Current status of aluminising research on titanium alloys

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; Abrasion resistance }

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 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].

1. EMBEDDING PENETRATION

The buried infiltration method is generally divided into: solid powder method and paste method, both of which are solid boron infiltration method[11]

(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 to the inside of the sample. Including boron donor, activator, and filler. [12]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 sodium fluoroicate 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[13].

(2) paste boron

Paste method boron is similar to solid method, ointment method boron is the paste boron agent coated on the surface of the workpiece, boron agent in addition to boron agent, activator and filling agent, also includes binder. The activator of ointment method is generally used by one or several mixed, commonly used activators are fluoride, chloride and potassium fluoroborate. The aste method can be divided into packing paste method, self-protection ointment method and non-packing local ointment method. The advantages of the ointment method are the high cost, large waste, poor thermal conductivity of the infiltration agent, long heating time, high energy consumption, low efficiency, it is not convenient to deal with large components, it is difficult to clean up[14].

1.1 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[15] et al In order to accelerate the growth of solid boron permeability layer on the surface of TC4 titanium alloy, the test of adding Y_2O_3 to 1050℃/ 8h in the process of solid powder infiltration, including not adding Y_2O_3 and 1%, 3%, 5% and 7%Y_2O_3 in the test. 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.

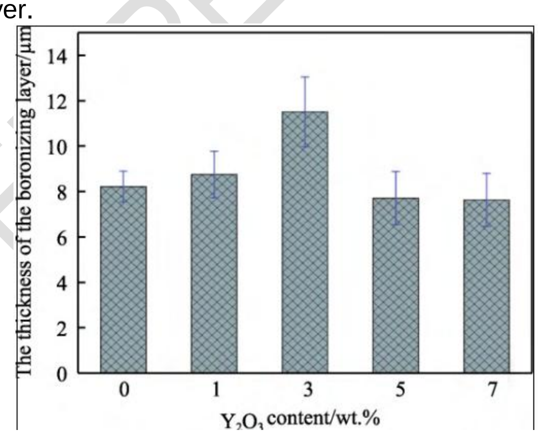

Fig.1Thicknessofboronizinglayerpreparedinpackmixtureswithdifferent Y2O3content

In order to improve the surface properties of TB2 alloy, Qudeyi et al[16]. used 4%La2O3 (mass fraction) for 1100℃, 20h, to study the composition and thickness, corrosion and wear properties of TB2 titanium alloy. The results show that La2O3 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 La2O3 can react with B to generate La-B active groups, which further promotes the growth of the boride layer. La2O3 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 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[17]. obtained a uniform and dense surface infiltration layer on the surface of Ti-6Al-4V alloy. The surface permeability layer is composed of TiB_2, 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.

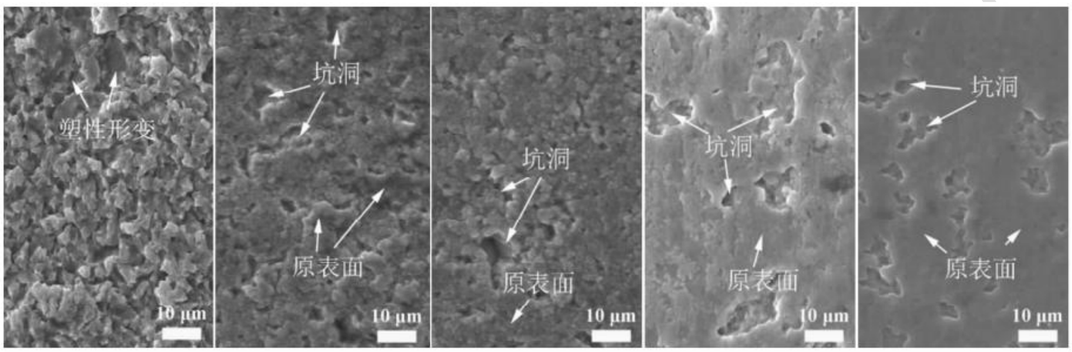

Fig. 2 SurfacemorphologyoftheTi─6Al-4Valloyspecimensafter12hofcavitationtesting

Xu Zhenyuan[18] et al. 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 / TiB_2 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 of high temperature of titanium alloy
Li Ping[19] chose TA2 industrial pure titanium as the substrate and used solid boron infiltration method
Face modification. 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_2Layer, 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. Was maximum 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 smaller 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 207.85kJmol-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, with a diffusion energy barrier of 0.8403 eV. The preferential diffusion path for B atoms in β -Ti is T-T 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[20].

