Microstructure and Oxidation Behavior of Nb-Si-Based Alloys for Ultrahigh Temperature Applications: A Comprehensive Review

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Abstract: Nb-Si-based superalloys are considered as the most promising high-temperature structural material to replace the Ni-based superalloys. Unfortunately, the poor oxidation resistance is still a major obstacle to the application of Nb-Si-based alloys. Alloying is a promising method to overcome this problem. In this work, the effects of Hf, Cr, Zr, B, and V on the oxidation resistance of Nb-Si-based superalloys were discussed. Furthermore, the microstructure, phase composition, and oxidation characteristics of Nb-Si series alloys were analyzed. The oxidation reaction and failure mechanism of Nb-Si-based alloys were summarized. The significance of this work is to provide some references for further research on high-temperature niobium alloys.

Keywords: multivariate alloy; microstructure; alloying; oxidation behavior; mechanism

1. Introduction

With the advancement of aerospace technology, the high thrust-to-weight ratio aero-engine puts forward higher requirements for the high-temperature resistance of structural materials. Due to the limitation of the melting point and high-temperature strength, the traditional Ni-based superalloys have gradually failed to meet the development needs of aerospace industry. Thus, there is a great need for a high-temperature structural material with better performance [1–3]. Nb-Si-based alloys have a higher melting point and lower density: an ideal candidate material [4–8]. The comparison of properties of Ni-based alloy and Nb-based alloy is shown in Table 1. The insufficient high-temperature oxidation resistance and high-temperature creep resistance of Nb-based alloys has greatly hindered its development and application [9,10]. The oxidation of Nb to Nb$_2$O$_5$ at high temperature leads to a sharp volume expansion, and the stress in the oxide layer increases gradually, resulting in cracks and spalling, which eventually leads to rapid oxidation failure of the alloy [11–13]. Various methods have been used to solve this problem, and one of the most common is alloying. Alloying elements can ameliorate the oxidation characteristics of the oxide layer, improve the density and integrity of oxide scales, and inhibit the permeation of O$_2$. Furthermore, alloying elements may also produce the intermediate phase with thermal expansion coefficient (hereinafter abbreviated as TEC) between the substrate and oxide layer, which can reduce the internal stress between the substrate and oxide layer, improve the bonding force of the oxide layer, reduce cracks, and optimize its antioxidant properties [14–20].

The weaker oxidation resistance of alloy is mainly due to the lack of protective oxide layer, and it also depends on the oxidation characteristics of the material itself. Although the metal surface coating technology can extend the oxidation life of the alloy effectively, once the metal coating fails, the antioxidant properties of the alloy become extremely
important [21–23]. Therefore, studying uncoated alloys is essential to determine how the material will respond when the coating fails. In the past few decades, people have studied a variety of alloying elements such as Hf, Cr, Al, W, Mo, Ti, Zr, V, B, Ge, Sn, and Ta [22–26]. Studies show that Al and Cr can form the protective Al$_2$O$_3$ and CrNbO$_4$ oxide layers [27], and B and Ge can facilitate the formation of SiO$_2$ protective film. Moreover, W and Mo can generate volatile WO$_3$ and MoO$_3$ [28–30] to reduce the internal stress and increase the adhesion of the oxide scales. In addition, Ti, Hf, and Sn can increase the fracture toughness of the alloy. Meanwhile, Hf and Sn can also inhibit the diffusion of O$_2$ and enhance the antioxidation properties of the alloy.

Table 1. Comparison of properties of Ni base superalloy and Nb base superalloy.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Melting Point (°C)</th>
<th>Density (g/cm$^3$)</th>
<th>Operating Temperature (°C)</th>
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<td>8.1–8.5</td>
<td>1150</td>
<td>[1,5,17,19]</td>
</tr>
</tbody>
</table>

At present, there are many related research studies on niobium alloy, but there is little summary or sorting of these studies. It is of great significance to summarize the effects of different alloy elements, temperature, element content, and other factors on the further study of high-temperature resistant alloy. In this work, the effects of Hf, Cr, Zr, B, and V on the oxidation resistance of multi-component Nb-Si-based superalloys were summarized. By analyzing the oxidation kinetics, oxide composition, and microstructure of the alloy, the oxidation and failure mechanisms of Nb-Si alloy were summarized, which have a certain reference significance for the further study of high-temperature niobium alloys.

