Improving the Performance of High-Temperature Titanium Alloys: Challenges and Advanced Solutions

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Abstract. High-temperature titanium alloys are vital in aerospace applications due to their exceptional strength, low density, and resistance to extreme temperatures and corrosion. These materials are critical for components like turbine engines and airframe structures, where weight reduction plays a key role in fuel efficiency and performance. Commonly used alloys, such as near-α and titanium aluminides (γ-TiAl), are designed to withstand elevated temperatures while maintaining their mechanical properties. However, challenges such as oxidation, embrittlement, and reduced tensile strength at high temperatures limit their broader application. Alloying with elements like aluminum, niobium, and molybdenum has enhanced oxidation resistance and high-temperature strength, while advanced surface treatments and coatings, including aluminide and silicide, provide further protection. Despite these improvements, issues like brittleness at room temperature and coating adhesion at extreme temperatures remain. Future advancements will likely focus on optimizing alloy compositions, refining surface treatments, and developing more robust coatings to further enhance the performance and durability of titanium alloys in aerospace and other high-temperature environments.

Keywords: Titanium alloy; aerospace; oxidation resistance.

1. Introduction

Titanium alloys have become essential in aerospace engineering due to their exceptional combination of high strength, low density, and strong resistance to extreme temperatures and corrosion [1-4]. These properties are critical for aerospace components, where weight savings directly contribute to increased fuel efficiency, payload capacity, and overall mission success. The ability of titanium alloys to maintain their structural integrity in harsh environments, such as those encountered in space shuttle engines and turbines, makes them a preferred material in the aerospace industry.

The most commonly used titanium alloys in high-temperature applications include near-α alloys, such as Ti-6Al-2Sn-4Zr-2Mo, and titanium aluminides like γ-TiAl. These alloys are specifically engineered to withstand elevated temperatures while maintaining strength and resisting creep deformation. For instance, near-α alloys offer excellent creep resistance and weldability, making them ideal for components exposed to sustained high-temperature environments. Titanium aluminides, such as γ-TiAl, are widely used in turbine blades due to their ability to operate at temperatures up to 725 °C while exhibiting lower density compared to nickel-based superalloys.

Despite these advantages, several challenges arise when titanium alloys are subjected to higher operating temperatures. Oxidation is a primary concern, as it weakens the material by forming brittle oxide layers that can peel off, exposing the substrate to further degradation. Additionally, titanium alloys can suffer from reduced tensile properties and brittleness at elevated temperatures, limiting their performance in critical aerospace applications.

There are various approaches proposed to solve the currently existing issues and elevate the temperature tolerance of titanium alloys. Alloying with elements such as aluminum, niobium, and molybdenum has been proven to enhance oxidation resistance and high-temperature strength. For example, aluminum forms protective oxide layers, while niobium reduces the oxidation rate by stabilizing titanium nitride on the surface. Additionally, advanced processing techniques such as heat treatment, vacuum arc remelting, and protective coatings like aluminide and silicide coatings have been employed to improve the high-temperature performance of titanium alloys.

While these approaches offer promising improvements, they are not without limitations. Alloy modifications can lead to increased brittleness at room temperature, and advanced coatings can face adhesion issues or become ineffective at temperatures exceeding 850 °C. Despite these challenges, ongoing research continues to refine these methods, aiming to enhance the durability and functionality of titanium alloys for even more demanding high-temperature aerospace applications.

2. Titanium and Titanium Alloys: Properties and Microstructure

2.1. Mechanical Properties

Titanium was discovered in 1791 and officially named in 1795. However, its commercial use did not begin until the mid-20th century due to the metal's tendency to react with oxygen and nitrogen, making it challenging to produce high-purity titanium. Titanium is considered one of the best elements for alloy bases due to its exceptional high-temperature resistance. It has a melting point of 1675 °C and a boiling point of 3260 °C, making it ideal for high-temperature environments.

In addition to its high-temperature resistance, titanium is favored for its high elasticity, electrical resistance, high strength, corrosion resistance, and, most importantly, its significantly lower density compared to steel. These exceptional mechanical properties have made titanium a popular choice in various industries, including aerospace engineering, which will be discussed in this article.

