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Review

Current Status Review of Corrosion Resistance Applications of Titanium Alloys in the Petroleum Industry

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Abstract: Because of its superior strength, low elastic modulus, and exceptional resistance to corrosion, titanium alloy is commonly used as a replacement for carbon steel in the construction of oil well pipes. This paper starts with the application of titanium alloy in oil well pipes in the petroleum industry, summarizes the research progress of its mechanical properties and corrosion properties in titanium alloy drill pipes and oil casing, and compares the fatigue life of several common carbon steel materials and titanium alloy in the petroleum industry. At the same time, the influence of adding metal elements and optimizing the manufacturing process on the corrosion resistance of titanium alloy is discussed. Finally, the problems that titanium alloys may face in the actual production and application process are put forward.

Keywords: titanium alloy; oil country tubular goods (OCTGs); corrosion resistance; application

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1. Introduction

Developed in the 1950s, titanium emerged as a significant metal in the field of structural engineering. Titanium alloy is a metal material made up of titanium, aluminum, manganese, vanadium, and other elements that possesses high strength, lightness, and resistance to corrosion. Despite having a significantly lower density, only 60% of that of steel, it boasts twice the strength. Titanium can form alloys with other metal elements to improve its mechanical properties and physical properties to meet different needs [1]. Titanium and its alloys possess remarkable characteristics including significant strength [2,3], a low elastic modulus [4], commendable resistance to corrosion [5–7], and excellent biocompatibility [8,9]. The tensile strength of ordinary titanium alloy is 280~1100 MPa, and the tensile strength of high-strength titanium alloy such as Ti-1023, Ti-15-3, or β-21s can reach 1270~1480 MPa, which exceeds the strength of many alloy structural steels, so the specific strength of titanium alloy is much greater than that of other metal structural materials. Therefore, titanium alloys are widely used in aviation, aerospace, medical, marine, and other fields.

The increasing demand for oil and gas resources both domestically and internationally can be attributed to the rapid advancements in modern science and technology, which have greatly enhanced people's quality of life. The oil industry is driven to pursue deep oil and gas field exploration due to the ineffectiveness of traditional oil and gas exploration technology in meeting the growing demand for oil and gas consumption [10]. As the exploration depth increases, the encountered environment becomes increasingly intricate. The stratum pressure reaches 150 Mpa, the temperature reaches 300 °C, and the well depth reaches 10 km. The content of H_2S and CO_2 is also increasing [11,12]. Therefore, the performance and quality of oil well pipe have received more and more strict requirements under such complex working conditions [10].

Most of China's traditional oil well pipes are made of carbon steel, such as G105, L80, N80, P110, etc. However, the oil and gas exploration environment in China is relatively harsh. The downhole service of oil well pipes not only faces the challenge of high temperature and pressure, but also suffers from the combined effect of H_2S, CO_2, high concentration brine/completion fluid, elemental sulfur, strong acid, and other corrosive environments [13], which means traditional carbon steel can no longer meet the requirements of the harsh service environment. According to research, every year, an average of 20,000 oil wells in China's Daqing, Changqing, and other oilfields experience corrosion in their oil pipes. The oilfield's security is significantly at risk due to substantial economic losses resulting from a 10% annual growth rate as the service duration progresses. According to statistics, China's annual consumption of oil well tubes exceeds 2 Mt, spending more than 200 billion yuan. At the same time, with the increase in consumption, the exploitation of oil and gas fields began to be carried out in harsh, high-pressure, high-temperature, and high-corrosion environments with complex geological conditions. As important equipment in the mining process, the corrosion resistance of oil well pipes is very important. Titanium alloy materials used in oil well pipes abroad mainly include UNS R56404 (Ti-6Al-4V-0.08Ru), UNS R55400 (Ti-5.5Al-4.3Zr-5.7V-1.3Mo-0.10O-0.06Pd), UNS R58640 (Ti-3Al-8V-6Cr-4Zr-4Mo), UNS R56260 (Ti-6Al-2Sn-4Zr-6Mo), etc. [14]. In China, the utilization of TC4 (Ti-6Al-4V) titanium alloy is increasingly being seen in oil well pipes due to its excellent corrosion resistance and exceptional specific strength, thanks to advancements in technology.

2. Research Progress in Microstructure and Mechanical Properties of Titanium Alloys

2.1. Common Additive Elements in Titanium Alloys

Titanium alloy is an important structural material, mainly composed of titanium and other alloying elements. Common titanium alloy components include the following:

(1) Titanium: A fundamental element of titanium alloy, with excellent properties such as low density, high strength, and corrosion resistance. It is an important structural material.
(2) Aluminum: The addition of aluminum can improve the strength and hardness of titanium alloys, while reducing density and improving heat and corrosion resistance.
(3) Vanadium: The addition of vanadium can improve the strength, hardness, and thermal stability of titanium alloys, as well as improve their processing performance and wear resistance.
(4) Iron: Iron has a certain effect on improving the strength and hardness of titanium alloys, but it limits their hot working ability and is usually controlled in content.
(5) Chromium: The addition of chromium can improve the corrosion resistance of titanium alloys, especially with good resistance to oxidation, vulcanization, and salt water corrosion.
(6) Zirconium: Zirconium can effectively improve the corrosion resistance and strength of titanium alloys while reducing their oxidation performance.
(7) Nickel: Nickel has a certain effect on improving the strength, toughness, and wear resistance of titanium alloys, but excessive nickel may reduce corrosion resistance.
(8) Copper: Copper can improve the strength and hardness of titanium alloys while affecting their corrosion resistance.

The above elements are common main alloying elements in titanium alloys, and their content ratio and combination method will affect the performance characteristics of the alloy, such as strength, hardness, corrosion resistance, heat resistance, etc. Different application fields and requirements may require selecting different types and composition ratios of titanium alloys.

2.2. Microstructure

At room temperature, the equilibrium structure of titanium alloy exhibits three common configurations: hexagonal close-packed (HCP) structure, body-centered cubic (BCC) structure, and a dual structure [15]. According to the metastable state, the microstructure can be divided into α type, near α type, α+β type, near β type, metastable β type, and β type, and there exist nearly 100 kinds of titanium alloys in various series [16,17]. At temperatures below 882 °C, the α phase forms a typical HCP structure. When the temperature exceeds 882 V, the α phase transforms into a β BCC structure [18]. Due to the difference in processing and production difficulty, α titanium alloy and α+β titanium alloy are more widely used. Nevertheless, the titanium alloy lacks high strength at room temperature, and α+β titanium alloy is a dual-phase alloy, with better organizational stability, toughness, and plasticity and resistance to high temperature deformation, making it the most widely used titanium alloy.

Among them, α titanium alloy cannot be strengthened by heat treatment, so its general strength does not exceed 689 MPa. Generally, it is mainly used for low-pressure fluid transmission pipelines, such as heat exchange tube bundles, cooling pipelines, etc. [19]. α titanium alloy has good high temperature performance and good welding performance and is the main component of heat-resistant titanium alloy, but the strength is low at room temperature and the plasticity is not high enough. Common alpha titanium alloys include industrial pure titanium (TA1, TA3), TA5, and TA16 [20]. α+β titanium alloy has an acceptable strength and toughness combination because it can be strengthened by heat treatment and can be used to prepare drill pipes and oil casings with higher strength requirements [21]. However, if there are higher requirements for strength and heat resistance, titanium alloy materials can be selected. β titanium alloys consist of a β phase and secondary α phase. By controlling the morphology and size of these two phases, titanium alloy pipes can obtain strength up to 1140~1242 MPa [22]. In the meantime, β titanium alloy or near β type titanium alloy also has better hydrogen resistance, which α type and α+β type titanium alloy does not have.

