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Progress of Titanium and Titanium Alloy Milling

Sanfeng Zhang, Jinzhou Meng and Wenge Li

School of Merchant Shipping, Shanghai Maritime University, 1550 Haigang Avenue, Pudong New District, Shanghai, China.

Abstract

Titanium alloy milling is a process that relies on chemical solutions to corrode and repair titanium alloy surfaces. The principles of development and classification of domestic titanium alloys are discussed. The reaction mechanism and evaluation index of titanium alloy milling are described. The various influencing factors of titanium alloy milling process are discussed, such as temperature, HF and HNO3 ratio, and stirring mode. Titanium alloy milling waste liquid is a kind of hazardous waste. Titanium ions and fluoride ions have great influence on the environment. The components of titanium alloy milling fluid will be measured and the waste liquid treatment will be discussed.

Keywords

Titanium alloy; Chemical milling; Crafts.

1. Introduction

Titanium and titanium alloys have very excellent comprehensive performance, which is of great significance for improving naval equipment and tactical performance, and improving the development of marine resources [1]. Therefore, since the 1980s in the 20th century, Western developed countries have begun to use their submarines and nuclear submarines. Aircraft carriers, surface ships and deep submersibles, and other equipment use Ti alloy materials to replace CuNi alloys, stainless steel and nickel-based alloys, to make power systems (steam generators and propeller propellers, etc.), sea pipeline systems, heat exchangers, Pressure-resistant housing, sonar system, smoke exhaust pipe, fire extinguishing system, pump valve system, communication system and other equipment and components [2-4], thus greatly extending the service life of the equipment, reducing maintenance costs and improving safety, Carrying capacity and maneuverability. In addition, in offshore oil drilling and production equipment, titanium alloys have also begun to be widely adopted to improve the safety and reliability of drilling and production equipment, reduce system weight and operation and maintenance costs. Will continue to expand.

However, at present, machining methods are mainly used to repair titanium alloys. Due to the low grinding ratio of titanium alloys, high grinding temperatures, and difficult to ensure surface quality, the maintenance efficiency of titanium alloys is low, and parts deformation, stress concentration, and failure are likely to occur. Problems such as ensuring the size requirements are one of the main problems that have troubled titanium alloy maintenance for a long time [5-6].

Compared with traditional metal materials, titanium and its alloys have poor processing properties, such as low thermal conductivity, low specific heat, low elastic modulus, and strong chemical activation.

Chemical milling is a special processing and maintenance process that relies on chemical solutions to dissolve and dissolve the surface of titanium alloys. It provides an effective method for the processing and maintenance of high-temperature titanium alloy structures and parts of marine gas turbines ^[7-10]. Certain types of engine titanium alloy blades, casings and other structural parts are processed by chemical milling to achieve weight reduction.

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1.1 Titanium and titanium alloy applications

Titanium and titanium alloys differ in their chemical milling and dissolution behavior due to their different composition and structure. Titanium has the phenomenon of allotropy. Pure titanium is a close-packed hexagonal (HCP) crystal at room temperature, called the Alpha (α) , which transforms into a body-centered cubic (BCC) mechanism, called the beta (β) phase at about 885 °C. Generally speaking, titanium alloys can be classified into α alloys, near- α alloys, $\alpha+\beta$ alloys, metastable β alloys, and β alloys according to the phase structure contained in the alloy in the metastable state.

Alpha titanium alloy (including near-alpha alloy)-that is, domestic brand TA. Such alloys generally have suitable strength, good welding performance, high creep strength and high thermal stability, and can be used as high-temperature titanium alloys and corrosion-resistant weldable titanium alloys, which are widely used in aerospace engines and ships, This alloy has good low temperature properties due to no plastic-brittle transition [11], and can be used at low temperatures. Common alpha alloys are Ti811 (Ti-8Al-1Mo-1V), Ti-6Al-2Zr-1Mo-1V, Ti-679 (Ti-2.25Al-11Sn-5Zr-1Mo-0.25Si), BT18 (Ti-7.7Al-11Zr-0.6Mo-1Nb-0.3Si) and Ti6242S (Ti-6Al-2Sn-4Zr-2Mo-0.1Si).

