference between molten salt electrolysis method and other methods is that boron infiltration does not need reducing agent, seepage agent pollution is small, and can be recycled [25].
(d) At high temperatures, molten salt has good electrical conductivity in the molten state. Generally, molten salt electrolysis is more efficient than aqueous solution electrolysis.

3.1 Research Status of Surface Molten Salt Electrolysis Method

Ma Xingfei et al. [26] used cyclic voltammetry and timing potential method to analyze the mechanism of $Na_2B_4O_7$-$CaCl_2$ molten salt electropermeability. The experiment showed that the sodium ions in the molten salt were reduced on the surface of titanium, and the resulting sodium atom reacted with the B_2O_3 generated in the molten salt to form boron atoms, and the boron atoms diffused into the titanium matrix to form the boride permeability layer. Secondly, a one-factor experimental study was conducted with 90%$Na_2B_4O_7$-10%CaCl= mixed molten salt, which investigated the effects of current density, electrolysis time and boron permeability temperature on the permeability thickness, morphology and material phase. Study showed that, with the increasing current density, The thickness of the seepage layer changes in a parabola, At the electrolysis temperature 1193K and time 60min, The current density of 500 A/m2 is about 4.5 μm, The surface hardness value of the sample is 1621HV; The layer thickness increased with the electrolysis time, At 1193K, the TiB2 thickness was 7.9 μ m, The maximum depth of the TiB embedded matrix is about 26.6 μ m, The surface hardness of the test sample is about 2696 HV; Boron infiltration at different temperatures, the rate of permeability formation increases with increasing temperature. Finally, the dynamics of permeability growth are analyzed and the diffusion constant K0 and diffusion activation energy Q are calculated [27].

Sarma et al. believe that the growth results of TiB2 and TiB crystals can be explained from the growth kinetic model. B goes through the TiB2, TiB and Ti phases respectively during the diffusion to the Ti matrix, and the diffusion velocity in the three phases is different. The diffusion coefficient of B in the TiB2, TiB and Ti phases is from large to small: D TiB> DTiB2> DTi. TiB and TiB2 are contained in the boride layer of all samples, but it is more difficult to generate TiB2 than TiB phase. At high temperature, the diffusion rate of the active B atoms in TiB is greater than that in titanium, and the active B atoms quickly pass through the TiB2 phase and directly react with the Ti matrix to form TiB2. Therefore, low temperature mainly favors TiB growth, while TiB2 growth is faster and TiB growth is slower at high temperature.

Liu Song Qing [28] with anhydrous borax ($Na_2B_4O_7$) molten salt electrolysis method of Ti permeability treatment, it is concluded that the molten salt electrolysis boron permeability layer thickness and treatment time, temperature and current density, including permeability treatment time square root and boron layer thickness is a linear relationship, permeability boron layer thickness relative to the treatment time is increased according to the parabola.

Thebault et al. and Feldman et al. are involved in the reaction dynamics of Ti-B system in their respective molten salt electrolysis studies, and reached a consistent conclusion: at a certain temperature, the reaction between Ti and B into TiB2 is a diffusion control process, and the diffusion of B atoms into the lattice of Ti matrix is the speed control link of the whole reaction. G.Kartal et al. believe that the boron permeability problem can be attributed to the diffusion of active B atoms in metals. The study found that the current density has an impact on the formation rate of active B atoms, thus affecting the growth rate of the boride permeability layer.

4. LIQUID PHASE PLASMA ELECTROLYTIC BORON INFILTRATION

The boron infiltration treatment of titanium alloy has the advantages of relatively simple process and short treatment time. Plasma electrolysis boron infiltration technology is a heat treatment method that quickly scans the permeable surface coated with the permeable agent with high-energy particle beam [29] changes the permeable agent of the heated surface coating under the bombardment of extremely high temperature and huge kinetic energy, and obtains the multiple permeable boron and quenching alloy tissue [30].

