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Application of Titanium Alloy Materials for the Pressure-Resistant Structures of Deep Diving Equipment

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Abstract: Herein, the development of titanium alloy deep-diving equipment is first summarized. Subsequently, the desired properties of titanium alloy materials are analyzed by considering the characteristics of deep-sea service conditions. In addition, the technical challenges, such as stress corrosion, compressive creeps, microstructure evolution, property attenuation, and dynamic response under impact loading, faced during the applications of deep-diving equipment are introduced. Finally, the key technologies in engineering applications are summarized, such as the technologies related to large materials, application evaluation, and efficient construction. To satisfy the urgent demand for titanium alloy equipment in the deep-diving domain, we propose to further increase the basic research and engineering applications of titanium alloy materials and promote innovative applications.
Keywords: deep diving equipment; pressure-resistant structure; titanium alloy; key technology

1 Introduction

Deep-sea equipment, such as deep-sea military equipment, manned/unmanned submersibles, deep-sea station/carrier platforms, underwater gliders, and rescue bells [1,2], is mainly used for exploration and development of deep-sea resources, construction of deep-sea monitoring information systems, deep-sea "tough" confrontation, three-dimensional resource supply, among others. Dominating the sea by depth is the basis and guarantee for China to become a strong maritime country, build the Maritime Silk Road, and transform its naval strategy from coastal defense to open sea defense.

In deep-sea conditions, many new characteristics are required for ensuring the proper servicing and functioning of the equipment. For example, the combined effect of extremely high external pressure due to sea water and structural stress of equipment would result in poor stress conditions of pressure structures, with the stress even approaching the yield stress of the equipment materials, while the equipment is required to repeatedly travel between deep sea and sea surface during a long service life [3].In addition, the reduced oxygen content in deep-sea conditions significantly affects the material-surface passivation, thereby accelerating the material corrosion and increasing the cracking tendency. These environmental characteristics necessitate some crucial requirements for ensuring the safety and reliability design of pressure-resistant structural materials. Titanium alloy, which is a structural material with light weight and excellent corrosion resistance to sea water, might solve problems such as insufficient buoyancy reserve, poor structural safety, and poor reliability in the long-term use of deep-sea equipment [4,5].

Compared with the traditional steel, the elastic modulus, manufacturing process, and failure form of titanium

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alloy materials used in pressure structures are different. Presently, some common basic problems between traditional steel and titanium alloy still need be solved. Simultaneously, many key technical problems that restrict the design, construction, and application of pressure-resistant structures are experienced in some engineering projects [6]. In this study, the development status of deep-sea titanium alloy equipment and the existing material technology problems are discussed to achieve the following two goals: first, to promote the research of the basic problem that is witnessed in the industrial applications of titanium alloy and, second, to facilitate the innovation and development of deep-sea equipment design and relevant material technology by improving the toughness and creep resistance of the equipment material.

2 Development of equipment

2.1 Military

Because of their high specific strength, satisfactory cold and hot forming properties, remarkable welding property, and excellent corrosion resistance to seawater, near-α titanium alloys and extra-low interstitial α alloys are gradually replacing hull steel and becoming the main structural materials for fabricating the pressure hulls of deep-submergence submarines. Reportedly [7], the former Soviet Union was the first to use a large amount of titanium alloy in submarine pressure hulls and successively built all-titanium hull nuclear-powered submarines of k-162, Alpha, Mike, and Sera classes. Although the United States has never built all-titanium hull submarines, titanium alloy is widely used in submarine masts, fasteners, and other parts to reduce the weight of the hull and optimize the performance [8,9].

2.2 Scientific research and deep-sea exploration

Titanium alloy offers unique advantages in the construction of the pressure hull of manned/unmanned deep-sea submersibles, especially because of its high specific strength and corrosion resistance to seawater. In addition, using titanium alloy significantly reduces the structure weight and corrosion-protection cost. Presently, many countries have performed research on and built titanium-alloy deep-sea submersibles.