Two-phase mixed $\alpha + \beta$ titanium alloy—namely, China brand TC. This alloy has good comprehensive properties, can be effectively adjusted by heat treatment, hot workability is better, and is widely used as structural materials ^[12]. Common Two-phase mixed $\alpha + \beta$ titanium alloy are TC4 (Ti-6Al-4V), TC6 (Ti-6Al-1.5Cr-2.5Mo-0.5Fe-0.3Si), TC11 (Ti-6.5Al-3.5Mo-1.5Zr-0.3Si), TC17 (Ti-5Al-2Sn-2Zr-4Mo-4Cr), TC19 (Ti-6Al-2Sn-4Zr-6Mo) and TC21 (Ti-6.2Al-2.8Mo-2Nb-2Sn-2.1Zr-1.3Cr).

Body-centered cubic structure (BCC) β -type titanium alloy (including near- β -type alloy)-that is, the China brand is TB. The β titanium alloy has good cold forming performance in the solid solution state, and has excellent hardenability and heat treatment response. Such metals have good cold workability, good fracture toughness and good heat treatment strengthening effect, and can be used in aerospace. And as a high-strength structural part in the ocean [13], common beta alloys Ti-1023 (Ti-10V-2Fe-3Al) Ti-1023, Ti-B20, Ti-20V-3Al-1Sn.

2. Chemical milling of titanium and titanium

In 1771, Schell discovered hydrofluoric acid, which provided the possibility of corrosion processing for titanium alloys that are difficult to machine [14-17]. In the mid-1960s, corrosion processing became a very practical production and processing method. The United States, Britain, France, Russia and other countries began to carry out related research on titanium alloy corrosion processing [18]. Coggins [19] disclosed a titanium alloy corrosion processing solution composed of hydrofluoric acid, nitric acid, carboxylic acid derivatives, and sodium benzoate in a 1978 US patent. This formula is used for milling, and the hydrogen absorption is very small and milling.

In the early chemical milling of titanium and titanium alloys, the HNO₃-H₂CrO₄ type was often used as the oxidant in the corrosion processing solution ^[20]. In the mid-term, the United States and the United Kingdom successively adopted HF-H₂CrO₄ based processing fluids. However, because H₂CrO₄ has the disadvantages of high cost, serious pollution, and prone to hydrogen embrittlement in processed parts, it is gradually abandoned. In the late 1980s, Chinese scholars such as Li Di, Zhu Yanhai, Qi Yunlian ^[21-23] now have common chemical milling fluids of the HF type: suitable for the hydrogen content of the base metal during the processing process. , Such as processing commercial pure titanium, Ti-25Cu, etc. HF-HNO₃ type: nitric acid is used as an oxidizing agent in chemical milling, while improving the surface brightness of the sample, it can also avoid hydrogen embrittlement, such as processing TC4, TA15, etc. At present, the most common application is the hydrofluoric acid-nitric acid type.

Now the main research direction is to optimize the corrosion processing technology and the post-processing of chemical milling.

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2.1 Quality evaluation criteria for milling

The evaluation of the quality of titanium and titanium alloy chemical milling usually includes three parts: chemical milling speed, surface roughness, and etching ratio [24].

The measurement method of chemical milling speed is usually to measure the thickness h_0 of the chemical milling part before processing and the thickness h_1 after processing. The formula of the corrosion processing speed is as follows

$$V = (h_0 - h_1)/T \tag{1}$$

Etching speed V (µm/min), etching processing time T (min)

The current surface roughness indicators are now expressed by Ra (mean deviation of contour arithmetic). Since the surface roughness will affect the fatigue strength, fracture toughness and other mechanical properties of titanium and titanium alloys, generally Ra \leq 1.6 μ m of the substrate is required, and now high-precision chemical milling should reach Ra \leq 0.6 μ m.

