In the present research, the Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho addition were prepared. Their microstructure, compressive properties and oxidation behaviors were investigated preliminarily. The results exhibit that the Nb-Si-Ti-Cr-Al-Ta-Hf alloy has coarse microstructure which is mainly composed of Nb solid solution, Nb5Si3 and Ti5Si3 phases. The minor Ho addition could refine the microstructure and suppress the precipitation of Ti5Si3 phase. Moreover, the Ho addition also leads to the formation of Ho2Hf2O7 which prefers to precipitate along the Nbss/Nb5Si3 phase interface. Compared with the Nb-Si-Ti-Cr-Al-Ta-Hf alloy, the minor Ho addition improves the room-temperature and high-temperature compressive properties of the alloy. Its room-temperature compressive strength and ductility obtain the maximum value of 1825 MPa and 16.5% when the Ho content is 0.1 at.%. Moreover, its best compressive strength at 873 K, 1273 K and 1473 K is 1495 MPa, 765 MPa and 380 MPa, respectively, when the Ho addition is 0.1 at.%. The oxidation behavior of the Nb-Si-Ti-Cr-Al-Ta-Hf alloy is diversified with the Ho addition. The oxidation rate of the alloy with 0.1 at.% Ho addition is the lowest while the alloy with 0.2 at.% Ho addition is the highest. Therefore, the 0.1 at.% Ho would be the appropriate content for the Nb-Si-Ti-Cr-Al-Ta-Hf alloy.

Keywords: Nb alloy; Nb5Si3 phase; Microstructure; Mechanical properties; Oxidation behavior

1. Introduction

In the few decades, intermetallic compounds have been paid great attention, since their excellent properties such as high structural stability, high strength, good thermal conductivity, and so on [1-4]. Especially in the aerospace, power, metallurgy industries, the increasing of working temperature has put forward higher requirements on the materials used as the high-temperature component [5,6]. Now, one method is fabrication the thermal barrier coatings with better performance, but their improvement is limited, due to the interface cracking [7,8]. The other method is developing the new materials with better high-temperature strength, better creep properties and good oxidation resistance [9,10]. As one typical intermetallic compounds, the niobium silicide (NbSi) has attracted more attention, because its ultrahigh melting point and excellent creep resistance [11,12]. Therefore, the NbSi based alloy has been considered as the most potential material to develop the new blade for high performance gas turbine [13]. However, the long range ordered structure of the NbSi phase makes it intrinsic brittleness, which is detrimental to its room-temperature ductility [14]. Moreover, the “pest” oxidation of Nb based alloy also restricts its application at high temperature [15]. Then, improving the room-temperature strength and oxidation resistance of the NbSi based alloy have become a critical issue before its application.

Among the methods to improve the properties of NbSi based alloy, the alloying has been considered as the most convenient and effective one. Especially for the intrinsic brittleness of NbSi intermetallic compound, the introducing of ductile phase is a feasible way. Recently, the researches [16,17] have improved the room-temperature mechanical properties of NbSi based alloy by microstructure optimization, which demonstrates the benefit of incorporated ductile phase on fracture toughness. The researches on Nb-Si alloy revealed that the doped Hf and Ti helped the formation of Nb3Si phase and the Cr and Al addition contributed the formation of Nb5Si3 phase [18,19]. However, Grammenos et al [20] studied the effect of Al, Cr and Ti addition on the microstructure of Nb-18Si-5Hf alloy and indicated that Ti could stabilize the Nb5Si3 phase and promote the formation of lamellar structure. Actually, the increased alloying elements

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would result in the phase transformation and precipitation along interface, which influences its high-temperature strength [21]. In addition, for the multi-phase alloy, how to take full use of the ductile phase and stiffness phase is another important factor that greatly affects the mechanical properties. The researches on multi-phase alloys with intermetallic compound indicated that the Rare Earth (RE) could refine the microstructure and contribute to the strength and ductility simultaneously [22,23]. Moreover, the added RE can purify the grain boundary by arresting the oxygen and impurities, which benefits the fracture toughness [2,24]. Then, it can be anticipated that the appropriate RE addition, cooperated with other alloying element, could improve the properties of the NbSi alloy effectively.

Therefore, in the present research, the Nb-Si-Ti-Cr-Al-Ta-Hf alloys with minor addition of holmium (Ho) was fabricated by conventional method. The microstructure, phase constituent, compressive properties and oxidation behavior of the alloys were investigated to demonstrate the appropriate Ho addition.