2.3. Mechanical Properties

Compared with carbon steel, titanium alloy has better mechanical properties in some respects. Titanium alloy drill rods have the advantages of low density, low elastic modulus, high flexibility, and excellent corrosion resistance, and are considered by many oilfield developers as an ideal substitute for steel pipes [23–26]. In the study by Peng et al. [27], tests were carried out to evaluate the hardness, flattening, and tensile strength of a titanium alloy drill pipe in difficult oil well conditions. The findings indicate that the titanium alloy drill pipe's hardness is comparable to that of steel pipes, and it possesses excellent toughness and plastic deformation capabilities. Mou et al. [28] conducted fatigue contrast tests on titanium alloy oil pipes and G105 steel oil pipes, and the fatigue life data under different stress levels are shown in Table 1. It can be seen from the data that the fatigue life of the titanium alloy sample is about twice that of G105 steel, and the difference between them increases slightly with the increase in stress level. However, when the material test results are extended to the macro properties of the titanium alloy drill pipe, the fatigue life of the titanium alloy drill pipe is 10~12 times greater compared with a G105 steel drill pipe under the same bending degree and axial force. Under the same bending strain, the stress level of the titanium alloy pipe is half that of the G105 steel pipe, and the performance of the titanium alloy in corrosion and fatigue environments is better than that of G105 steel.

Many scholars believe that a series of improvement treatments can enhance some properties of titanium alloys. Chen et al. [29] attempted to modify Ti6Al4V titanium alloy by adding micro-alloyed Fe elements and compared the microstructure characteristics and mechanical properties of the prepared Ti6Al4V0.55Fe alloy with other Ti6Al4V alloys. The final experimental results indicate that the Ti6Al4V0.55Fe alloy exhibits better fracture toughness under heat treatment conditions than before modification, while maintaining the same strength, hardness, and elongation. Zhao et al. [30] investigated the mechanical properties, microstructure, and fracture morphology of TA15 titanium alloy after annealing. Based on the findings, it can be concluded that the mechanical properties of TA15 alloy experience a considerable enhancement through annealing treatment. As the annealing temperature rises, there is a noticeable increase in the interface between the α/β phase and the secondary α phase, while the volume fraction of the primary α phase declines. As a result, there is an increase in strength while toughness decreases. After secondary annealing, more secondary α phases are obtained, resulting in better overall performance. Mantri et al. [31] reported that β titanium alloys have very high tensile strength (UTS 1200–1810 MPa), but the elongation is low when using solid solution and double-aging treatment, ranging from 4% to 6.5%. The investigation by Wu and colleagues [32] focused on the strength enhancement in Ti-5.5Al-2Zr-1Mo-2.5V alloy tubes with a Weinstein structure due to the presence of a fine secondary A-phase. They found that the yield strength (YS) of the 920 °C solution and the 450 °C aged sample significantly increased to 1064 MPa, and the elongation (EL) remained at 10.5%. Feng et al. [33] looked at how aging affected the mechanical and microstructure characteristics of a drill pipe made of the titanium alloy Ti-5Al-3v-1.5Mo-2zr. After aging treatment at different temperatures, the mechanical properties of the titanium alloy drill pipe materials changed significantly. According to the research findings, there was an increase in the grain size of the Ti-5Al-3V-1.5Mo-2Zr titanium alloy, resulting in a clearer grain boundary. Additionally, the aggregation of phases and grain boundaries was diminished. The researchers noted that the growth in primary and secondary phase grains leads to an increase in their volume fraction. Nevertheless, elongation decreases as strength increases. As the temperature for aging increases, there is initially a rise in hardness followed by a decline (as shown in Figure 1a). Figure 1b clearly illustrates that the new sample exhibits significant enhancements in both its tensile strength and yield strength in comparison to the original sample. However, the elongation is decreased. In contrast, the Ti-5Al3V-1.5Mo-2Zr titanium alloy drill pipe material does not exhibit a significant yield phenomenon, and the stress–strain curve (depicted in Figure 1c) lacks a prominent yield platform. The strength of the alloy is enhanced through the improvement in interfacial dislocation stacking near phase boundaries after undergoing aging. As the number of secondary phase precipitates increases, the effectiveness of strengthening decreases. The greater the number of secondary phase precipitates, the lesser the strengthening effect.

Table 1. Fatigue life data of two materials under different stress levels [20].

Material	Stress (MPa)	150	180	200	240	300
Titanium alloy	Fatigue life/N	$>10^7$ $>10^7$	$>10^7$ $>10^7$	$>10^7$ $>10^7$	$>10^7$ 9,549,930	2,296,180 1,091,520
G105	Fatigue life/N	$>10^7$ $>10^7$	9,004,860 9,851,450	5,264,400 7,965,280	4,234,690 3,054,370	1,258,940 1,584,790
Material	**Stress (MPa)**	**380**	**465**	**550**	**620**	
Titanium alloy	Fatigue life/N	1,023,290 1,318,260	651,893 551,247	199,526 431,131	168,825 194,984	
G105	Fatigue life/N	281,838 630,957	304,639 231,405	128,489 81,283	91,398 59,432	

Titanium alloy tubing and casing will bear large external pressure loads underground. Wu et al. [34] first established a compression and tensile test method for titanium alloy pipes, and based on the test data, studied the downhole mechanical behavior of titanium alloy drill rods from the aspects of buckling, contact force, and friction with actual complex wells. At the same time, the mechanism of reducing friction was analyzed and discussed. The research results indicate that the strength of titanium alloy drill rods is equivalent to that of steel pipes, and they have good plastic deformation ability. Titanium alloy drill rods are more prone to buckling during operation, but their contact force is smaller, which can effectively reduce friction during operation. Liu Qiang et al. [35] established a new strength prediction model for titanium alloy tubing and casing based on the strength compression criterion model to calculate and compare the compressive strength of titanium alloy tubing and steel pipes with different key parameters. The experimental results show that the compressive strength of titanium alloy pipe is less than that of steel pipe with the same specification. The titanium alloy tubing and casing's compressive strength plays a major role in the downhole string's safety.