2. Nb-Si-Based Alloys

The Si element has strong stability, and Nb-Si intermetallic compound is one of the most common high-temperature structural materials. After the oxidation of Si at high temperature, the flowing SiO$_2$ glass film is generated, which has an excellent repair and protection effect on the alloy substrate [31–34]. The phase composition of Nb-Si-based alloys mainly includes niobium solid solution (Nbss), Nb$_3$Si, and Nb$_5$Si$_3$. Nbss has excellent ductility, but its high-temperature oxidation resistance is poor. The pesting phenomenon occurs at medium-low temperature (700 °C); thus, the alloy is difficult to use at high temperatures [35–37]. Alloying can alleviate the problem of insufficient high-temperature oxidation resistance of Nb-Si alloys to a certain extent. Unfortunately, the oxidation resistance and mechanical properties of ternary Nb-Si-based alloys, such as Nb-Si-Al and Nb-Si-Cr, are still insufficient. Therefore, it is significant to optimize the comprehensive properties of Nb-Si series alloy by further alloying. Based on this, the focus of the research has been shifted to multi-component high-temperature-resistant niobium alloys.

3. Modified Nb-Si-Based Multi-Element Alloys

3.1. Nb-Si-Based Alloys Modified with Hf Elements

In order to promote the high-temperature oxidation resistance of Nb-Si-based alloys, researchers have tried to add different kinds of elements, and Hf is a common addition element. Geng et al. [38] produced the Nb-Si-Al-Cr alloy by a non-consumption arc-melting process and the effects of Ti, Mo, and Hf on the oxidation behavior of the alloy at different temperatures were studied. Figure 1 shows cross-sections of the oxidized alloys. The scales of the alloy were a complex mixture of Nb and Ti oxides; oxygen was dissolved in the niobium solid solution (Nbss) below the oxide scale of the alloy. The oxidation kinetics curve is shown in Figure 2a. It can be seen that the oxidation of these alloys includes two stages: the initial linear stage and the later parabolic stage. The weight gain rate of the alloy with the Hf element decreases gradually after 55 h of oxidation, while its oxidation
resistance becomes worse after heat treatment. Furthermore, Geng et al. [39] have also studied the effects of Ti, Hf, and Sn on the oxidation resistance of the Nb-Si-Al-Cr-Mo alloy, and the oxidation weight gain curve is shown in Figure 2b. It is clear that the addition of Hf decreases the oxidation rate of as-cast alloy but increases the oxidation rate of heat-treated alloy. The oxidation behavior of these alloys is mainly controlled by the oxidation of Nbss, and the volume fraction of Nbss has a great impact on the oxidation resistance of the alloy.

![Figure 1. BSE images of the microstructures of cross-sections of the (a) Nb-24Ti-18Si-5Al-5Cr-2Mo and (b) Nb-24Ti-18Si-5Al-5Cr-2Mo-5Hf after oxidation at 800 °C. Copyright 2006 Elsevier.](image)

![Figure 2. Weight change curves of Nb-Si-based alloys with Hf addition oxidized at (a) 800 °C and (b) 1200 °C. (c) Cyclic oxidation curves for Nb-20Si-20Cr-(5, 10 at.%) Hf alloys. (d) Oxidation weight gain histogram of Nb-22Ti-16Si-3Cr-Al-2B-xHf (x = 0 at.%, 2 at.%, 4 at.%, 8 at.%) alloys at 1250 °C. Copyright 2006 Elsevier, 2011 Elsevier and 2015 Elsevier.](image)

In addition, Vazquez et al. [40] also studied the effects of Hf element on the antioxidant properties of Nb-Si-based alloys. The microscopic morphology of the alloy after oxidation is shown in Figure 3. Analysis shows that the products of oxidation are Nb_2O_5, HfO_2, and un-reacted NbCr_2. Nbss in the alloy is prone to selective oxidation. After long-term...
oxidation at 700 °C, there are a large number of powder oxides and cracks in the oxide layer, which has no protective effect. Figure 2c shows the oxidation curves for both alloys doped with 5Hf and 10Hf (at.%) at 700, 800, and 1400 °C, respectively. The oxidation experiments reveal that both alloys exhibit a good oxidation resistance at 700 °C, the 10Hf alloy has lower oxidation weight gain than 5Hf alloy at all temperatures. The researchers attribute the alloy’s better oxidation resistance to the formation of a thin protective layer.

Figure 3. Microstructure of Nb-20Cr-20Si-5Hf alloy (a,c) and Nb-20Cr-20Si-10Hf alloy (b,d) after short-term oxidation at 1400 °C and long-term oxidation at 700 °C. Copyright 2011 Elsevier.