2. Experimental procedures

The Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho contents were prepared by the vacuum arc furnace with the definite composition, as shown in TABLE 1. The pure metals of niobium (99.9%), silicon (99.9%), titanium (99.9%), chromium (99.9%), aluminum (99.9%), tantalum (99.9%), hafnium (99.8%) and holmium (99.7%) were arc-melted in a water-cooled copper crucible. The alloy buttons were turned over and remelted for five times to homogenize the chemical composition. Due to the elemental losses were almost less than 0.5% in mass, the nominal compositions of the alloys were considered as their real composition.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ho</th>
<th>Hf</th>
<th>Ta</th>
<th>Al</th>
<th>Cr</th>
<th>Ti</th>
<th>Si</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Ho</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>6</td>
<td>22</td>
<td>16</td>
<td>49</td>
</tr>
<tr>
<td>0.1Ho</td>
<td>0.1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>6</td>
<td>22</td>
<td>16</td>
<td>48.9</td>
</tr>
<tr>
<td>0.2Ho</td>
<td>0.2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>6</td>
<td>22</td>
<td>16</td>
<td>48.8</td>
</tr>
</tbody>
</table>

The TEM observation was observed on JEOL-2100 to characterize the crystal structure and defects. Rectangular compression specimens with the dimensions of 4 mm × 4 mm × 6 mm were cut from the buttons by electro-discharge machining (EDM) and the major surfaces were mechanically ground with 600-grit SiC abrasive prior to compression test. The compression tests were conducted in air using a Gleeble 1500 testing machine with an initial strain rate of 1×10⁻³ s⁻¹ and the recorded load-time curves were converted to true stress-strain curves by taking constant volume into account.

The specimens for oxidation tests were cut from the alloys with the dimension of 10 mm × 10 mm × 3 mm and ground with 2000-grit SiC abrasive. The oxidation tests were performed in an open-ended tube furnace at 1100°C. Each specimen was placed in a separate alumina crucible during the test. The specimens were removed from the furnace at the intervals of 2, 3, 5, 10, 25, 40, and 60 h and weighed together with the crucible using a precision analytical balance (Model CPA225D, Germany) with an accuracy of 0.00001 g. The oxidized surfaces of the specimens were observed by the SEM S-3400. The phase constituents of the oxides were analyzed by the XRD.

3. Results and discussion

3.1. Microstructure and phase structure

The SEM observations on Nb-Si-Ti-Cr-Al-Ta-Hf alloys with and without Ho addition have been shown in Fig. 1. Clearly, the alloy mainly comprises three kinds of phases. In the Nb-Si-Ti-Cr-Al-Ta-Hf alloy without Ho addition, the gray-white Nb solid solution (Nbss) is the matrix embellished with coarse gray Nb₅Si₃ phases and relative small black Ti₅Si₃ phases, as shown in Fig. 1(a). Moreover, the Nbss and Nb₅Si₃ phases have formed the eutectic structure in some regions. With the addition of 0.1 at.% Ho, the microstructure becomes fine and demonstrates the near-eutectic morphology, as shown in Fig. 1(b). Though the

![Fig. 1. Microstructures of Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho addition: (a) 0 Ho, (b) 0.1 Ho, (c) 0.2 Ho](image-url)
distribution of Ti$_2$Si$_3$ phases is more homogeneous, the amount tends to decrease a little. In addition, some white phase can be observed along the Nbss and Nb$_2$Si$_3$ phase interface. The EDS test shows the white phase is rich of Hf, Ho and O, which indicates it should be the oxides of Hf and Ho. When the Ho addition is increased to 0.2 at.%, the microstructural refinement is more distinct, which promotes some Nbss/Nb$_2$Si$_3$ lamellar eutectic structure, as shown in Fig. 1(c). Furthermore, the quantity of white phase is increased but their size almost changes little, compared with the 0.1 at.% Ho doped alloy.

The XRD has been employed to analyze the phase constituent in the Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho addition and the results are shown in Fig. 2. It can be found that the Nbss and Nb$_2$Si$_3$ are the main phases in all alloys, but the Ho addition has resulted in the phase evolution. Compared with the Nb-Si-Ti-Cr-Al-Ta-Hf alloy, the Ho addition has restrained the formation of Nb$_5$Si$_3$ phase. Especially in the 0.2 at.% Ho doped alloy, the diffraction peaks strength of the Nb$_5$Si$_3$ phase have decreased obviously. In addition, the Ho addition has led to the little deviation of Nbss diffraction peaks, which indicates it has caused lattice parameters changing in Nbss phase. Comparatively, the diffraction peak strength of Ti$_2$Si$_3$ phase has decreased greatly with the Ho addition. The diffraction peak evolution of XRD patterns has confirmed the microstructural observations.