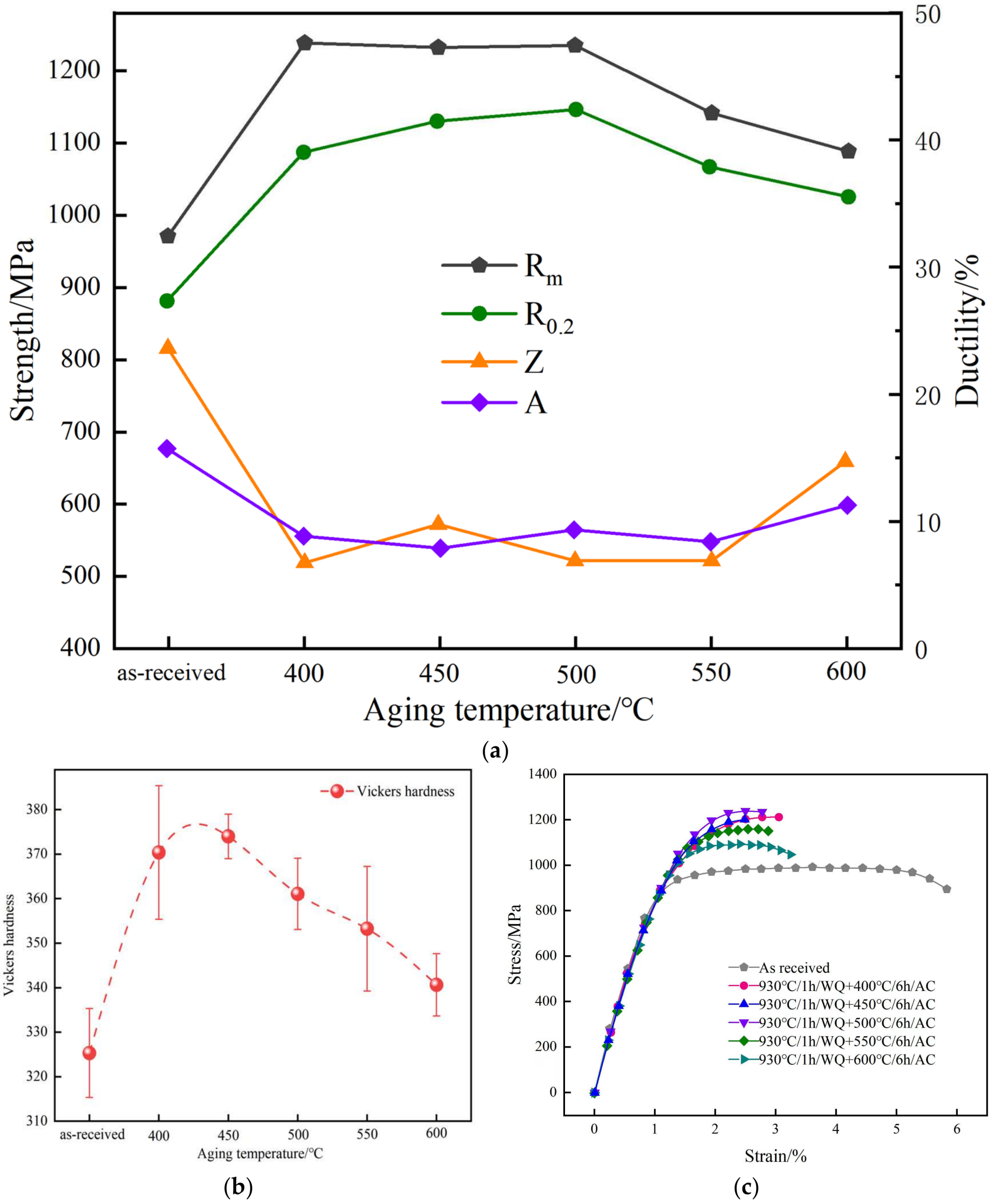

Figure 1. Effect of aging treatment on mechanical properties of Ti-5Al-3V-1.5Mo-2Zr titanium alloy drill pipe: (**a**) tensile property curve, (**b**) hardness change, (**c**) stress–strain curve (adapted from [21]).

2.4. Chemical Properties

Titanium and titanium alloys can react with dissolved oxygen in aqueous solutions, forming an oxide film on their surface with a thickness of about tens to hundreds of nanometers. The structure is relatively dense, and the chemical properties are stable, which can effectively inhibit further corrosion of the matrix by corrosive ions [36,37]. However, with the widespread application of titanium alloys in industry, the service environment has become increasingly harsh; especially when titanium alloys are in strong acidic environments, the corrosion behavior patterns become more complex [38,39]. R.W. Schutz et al. [40] exposed UNS R56404 titanium pipe to liquid mercury, and conducted high-stress, continuous tensile and cyclic loading experiments on it under relevant oil and gas production conditions. It was found that in liquid mercury at 232 °C, titanium pipe can completely resist liquid metal embrittlement and other forms of environmental degradation. They also studied the acid service qualification of UNS R55400 titanium alloy under the ANSI/NACE MR0175/ISO 15156 standard. UNS R55400 belongs to $\alpha+\beta$ titanium alloy, and it is a new high-strength titanium alloy specially developed for high-temperature and high-pressure oil and gas production [41]. They found that UNS R55400 titanium alloy can be used in an acidic salt water environment with up to 198 gpl chloride (i.e., saturated), and can be used in H_2S and CO_2 partial pressure up to 3.45 MPa and 6.9 MPa, respectively, at 288 °C in acidic environment.

To sum up, the corrosion resistance of titanium alloy oil well pipe is better than that of traditional carbon steel. Aging treatment enhances the mechanical properties of titanium alloy oil well pipe, and it showcases outstanding resistance to liquid metal embrittlement, sulfur, and acid. However, under the service environment with large external pressure load, the compressive strength of titanium alloy oil well pipe is far less than that of carbon steel pipe. There is little research on how to improve the compressive and flexural strength of titanium alloys in China. Maintaining or even enhancing the strength of titanium alloys in high-stress conditions is of utmost importance.

2.5. Processing Methods of Titanium Alloys

The processing difficulty of titanium alloys is relatively high, so the selection of processing methods is very important.

(1) Cutting processing

Cutting is the most commonly used method in titanium alloy processing, including turning, milling, drilling, etc. This method is suitable for machining complex shaped parts, but it is prone to generating chips and high temperatures during the machining process, resulting in severe tool wear and high surface roughness.

(2) Chemical processing

Chemical processing is the process of coating a layer of chemical material on the surface of titanium alloy, followed by a corrosion reaction, in order to obtain the desired shape and size of the parts. This method has the advantages of high precision and high surface finish, but the process is cumbersome, and the cost is high.

(3) Electrical discharge machining

Electrical discharge machining (EDM) is a method of machining titanium alloys by heating them with discharge. This method has high machining accuracy and surface smoothness, but the machining process is time-consuming and will affect the original mechanical properties of the produced titanium alloys.

In summary, different processing methods have their own advantages and disadvantages. Choosing a suitable processing method can improve processing efficiency, reduce production costs, and ensure the quality and durability of titanium alloy parts. Therefore, when selecting processing methods, it is necessary to comprehensively consider the processing requirements and process conditions.

3. Application of Titanium Alloy in Petroleum Industry

With the continuous development of unconventional oil and gas resources exploration such as deep water, high temperature and pressure, and high corrosion in oil and gas exploration [42–45], the shallow surface oil and gas resources that are easy to exploit are increasingly scarce, the water cut from old oilfields is getting higher and higher, and the exploitation environment is getting worse and worse. The existing oil well tubing materials can no longer meet their use conditions [46]; thus, the development of new drill pipe materials has become an urgent task. Titanium alloy oil well pipe has the advantages of good corrosion resistance; high strength; low elastic modulus; easy cold forming; seawater corrosion resistance [46–48]; and being appropriate to apply to deep wells, ultradeep wells, short-radius horizontal wells, and high-acid oil and gas wells, and will become a powerful tool to support oil well pipe development.