2.2.1 The United States

Before the 1960s, the pressure hulls of deep submersibles in the United States were mainly made of high-strength steel, for example, the first deep-diving research submersible Alvin, which was manufactured by the Woods Hole Oceanographic Institution (WHOI). However, because the density of steel is significantly higher than that of titanium alloy, the submergence depth of Alvin was considerably limited. Moreover, expensive corrosion-protection procedures had to be annually performed for Alvin. Therefore, since the year 1973, WHOI has made major upgrades to Alvin by replacing its steel pressure hull with the titanium-alloy one, i.e., using the Ti–6Al–2Nb–1Ta–0.8Mo alloy instead of HY100 high-strength steel to build a new shell, and using the Ti-6A1-4V alloy to make buoyancy balls and high-pressure gas cylinders. After the upgrade, the new Alvin, with the diving depth of 6500 m, can operate across 98% of the world’s sea area and has completed a significant number of deep-sea explorations (more than 4600 dives) [7].

2.2.2 Japan

Japan began studying deep-sea submersibles considerably early. In the 1980s and 1990s, the Ti-6Al-4V ELI alloy was used to build a manned submersible with the diving depths of 2000 m and 6500 m, respectively. The latter, particularly, with the large submergence depth and access to a wide range of sea areas, has completed many deep-sea exploration missions, thereby significantly contributing toward the deep-sea development and research in Japan [7].

2.2.3 China

Although the research on manned titanium-alloy deep submersibles began late in China, it developed considerably fast. The *Jiaolong* manned submersible, which was built in the year 2003, weighs 22.9 t and has a pressure hull made of TC4 ELI alloy with the diameter of 2.1 m. In the year 2012, with the cooperation of the overall design institutes, equipment manufacturers, and material (especially, titanium alloy) research institutes in China, *Jiaolong* successfully completed a 7000-m dive test and set the record of achieving the largest diving depth among the same types of research submersibles in the world. This shows that China has mastered both the preparation of relevant brands of titanium alloys, and forming and welding technologies, as well as realized the complete independent design, research, and manufacturing of hulls [7]. China continues to implement the research and development of the Deep Sea Warrior, which is a manned submersible, with fully independent intellectual property rights and completed the dive test on schedule in the year 2017. This again shows that China has made a significant breakthrough in the material development and processing technology and development of deep-sea titanium alloy, thereby entering the world's advanced ranks.

In addition, Nautilus of France and two MIR manned submersibles of Russia were built using titanium alloy. Kindly refer to Table 1 for information on the development of titanium alloy deep submersibles.

Table 1 List of manned deep-sea submersibles in the world.

Program	Alvin	New Alvin	Shinkai 6500	Jiaolong	Deep Sea Warrior	Nautilus	Mir
Country	USA	USA	Japan	China	China	France	Russia
Dive depth (m)	4500	6500	6500	7000	4500	6000	6000
Weight (t)	17	19.7	25.8	22.9	25	19.5	24
Inner diameter of the spherical hull (m)	1.98	2.1	2.0	2.1	2.1	2.1	2.1
Payload (kg)	205	180	200	220	220	200	400
Service year	1964	2010	1990	2011	2016	1984	2000

2.3 Oil and gas exploitation

Energy is the most important resource for human survival and development. Because of the increasing consumption of petrochemical energy, the search for new energy sources has gained considerable attention. Notably, 70% of the earth surface are oceans, which are rich in oil and gas resources. Therefore, we must accelerate the exploration and development of deep-sea resources. Accordingly, China has clearly proposed the development goal of "building China into a maritime power."