Zhang et al. [41] studied the effects of Hf, B, and Cr on the antioxidant properties of Nb-Si-based superalloys. The research shows that the weight gain per unit area of the alloy decreases from 157 to 139 mg/cm² after oxidation at 1250 °C for 50 h. Meanwhile, the synergistic addition of Hf, B, and Cr makes the oxidation resistance of the alloy more excellent. Zhang et al. [42] also studied the antioxidant properties of Nb-Si-based alloys with different Hf contents and found that the oxide layers of these alloys fell off and had poor adhesion. The cross-sectional BSE image of the alloy after oxidation is shown in Figure 4. The oxides of the alloys are TiO₂ and HfO₂, as determined by EDS. HfO₂ is mainly found at the interface between Nbss and (Nb,X)₅Si₃ (rod-like morphology) or at the edges of silicide blocks (needle-like morphology). More severe internal oxidation occurs with Hf addition. With the addition of Hf, the formation of α(Nb,X)₅Si₃ was inhibited, while the formation of γ(Nb,X)₅Si₃ was promoted, and the former has better oxidation resistance, since the former phase is not attacked, while the latter phase is partly oxidized. The histogram of oxidation weight gain is shown in Figure 2d. It is obvious that the weight change of the alloy decreases first and then increases with the increase in Hf, and the alloy with 2Hf (at.%) has the least weight gain. It may be due to the large size of Hf atoms, which inhibited the diffusion of other metal atoms. Although the addition of 8Hf (at.%) did not improve the oxidation resistance of the alloy, it increased the room temperature fracture toughness of the alloy, and the eutectic structure in the alloy has been refined significantly. It can be seen that the contents of Hf have a great influence on the comprehensive performance of the alloy.
3.2. Nb-Si-Based Alloys Modified with Cr Elements

Chromium has the advantages of high melting point, excellent chemical stability, and easy alloying with other elements. It is widely used in Fe-based and Ni-based alloys. The $\text{Cr}_2\text{Nb}$ phase formed after the addition of Cr element in niobium alloy has the advantages of high melting point and oxidation resistance [43–45]. The oxide $\text{CrNbO}_4$ has better oxidation resistance than $\text{Nb}_2\text{O}_5$, and it can also improve the adhesion between the oxide layer and substrate [46,47]. Zhang et al. [41] studied the effects of Hf, B, and Cr elements on the microstructure and properties of Nb-Si-based superalloys by a vacuum non-consumption arc-melting process. (The alloy with $x$ at.% Hf, $y$ at.% B, and $z$ at.% Cr content is denoted by $x\text{Hf}-y\text{B}-z\text{Cr}$ below.) The histogram of the oxidation weight gain of alloys with different compositions is shown in Figure 5a. Obviously, the 0Hf-0B-0Cr alloy (base alloy) has the most weight gain after oxidation (157 mg/cm$^2$ for 50 h), displaying the worst oxidation resistance. The oxidation weight gain decreases from 157 to 139 mg/cm$^2$ after Hf addition (4Hf-0B-0Cr alloy), and the oxidation resistance is slightly ameliorated. Furthermore, the synergistic effects of Hf, Cr, and B enhance the oxidation resistance of the alloy significantly, and the weight gain of the 4Hf-2B-5Cr alloy is 91 mg/cm$^2$ at 50 h. The room temperature fracture toughness of the alloy decreases with the addition of Cr, and the microhardness increases with the addition of Cr. In addition, Wang et al. [46] prepared the Nb-22Ti-14Si-2HF-2Al-$x$Cr ($x$ = 2 at.%, 6 at.%, 10 at.%, 14 at.%, 17 at %) alloys, and the effect of Cr on oxidation resistance and mechanical properties of the alloy were studied. Figure 5b shows the oxidation kinetics curve of these alloys at 1250 °C. It is obvious that with the increase in the contents of Cr, the oxidation weight gain decreases gradually, and the oxidation resistance of the alloy improves gradually. The 17Cr (at.%) alloy has the best antioxidant properties, which may be due to the formation of the protective $\text{Cr}_2\text{O}_3$/SiO$_2$ film. In addition, with the increase in Cr content, the fracture toughness of the alloy decreases, and the hardness of Nbss increases. Moreover, the studies of Zelenitsas [48] and Esparza [49] show that the synergy of Cr and Al can form the protective $\text{Al}_2\text{O}_3$/CrNbO$_4$ film and reduce the oxidation rate inside the alloy. The Cr element has stronger O affinity than Nb, and the formation of stable $\text{Cr}_2\text{O}_3$ can improve the compactness and stability of the oxide layer [50–52]; thus, the alloy has better oxidation resistance.
3.3. Nb-Si-Based Alloys Modified with Zr Elements