As early as the 1990s, titanium alloys were used in the petroleum industry because of their excellent comprehensive properties. In the 1990s, RMI Company [49] of the United States developed an excellent α+β titanium alloy pipe. Later, RMI Company (Basalt, CO, USA) developed a series of titanium alloy materials suitable for the petroleum industry on this basis, such as Ti-Bcta-C, 3-2.5RU, etc. The titanium alloy oil well pipe in China is developed by the China Petroleum Pipeline Engineering Technology Research Institute. It is lighter, stronger, more corrosion-resistant, and more fatigue-resistant than traditional steel pipes. Titanium alloy will become a popular oil well pipe material in the future. The problem of corrosion failure of oil well pipelines under harsh working conditions is solved by using it.

3.1. Drill Pipe

For drill rods, common ones include steel drill rods, aluminum drill rods [50], and titanium drill rods, among which steel drill rods are currently the most widely used drill rods. Although some thin-walled and lightweight ultrahigh-strength steel drill rods can be used to solve drilling problems in ultradeep wells, high-displacement wells, and deepwater drilling, high-strength steel is prone to brittleness at low temperatures [51], and the impact toughness and tensile strength of drill rods do not match the environment [52]. In complex wells, the drill pipe needs to be cycled under high stress levels for a long time under a small curvature radius. Conventional steel drill pipes can experience a sharp reduction in lifespan or even failure due to fatigue cracks, wear, and high bending stress, posing safety hazards to drilling operations. Therefore, unconventional oil and gas wells such as deep wells, ultradeep wells, and horizontal wells should use lightweight and high-strength drill rods. For some wells drilled with special technology, the use of titanium alloy drill pipe is the future development trend [24]. Titanium alloy drill rods have stronger flexibility, lower structural stress, better fatigue resistance, corrosion resistance, and lighter weight than commonly used steel drill rods. They have great application prospects in high-curvature well drilling applications. However, titanium alloy has low hardness and poor wear resistance, and it is easy to generate adhesion during the wear process, which makes the components invalid in early use. Grant Prideco (Houston, TX, USA), a subsidiary of Weatherford, and RTI Energy Systems (Houston, TX, USA) developed a titanium alloy drill pipe using the hot rolling process [53]. It not only has the strength of steel pipe, but also has the flexibility of synthetic materials. It is lighter, corrosion-resistant, and durable [54–56].

Compared with foreign countries, China's titanium alloy drill pipe technology started late, but developed rapidly. The titanium alloy drill pipe body is made of Ti-6Al-4V hot-rolled seamless pipe. Designed and processed, the titanium alloy drill pipe has an outer diameter of Φ73.02 mm, wall thickness of 9.19 mm, and length of 9.15 m. The drill pipe body is made of Ti-6Al-4V alloy, which has fatigue strength and high tensile strength, good corrosion resistance, low elastic modulus, and low cost. In addition, Ti-6Al-4V material also has good hot forging, processing, and welding properties. Figure 2 shows the hardness test results of G105, S135, V150, and titanium alloy drill pipe samples. It can be seen from Figure 2 that the hardness distribution of drill pipe is relatively uniform. The elastic model and density of titanium alloy drill pipe are lower than those of steel drill pipe, but the hardness of titanium alloy drill pipe is higher than G105 and S135, which may improve the corrosion resistance of it [39]. The taper transformation in the end wall thickness of titanium alloy-thickened drill pipe can significantly reduce the bending stress at the joint between the drill pipe joint and the drill pipe body, so that the bending stress of the drill pipe joint is evenly distributed along the axial direction, thus greatly improving the fatigue resistance of the titanium alloy drill pipe [57]. Titanium alloy drill pipe is more suitable for complex-trajectory wells with a short radius, long horizontal section, and corrosive environment [39].

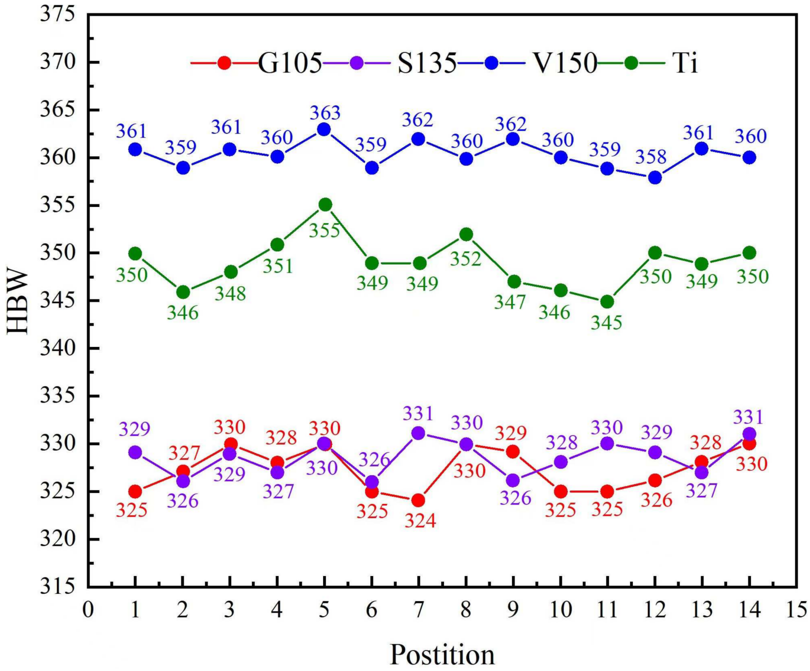

Figure 2. Hardness distribution of different drill pipes (adapted from [37]).

3.2. Oil Casing

Most of China's natural gas resources are sulfur-containing gas fields, such as the Tarim Basin in Xinjiang and Sichuan Basin. The development of highly corrosive oil and gas fields has become a major problem faced by the oil and gas industry. Many years of research have been carried out at home and abroad on the corrosion prevention of pipes with high H_2S and CO_2 content in oil and gas fields. There are roughly three types of corrosion prevention measures: adding corrosion inhibitors, anti-corrosive coating, and corrosion-resistant pipes. The first two can play an anti-corrosion role to a certain extent, but they cannot solve the corrosion in long-term service under high-temperature and high-pressure conditions. Therefore, the selection of high-quality corrosion-resistant materials for pipes has become the dominant trend. To ensure the normal operation of the drilling process and the entire well after completion, petroleum casing is used to support the steel pipes on the wellbore of the oil and gas well [58]. Several layers of casing are used for each well according to different drilling depths and geological conditions. Cement is be used for cementing after the casing is put into the well. It is different from tubing and drill pipe and cannot be reused. It is a one-time consumable material. The consumption of casing accounts for more than 70% of all oil well pipes. Therefore, casing material improvement is a matter of urgency.