Marine development is inseparable from offshore drilling platforms, deep-sea detectors, and other important operation equipment, all of which have bad service conditions and suffer from long-term sea-water-induced corrosion and wave impact. Because of their unique advantages, titanium alloys might be widely used to manufacture the above-mentioned equipment. However, the cost issue has been hindering the expansion of its application. With the development of titanium alloy manufacturing technology and the breakthrough research on the low-cost titanium alloy research, the economic concerns have been significantly reduced. Titanium alloy has been widely used in offshore oil platform pillars, plate heat exchangers, among others in the United States; in the year 1991, it was applied to offshore platform lifting devices, solving the structural corrosion and fatigue problems in sea-water conditions. Via comprehensive evaluation, it was observed that using titanium alloy parts offers satisfactory cost-effectiveness [10,11]. Accordingly, during the development of oil- and gas-exploitation equipment in Southwest China, a significant number of titanium alloy materials with high resistance to the H_2S + CO_2 corrosive medium were used to ensure corrosion resistance, while considerably reducing the equipment weight and obtaining satisfactory comprehensive income.

3 Material development

3.1 Current status of material research

Both titanium and titanium alloy are excellent materials in the domain of ocean engineering. Many countries attach significant importance to their research and applications and have, therefore, developed a series of titanium alloys for marine engineering. The former Soviet Union/Russia, and the United States are the first countries that specialized in the research of titanium alloy for marine engineering, and each of these countries formed a titanium alloy system based on marine engineering. However, Russia ranks first in terms of the research and practical application level of titanium alloy in marine engineering. It developed a series of special titanium alloys, whose strength grades were 490, 585, 686, 785 MPa, etc., for marine engineering [12]. In the 1960s, the United States began to study the technology of titanium alloy for marine engineering, developed a series of titanium alloy materials, and established a complete assessment system for the application of titanium alloy for marine engineering.

3.2 Performance requirements for service environment and structural characteristics

Being immersed in sea water for a long time, deep-sea equipment must withstand the extremely high sea-water pressure load and sea-water-induced corrosion. In addition, because of its long-term service between deep sea and sea surface, deep-sea equipment must bear various types of marine environments, such as the near-shore sea area while entering a port, and the shallow and deep sea levels while going to sea. This necessitates higher requirements for the safety, reliability, durability, and maintainability of the structure. In the long self-sustaining condition, we must consider the possible unconventional conditions, such as storm impact, physical impact, and explosion impact. Therefore, the all-sea-area, all-sea-depth, all-weather, and long-term operation, coupled with extreme environmental conditions, necessitate high requirements for ensuring the performance of titanium alloy materials.

The design of deep-sea equipment should not only follow the basic principles of structural mechanics and hydrodynamics but also be combined with the development of engineering technology, to adapt to the current industrial material preparation technology and shipbuilding technology. On the basis of the working condition of deep-sea equipment and the current situation of material technology system, titanium alloy materials should meet the following basic requirements.

(1) The strength grade of the material should meet the structural design requirements. According to the analysis results of a designer, the strength of pressure-resistant structural materials must be moderately increased with increase in the submergence depth. Considering the structure manufacturing, plastic toughness, and processability of materials, the strength of materials should not be significantly high, and α-Ti alloys should be mainly selected for the material design [13].

(2) The material should have satisfactory plastic toughness, sufficient stress-corrosion resistance, and low cycle fatigue resistance in corrosive marine environments (such as sea water and marine atmosphere) to meet the requirements of equipment safety and reliability in the long-term use or in some special working conditions.

(3) Satisfactory process adaptability of material. The process should match the characteristics of hulls and ship equipment; for example, the method of casting, forging, and cold and hot forming should meet the manufacturing process requirements of low-cost titanium-alloy structural parts. In addition, for welding, the material should have satisfactory weldability, and the welding can be generally implemented without heat treatment after it. The material and process should meet the requirements of large ship equipment, and they should be supported by corresponding shaping, non-destructive testing, and other technologies.

3.3 Equipment safety problems restricted by material toughness

It is not uncommon for the early welded hulls to suffer from brittle failure, which compels designers to analyze and solve the problem via mechanics and metallurgy. In the early 1950s, the major countries involved in shipbuilding performed researches on the drop weight test, dynamic tearing test, explosion crack starter test, and impact tests in a series of temperatures for hull materials. They analyzed the toughness of materials with the change in environment and evaluated whether they could be used to build hulls [14].