2.2. Microstructure Overview

The titanium also has an allotropic phase change temperature of 882 °C, changing between a close-packed hexagonal structure $\alpha - phase$ (at lower temperatures) and a body-centered cubic structure β-phase(at higher temperatures). The exact transformation temperature varies with substitutional and interstitial elements in titanium and heavily depends on the purity of titanium.

Fig. 1a below shows the HCP unit cell of low-temperature $\alpha - phase$, with three of the most densely packed lattice planes in the unit cell at lattice parameters at room temperature.

Fig. 1b shows the BCC unit cell of high-temperature β-phase, with one variant of {110} lattice planes, which is the most densely packed and lattice parameter at 900 °C [1].

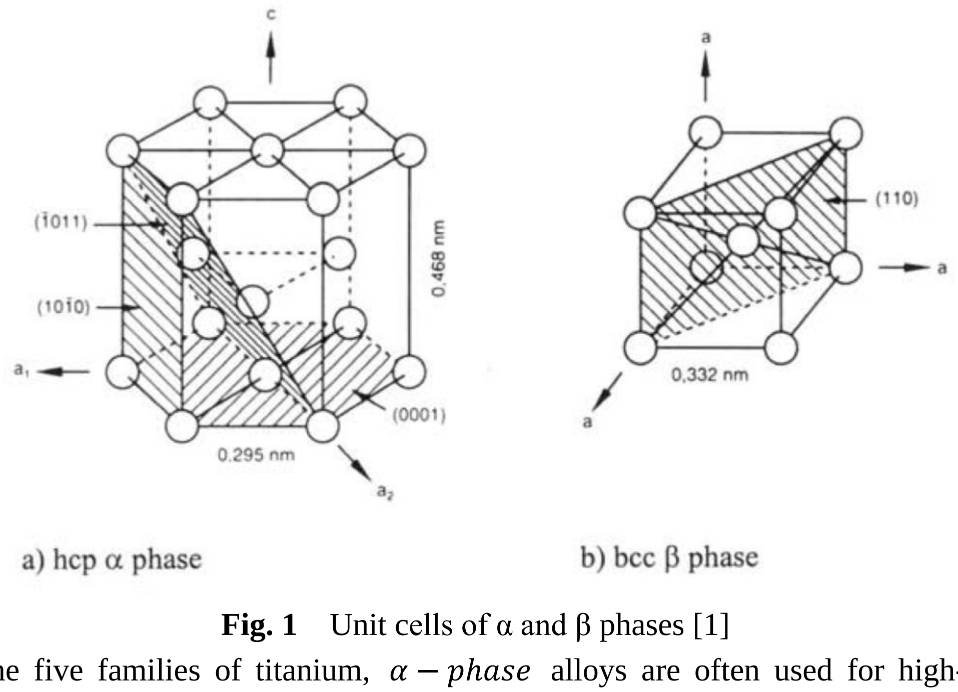

Fig. 1 Unit cells of α and β phases [1]

Among the five families of titanium, $\alpha - phase$ alloys are often used for high-temperature applications because of their better creep properties. β-phase alloys have excellent forgeability and corrosion resistance.

The near-α alloys contain Al, Sn, and Zr with small amounts of β-stabilizers like Mo or Nb and some Si. They have excellent creep resistance, weldability, fatigue resistance, and damage-tolerant properties. However, they are not heat-treatable and are seldom used as sheet products due to lower β-phase content. The maximum service temperature is affected by surface oxygen absorption, leading to the formation of an oxygen-enriched brittle surface layer known as α-case.

$\alpha - \beta$ alloys are made by a combination of α and β phases and have better mechanical properties than either phase on their own. They are the most widely used titanium alloys for structural applications, with higher β-stabilizer contents between 4-6% (weight percentage). As a result, they contain a higher β-phase content than near-α alloys, which allows them to be processed with heat treatment to achieve higher strengths.