Chevron has prepared Ti-6Al-2Sn-4Zr-6Mo, Ti-6Al-4V-Ru, Ti-6Al-4V, Ti-3Al- 8V-6Cr-4Zr-4Mo, and other titanium alloy tubing and casing materials, which have been used in some high-pressure, high-temperature, and ultrahigh-pressure high-temperature wells in the Gulf of Mexico [22]. Among them, the titanium alloy casing used in thermal production wells is made of Ti-6246 alloy. Titanium alloy casing of 145 steel grade has been used in thermal recovery wells. Since 2003, it has been used in thermal recovery wells with a depth of 1524 m and a temperature of 260~287 °C and has achieved excellent results. RMI Company has successfully developed titanium alloy casing, tubing, and coiled tubing by using the hot rotary pressure piercing pipe rolling process. According to the National Association of Corrosion Engineers (NACE), the titanium alloy oil well pipe produced by RMI Company can be completely resistant to H_2S, CO_2, and Cl^- corrosion below 330 °C. The service practice of Gr29 titanium alloy pipe in sour oil and gas wells has proved that its corrosion resistance is higher than that of C276 nickel base alloy and its cost is lower than that of G3 nickel base alloy oil casing [59,60].

China's Baotai Group upgraded and modified the Ti-6Al-4V alloy, and mass-produced Φ90~Φ120 mm extruded titanium alloy pipe, which is applied in Yuanba gas field with the burial depth of 6800 m, a H_2S volume fraction of 5.77%, and a formation temperature of 158 °C. The sulfide resistance stress is similar to or even better than that of nickel base alloy oil well pipe. The CNPC Petroleum Pipe Engineering Technology Research Institute developed P110 steel-grade titanium alloy oil well pipe based on α+β titanium alloy and cooperated with the Canadian CFer Center to carry out research on the gas sealing mechanism in specially threaded joints in oil and casing pipe. They developed a special threaded titanium alloy gas sealing joint from a tooth-shaped design, interference calculation, and sealing structure to give consideration to anti-gluing performance, which was proved to exceed the requirements of the API Spec 5CT-2011 standard for steel grade P110 by running CNOOC tests [61].

4. Research Progress on Corrosion Resistance in Titanium Alloy Oil Well Pipe

The essence of corrosion resistance in titanium alloys is that titanium is a thermodynamically unstable element, and the standard electrode potential is only −1.63 V (standard hydrogen electrode HSE) [62]. Therefore, it is very easy for titanium and titanium alloys to form a continuous, dense, and extremely thin surface oxide film in air or even water, which is composed of Ti_2O_3 in the inner layer and TiO_2 in the outer layer and thickens with the redox reaction. The coating of oxide film on the surface of titanium alloy hinders the transmission of reactive charge, thus reducing or inhibiting the dissolution of titanium alloy in corrosive medium, resulting in passivation. However, titanium alloys have higher positive potential than other alloys. When they are coupled with different alloys, titanium alloys are protected as cathodes, accelerating the corrosion of coupling metals, which can lead to structural damage [63]. The corrosion resistance of titanium alloy in drill pipe and oil casing has also been studied by scholars.

4.1. Corrosion Resistance in Titanium Alloy Drill Pipe

In 1982, the United States Unocal found that β-C titanium alloy could solve the corrosion problem caused by H_2S and CO_2 when developing geothermal wells, which promoted the development and application of titanium alloy in the oil and gas field. The research of RMI [64] in the United States on the corrosion behavior of titanium alloy in high-concentration hydrochloric acid solution shows that temperature and concentration significantly accelerate the corrosion rate of titanium alloy. Alcoa [65] of the United States established a laboratory corrosion test database of UNS R55400, UNS R56260, UNS R56404, and other titanium alloys under a hot hydrochloric acid environment through a large number of experiments and conducted tests in a series of related high-temperature and high-pressure oilfield well environments. A practical environmental limit framework for oil wells and chemical services using high-strength titanium alloys was constructed. In the early 21st century, Grant Prideco, a subsidiary of Weatherford International Co., LTD. (Weatherford), and Texas, a subsidiary of RTI, used Ti-6Al-4V titanium alloy to develop a titanium alloy drill pipe with light weight and high corrosion resistance, strength, and deflection to meet the requirements of the field. It has a yield strength of up to 840 MPa and was successfully applied to the drilling of a number of highly angled directional wells in the US state of Texas in 2000, with good results. Peng Xianbo et al. [39] evaluated the fatigue performance of titanium alloy drill pipes. The results show that the fatigue life of drill pipes will be prolonged with the increase in steel grades in air, and the titanium alloy drill pipes have the best fatigue performance in drilling mud. Figure 3a shows the fatigue curves of different drill pipe samples under H_2S mud at room temperature. The presence of H_2S mud greatly reduces the fatigue life of each drill pipe sample, indicating that drill pipes are highly sensitive to H_2S mud. In a H_2S mud environment, the fatigue life of the titanium alloy drill pipe is significantly higher than that of G105, S135, and V150 steel drill pipes. Figure 3b plots the S-N curves of different drill pipes in 100 °C H_2S mud, showing that the fatigue life at 100 °C of G105, S135, and V150 and the Ti samples is significantly reduced compared to that in room-temperature air. The coupling factor of H_2S mud and temperature has greater influence on the fatigue life of the drill pipe than any single factor. Under this coupling condition, the fatigue life of titanium drill pipe is still superior to that of other drill pipes.