2. SURFACE-BASED MOLTEN SALT ELECTROLYSIS METHO

The molten salt electrolysis technology with anhydrous borax as boron infiltration agent is a new technology developed in recent years, which has a series of advantages such as simple leach, low cost, convenient operation, objective thickness, small pollution and reproducible application of leach. Generally speaking, the process of molten salt electrolysis includes several important process parameters, namely, electrolysis time, current density and electrolytic temperature, any one factor will have a huge impact on the seepage layer[21].
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 beCycle reuse[22].
（d）At high temperature, the molten salt has good conductivity in the molten state, and usually the efficiency of molten salt electrolytic than that of aqueous solution
tall.

2.1 Research status of surface molten salt electrolysis method

Ma Xingfei[23] et al. 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 show 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 μ m, The surface hardness value of the sample is 1621 HV; The layer thickness increased with the electrolysis time, At 1193K, the TiB_2 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 K_0 and diffusion activation energy Q are calculated[24].

Sarma et al. believe that the growth results of TiB_2 and TiB crystals can be explained from the growth kinetic model. B goes through the TiB_2, 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 TiB_2, TiB and Ti phases is from large to small: $D_{TiB} > D_{TiB2} > D_{Ti}$. TiB and TiB_2 are contained in the borization layer of all samples, but it is more difficult to generate TiB_2 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 TiB_2 phase and directly react with the Ti matrix to form TiB_2. Therefore, low temperature mainly favors TiB growth, while TiB_2 growth is faster and TiB growth is slower at high temperature.

LiuSongQing[25] 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 TiB_2 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.

3.LIQUIDPHASE 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[26], 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[27].

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, NaCO 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 content of water in the electrolyte has a great influence on the electrical parameters, usually control the water content of the added solution is 5%~10%. If less than 5% increases the critical breakdown voltage; if more than 10% increases the slope of the voltage-temperature curve[28].

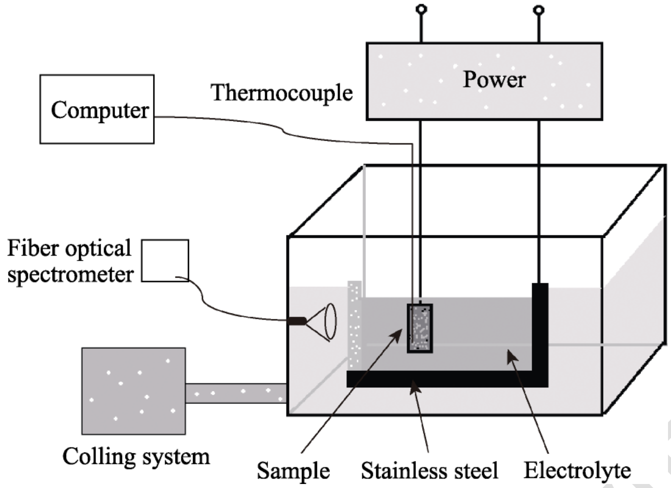

Fig. 3 Schematicdiagramoftheplasmaelectrolyticboridingequipment

3.1 Research status of Liquid phase plasma electrolytic boron

Miao Qianqian[29] et al 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 TiB_2, 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 less resistance to corrosion

Aliofkhazraei[30] et al. studied the size and morphology structure of nanocrystalline compounds after cathode plasma electrolytic boron and carbon co-infiltration (CathodePEB / 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.

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.

4. CONCLUSION

The top three boron infiltration techniques of titanium alloy can greatly change the surface structure of the alloy, improve the surface hardness and strength, improve the wear, fatigue and corrosion properties of the alloy to a certain extent, expand the use field of titanium alloy, and prolong the service life of titanium alloy. In general, the three methods of titanium alloy boron infiltration have both advantages and disadvantages. In addition, from the characteristics of permeability layer, boron permeability is a chemical heat treatment with potential in the future. Embedded infiltration in the composite permeability is the focus of the research, follow-up research can continue to explore a variety of elements permeability process and composite permeability dynamics and thermodynamics analysis, molten salt electrolysis boron permeability in addition to the system research process parameters of the permeability thickness, also need to further study under the near phase transition temperature permeability growth thermodynamics and dynamics. Study on the boron infiltration technique of anode plasma electrolytic system. The ion electrolysis technique focuses on the cathode plasma electrolysis technique, while the performance of the anode plasma electrolysis boron layer is rarely explored. In addition, to clarify the difference in the boron permeability mechanism of the anode and cathode plasma is of great value for the study of the plasma electrolysis mechanism, and the research on this aspect can be added in the future.

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