There is another class of titanium-based alloys known as Ti-based intermetallic compounds, which have higher temperature capabilities compared to the near-α alloys. These alloys are based on two ordered intermetallic phases, Ti_3Al (α2) and TiAl (γ). Currently, the only alloy of this type used in production engines is the γ alloy, as it exhibits satisfactory high-temperature properties up to about 725 °C, allowing it to be used at higher temperatures than conventional Ti alloys and to replace some Ni alloys. TiAl also has approximately 50% lower density than the Ni-based alloys it replaces [4].

3. Current Titanium Alloys for High-Temperature Applications

3.1. Titanium-based Intermetallic Compounds

Titanium aluminide alloys, like γ (TiAl), can be manufactured through casting, powder metallurgy, and heat treatment processes. These alloys typically contain titanium, 38-46 at.% aluminum, and 5-10 at.% of niobium, with small amounts of Cr, Si, and Ni added based on the desired properties. Titanium aluminide alloys are known for their low density, high rigidity, and excellent corrosion resistance. In their solid state, they exhibit hexagonal (α) domains, two-phase structures (α-β), and body-centered cubic β phase and/or γ phase.

The TiAl alloy is a new intermetallic compound-based alloy known for its lightweight and high strength. It is commonly used in airplane and industrial engine blades, as well as in exhaust valves and turbochargers for passenger vehicle engines.

The TiAl alloys, known for their low density, excellent high-temperature strength, good oxidation resistance and other outstanding properties, have gained significant interest from researchers and businesses. However, these alloys have shortages such as their brittleness under room temperature, with relatively low fracture toughness.

The TiAl-based alloys' mechanical properties are primarily influenced by three factors: interlamellar spacing, the size of the lamellar colonies, and the alloying elements present. For example, smaller lamellar colony sizes of alloys can improve the ductility at room temperature, while the alloy's strength at both elevated temperature and room temperature can be enhanced by reducing the interlamellar spacing [2].

3.1.1 γ based titanium aluminide

Intermetallic phase γ base titanium alloys (TiAl) with a tetragonal structure and containing small amounts of intermetallic phase α2 (Ti_3Al) with a hexagonal structure in addition to the main phase γ (TiAl) have been specifically studied for industrial applications. These γ titanium aluminide alloys have), high elastic modulus, high rigidity, high creep resistance up to 700 °C, and low densities (3.85-4.2 g/cm^3). These properties make them ideal to be lightweight construction materials under elevated temperatures, for example, to build turbine buckets used in aircraft engines and stationary gas turbines, as well as hot gas ventilators and engine valves.

Although γ based alloys (TiAl), along with other types of titanium aluminide, are known for their remarkable properties that make them suitable for high-temperature applications, their low plastic malleability and fracture toughness hinder their use in certain applications. Extensive research has been conducted to optimize the structure of TiAl alloys to overcome these drawbacks.

To develop this alloy, researchers added niobium to improve its oxidation resistance and high-temperature strength, and the appropriate Nb concentration in the Ti-Al-Nb ternary system was investigated (Fig. 2). The effects the fourth element added has on the ternary alloy were also studied, in order to choose appropriate additives. The turbine wheels made from the newly developed alloy were used to evaluate their material properties and durability in a realistic environment, and the properties of the alloy were compared to conventional titanium aluminides and Inconel 713C, which are currently put to application.

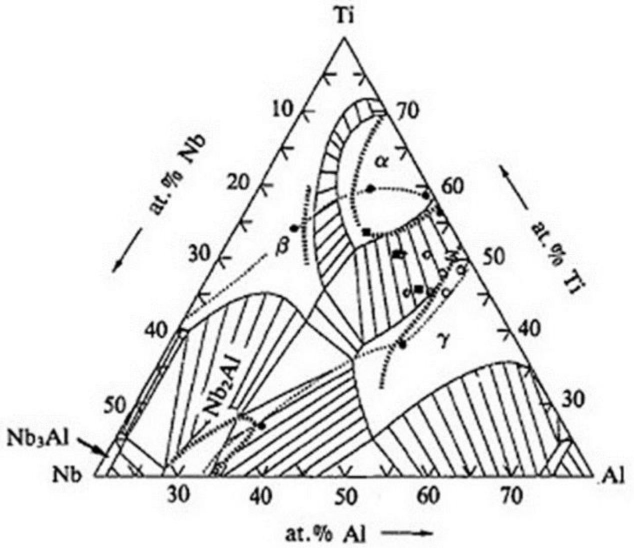

Fig. 2 Ti-Al-Nb ternary equilibrium phase diagram (1473 K isothermal section) [3]