Presently, the main methods to evaluate the fracture toughness of titanium alloy are plane strain fracture toughness, J-integral, crack opening displacement δ, Charpy impact fracture toughness A_K, among others. Generally, the critical stress intensity factor K_{Ic} is related to the specimen thickness B, and crack length and width of the ductile zone. Only when the specimen thickness satisfies $B \geq 2.5\ (K_{Ic}/\sigma_s)^2$, can stable K_{Ic} be obtained. Compared with the α+β two-phase titanium alloy and metastable β titanium alloy, the yield strength of the near-α titanium alloy has lower σ_s and higher K_{Ic}. Therefore, the required thickness of the sample will be large, and the test not only consumes considerable amount of materials but also requires large test equipment. To avoid this problem, the critical value of the J-integral ($J_{Ic} = K^2{}_{Ic}\ (1\text{-}\nu^2)/E$), or the critical value of crack tip opening displacement ($\delta_c = K^2{}_{Ic}\ /(E\sigma_s)$), are often measured and then converted to K_{Ic}. However, the tests for measuring J_{Ic} and δ_c are time consuming and expensive. Therefore, to quickly evaluate the fracture toughness of materials in engineering applications, the Charpy impact fracture toughness A_K is usually used instead of K_{Ic}. Instead, sometimes, the Charpy absorption energy can be converted to K_{IC} according to the empirical formula $A_k = (4\ K^2{}_{Ic} + \sigma_s{}^2)/\ (20\sigma_s)$ to quickly evaluate the fracture toughness of materials [15,16].

This type of method is used to evaluate several titanium alloy materials in the United States to check their adaptability to hull materials. In addition, the damage characteristics of titanium for hull materials are classified according to the damage classification method of steel. Presently, the relationship among the critical crack size ac,

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fracture toughness X_c, and fracture stress σ_f has been established. In the condition of plane strain, if the crack surface is perpendicular to the external stress, the opening-mode plane-strain fracture toughness K_{Ic} can be used instead of X_c; therefore, the toughness value can be used for performing design-related quantitative calculations. Although a similar research was performed in China in the 1960s, it was stopped because titanium was not used for hulls at that time.

The experience related to the modern ship design shows that when the required strength of structural materials is achieve, the higher the toughness, the better is the performance. The sensitivity to the stress-corrosion cracking of titanium alloy will increase in seawater, and the impact and fracture toughness show obvious differences. (1) For titanium alloys of the same strength grade but different compositions and microstructures, the difference of corrosion-fatigue-induced crack growth rate can be over 100%, and the difference of stress-corrosion fracture toughness can be over 50%. The joint action of the two makes the local fatigue-life calculation of the main structure be over three times different. (2) The fracture toughness and impact toughness of titanium alloy with the same strength grade and different grades differ by 1.5–2 times, and the deformation and fracture characteristics at medium and high deformation rates are significantly different from those at low deformation rates, significantly affecting the failure mode of the equipment in extreme conditions. For the selection and design of materials for deep-sea pressure structures, the strength of the near-α titanium alloy is the key to meeting the lightweight-design requirements of deep-sea pressure structure, and the fracture toughness is the key to ensuring the safety and reliability of deep-sea pressure structures in service [13,17]. Unfortunately, the strength and fracture toughness of titanium alloys usually are inversely proportional to each other. Therefore, how to quickly and accurately evaluate the fracture toughness of the near-α titanium alloy, and how to improve the fracture toughness to the maximum possible extent under the premise of ensuring the alloy strength, have become the topics of future research.