The etching ratio is the ratio of the lateral corrosion length to the longitudinal corrosion length (corrosion depth) of the chemical milling parts, generally 0.9 to 1.2. If the etching ratio is too small or too large, it will increase the difficulty of chemical milling, and it is difficult to meet the requirements of tolerance matching.

$$K = A / B \tag{2}$$

A is the length of lateral corrosion; B is the depth of sample corrosion;

2.2 Composition and function of miling liquid

Hydrofluoric acid-nitric acid type as a common titanium alloy milling solution, usually milling liquid by corrosive agent, oxidant, additives. Due to the strong oxidation of titanium and titanium alloy, it has a good corrosion resistant layer when contacting with air. HF is used as the corrosion agent. HNO3, as an oxidant, oxidizes hydrogen to prevent hydrogen embrittlement from causing damage to the matrix. Meanwhile, it can improve the finish of the matrix milling surface.

$$2Ti+6HF=2TiF_3+3H_2\uparrow$$
 (3)

$$3Ti+10HNO_3=3TiO(NO_3)_2+5H_2O+4NO\uparrow$$
 (4)

$$3Ti + 12HF + 4HNO_3 = 3TiF_4 + 8H_2O + 4NO\uparrow$$
 (5)

2.2.1Additives

In the process of titanium alloying milling, in addition to the necessary corrosive agent and oxidant, in order to turn the milling quality, also need to add the necessary additives. The additive can reduce the hydrogen absorption of titanium alloy, increase the corrosion rate and improve the surface quality. In order to inhibit the toxic nitrogen oxide gas produced in the process of milling, amide compounds, such as urea, should be added in general, in principle, it is required to neither affect the mechanical properties of the substrate nor react with the milling liquid, in which the nitrogen oxide inhibition equation of urea is expressed in the following formula:

$$NO + (NH2)2CO \rightarrow NH4NO3 + CO2 + N2 \uparrow$$
 (6)

2.2.2 Inhibitor

In order to reduce the corrosion rate and improve the uniformity of the chemical milling surface, it is generally necessary to add an inhibitor, which has a certain viscosity. After being dissolved in the chemical milling solution, it can reduce the diffusion speed of the ions in the solution and make the surface react. The speed is more uniform, improving the flatness of the surface.

2.2.3 Surface active agent

The addition of surface active agent can reduce the reaction interfacial tension, make the chemical milling solution and substrate surface fully wet, thereby directly increasing the reaction area and increasing the corrosion rate. For nonionic surfactants, the surface tension of the substrate can be reduced, so that the substrate and the chemical milling fluid can be fully contacted, so that the gas

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generated on the reaction surface of the substrate can be discharged in the form of small bubbles, and the surface roughness of the chemical milling surface is improved.

2.3 Chemical milling corrosion mechanism

The alloy components and different phase compositions in the titanium alloy have different dissolution behaviors during the corrosion process, which causes corrosion differences in various areas of the titanium alloy surface. Figure 1 shows P.Y.Lim [25] of Taiwan, China, etc. studied the microstructure of the surface of $\alpha + \beta$ titanium alloy after different annealing treatments eroded in the corrosion processing solution. The XRD and SEM analysis found that the β phase A microbattery is formed with the α phase, the β phase serves as the cathode, the α phase preferentially dissolves, and the corrosion proceeds in a localized manner.

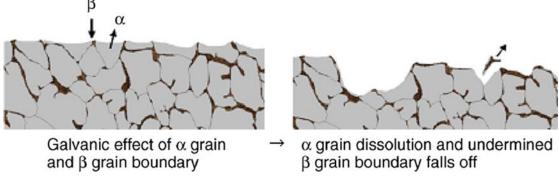


Figure 1 Schematic diagram of local dissolution of TC4 titanium alloy

At this stage, the dissolution mechanism of titanium alloy milling is mainly focused on the diffusion behavior of titanium alloy during milling and the micro-region dissolution behavior. Lin Cui ^[26] of Nanchang Aerospace University used E-t curve and polarization curve to analyze the dynamics of chemical milling by changing the composition and temperature of Ti-6Al-4V titanium alloy milling fluid. It is an iterative process of "etching-dissolving-passivation". Figure 2 shows the curve of anode solvent velocity with time when the volume ratio of nitric acid to hydrofluoric acid is 2: 1 and 3: 1. At different temperatures, at the beginning of the first tens of seconds of the curve, the corrosion rate rises rapidly. This stage is the rapid dissolution process of the titanium oxide surface oxide film in the strong reduction of hydrofluoric acid. The second stage is a stable stage, mainly because the substrate and nitric acid are directly contacted to form a passivation film with strong corrosion resistance after removing the oxide film. The ring-breaking speed reaches a dynamic balance, and the corrosion speed also tends to be gentle.