The study has found that the ideal concentration of Nb is generally around 7 at.%, considering mechanical properties, oxidation resistance, specific gravity, and production costs. In addition, Cr, Si, and Ni are beneficial additives in the production of turbine wheels. The elements added to the Ti-Al-7 Nb alloy depend on the application and size of the turbine wheel.

The specific high-temperature strength of the newly developed TiAl alloy turbine wheel surpasses that of the conventional TiAl alloy and even exceeds Inconel 713C when hot isostatic pressing treatment is applied. During the engine endurance test, the conventional alloy turbine wheel blades eroded severely, while the newly developed alloy blades showed negligible erosion. This difference is attributed to the variance in the microstructure of the two materials [3].

3.1.2 Ti_2AlNb alloy

The maximum service temperature for this orthorhombic Titanium alloy is 750 °C for long periods of service time and up to 900 °C for short. It has excellent properties, including strength and oxidation resistance. The high quality of this alloy is ensured through melting processes of up to five times using vacuum arc melting. It was developed to replace nickel-based alloys for high-temperature applications.

3.1.3 Ti_3Al alloy

For the Ti_3Al alloy, the maximum service temperature is 700 °C for long service time and up to 850 °C for short-term use. When compared with standard alloys In-625 and In-718, Ti_3Al exhibits very high strength at elevated temperatures. It also offers advantages such as higher fatigue strength, high fatigue strength at room and elevated temperatures, and 40% lower density. However, it is important to note that this material is expensive and more difficult to weld while processing is required.

4. Challenges in Using Titanium Alloys at Elevated Temperatures

4.1. Oxidation

The TiAl alloy is a new intermetallic compound-based alloy known for its lightweight and high strength [5,6]. It is commonly used in airplane and industrial engine blades, as well as in exhaust valves and turbochargers for passenger vehicle engines.

At high operating temperatures, titanium alloys and titanium aluminides usually undergo oxidation through the following chemical equations:

$$\frac{1}{2}Ti(s) + O_2(g) \Rightarrow TiO(s) \tag{1}$$

$$TiO(s) + \frac{1}{2}O_2(g) \Rightarrow TiO_2(s) \tag{2}$$

Among which TiO has an anion vacancy and is highly unstable; hence, it will quickly oxidize into the dioxide TiO_2 , which is more commonly found in practice.

The oxidation process occurs when oxygen penetrates the surface, causing the oxidation film to thicken as oxygen diffuses internally. This weakens the bond between the oxidation film and the substrate, leading to the film peeling off from the substrate. Additionally, ordered phases and brittle layers form on the substrate surface, causing lattice distortion and reducing the mechanical properties of the substrate [7].

4.2. Tensile Properties

Titanium has always been favored in various industries due to its high specific strength. However, it may not perform as well in terms of tensile properties at elevated operating temperatures. Researchers have examined the performance of several titanium alloys at higher temperatures to assess their tensile properties, including ASTM_Gr.04, Exhaust-XT, and KS1.2ASNEX. The stress-strain curves of the tested alloys indicated that they begin to soften at 700 °C and become less ductile due to the precipitation of silicide added to the alloys at 500 °C [8].

5. Strategies for Enhancing the High-temperature Performance of Titanium Alloys

5.1. Alloy Composition Modifications

Alloy composition changing, or so-called solution strengthening, involves introducing other elements into the metal matrix. This process reduces the gap between atoms and increases the mutual blocking effect between crystals, ultimately enhancing the strength and hardness of the material. As a result, titanium alloys perform better at high temperatures.