Among the many types of alloy systems, Zr addition can refine the microstructure and promote the oxidation resistance of the alloy [53–56]. After the oxidation of Zr, ZrO$_2$ is formed, which has the characteristics of low thermal conductivity, excellent thermal vibration resistance, and oxidation resistance. In the work of Zhang et al. [57], the effect of V, Zr, and other elements on the antioxidant properties of Nb-15Si-24Ti-4Cr-2Al-2Hf (at %) alloy was investigated. The surface SEM images of the alloy oxide upon 1250 °C for 100 h are shown in Figure 6a–c; Figure 6(a1–c1) show the macroscopic morphology after oxidation. It is apparent that the alloy has a rough and porous surface, and the oxide layer is seriously peeled off. The condition has not been improved after adding V, but the oxide layer is relatively dense and complete after adding Zr. Figure 6d–f shows the SEM morphology of the oxidation cross-section, and the oxide layer consists of inner and outer layers. The surface of the base alloy and 1 V alloy after oxidation is loose and porous after peeling off. Although the oxide layer of 1Zr alloy falls off also, an oxide layer rich in silicon and oxygen is formed on the surface. Combined with the oxidation kinetics curve in Figure 7a, it can be inferred that a protective oxide layer is produced on the surface of the 1Zr alloy. The results of WDS and EPMA analysis show that an SiO$_2$ film is formed in the oxide outer layer, which inhibits the diffusion of O$_2$ and protects the alloy substrate.

Figure 5. (a) Oxidative weight gain histogram of the Nb-Si-based alloys oxidized at 1250 °C. (b) The oxidation weight gain curve of Nb-Si alloy with different Cr content at 1250 °C. Copyright 2012 Elsevier and 2015 Elsevier.

Figure 6. Surface SEM images of Nb-Si-based alloys after oxidation at 1250 °C for 100 h: (a) base alloy, (b) 1V alloy, (c) 1Zr alloy. a1–c1 are the corresponding macroscopic morphology. Cross-sectional SEM images of Nb-Si-based alloys after oxidation: (d) base alloy, (e) 1 V alloy, (f) 1Zr alloy. Copyright 2017 Springer Nature.
Figure 7. Weight gain versus time for Nb-Si-based alloys oxidized at 1250 °C for 100 h (a). Oxidation weight gain curve (b) and oxidation weight gain histogram (c) of Nb-Si-based alloys with different Zr contents. Copyright 2017 Springer Nature, 2019 Elsevier and 2017 Elsevier.

In order to ascertain the influence of Zr content on the oxidation resistance of Nb-Si-based alloy, Zhang et al. [58] designed the Nb-Si-based alloys with different Zr content, and the oxidation behavior of the alloy at 1300 °C was studied. The microstructure of the oxide layer on the alloy surface is shown in Figure 8a–d. It is apparent that the oxide on the surface of 0Zr and 3Zr alloys is rod-like, rough, and porous. When the Zr content reaches more than 5 at.%, the oxides have a polygonal structure and compact arrangement. Figure 8e–h show the oxidation fracture surface microstructures of 0Zr, 3Zr, 5Zr, and 7Zr, respectively, and the oxide layer is mainly composed of TiO$_2$, Nb$_2$O$_5$, TiNb$_2$O$_7$, and Ti$_2$Nb$_{10}$O$_{29}$. A small amount of ZrO$_2$ is detected in the 7Zr alloy. Meanwhile, no SiO$_2$ is detected in the oxide, which may be attributed to the amorphous state of SiO$_2$. Figure 7b shows the oxidation kinetics curve of the alloy. It is obvious that the weight gain of the alloy decreases with the increase in Zr. The weight gain curves of 1Zr and 3Zr alloys almost coincide, while the weight gain of 7Zr alloy is about 44% lower than that of 0Zr alloy. Combined with the macroscopic morphology of these alloys after oxidation, it can be seen that the 7Zr alloy has the best oxidation resistance.

Figure 8. Surface morphologies and cross-sectional microstructures of Nb-15Si-24Ti-4Cr-2Al-2Hf-xZr (x = 0 at.%, 3 at.%, 5 at.%, 7 at.%) alloys after oxidation at 1300 °C for 100 h. (a,e) 0Zr; (b,f) 3Zr; (c,g) 5Zr; (d,h) 7Zr. Copyright 2019 Elsevier.

In addition, Qiao et al. [59] also carried out a similar study on the effect of Zr content on the microstructure and properties of Nb-Si-based alloys. Figure 9 shows the cross-section BSE image of the alloy after oxidation at 1250 °C for 20 h. It is evident that there are many cracks and holes in the oxide layer, and the thickness of the oxide layers ranges from 260 to 380 µm. The EPMA-WDS analysis shows that the phase composition of the outer layer is TiNb$_2$O$_7$ and TiO$_2$, and the inner layer is Ti$_2$Nb$_{10}$O$_{29}$ and Nb$_2$O$_5$. In addition, ZrO$_2$ was also detected in the scales of 4Zr and 8Zr alloys. Obviously, the weight gain of the sample decreases with the increase in Zr, as shown in Figure 7c. It can be seen that Zr plays an important role in advancing the antioxidant properties of Nb-Si-based
alloys; meanwhile, the addition of Zr improves not only the room-temperature fracture toughness but also the high-temperature strength and compressive strength of the alloy. In addition, Ma et al. [60] showed that adding Zr or V alone can improve the oxidation resistance of Nb-Si series alloys, but the simultaneous addition of Zr and V will form the CrVNbO$_6$/VNb$_9$O$_{25}$ harmful oxides, which will reduce the service time of Nb-Si alloys. Moreover, the addition of Zr improves the room-temperature fracture toughness and compressive yield strength of the alloy, and the phase microhardness is also improved due to the solution strengthening effect of Zr.