4 Basic problems of materials

4.1 Microstructural evolution and property degradation of titanium alloys in long-term service

Because of the long-term effects of stress field and corrosion field, titanium alloys show the phenomena of damage and fracture acceleration on the macro scale. Research on these phenomena indicate the following: 1) on the mesoscale, the dynamic dissolution and healing law of titanium-alloy passivation films under the long-term action of deep-sea environment is still being explored; 2) on the microscale, the evolution of the microstructure of titanium alloy under long-term high-stress loads and its influence mechanism on the crack acceleration and growth are not clearly understood; 3) on the macroscale, the load-time-damage law of titanium alloys used in the main structure lacks sufficient data accumulation. Therefore, we must analyze both the microstructure evolution and performance deterioration of titanium alloys for improving their damage resistance and, consequently, the safety of the main structure of deep-sea equipment.

4.2 Dynamic stress and crack initiation and propagation mechanism of titanium alloy under impact

Deep-sea equipment experience impact, collision, and other accidental phenomena while in service. Therefore, we must study the deformation damage and dynamic fracture characteristics of titanium alloy under different strain rates for improving its material properties and optimizing the structural safety. For various loading rates, the micro deformation mechanism and the crack initiation and propagation mode of titanium alloy are fairly different from one another, resulting in the obvious difference in the macro mechanical properties and damage characteristics of titanium alloys, thereby significantly affecting the fracture mode of the structure. Presently, the research on the dynamic response and failure mechanism of titanium alloys under medium- and high-speed dynamic load, as well as on microstructure damage, crack initiation and propagation, and dynamic fracture toughness, are being performed. In addition, the development of other characterization methods, such as dynamic fracture characteristics in service environment, is in progress.

4.3 Possible creep problems in the application of titanium alloy in deep-sea pressure structures

Compared with structural steel, titanium alloys suffer from obvious compression creep effect during their application in deep-sea pressure structures, thereby reducing the service reliability of titanium alloy pressure structures [18,19]. The creep effect is mainly attributed to the following two aspects: (1) the modulus of elasticity of titanium alloy is approximately half of that of steel, and, consequently, the elastic strain of titanium alloy is approximately twice of that of steel for the same strength load; (2) the α phase in titanium alloy is a hexagonal close packed structure, which has obvious anisotropy and Bauschinger effect. Presently, the research on the creep behavior of titanium alloy mainly focuses on the aspect of high-temperature tensile creep behavior of aerospace vehicles, and only a few research works exist on the compressive creep behavior of deep-sea titanium-alloy pressure structures. To reveal the damage mechanism of deep-sea titanium-alloy pressure structures, the compression creep behavior of titanium alloys near the yield stress level in the seawater-induced corrosion medium is being studied in China.

5 Key technologies of material engineering

5.1 Technologies of large plates and supporting materials

The construction of the pressure structures of deep-sea equipment mainly involves the forming of curved surfaces and welding of medium and thick titanium alloy plates; this requires high-level preparation technology of large and sensitive alloy plates and corresponding welding wire materials. Because of the characteristics of titanium and titanium alloy slabs, such as narrow temperature range during hot working, rapid cooling, hydrogen and oxygen absorption at high temperature, significant change in deformation resistance with temperature change, and high possibility to crack, the rolling temperature control has to be very strict. This makes it difficult to establish the hot-rolling production lines of titanium and titanium alloy plates, stabilize the rolling process, and improve the dimensional accuracy of products.

Thick plates are currently produced using steel processing equipment; i.e., these rolling production lines are designed based on the characteristics of steels. Hence, these produce lines lack the targeted design for the production of titanium and titanium alloys and cannot satisfactorily adapt to their heating and processing characteristics, thereby making the quality of finished products not significantly ideal [20]. Therefore, we must perform research on the technical problems of uniformity and stability of performance and process stability of large titanium-alloy sheets, study the forming process and methods to optimize the microstructure and performance of high-performance large titanium-alloy sheets, and promote the comprehensive performance of large titanium-alloy sheets, to meet the requirements of the deep-sea engineering domain and support the development there of [21].