5.1.1 Aluminium

Aluminum can provide titanium with protective oxide scales because it has great compactness, good adhesion, and a relatively low growth velocity. This makes it an ideal alloying element to improve the high-temperature oxidation resistance of titanium alloys. Sufficiently high concentrations of aluminum can be selectively oxidized into a single alumina scale, which effectively hinders the diffusion of titanium and oxygen, significantly improving the high-temperature oxidation resistance of titanium alloys and titanium aluminides. Additionally, the addition of aluminum reduces the density of the alloys, improves the atomic bonding force of the solid solution, and enhances the high-temperature strength of the alloys.

5.1.2 Niobium

Niobium effectively enhances titanium alloys and titanium aluminides’ oxidation resistance at elevated temperature levels through multiple mechanisms.

Titanium nitride acts as an effective barrier, preventing oxygen ions from penetrating the substrate. When exposed to high temperatures in the presence of air, a titanium-enriched nitride layer forms on the alloy surface. Additionally, niobium plays a positive role in stabilizing titanium nitride, reducing its conversion to titanium oxide and decreasing the oxidation rate of the alloys.

Adding niobium can decrease the bonding strength between aluminum and other atoms while increasing the bonding strength between metal atoms and titanium. As a result, the addition of niobium promotes the external diffusion of aluminum by significantly decreasing titanium’s activity and increasing aluminum's activity relative to titanium. It can also decrease the critical aluminum content required to form the desired continuous and compact Al_2O_3 oxide scales on the surface of products.

5.1.3 Molybdenum

Adding molybdenum to titanium aluminides does not significantly improve their oxidation resistance, but it can enhance their creep resistance at specific temperatures. For pre-alloyed Ti6Al4V with 2 to 6 wt.% molybdenum, the microstructure changes from equiaxed primary alpha and Widmanstätten($\alpha - \beta$) into a duplex and globular model, with varying pore distribution. The resulting product Ti6Al4V-4Mo has good mechanical properties, including high yield stress (1174 MPa) and ultimate tensile strength (1368 MPa). Moreover, Ti6Al4V-6Mo has the highest microhardness among all compositions of 370 HV500 [5].

5.1.4 Rare earth elements

Alloying with rare earth elements can refine the nucleation and growth of grains, which encourages the development of dense oxide layers made up of fine particles. Rare earth elements also have a strong affinity with oxygen, so they can help to reduce the oxygen partial pressure through internal oxidation [6].

5.2. Advanced Processing Techniques

5.2.1 Heat treatment

As materials age, their strength and hardness can increase, while annealing can raise the melting point. Both processes can improve the ability of titanium alloys to withstand higher temperatures and enhance their performance at elevated temperatures. An example of this is the in-situ heat-treated Ti-6Al-4V alloy. In this example, 'S' represents single scanning (without in-situ heat treatment), 'D' represents double scanning (with in-situ heat treatment), and the associated numbers with the letters represent the corresponding laser powers. According to Fig. 3, 300D exhibits the highest stress and tensile strength. This is due to the effective elimination of residual stresses in the in-situ heating process and the redistribution of internal stresses within the material. Consequently, the sharp notches of the cracks changed to blunt ones, reducing the crack propagation rate and contributing to the enhancement of strength [9].

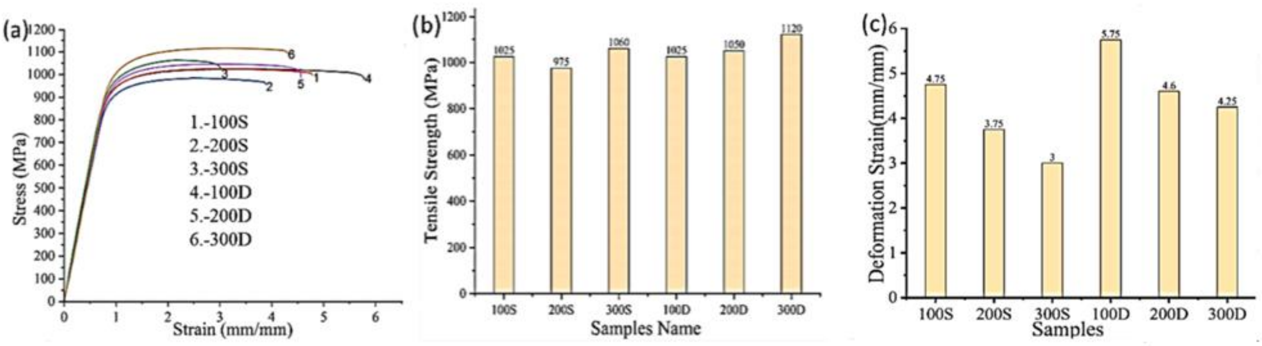

Fig. 3 (a) stress-strain curves (b) tensile strengths (c) deformation strains [9]