3.4. Nb-Si-Based Alloys Modified with B Elements

B elements can refine the grain size and improve the toughness of materials. Studies have shown that the borosilicate glassy layer formed by B and Si in Mo-Si-B alloys has a good repairing effect on cracks and holes in oxide scales [61–66], which is of great significance to ameliorate the comprehensive properties. Zhang et al. [65] prepared the Nb-$22$Ti-$16$Si-$5$Cr-$4$Hf-$3$Al alloy with different contents of B and studied the effect of B on the microstructure and properties of the alloy. The layer is composed of TiNb$_2$O$_7$, (Ti, Nb, Cr)O$_2$, and Si, as shown in Figure 10. Unexpectedly, no silicon oxide was detected in the oxide layer, which may be due to the formation of amorphous silicate. The oxidation weight gain of 0B, 2B, and 5B alloys are 127.1, 90.5, and 67.6 mg/cm$^2$, respectively, and the thickness of the oxide layer decreases from 882 to 441 µm. Obviously, the antioxidant performance of the sample increases gradually with the increase in B content. The fracture toughness of the alloy increases first and then decreases, while the microhardness of Nbss increases slightly with the increase in B content. Furthermore, Zhang et al. [41] also studied the synergistic effects of B, Hf, and Cr, and the results showed that the synergy of B and Cr had a better oxidation resistance, while the addition of Hf was not conducive to enhancing the oxidation resistance of the alloy. The fracture toughness of the alloy decreases with the addition of B, while the macroscopic hardness does not change significantly. Moreover, in the work of Thomas et al. [67], the effect of different Si and B content (at %) on the oxidation resistance of Nb-$25$Cr-$15$Mo-xSi-yB alloy was studied (hereinafter, it is abbreviated as xSi-yB alloy). The oxidation products of 20Si-10B and 20Si-15B (at.%) alloys are mainly CrNbO$_4$ and SiO$_2$. The weight gain of 20Si-15B alloy is the minimum at 1200 and 1400 °C, while the weight gain of 15Si-15B alloy is the minimum at 900 °C, which may be attributed to the occurrence of pest oxidation and the spalling of the oxide layer, as shown in Figure 11. Therefore, the high content of Si and B is more beneficial to enhance the oxidation resistance of the Nb alloys. Moreover, the research of Su et al. [68] shows that the synergy of B and Ge can facilitate the production of continuous and dense oxide film in the alloy and reduce the penetration rate of O$_2$. It is worth noting that the dissolution of B$_2$O$_3$ and GeO$_2$ in silicide can also improve the TEC of the oxide scales and make it more compatible with the substrate so as to suppress the occurrence of cracks and improve the oxidation life of the alloy.
Figure 10. Cross-sectional BSE images of the Nb-22Ti-16Si-5Cr-4Hf-3Al-xB (x = 0 at.%, 2 at.%, 5 at.%) alloys after oxidation at 1250 °C: (a) 0B, (b) 2B, and (c) 5B. Copyright 2014 Elsevier.

Figure 11. Long-term oxidation curves for alloys at (a) 900 °C, (b) 1200 °C, and (c) 1400 °C. Copyright 2015 Elsevier.