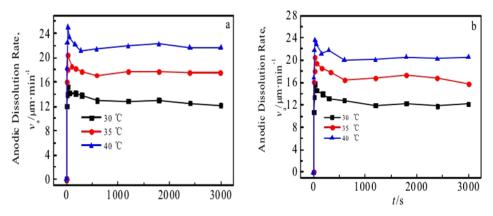


Fig. 2 Change of anodic dissolution rate of Ti-6Al-4V in corrosion processing solution with time

2.4 Chemical milling process

Process flow: degreasing \rightarrow washing \rightarrow drying with cold wind \rightarrow coating protective glue and curing \rightarrow engraving \rightarrow mounting \rightarrow activation \rightarrow corrosion processing \rightarrow hot water washing \rightarrow cold water washing \rightarrow drying \rightarrow Removing protective glue and acceptance.

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2.4.1 Pretreatment

Whether the oil stain on the surface of the parts is thoroughly cleaned is an important preparation process before the chemical milling process. The oil removal is not clean and the corrosion is prone to unevenness, and even local over corrosion. The common oil removal methods for chemical milling of titanium alloys include organic solvents. And chemical degreasing and other methods. If there is scale and foreign impurities on the surface, the purpose of sand blowing or corrosion is to improve the bonding force between the protective glue and the part substrate. Sand blowing can also remove shallow defects such as oxide layer on the surface of metal materials, so it is a better method than pre-corrosion. There are two types of sand blowing: dry sand blowing and wet sand blowing. Wet sand blowing is also called water sand blowing, and is a surface cleaning method for sand blowing with corundum sand mixed with water. Because water is added to the sand, the impact of the sand on the parts is slowed, the surface roughness of the parts is lower than that of dry sand blow, and the amount of removal is also less, so it is best to use wet sand blow. Before the parts are dry blown, the surface must be clean and dry. The parts with particularly complicated shape and structure are not suitable for the subsequent application of protective glue, so dry sand blowing should not be used. In order to prevent pollution, the sand blower used for titanium alloy parts should be used separately. When the wet sand blowing and dry sand methods are not applicable, the surface can be cleaned using the pre-corrosion method. Pre-corrosion is to place the parts in an acidic solution for weak corrosion to remove a thin layer of metal oxide film uniformly on the surface of the material and leak out the fresh base metal surface. Titanium alloy pre-corrosion formula generally uses a mixed solution containing nitric acid and hydrofluoric acid.

2.4.2 Engraved

Before chemical milling of the titanium alloy work-piece coated with a protective layer, the protective layer of the part to be milled must be removed. This process is called engraving. The scoring method is to use a scoring knife to cut the protective layer along the outline of the defined corrosion site, and then remove the unnecessary protective layer. Traditional manual scribing has the disadvantages of low efficiency, complicated coordination relationship, large error, poor accuracy, and difficulty in ensuring accuracy requirements. With the development of laser technology, Sun Xin [27] and others of AVIC Aircraft used laser engraving technology to adjust laser intensity parameters according to coatings of different thicknesses to obtain the effect of laser engraving on chemical milling erosion ratio and the calculation method of laser engraving chemical milling etching allowance completely replaces the traditional manual engraving.

2.4.3 Protective glue

The protective glue is a temporary protective coating on the parts that do not need to be processed during the chemical milling process, and is a peelable coating. The thickness of the coating is uniform, with a thickness between 250 and 300 μm . The coating methods of protective glue include spraying, brushing and dipping, and the coating method suitable for the parts is selected according to the structural complexity and size of the parts.