Fig. 2. XRD patterns of the Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho addition

To further study the phase and crystal feature, the TEM observations have been performed on the 0.2 at.% Ho doped Nb-Si-Ti-Cr-Al-Ta-Hf alloy. The bright-field TEM observation on the matrix reveals the fine eutectic structure, as shown in Fig. 3(a). Clearly, the Nb$_2$Si$_3$ phases have precipitated in the Nbss matrix with the ultrafine lamellar structure. The inset selected area electron diffraction (SAED) pattern indicates the Nb$_2$Si$_3$ phase has the tetragonal crystal structure with $a = b = c = 0.5206$ nm and Fm$ar{3}$m space group, which indicates it is Hf$_2$Hf$_2$O$_7$ phase. Due to the high stiffness of this kind of oxides, the formed Hf$_2$Hf$_2$O$_7$ phase could handicap the movement of dislocations and increase the strength [26]. In addition, the active Ho could promote the formation of specific oxide and dense oxide layer.

3.2. Compressive properties

The compression tests at different temperatures have been performed on the Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho additions and the results are shown in Fig. 4. Due to the presence of ductile-brittle transition of the NbSi based alloy, the compressive strain would be improved obviously with increased temperature, and only the compressive strain at room temperature is studied. As shown in Fig. 4(a), the room-temperature compressive strength and strain of the alloy without Ho addition are 1640 MPa and 12.5%, respectively. With 0.1 at.% Ho addition, the compressive strength and strain of the alloy are improved to 1825 MPa and 16.5%, respectively. When the Ho addition is increased to 0.2 at.%, the compressive properties are decreased a little with the compressive strength and strain of 1800 MPa and 16%, respectively. Generally, the minor Ho addition is beneficial to the compressive strength and strain, which should be mainly ascribed to the refined microstructure. With the test temperature increasing, the compressive strength of the alloy with different Ho addition has decreased.
less than 20% at 873 K. The compressive strength of the Nb-
Si-Ti-Cr-Al-Ta-Hf alloy with 0, 0.1 and 0.2 at.% Ho addition
is about 1350 MPa, 1495 MPa and 1450 MPa, respectively.
When the test temperature increases to 1273 K, the compres-
sive strength of the Nb-Si-Ti-Cr-Al-Ta-Hf alloy with 0, 0.1
and 0.2 at.% Ho addition has an obvious drop and their values are
695 MPa, 765 MPa and 741 MPa, respectively. With the test
temperature increasing to 1473 K, the compressive strength of
the Nb-Si-Ti-Cr-Al-Ta-Hf alloy with 0, 0.1 and 0.2 at.% Ho ad-
dition has decreased to 300 MPa, 380 MPa and 360 MPa,
respectively. Comparatively, the compressive strength of the
alloy has decreased gradually with the temperature. Especially
at the temperature above 1273 K, the compressive strength drops
significantly. Such a phenomenon could be attributed to the
softening of the Nbss, which results in the decreased strength.
The minor Ho addition improves the compressive strength at
elevated temperature, which should be mainly attributed to the
refined Nb₅Si₃ phase. The microstructure evolution could take
full use of the strengthening phase and restrain the dislocation
movement. In addition, the well distributed Ho₂Hf₂O₇ phases
also benefits the strength by handicap the dislocation movement.

3.3. Oxidation behavior

The oxidation behavior of the NbSi based alloy is an im-
portant issue, because of the “pest” oxidation phenomenon [15].
Though the Cr and Al addition could help to form the oxidation
resistance surface layer, however, the rapid inner oxidation
could destroy the protective layer. Actually, the active RE could
induce the formation of specific oxide and help the oxidation
resistance [27]. To study the effect of Ho addition on the oxida-
tion behavior of the Nb-Si-Ti-Cr-Al-Ta-Hf alloy, the oxidation
at 1373 K has been performed and mass variation of alloys is
present in Fig. 6. Clearly, the Nb-Si-Ti-Cr-Al-Ta-Hf alloys with
Ho addition have experienced great stress and almost crashed
during the compression, as shown in Fig. 5(a). Moreover, the
cracks could be observed in the Nbss matrix with similar propa-
gating direction, which indicates the rapid stress transfer and
less using of the ductile phase. In the Ho doped Nb-Si-Ti-Cr-Al-
Ta-Hf alloy, the cracks with diversified propagating direction
have distributed in the Nb₅Si₃ phases, as shown in Fig. 5(b).
Moreover, there is almost no crack in the Nbss matrix. Such
a feature indicates the stress has been changed by the synergistic
deformation of Nbss and Nb₅Si₃ phases. Then, it can be con-
cluded that the refined microstructure could well take advantage
of the ductile and stiffness phases, which contributes to the
strength and ductility simultaneously.