3.5. Nb-Si-Based Alloys Modified with V Elements

It is found that the V element has a positive effect on the oxidation resistance and mechanical properties of Nb-Si-based alloys [69,70]. Guo et al. [69] studied the effect of V (1 at.%) on the fracture toughness and oxidation resistance of the Nb-15Si-24Ti-4Cr-2Al-2Hf alloy. Compared with V free alloy, 1 V alloy has better fracture toughness. Figure 12 shows the cross-section morphology of the alloy oxidized at 1300 °C for 100 h. V is mainly distributed in Nbss, and V will be oxidized preferentially within Nbss due to its stronger O affinity than Nb. The oxidation kinetic curve of the alloy is shown in Figure 13a. After oxidation for 20 h, the V-free alloy increases linearly, while the 1 V alloy still increases its parabola. The author believes that although the microstructure of the alloy has no obvious change, the oxidation characteristics of Nbss have been ameliorated; thus, the antioxidant properties of the alloy have been enhanced. Ma et al. [60] studied the synergistic effect of V and Zr on the microstructures and properties of the Nb-22Ti-15Si-5Cr-3Al-2Hf alloy. Figure 13b shows the histogram of oxidation weight gain and macroscopic morphology of the alloy. The study shows that the addition of V or Zr alone can enhance the oxidation resistance of the alloy, while the effect of adding both at the same time is the opposite. The addition of V can reduce the difference in the oxidation rate of Nbss and silicide, which is beneficial to the formation of a continuous and dense oxide layer, thereby improving the oxidation resistance of the alloy. However, the addition of Zr has the opposite effect [71,72]. The addition of V can also improve the fracture toughness and compressive yield strength of the alloy. However, there are some different views about the effect of vanadium on the antioxidant performance of Nb-Si-based high temperature alloys.
Figure 12. Cross-sectional microstructure of Nb-15Si-24Ti-4Cr-2Al-2Hf-1V (at.%) alloy in outer layer (a) and inner layer (b) after oxidation, and the enlarged images of the yellow rectangular zones (b1). Copyright 2017 Elsevier.

Figure 13. Weight gain curve of Nb-Si-based alloys after adding V. (a) Nb-15Si-24Ti-4Cr-2Al-2Hf-xV (x = 0, 1 at.%). (b) Nb-22Ti-15Si-5Cr-3Al-2Hf-xV-yZr ((x, y) = (0, 0), (3, 0), (0, 4), (3, 4) at.%). (c) Nb-15Si-24Ti-4Cr-2Al-2Hf alloys with separate V, Ta, W and Zr additions. (d) Nb-22Ti-15Si-5Cr-5Mo-4Zr-3Al-2Hf-xV (x = 0, 3, 5, 10 at.%). Copyright 2017 Elsevier, 2021 Elsevier, 2017 Springer Nature and 2020 Elsevier.

The study by Zhang et al. [57] showed that V reduces the oxidation resistance of Nb-Si-based alloys, and the oxidation weight gain curve of the Nb-15Si-24Ti-4Cr-2Al-2Hf alloy with different modification elements (V, Ta, W, and Zr) is shown in Figure 13c. The oxide layer composed of Nb₂O₅, TiNb₂O₇, Ti₂Nb₃O₉, and TiO₂ has no protective effect on the substrate, which may be the reason for the poor oxidation resistance of the
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of 17

alloy [73,74]; besides, volatile $V_2O_5$ produced after V oxidation will cause the oxidation holes and accelerate the oxidation failure process. In addition, Ma et al. [75] studied the oxidation behavior of Nb-22Ti-15Si-5Cr-5Mo-4Zr-3Al-2Hf-xV (x = 0 at.%, 3 at.%, 5 at.%, 10 at.%) alloys at 1250 °C. Figure 14 shows the cross-section morphology and the magnified BSE image of the alloy after oxidation at 1250 °C for 1 h. It is clearly that the oxide layer is divided into internal and external layers. The outer layer is composed of TiNb$_2$O$_7$, Nb$_2$O$_5$, TiO$_2$, SiO$_2$, CrVNiO$_6$, and Nb$_9$VO$_{25}$, while the inner layer is composed of Nbss and silicide. It can be seen from Figure 13d that with the increase in V content, the weight gain per unit area of oxidation increases gradually, and the thickness of the oxide layer increases gradually also. Meanwhile, the pores caused by $V_2O_5$ volatilization are also increasing. Although the pores are beneficial to relieve the internal stress of the oxide layer, they also accelerate the internal diffusion of O$_2$, thus worsening the antioxidant properties of the alloy. The fracture toughness of the alloy increases first and then decreases with the increase in V content, and the microhardness of the alloy increases with the increase in V content, while the compressive strength decreases. However, there is still a controversy about the effect of vanadium on the antioxidant performance of Nb-Si-based alloys, which may be related to the substrate composition, alloy preparation process, oxidation conditions, V content, and other factors.

Figure 14. Cross-sectional and enlarged (a$_1$–d$_1$, a$_2$–d$_2$) BSE images of scales of the Nb-Si-based alloys with different V content oxidized at 1250 °C for 1 h: (a) (a$_1$, a$_2$) 0 at.% V. (b) (b$_1$, b$_2$) 3 at.% V. (c) (c$_1$, c$_2$) 5 at.% V. (d) (d$_1$,d$_2$) 10 at.% V. Copyright 2020 Elsevier.