The electrolyte of liquid plasma lysis and boron infiltration is usually composed of two parts. The first part includes some soluble salts, such as NaCl, Na2CO$_3$ or NaOH, which can improve the conductivity of the electrolyte in order to form a stable discharge arc. The second part is some commonly used organic compounds, which can provide B, C, N and other active particles in the process of plasma electrolysis permeability boron (PEB) or multiple permeability boron (PEB / C, PEB / N and PEB / C / N, etc.) In addition, the water content in the electrolyte has a great influence on the electrical parameters. The water content added to the solution is usually controlled to be 5% to 10%. If the content is less than 5%, the critical breakdown voltage will increase; if it is more than 10%, the slope of the voltage-temperature curve will increase rapidly [31].

4.1 Research Status of Liquid Phase Plasma Electrolytic Boron

Miao Qianqian et al. [32] also used the anode plasma electrolysis technology to treat the surface of titanium alloy. After the boron treatment, a continuous and dense boron layer can be made. The boron layer is composed of TiB and TiB2, and the oxide and the boron layer work together to improve the wear resistance of TC4 titanium alloy surface. However, compared with raw materials, the permeability of TC4 titanium alloy has weak resistance to corrosion.

Aliofkhazraei et al. [33]. studied the size and morphology structure of nanocrystalline compounds after cathode plasma electrolytic boron and carbon co-infiltration (Cathode PEB / C) of γ -TiAl and pure titanium under different voltages, frequencies and duty ratio. The results showed that reducing the average size of the generated compounds by adjusting the appropriate boron permeability parameters will significantly improve the performance of the samples after the boron permeability treatment.

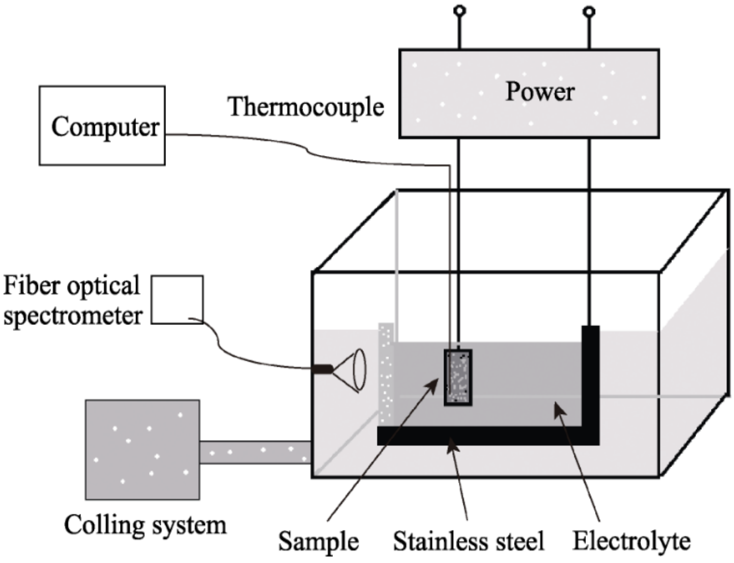

Fig. 4. Schematic diagram of the plasma electrolytic boriding equipment

Taheri, Kim and Kusmanov, etc. explored the plasma electrolytic boron (PEB / C / N). Through comparative analysis with PEB and PEB / C, PEB / C / N usually has thicker boron layer and higher boron efficiency than PEB and PEB / C.

5. CONCLUSION

The three titanium alloy boronizing techniques mentioned above can significantly alter the surface structure of the alloy, enhance surface hardness and strength, and to some extent, improve the alloy's properties such as wear resistance, fatigue resistance, and corrosion resistance. This broadens the application scope of titanium alloys and extends their lifespan. Composite boronizing in solid pack boronizing is currently a hot topic in research. Further studies can explore various elements' co-infiltration processes and conduct kinetic and thermodynamic analyses of composite boronizing.

In the case of molten salt electrolysis boronizing, besides systematically studying the influence of process parameters on the thickness of the boride layer, further research is needed to deeply understand the thermodynamics and kinetics of boride layer growth near the phase transition temperature.plasma electrolytic boriding technology primarily focuses on cathodic plasma electrolytic boriding, while research on the performance of boride layers formed under anodic plasma electrolytic boriding is scarce. Future research could include investigations into this aspect.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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