The chemical milling protection peelable coatings are mainly imported products from Germany and the United States represented by TURCO5580G and AC-850 chemical milling protection coatings. Li Qingcai and others ^[28] of Zhonghao North Coatings Industry Research and Design Institute Co., Ltd. chose a new type of polymer block copolymer as the matrix material, self-made thermosensitive tackifying resin that is non-reactive to hot alkaline liquid, and combined with reinforcing filler and pigment, Additives and solvents, balance the peelability and adhesion, and make a new type of chemical milling temporary protection peelable coating, which fills the lack of chemical milling protective glue in China. The paint film is smooth and even, with certain adhesion and good physical and mechanical properties. At the same time, the paint has the characteristics of convenient use, good chemical corrosion protection and easy manual stripping

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2.4.4Mount

The chemical milling process is a violent chemical reaction that will generate a lot of gas and heat. If it is not eliminated in time, it will affect the chemical milling uniformity and chemical milling speed. If the parts are stationary during chemical milling, there will be obvious air washout marks on the surface of the parts after chemical milling. In order to eliminate this flow mark, the method of stirring the solution is usually used, but for the complicated shape, especially the large parts cannot guarantee the uniformity in all directions simply by stirring, special tooling needs to be designed to rotate the parts in the solution, and Change direction regularly to avoid occlusion due to part shape. The tooling materials are pp material, polytetrafluoroethylene, and stainless steel materials OCr17Ni2Mo2 (SUS316) and OCr18Ni9 (SUS304) for test comparison [29]. SUS316 has better corrosion resistance than SUS304, but when both are used, protective glue must be applied.

In the tooling process, the adhesive can be epoxy resin, 502 glue, PVC water glue. Plastic welding and hot-melt welding can be used to weld non-metallic materials. For the load-bearing parts with stainless steel as tooling, the protective glue can be coated on the work-piece by hot dipping PVC method or coating method.

2.4.5 Chemical milling

The chemical milling process requires uniform corrosion of the parts, smooth and smooth surface, to prevent defects such as small holes and roughness, and to meet the mechanical properties of the base material. Chemical milling is to put the uncovered parts into a chemical milling solution containing nitric acid, hydrofluoric acid and additives to remove metal materials until the thickness reaches the required level. During chemical milling, in order to eliminate the erosion of the part by the gas generated by the reaction of the part with the chemical milling liquid and produce uneven flow marks, the solution needs to be stirred. There are generally two kinds of stirring methods: one is to pass the solution into the dry and clean compressed air that is filtered by the oil-water separator, and the other is to design a special tooling that drives the parts to rotate in the bath and can also be performed with a magnetic stirrer Stir.

After chemical milling, the parts need to be thoroughly cleaned in a cold water tank to avoid residual acid and alkali on the surface. For commonly used chemical milling materials, the corrosion process will leave a layer of oxide film and reactive deposits on the surface, and these substances cannot be removed by water washing alone. Titanium alloy materials are generally removed in a mixture containing hydrofluoric acid and nitric acid. Use a certain pressure of water to rinse the parts after washing to completely remove the residual substances on the surface of the parts.

3. Factors affecting the quality of titanium and titanium alloy milling

3.1 Effect of material state on chemical milling

- (1) The influence of the metallurgical state of the metal material: the metallurgical state of the substrate surface has a certain influence on the chemical milling process. Generally, the forged, extruded and rolled parts are denser and more uniform than the cast parts. The surface roughness after chemical milling is low and the brightness is high. For the chemical milling of titanium alloy materials, the parts made by forging have better surface quality and higher uniformity than the plate. The grain size of the material generally has no effect on the chemical milling speed. Materials with high hardness are generally not easy to chemically mill, and their chemical milling speed is lower than materials with low hardness.
- (2) The effect of cold work hardening: cold work hardening is due to the distortion of the material lattice during the machining or sheet metal forming of the parts, the internal stress of the material is increased, and the corrosion of the material is accelerated during chemical milling. If the internal stress of the cold-work hardened parts is not eliminated, the possibility of corrosion of the base material will increase, and the stress of the cold-work hardened parts needs to be eliminated before the milling.

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(3) Effect of surface roughness: Under the same conditions, the lower the surface roughness value of the base material of the part before chemical milling, the lower the surface roughness value of the part after chemical milling. Chemical milling will reduce the surface roughness of the parts. In general, the value after chemical milling is about twice lower than the value before chemical milling. And the chemical milling speed with low roughness is faster.