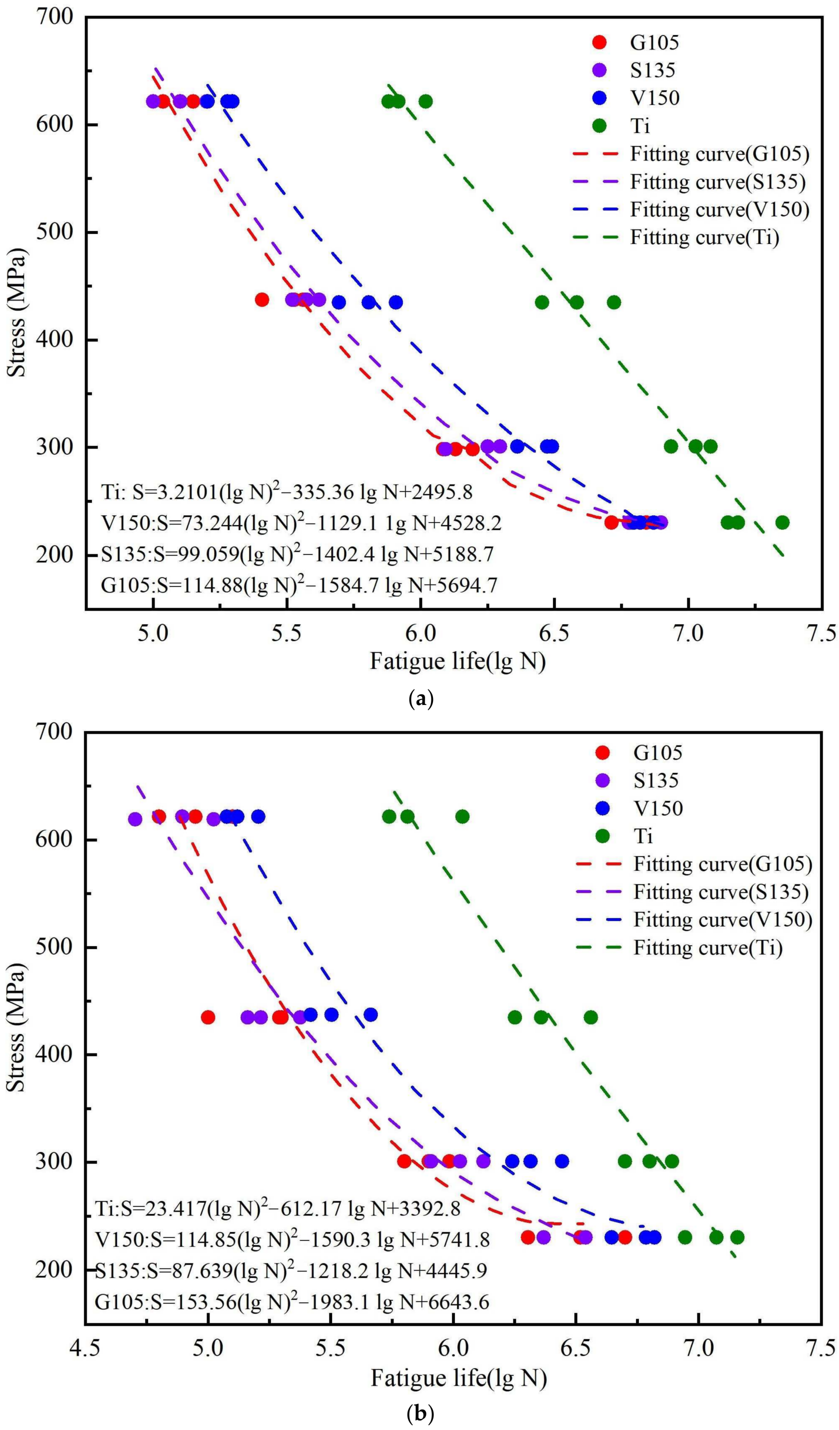

Figure 3. Fatigue curves of different drill pipe samples in H_2S mud (**a**) at room temperature and (**b**) at 100 °C (adapted from [37]).

Under the conditions of H_2S partial pressure at 6.9 MPa, CO_2 partial pressure at 3.4 MPa, Cl^- mass concentration at 0.2 g/L, elemental S mass concentration at 1 g/L, and temperatures of 177 and 218 °C, there is no gap corrosion or pitting corrosion on the titanium alloy caused by high-temperature sulfur-containing natural gas in Mobile Bay, USA [66]. D. R. KANE et al. [67] found that Ti-3Al-8V-6Cr-4Mo-4Zr titanium alloy had serious corrosion and hydrogen absorption at 25 °C in an HF system with a 12.0% HCl + 3.0% volume fraction. In the HCl system with a volume fraction of 15.0%, the corrosion and hydrogen absorption are serious at 120 °C, while in the HCl system with a volume fraction of 10.0% and HCl system with a volume fraction of 7.5%, corrosion occurs at 100 °C. In the NaCl system with 10.0% formic acid by volume, 10.0% acetic acid by volume, and 10.0% acetic acid by volume + 10.0% by volume, corrosion and hydrogen embrittling do not occur at 232 °C. Chen Xiaowen et al. [68] used a new surface treatment micro-arc oxidation technology to prepare a micro-arc titanium oxide film on the surface of a TC4 titanium alloy drill pipe. The micro-arc oxidation film of titanium alloy was coated by adding sodium tungstate of different concentrations into the oxidation solution. The research shows that the improvement in hardness and corrosion resistance of TC4 titanium alloy drill pipe is related to tungsten doping. It was concluded that when the concentration of sodium tungstate is 3 g/L, the comprehensive performance of micro-arc oxide coating on titanium alloy drill pipe is the best.

In conclusion, the corrosion fatigue life of titanium alloy drill pipe is better than that of steel drill pipe in high-temperature and high-sulfur environments, and the hardness and corrosion resistance of the drill pipe can be effectively improved by coating metal film on a TC4 titanium alloy surface [69]. However, at present, the research on improving the corrosion resistance of titanium alloy drill pipe by surface treatment or doping metal is still rare. Therefore, this provides a direction for researchers to study in the future.

4.2. Corrosion Resistance in Titanium Alloy Oil Casing

Around 1985, the first set of titanium alloy bushings for SaltonSea was officially produced and would be installed in 1986, and the first material for this service was Ti-38644 (beta-C, UNSR58640), a high-strength, age-hardened beta titanium alloy. After the development of ASTM Grade29 (UNS R56404) titanium casings, the vast majority have been in service at SaltonSea for more than 15 years with no signs of corrosion or cracking. [70] Hargrave et al. [22] studied in detail the corrosion resistance of Ti-6246 (135 ksi) titanium alloy tubing under simulated harsh drilling and completion conditions, and the final results showed that Ti-6246 (135 ksi) titanium alloy tubing had excellent corrosion resistance and resistance to environmental stress cracking in production, workover, and completion environments. Sumitomo Metal of Japan and other companies studied the corrosion behavior of titanium alloy pipes under simulated production conditions and proved that titanium alloy materials have great advantages in oil and gas development [71]. Schutz et al. [71] studied the preparation process of Ti-6Al-4V-Ru oil well pipe and made seamless pipe by using the hot rolling method above the β phase transition temperature to a obtain needle-like alpha phase or Weil structure with a strength of 758 MPa and a hardness of 35 HRC. Systematic corrosion performance tests have proven that this titanium alloy has good resistance to crack corrosion and stress corrosion cracking in acidic oil and gas fields, and the high-temperature corrosion resistance limit of the alloy is increased to 300 °C [72]. The research group of Wang et al. [73] studied the titanium alloy material TC4, which can be used as oil casing. They found that under the acidic corrosion environment, there is local electrochemical corrosion on the surface of TC4 alloy, mainly spot corrosion. In the completion fluid containing CO_2, the corrosion degree of TC4 alloy is serious, but the corrosion resistance in the formation water containing CO_2 is relatively acceptable. In the above two CO_2-containing corrosion media, TC4 alloy has excellent stress corrosion cracking resistance. Compared with the terrestrial environment, TC4 alloy is more sensitive to crack corrosion and stress corrosion cracking in deep-sea environments. At the same time, Wang's research group [74] also studied the corrosion resistance mechanism of TC4 titanium alloy under different stress loading conditions. They found that pits appeared on the surface of the specimen loaded with elastic stress, but the degree of pitting corrosion was relatively low, and the surface film layer showed n-type semiconductor properties, with cation-selective permeability. When the pits on the surface of the specimen subjected to plastic stress are deeper and wider, and the semiconducting type of the surface film layer changes to the p-type, anions such as Cl^- and $CO_3{}^{2-}$ are more likely to adsorb and damage the protective film and contact the matrix through the protective film, which leads to a decline in the corrosion resistance of TC4 titanium alloy.

At present, the working conditions of unconventional oil and gas fields are poor. High temperature reduces the elastic modulus and yield strength of tubing and casing. High pressure increases the pressure of tubing and casing. Under the action of H_2S, CO_2, and Cl^-, alone or jointly, the corrosion of oil and casing is becoming more and more serious. Titanium alloy tubing and casing can effectively solve the problem of downhole corrosion failure, but the research on the corrosion resistance of titanium alloy tubing and casing is not perfect at present, warranting further research [75].