3.6. Nb-Si-Based Alloys Modified with Other Elements

The oxidation and mechanical properties of the alloys are shown in Table 2. Apart from the alloying elements mentioned above, the researchers also studied the effects of Ti, Al, Mo, Ta, and other elements on the oxidation behavior of Nb-Si-based alloys. Geng et al. [38,39] found that Ti can effectively increase the oxidation resistance of the Nb-Si-Cr-Al alloy at 800 °C. It may be attributed to the preferential oxidation of Ti in Nbss, forming a large number of stable Ti oxide particles, which enhance the oxidation resistance of Nbss. This is consistent with Yonosuke et al. [76]. The Al$_2$O$_3$ protective film will be produced after the oxidation of Al, which has a good protective ability on the substrate. Esparza [49] and Su [52] et al. point out that a certain amount of Al is beneficial to prolong the service life of
Nb-Si-based superalloys. However, because Al reduces the melting point of the alloy, this alloy is not suitable for a high-temperature oxidation environment. Mo can improve the melting point and high-temperature strength of the alloy [77]. The research of Geng [38] and Ma et al. [78] shows that the low content of Mo (2 at.%) can form the volatile MoO$_3$ after oxidation, reduce the internal stress of oxide scales, and enhance the antioxidant capacity of the oxide layer. However, a large amount of MoO$_3$ volatilizes and causes holes in the oxide layer, which will deteriorate the oxidation resistance of the alloy. The study by Zelenitsas [48] and Zhang [57] et al. showed that Ta can slightly advance the oxidation properties of Nb-Si-based alloys. Moreover, other studies show that an appropriate amount of elements such as W, Y, Er, Ce, Sn, and Ge can also enhance the oxidation resistance of Nb-Si-based super alloys to some extent [39,57,68,79–81].

<table>
<thead>
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<th>Alloy Composition (at.%)</th>
<th>Oxidation Conditions (°C and h)</th>
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<th>Room Temperature Fracture Toughness (MPa m$^{1/2}$)</th>
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<td>14.1</td>
<td>[42]</td>
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<tr>
<td>Nb-22Ti-14Si-2Al-2Hf-17Cr</td>
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<td>60</td>
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<td>[46]</td>
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<tr>
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<td>[59]</td>
</tr>
<tr>
<td>Nb-22Ti-16Si-5Cr-4Hf-3Al-5B</td>
<td>1250/50</td>
<td>67.6</td>
<td>11.0</td>
<td>[65]</td>
</tr>
<tr>
<td>Nb-15Si-24Ti-4Cr-2Al-2Hf-1V</td>
<td>1300/100</td>
<td>148.5</td>
<td>12.98</td>
<td>[69]</td>
</tr>
<tr>
<td>Nb-22Ti-15Si-5Cr-5Mo-4Zr-3Al-2Hf-10V</td>
<td>1250/20</td>
<td>302.8</td>
<td>6.42</td>
<td>[75]</td>
</tr>
</tbody>
</table>

The oxidation behavior of niobium alloy is affected not only by the type and amount of alloying elements but also by the alloy preparation process and oxidation conditions. For instance, the research of Guo et al. [82,83] shows that the alloys prepared by selective laser melting (SLM) have a finer microstructure, denser oxide layer, and better oxidation resistance than vacuum induction melting (VIM). The research of Mathieu [84] and Alvarez et al. [85] shows that Nb-based alloys are more prone to pesting oxidation at medium and low temperature (700 °C), resulting in the pulverization of the oxide layer. At high temperature, the oxidation weight gain is more severe, the outer oxide layer spalls gradually, and the alloy fails faster.

4. Mechanisms of Oxidation and Failure

The oxidation reaction of niobium alloy usually proceeds gradually from the outside to the inside. At the beginning of the oxidation reaction, O atoms dissolve and diffuse to Nbss to form an oxide layer firstly; then, O atoms diffuse to the substrate along the cracks and holes of the oxide layer, and oxidation occurs inside the alloy. The thickness of the oxide layer increases gradually with the increase in oxidation time and temperature. Due to the distinction of TEC between the oxide layer and substrate, the layer expands and falls off, loses its protective effect eventually. Thereby, it is vital to strengthen the oxidation performance of the oxide layer.