5.2.2 Differential speed rolling

Differential speed rolling (DSR) is a cold treatment method in which the linear velocity of the upper roll is four times higher than the bottom roll. It induces dynamic recrystallization and formation of shear texture components to enhance mechanical properties and reduce the chance of failure.

In the following example of alloy Haynes282, DSR treated alloy plate is compared with solid solution treated plate (SSA) and equal speed rolling (ESR) treated plates where the linear velocity is the same for the upper and bottom roll. From Fig. 4, it can be derived that DSR provides the best mechanical properties for the plates, which can reduce the chances of titanium alloys failing at high operating temperatures [10].

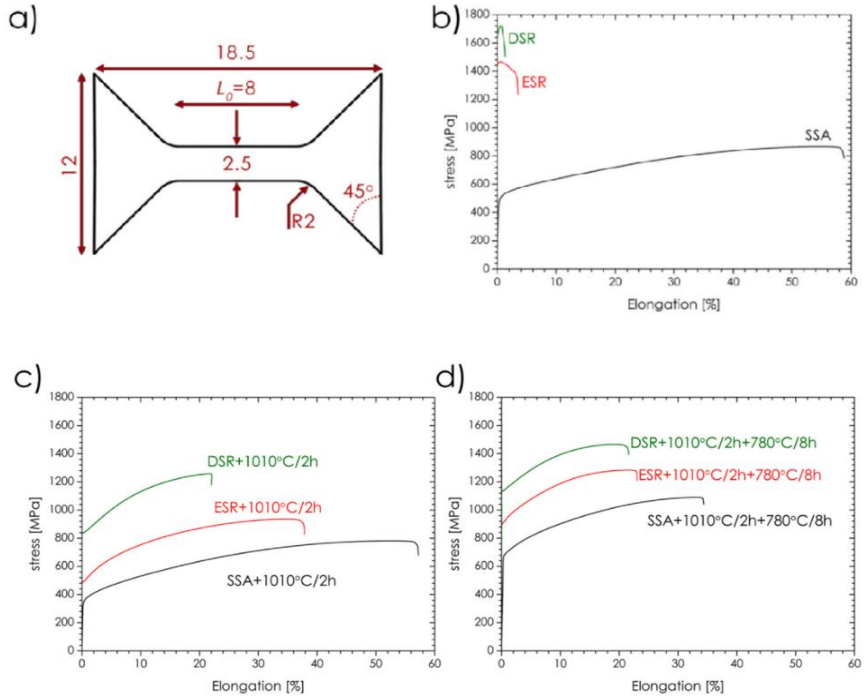

Fig. 4 The results of room temperature static tensile test of Haynes® 282® alloy carried out on miniaturized specimens (a) cut off from SSA and cold deformed materials (b) and then subjected to the first stage aging at 1010 °C/2 h (c) and the full heat treatment at 1010 °C/2 h + 780 °C/8 h (d). [10]

5.2.3 Vacuum arc remelting

Vacuum arc remelting, or VAR, has been used in processing titanium alloys to achieve ideal qualities and properties. In the case of Ti-SF61, it underwent triple vacuum arc melting to attain rotor grade quality, high fatigue strength, high creep resistance, and the ability to maintain high creep strength of up to 820 °C. The use of VAR results in reduced gas and oxide content in the final alloy, enhancing the homogeneity of the resulting ingots, improving the ductility of the product, and ensuring more uniform features in both transverse and longitudinal directions [11].