4.3. Factors Affecting Corrosion Resistance of Titanium Alloy Oil Well Pipe

Well pipes are mostly affected by environmental aspects, such as temperature, pH, and moisture and other impurities in the air. When the pH value is less than 4, Ti becomes active, the oxide film begins to dissolve, the turning point of passivation–activation is no longer within the potential range of -0.7~-0.3 V, and the corrosion reaction speed is accelerated, accompanied by the formation of TiHx. If the surface of titanium alloy is enriched with Pd or Ru, the corrosion rate is inhibited. Even in a high-temperature and strong acid environment, due to the enrichment of Pd and Ru, the reduction in hydrogen ions is promoted, the corrosion potential of the titanium alloy shifts positively, and the surface is passivated. In an oxygen-rich environment, the corrosion potential of titanium alloy is greater than -0.3 V, and it is in the passivation state, even if the temperature is higher than 100 °C. The influence of the environment and temperature on corrosion rate is very small. In the active state, such as in an acidic or alkaline environment, the corrosion rate of titanium alloy increases with the increase in temperature. However, in the passivation state, the temperature has little effect on the corrosion rate of titanium alloy. As the temperature rises to 70 °C, the higher crystallinity of the passivation film on the surface of titanium alloy is caused by water absorption, and cracks or defects begin to appear [76]. The test conditions for high-temperature sulfur-containing natural gas wells in Mobile Bay, USA are as follows: H_2S partial pressure is 6.9 MPa, CO_2 partial pressure is 3.4 MPa, and with 20%NaCl solution and 1 g/L elemental sulfur, the temperature is 177 °C and 218 °C. No slot corrosion or pitting corrosion occurred in the titanium alloy under the above test conditions. Kane et al. [67] studied the corrosion, cracking, and hydrogen embrittlement of Ti-3Al-8V-6Cr-4Mo-4Zr in different acids. The results show that the corrosion rate of Ti-3Al-8V-6Cr-4Mo-4Zr decreases significantly when the molybdate corrosion inhibitor Na_2MoO_4 is added to HCl solution, and there is no hydrogen embrittlement. However, even with the use of molybdate corrosion inhibitor, the sulfide stress corrosion of Ti-3Al-8V-6Cr-4Mo-4Zr occurs in 10% HCl solution at 204 °C and 15%HCl solution above 177 °C. The corrosion of Ti-3Al-8V-6Cr-4Mo-4Zr in organic acids is much lower than that of inorganic acids, and there is no corrosion, hydrogen brittleness, or sulfide stress corrosion in organic acids. R. W. Schutz et al. compared the corrosion resistance of UNS R55400 alloy pipe with that of other oilfield titanium alloy pipes [65]. The laboratory corrosion test data for the development of UNS R55400 pipeline showed that the resistance of titanium alloy to SSC and local pitting and crevice corrosion was improved in the highly acidic and non-acidic chloride-rich water environments related to the oilfield industry. Table 2 shows the different types of approximate environmental service limits of titanium alloys in different oilfield environments. It can be seen that UNS R55400 and UNS R56404 titanium alloys have the highest performance in acid and non-acid chlorine water environments, and that with the highest strength is the UNS R58640 beta titanium alloy.

Wei Ya et al. [49] studied the relationship between the microstructural evolution and corrosion behavior of Ti Mo titanium alloy in hydrochloric acid and annealing temperature.

They found that with the increase in annealing temperature, after the temperature exceeded 850 °C, the dissolution of MoO_3 and TiO_2 passive films on the surface of the titanium alloy accelerated, as shown in Figure 4; the corrosion rate increased; and α phase harmony β phase micro-galvanic cells formed. In addition, the passivation film shows n-type semiconductor properties independent of annealing temperature.

Table 2. Comparison of approximate service limits of titanium alloys in different oilfield environments [46].

Oilfield Environment	Service Limits			
	UNS R55400	UNS R56404	UNS R56260	UNS R58640
Sour brine	288 °C * 3.45 MPa H_2S * 6.9 MPa CO_2 * with or without S^0, 25 wt.% NaCl	288 °C * 6.9 MPa H_2S * 3.45 MPa CO_2 * with or without S^0, 25 wt.% NaCl	<288 °C * 1.0 MPa H_2S 6.9 MPa CO_2 with or without S^0, 33 wt.% NaCl [SCC **]	150–204 °C 6.9 MPa H_2S 3.4 MPa CO_2 20 wt.% NaCl [SCC/crevice attack] **
Seawater (naturally aerated)	288 °C *	300 °C *	<288 °C * [SCC, low K_{SCC}] **	~200 °C [SCC, crevice attack] **
13.5 ppg $CaCl_2/CaBr_2$ completion fluid brine (sour or naturally aerated)	≤288 °C ***	288 °C *	<288 °C [SCC] **	<232 °C [SCC] **
Acetic + formic organic acids	204 °C *	204 °C *	-	-
10–15 wt.% HCl [w/molybdate inhibitor]	105 °C * [>105 °C]	105 °C * [>105 °C]	<100 °C [>105 °C]	105 °C
Methanol–water solutions @RT	≥3 wt.% water or ≥9 wt.% water ****	>9 wt.% water	>5 wt.% water	>4 wt.% water

* Not true limit, but highest value tested; ** [limiting mode of corrosion]; *** depending on oxygen level in brine; **** depending on pipe heat treatment/strength condition.

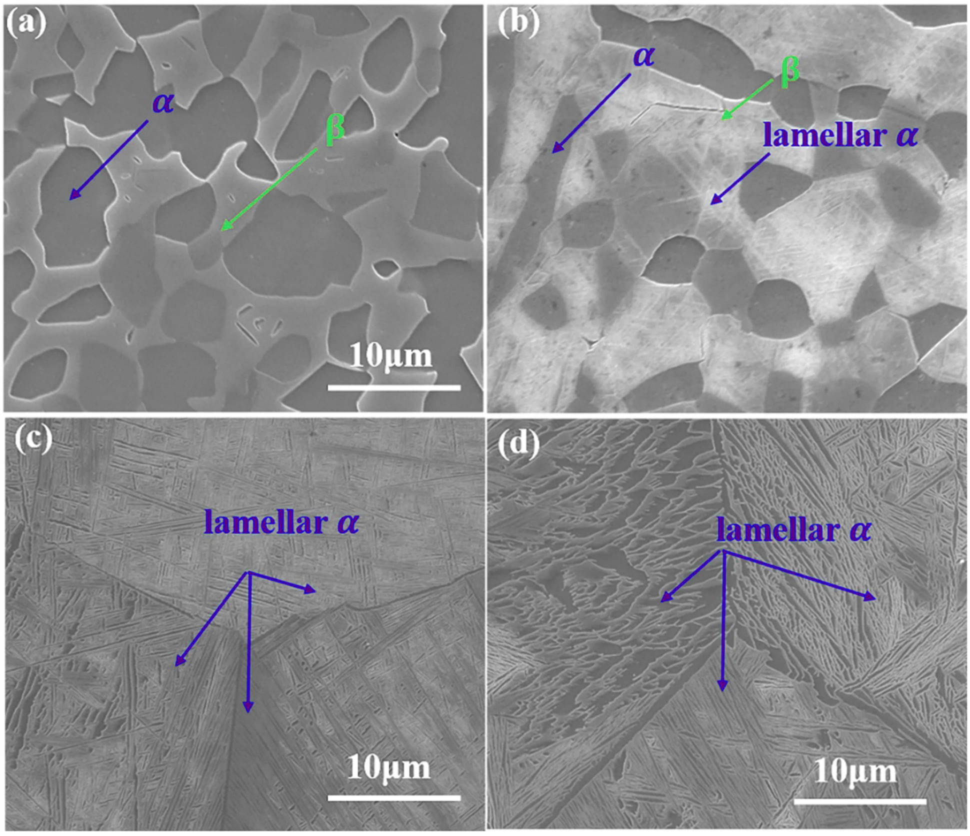

Figure 4. Microstructure of Ti-3Mo titanium alloys after annealing at different temperatures: (**a**) 750 °C, (**b**) 850 °C, (**c**) 950 °C, and (**d**) 1050 °C (adapted from [47]).