Figure 15 shows the oxidation behavior and failure mechanism of Nb-Si-based alloys. After Nbss is oxidized, Nb$_2$O$_5$ is formed as the volume sharply expands, and there is no protection. Si, Al, Zr, Cr, B, etc. can form the protective oxide films, SiO$_2$, Al$_2$O$_3$, borosilicate, and other fluid oxide films can fill the cracks and holes timely in the oxide scales, inhibit the permeation of O$_2$, and improve the oxidation resistance of the oxide layer. In addition, elements such as Al, Cr, Hf, Si, and Ti have a stronger O affinity than Nb, and the selective oxidation of these elements in Nbss can increase the oxidation resistance of Nbss. Furthermore, Si, Cr etc. can also reduce the diffusion rate and solubility of O atoms in Nbss and inhibit the oxidation reaction of Nbss, thereby improving the antioxidant performance of the alloy. In addition, an appropriate amount of V can enhance the adhesion of oxide scales, ameliorate the oxidation performance of the alloy. However, the excessive addition of V will cause a large number of oxide pores, which will deteriorate
the antioxidant properties of the alloy. In addition, an appropriate amount of Hf can participate in the formation of amorphous silicate and improve the oxidation resistance, while an excessive amount of Hf will increase the brittleness of scales and deteriorate the oxidation performance of the alloy. Therefore, the content of modified elements also has a significant effect on the oxidation resistance of the alloy. The excellent oxidation characteristics of the oxide layer is essential for the oxidation resistance of the niobium alloy. A protective oxide layer can suppress the diffusion of $O_2$ effectively and strengthen the anti-oxidation performance of the alloy. The non-protective oxide layer is often loose and porous due to the discrepancy in the TEC of the oxides, and the oxide layer is prone to peeling and crushing. In addition, the volatile oxides in the oxide layer can also cause the cracks and holes, resulting in rapid oxidation failure of the alloy.

Figure 15. Schematic diagram of oxidation behavior and failure mechanism of Nb-Si-based superalloys.

5. Conclusions and Prospect

Niobium silicon series alloys are widely used in propulsion systems of aerospace and spacecraft, military weapons, and ultrahigh-temperature hot end parts, and they are the most promising new high-temperature-resistant structural materials. Studies show that some modifying elements such as Hf, Cr, Zr, B, and V can promote the oxidation resistance of Nb-Si-based alloys to some extent. Furthermore, the type and content of modified elements, alloy preparation process, and oxidation conditions will also have a great impact on the oxidation performance of materials.

Studies show that adding an appropriate amount of Hf can improve the antioxidant properties of Nb-Si-based alloys, but an excessive amount of Hf will aggravate the brittleness and porosity of the oxide layer, which is not conducive to the generation of a protective oxide layer, which will lead to the deterioration of the antioxidant properties of the alloy. Cr elements can reduce the diffusion rate of O atoms in Nbss and improve the compactness and stability of the oxide layer. In the Nb-Si-based alloys, an oxidation-resistant $\text{Nb}_2\text{Cr}$ phase will be formed if enough Cr is added. With the increase in Cr content, the volume fraction of $\text{Nb}_2\text{Cr}$ and $\text{Nb}_5\text{Si}_3$ increases, while the volume fraction of Nbss decreases. $\text{CrNbO}_4$ oxides can strengthen the adhesion of scales and have better oxidation resistance than $\text{Nb}_2\text{O}_5$. The addition of Zr can refine the macrostructure and promote the generation of a glassy SiO$_2$ oxide film, which is beneficial to improve the compactness and integrity of the oxide scales and enhance the anti-oxidation performance of the alloy. The B elements can refine the grain, and the dissolution of B and Ge in the oxide layer will facilitate the formation of continuous SiO$_2$ film and inhibit the diffusion of O$_2$. In addition, B can also alleviate the problem of mismatch between the TEC of the oxide layer and substrate, enhance the adhesion of oxide scales, and reduce the cracks and spalling. The effect of V addition on the oxidation properties of Nb-Si-based alloy is still controversial. Some studies suggest that V will form volatile V$_2$O$_5$ in the alloy, which is not conducive to the formation of the protective oxide scales and deteriorates the oxidation resistance of the
alloy. It is also considered that V has a stronger O affinity than Nb, which improves the oxidation characteristics of Nbss, reduces the oxidation rate difference between Nbss and silicide, and makes the oxide layer more compact and complete, thus promoting the oxide resistance of the alloy.

To improve the high-temperature oxidation resistance of metal by alloying, it is necessary to accurately control the content of modified elements. The oxidation resistance of the alloy cannot be improved effectively if the content of modified elements is insufficient, while excessive modified elements will reduce the mechanical properties such as the fracture toughness and high-temperature creep property of the substrates. Alloying makes it difficult to keep the balance between high-temperature oxidation resistance and mechanical properties. In recent years, the rapid development of metal surface coating technology can better solve this problem; high-temperature resistant coating is formed on the substrate surface of a layer of heat insulation or the oxygen isolation protective layer, with a certain fluidity and thickness. Among them, silicide ceramic high-temperature-resistant coating is the most widely used, its preparation process is relatively simple and low cost, and it has excellent high temperature resistance, giving it broad potential as a high-temperature coating. In addition, oxide coating, precious metal coating, composite coating, etc. also have their own advantages. High-temperature-resistant coating technology greatly makes up for the deficiency of the high-temperature oxidation resistance of metal substrates, and it is an excellent improved process, which is worthy of further study in the field of high-temperature-resistant materials.

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