5.2 Material selection and application assessment

Engineering design and construction require the establishment of a scientific material-evaluation system. The physical and chemical properties, and performance related to the preparation, process, and service of materials must be quantifiable and assessable. However, the foundation of this aspect is relatively weak, which has become one of the important factors that restrict the application of titanium alloy materials in deep-sea equipment.

Considering the requirements of pressure bearing, high-strength titanium alloy is preferred for deep-sea pressure structures; regarding the safety of manned spherical-hull structures, titanium alloy materials are required to have not only sufficient strength but also appropriate fracture toughness. Many shipwrecks are a result of the lack of sufficient fracture toughness of structural materials. For example, the *Titanic* shipwreck was attributed to the low-impact fracture toughness at low temperature of the steel used. Because of the long-term use of deep-sea pressure structures in seawater, the critical strength factor of the stress corrosion of materials in seawater should also be considered. From the viewpoint of construction technology, titanium alloy material should have satisfactory formability and weldability.

Therefore, in the stages of material preparation and process research, we must establish a comprehensive evaluation system of titanium alloys for pressure structures, define the standards and methods to evaluate the basic properties and performance in the stages of material preparation and processing, ensure the quality stability of titanium alloy materials in the construction process, and meet the reliability of equipment in long-term use and extreme conditions.

5.3 Efficient and high-quality construction technology

Deep-sea pressure structures mainly comprise ring-stiffened cylindrical shells and hemispherical heads, which have the characteristics of large size and high dimensional accuracy requirements. However, the existing titanium alloy technologies cannot completely meet the accuracy requirement. Because the welding work of large hull structures accounts for more than half of the total assembly work of shipyards, we must introduce a break-through and efficient titanium alloy construction technology.

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The welding methods of titanium alloy heavy plates are divided into narrow-gap wire-filling welding and electron-beam welding. The electron-beam welding is characterized by high automation, fast welding speed, short construction period, stable process, and high efficiency; however, although the cooling speed of the fusion zone of the titanium alloy weld is fast, the toughness of the weld is slightly low; in addition, because of the limitation of equipment conditions, the weld of large and complex-shape components is not easy to realize. However, the narrow-gap welding has a long period and imposes high requirements for the comprehensive capabilities of welding technicians, and there are many other factors that affect the processing. Because the existing engineering technologies have low efficiency and poor construction adaptability [22], we must develop a more efficient and stable high-adaptability and intelligent titanium alloy welding technology.

In addition, we must study other technologies that are required for titanium alloy equipment in the marine environment, as soon as possible. Because of different material grades, the joints between various parts of the hull, equipment, and pipelines unavoidably suffer from the problem of electrochemical corrosion of dissimilar metals; how to take effective electrical insulation or compensation measures is a technical problem that must be considered in the engineering application of the titanium alloy materials. Furthermore, titanium alloys have satisfactory biocompatibility. Accordingly, the phenomenon of marine biological attachment and growth in the marine environment will result in pipeline blockage, weight increase, and other adverse effects. Therefore, we must have practical means to solve the problem of long-term antifouling.

6 Conclusion

The successful applications of titanium alloy materials in the pressure structures of deep-sea equipment, such as manned submersibles, provide a satisfactory demonstration for the material selection and innovative use of deep-sea equipment.

Because more types of deep-sea equipment are required for making China the future maritime power, the industry departments should implement the following steps: deepen cooperation and scientific division of labor; strengthen the basic research of titanium alloy materials; break through the mechanical mechanism of titanium alloy materials used in deep-sea pressure structures via measures such as strengthening, toughening, and corrosion-resistance development; optimize the engineering technology such as the welding of large-thickness titanium plates; and establish a system to evaluate titanium alloys in extreme working conditions to eliminate the safety risks and ensure reliability. By considering the top-level requirements such as overall design, material technology, and other aspects of deep-sea equipment, we significantly contribute toward accelerating the research and application innovation in the domain of deep-sea equipment in China.

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