3.2 Effect of chemical milling fluid on chemical milling

Temperature plays an important role in the removal of metals caused by the acid reaction of titanium and titanium alloys. Titanium alloy chemical milling is an exothermic reaction. The chemical milling speed is directly proportional to the temperature. However, after the temperature is higher than 46 °C, hydrofluoric acid will volatilize a lot, which is easy to cause harm to the experimenters $^{[30]}$, and hydrofluoric acid volatilization will cause chemical .The composition of the milling fluid changes, which reduces the service life of the chemical milling fluid. At the same time, excessively high temperature can easily lead to foaming failure of the protective glue $^{[31]}$. The most suitable temperature range is $25 \sim 30$ °C. To control the temperature, an ice bath can be used to maintain the temperature of the chemical milling fluid.

In the initial chemical milling fluid, the titanium ion content is low, the chemical milling speed is fast, and the surface smoothness is good, but the surface is rough. In the middle and later stages, as the reaction progresses, the titanium ions in the solution increase, so that the viscosity of the solution increases, and the contact speed between the milling fluid and the substrate slows down, resulting in poor surface uniformity. At the same time, the concentration of the solution per unit area is relatively reduced, which reduces the milling rate. Titanium ions have a corrosion inhibitory effect. As the content increases, the surface roughness is improved.

Stirring speed. The chemical milling process is accompanied by agitation, so that the chemical milling fluid maintains contact with the metal surface and reacts uniformly. Generally speaking, the stirring speed has no obvious effect on the surface roughness; the stirring speed is proportional to the chemical milling speed, but when the chemical milling speed is too fast, the chemical milling speed is too fast, and the contact flow velocity of each part of the chemical milling surface is different, resulting in The uniformity of the work-piece becomes poor. Therefore, the stirring speed is generally $150 \sim 200 r / min$ [33].

3.3 The effect of chemical milling on the performance of the substrate

Although chemical milling cannot avoid deformation of parts due to mechanical processing stress, as shown in Figure 3, due to the chemical reaction has isotropy and protective effect of the glue layer, its horizontal direction will be continuously eroded, resulting in reinforcing ribs The upper edge of the edge forms a sharp edge. As the depth of chemical milling increases, the sharp edge will become sharper and sharper, causing excessive stress concentration [32]. At present, the method of removing sharp edges mainly includes the mechanical vibration method, which uses the principle of three-dimensional vibration to make parts and grinding media rub against each other on special equipment to remove the purpose of sharp edges. Wang Hui [34] of China Aviation Industry Corporation used hydrofluoric acid, nitric acid, etc. to form corrosive fluids, and adopted the secondary milling method for the removal of sharp edges, which can remove the sharp edges with high efficiency, low cost, and stability, but it will cause size of attrition.



Figure 3 Titanium alloy milling sharp edge [34]

Titanium and titanium alloys are very sensitive to hydrogen, and they are continuously processed in chemical milling. As the percentage of hydrofluoric acid increases, the reaction surface is exposed to

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more hydrogen content, and the amount of hydrogen absorption continues to increase ^[35]. Hydrogen is an indicator that must be strictly controlled. Generally speaking, the hydrogen content in titanium and titanium alloys should not be higher than 0.0125% ~ 0.015%, otherwise hydride will be precipitated on the tissue ^[36], and obvious hydrogen embrittlement will occur. In order to avoid this phenomenon, inhibitors are added to suppress the production of the mixture during the pickling process, thereby reducing the hydrogen content and improving the surface characteristics. Due to the occurrence of hydrogen embrittlement, the depth of the existing chemical milling and milling is generally not more than 2mm ^[37]. QingChun Li^[38] of Harbin Institute of Technology studied the chemical milling of TA12 titanium alloy greater than 2mm, and found that the chemical milling depth reached at 2.4mm, the hydrogen content has increased, but hydrogen embrittlement has not occurred. When the chemical milling depth reaches more than 5mm, the hydrogen increase is about 50ppm.

4. Optimization of titanium alloy chemical milling process

4.1 Research on the post-treatment of chemical milling fluid

The titanium alloy milling corrosion solution is usually composed of HF, HNO3, additives and processing by-product Ti (IV). Generally speaking, the titanium capacity of the chemical milling fluid is 50g / L, and the subsequent titanium solution capacity is adjusted to 70g / L. When the mass concentration of titanium ions in the solution reaches 70-90g / L, the milling speed of the titanium alloy sample decreases, the surface quality decreases, and the solution reaches the dissolution limit of the scrap state. After being scrapped, the corrosive processing fluid not only has strong acidity, high concentration, and a large amount of waste liquid, but also contains a large amount of metal ions in the solution. In the discharge, if not properly handled, it will not only cause serious damage to the environment. And it is a great waste of resources. The current chemical milling fluid is used by adding CaF_2 [$^{139-41}$] and the extraction of titanium ions to rationally use the waste fluid.