5.3. Protective Coatings

5.3.1 Aluminide coating

Aluminum is a major focus in developing high-temperature anti-oxidation coatings due to its ability to form a protective Al2O3 layer. Researchers have explored various intermetallic systems, incorporating elements such as silicon, chromium, niobium, carbon, sulfur, and molybdenum. Among the coating methods, hot-dip aluminizing immerses the alloy in molten aluminum, significantly enhancing surface properties and resistance to heat and corrosion.

Gas-phase aluminizing, which includes chemical and physical vapor deposition, utilizes gaseous reactants to minimize unwanted phases and contaminants. Additionally, laser-cladding aluminizing applies alloy powders using high-energy laser beams, improving microstructural properties, although high costs and potential cracking may hinder it.

Low-activity aluminizing at elevated temperatures relies on outward diffusion, risking defects due to the Kirkendall effect. At the same time, high-activity aluminizing enables inward diffusion at lower temperatures, albeit at a higher complexity and cost.

Despite the advantages of aluminized coatings, challenges like cracking and poor adhesion can arise, particularly above 800 °C. To counter these issues, silicon is often added to create Ti-Al-Si layers that improve oxidation resistance up to 800–850 °C. Silicide-aluminide coatings, formed on Ti-6Al-4V through slurry cementation at 900 to 1100 °C, exhibit a layered structure with aluminum-rich phases on the surface and titanium-rich phases near the substrate, contributing to exceptional mechanical and corrosion resistance. These coatings also show impressive resistance to cyclic oxidation and possess self-healing properties, as microcracks can be filled with alumina. Furthermore, additional elements like chromium, platinum, and niobium are incorporated to enhance the overall performance of the aluminide system [12].

5.3.2 Molybdenum interlayer in coatings

Some commonly used protective coatings, such as SiAlN, have good oxidation resistance but also interfacial performance issues. This can be mitigated by attaching a molybdenum interlayer between titanium alloy and SiAlN, as shown in Fig. 5 below, as Mo has strong diffusivity in Ti and intermediate thermal expansion coefficient, to make the surface more robust and enhance the coating adhesion [12].

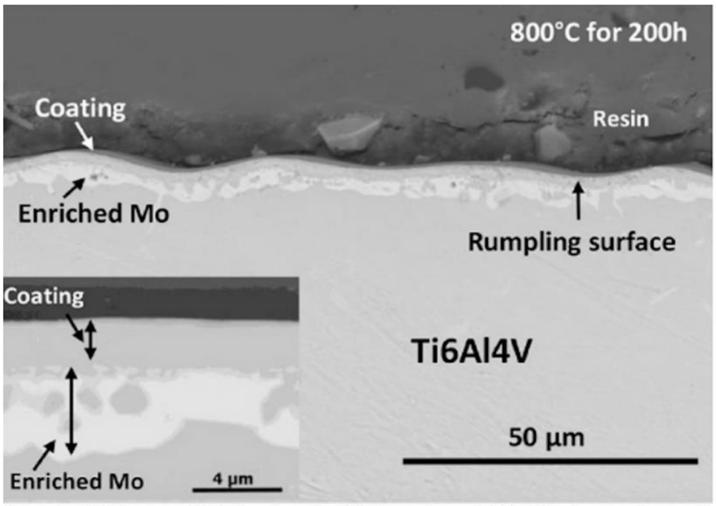

Fig. 5 SEM images showcasing the Mo interlayer within the SiAlN coating on a Ti6Al4V substrate after undergoing cyclic oxidation at 800 °C for 200 hours in air, with an inset highlighting a magnified view of the interface [12]

6. Conclusions

Titanium alloys play a crucial role in high-temperature aerospace applications due to their exceptional strength, low density, and ability to withstand extreme environments. However, these alloys face challenges such as oxidation, brittleness at room temperature, and reduced mechanical performance at higher temperatures. Researchers have addressed these issues by alloying with elements like aluminum, niobium, and rare earths, improving processing techniques, and applying advanced protective coatings. Moving forward, the focus should be on optimizing the microstructure of titanium alloys and developing innovative approaches such as hybrid coatings and next-generation alloy compositions. These advancements can potentially enhance the performance of titanium alloys, ensuring they remain the leading high-temperature material solutions for aerospace and other demanding applications.

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