Based on the above research results, it is found that the annealing temperature, a high-acid or non-acid chloride-rich water environment will affect the corrosion resistance in titanium alloys, which has guiding significance for the optimization of titanium alloy materials in the future.

5. Preparation and Optimization of Titanium Alloy

In order to solve the problem of early steel drill pipe fatigue in short-radius horizontal wells, Grant Prideco and RTI Energy jointly developed a titanium alloy drill pipe [77]. The titanium alloy drill pipe has high strength, light weight, and corrosion resistance. R. W. Schutz and H.B. Watkins [25] utilized traditional α+β titanium alloy to maximize the fracture resistance in TC4 titanium alloy drill pipe by limiting the maximum alloy element content in the alloy (that is, the highest ELI rating is 0.13% O). By adding 0.1% Ru into the alloy, Ti-6Al-4V-Ru and Ti-3Al-2.5V-Ru were developed, which are two low-cost, corrosion-resistant, high-strength titanium alloy drill pipes, and they were successfully applied to geothermal brine wells, offshore riser cone stress joints, and deep-sea offshore drilling platforms. The addition of trace alloying element Ru makes the alloy have stress corrosion resistance. When the service temperature is up to 330 °C and the pH value is as low as 2.3, the corrosion resistance is still competitive [78,79]. The optimized titanium alloy drill pipe has outstanding corrosion resistance, low cost, and high strength.

The LMD process has a high degree of interaction between process parameters in metal deposition technology, which plays an important role in performance. Based on the LMD process, Mahamood et al. [80,81] studied the effects of scanning rate, laser power, gas flow rate, and powder flow rate on the microstructure, Vickers hardness, and surface finish of Ti6Al4V alloy during deposition, optimized the process parameters, and obtained the best surface finish and better mechanical properties. Chen et al. [82] and Zhou et al. [83] studied the mechanical properties and microstructure of Ti-20Mo and Ti-10Mo alloys after cold rolling and heat treatment, and the results showed that Ti-Mo alloys showed excellent corrosion resistance, among which Ti-10Mo alloys had good ductility and low yield strength compared with other metal materials with more broad application prospects. The excellent properties of β-Ti alloy have attracted the attention of researchers at home and abroad. Mihai Buzatu et al. [84] studied the mechanical properties (hardness, compressive strength, and elastic modulus) of Ti-15Mo-W alloy. Ti-15Mo alloy was selected as the starting material, 3.88% to 12.20% tungsten was added, and the sample was continuously melted in a water-cooled copper crucible in a vacuum arc furnace. After microstructure study, it was found that the alloy has a uniform structure and shows the advantage of β phase. The alloys studied had good mechanical properties, with average Vickers microhardness values ranging from 251 to 321 HV, compressive strength values ranging from 717 to 921 MPa, and an elastic modulus ranging from 17.86 to 45.35 GPa. Zhang et al. [85] optimized the two-step chemical polishing process based on the additive processing of TC4 alloy and obtained a better surface. After polishing, the weight loss rate of TC4 alloy was only 2.51%. The surface roughness of TC4 was reduced by 71.86%, and the surface quality was significantly improved. A uniform and stable TiO_2 passive film was formed on the alloy surface. Compared with the unpolished TC4, the thickness of the passivation film on the polished sample surface was decreased, and the resistance value and corrosion resistance of the passivation film were higher. Zhang et al. [56] studied a new experimental design of laser processing, as shown in Figure 5. Ti-Al-V-xC alloy was deposited to clarify the solid solution relationship among C, Al, and V in the matrix and the effect of C on TiC precipitation behavior. The research results indicate that the elastic modulus, indentation hardness, and yield strength of titanium based alloys were all improved by the solid solution strengthening of C and the continuous precipitation of TiC. This work lays the foundation for the design of optimized titanium matrix composites for laser additive manufacturing and other laser processing technologies. Zhao et al. [86] proposed that the addition of silicon is conducive to improving the strength, creep resistance, and oxidation resistance in titanium alloys in high-temperature environments in the study of the influence of silicon on the properties and strengthening mechanism of high-temperature titanium alloys, but this also has the disadvantage of reducing the plasticity in titanium alloys. This research provides a new research direction for the preparation of oil well pipes serving at high temperature.

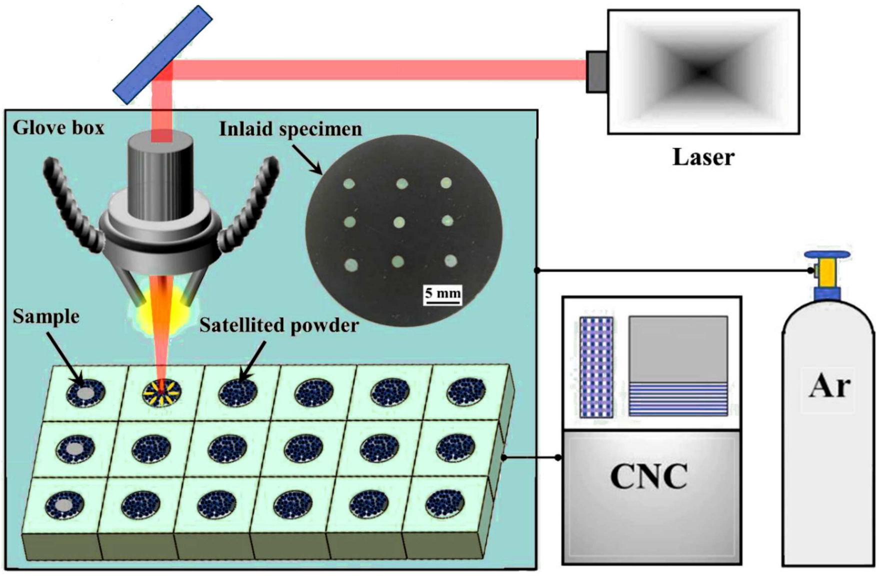

Figure 5. Schematic of the laser micro-alloying process and the inlaid specimen (adapted from [24]).

6. Summary and Outlook

Although there have been many research results on titanium alloys, there are still some problems to be solved. For example, poor oxidation resistance, low hardness, poor weldability, low surface hardness especially, poor thermal conductivity and wear resistance, the thread-gluing problem of titanium alloy pipes, whether oil well pipes made of optimized materials can be used in high-CO_2 and high-H_2S environments for a long time, and the welding performance of materials may need to be considered according to actual use needs. The further breakthrough in these problems will be of great significance to the expansion of the titanium alloy application field.

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