4.2 Titanium ion extraction

Research on the corrosion waste liquid of titanium alloy with hydrofluoric acid-nitric acid as the main body. In cold water and inorganic acid, sodium fluorotitanate is slightly soluble in cold acid, by reducing the temperature, the potassium fluorotitanate or sodium fluorotitanate in the corrosion waste liquid is precipitated, and the corrosion with extremely low titanium ion content can be obtained by filtration Waste liquid, in which potassium fluorotitanate can be used to prepare titanic acid and titanium, and sodium fluorotitanate can be used as an additive or to produce titanium dioxide, all have certain industrial production value.

Zhao Qing [42] obtained the pure K₂TiF₆ crystals by continuously precipitating the titanium ions in the TC4 titanium alloy milling fluid under low temperature environment with potassium fluoride. Replenishing acid liquid and additives, so as to recycle waste liquid, improve the life of chemical milling liquid, so that waste liquid can be reused.

4.3 Comprehensive evaluation of the chemical milling process

The milling process of titanium and titanium alloys is a controllable process [43]. In order to accurately control the milling depth and milling quality of titanium and titanium alloys, it is necessary to comprehensively consider factors such as temperature, chemical milling fluid ratio, and stirring.

Liang Jing ^[44] of Nanchang Aerospace University adjusted the TA15 titanium alloy corrosion processing solution formula and used orthogonal experiment methods to change the components of the chemical milling fluid. It was concluded that HF is the main factor affecting the corrosion processing speed, and HNO₃ is the surface. The main reason for roughness, and additives also have a greater impact on the corrosion-processed surface.

Titanium and titanium alloy milling is a process affected by a mixture of factors. In the past, when we studied titanium alloy milling, we only used a single factor as a variable to determine its impact, and did not consider the cross-effect between various factors. Lu^[45] adopted the uniformly designed experimental method, taking four influencing factors of chemical milling (temperature, titanium ion

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concentration, HF content, HNO₃ content) as 4 factors, and obtained the milling speed and erosion ratio using Minitab With the regression equation of 4 factors, the following equations (7), (8), (9) are obtained, and the degree of mixed influence of each factor is determined, and the parameter control under different titanium ion concentrations is obtained, as shown in Table 1 below

$$V = -0.0922 + 0.00189T + 0.000735C_{F}$$
(7)

$$P=1.21-0.0219C_{T}+0.0156C_{F}-0.0108C_{N}$$
(8)

$$C_F = 0.7C_N + 1.4C_{T} - 19.8 \tag{9}$$

Where V is milling speed; T is temperature; P is erosion ratio; C_T is titanium ion concentration; C_F is HF content; C_N is HNO₃ content.

5. Summary and Outlook

As a controlled machining technology, titanium and titanium alloy milling not only have absolute advantages in weight reduction and forming of titanium alloys, but also can process and repair some titanium alloy parts with complex contours. Because this kind of chemical milling can remove the surface oil stains and descaling of titanium alloy forgings, castings and other parts, at the same time, it avoids the hazards of tool wear, cutting stress and deformation caused by machining. It is widely used in aerospace, offshore engineering, Medical equipment and other fields.

Titanium and titanium alloy milling has been greatly developed in recent decades, but the following processing technology and theory still need to be strengthened.

- (1) Because there is no complete system for titanium and titanium alloys and the proportions of titanium and titanium alloys are different, the current chemical milling research is often only the characterization of a single titanium alloy, and it cannot fully reflect the chemical milling characteristics of the entire system of titanium alloys.
- (2) Titanium alloy milling waste liquid is highly polluting. In order to reduce pollution, you can choose fluorine-containing compounds, fluorosilicic acid and other substances to replace hydrofluoric acid [46].
- (3) At present, the research mainly focuses on the improvement of chemical milling processing technology and the study of individual factors, which cuts off the internal interactions between temperature and chemical milling fluid composition, and lacks a complete evaluation system

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