Fig. 4. Compressive properties of the Nb-Si-Ti-Cr-Al-Ta-Hf alloys
with different Ho addition: (a) Compressive strength and strain at room
temperature, (b) Compressive strength at elevated temperature

The typical cross-sectional microstructures of the Nb-Si-
Ti-Cr-Al-Ta-Hf alloys with and without Ho addition after room-
temperature compressive test have been observed and given in
Fig. 5. It can be seen that the Nb₅Si₃ phases in the alloy without

Fig. 5. SEM observations of the crack morphology in the Nb-Si-Ti-
Cr-Al-Ta-Hf alloys with different Ho addition compressed at room
temperature: (a) 0 Ho, (b) 0.1 Ho

Fig. 6. Oxidation kinetics curves of the Nb-Si-Ti-Cr-Al-Ta-Hf alloys
with different Ho addition at 1373 K
different Ho addition all demonstrate the increased mass with the time extending. Moreover, the mass variation curves exhibit the parabolic feature, which has rapid increasing rate at initial stage and then the increasing rate drops keeping at a certain value. Comparatively, the Nb-Si-Ti-Cr-Al-Ta-Hf alloy without Ho addition has the higher mass increasing at the initial stage, but it decreases a little in the following time and keeps at the medium value. The Nb-Si-Ti-Cr-Al-Ta-Hf alloy with 0.1 at.% Ho addition has the better oxidation behavior with the lowest mass increasing rate in all time. However, the 0.2 at.% Ho doped Nb-Si-Ti-Cr-Al-Ta-Hf alloy has the higher mass increasing rate at initial stage and the highest value in the following time.

The XRD analyses on the oxidized surfaces of Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho addition are shown in Fig. 7. It is clear that the high-temperature oxidation has resulted in complex oxides. Clearly, the surfaces of alloy are mainly composed of Nb₂O₅ based oxide. Due to the coexistence of Ti, and Ta elements in the Nb₅Si₃ and Ti₅Si₃ phases, the Nb₂O₅ almost forms with TiO₂ and Ta₂O₅ phases synergistically. Moreover, the diffraction peaks of NbSi₂ can be observed in the XRD patterns, which can be ascribed to the consumption of Nb during oxidation. With the consumption of Nb, the Nb content in the Nb₅Si₃ phase would be decreased, which leads to the transformation of Nb₂Si₁₃ to Nb₂Si₅. In addition, the AlNbO₄ and CrNbO₄ also can be calibrated in the XRD patterns, which should be attributed to the solid solution of Al and Cr in Nb₅Si₃ matrix. Based on the XRD patterns, the Ho addition exerts little effect on the oxide types, except the formation of HfO₂ and Ho₂Hf₂O₇.

SEM observations on the oxidized surfaces are exhibited in Fig. 8. It can be found that the surface of Nb-Si-Ti-Cr-Al-Ta-Hf alloy without Ho addition is mainly covered by the rod-like phases with dual size, as shown in Fig. 8(a). The rod-like phases are intersected with each and there are some small particles interspersed inside. Moreover, the rod-like phases with different sizes prefer to aggregate separately. Combining with the XRD analyses, the rod-like phase should be Nb₂O₅ and the size may be related with the coordinated formed phase. With the 0.1 at.% Ho addition, the surface morphology has changed a little. As shown in Fig. 8(b), though the rod-like phase still has the high proportion, the size has decreased obviously, compared with those formed on the alloy without Ho addition. When the Ho addition increases to 0.2 at.% , the oxides are refined further, which almost changes the rod-like shape to small particles, as shown in Fig. 8(c). Furthermore, the micro-gaps could be observed in the oxidized surfaces, which indicates the relative loosening oxide film. However, the Ho addition could decrease the ratio of micro-gap with big size, which is helpful to improve the oxidation resistance.

To demonstrate the effect of Ho addition on the oxidation permeation, the cross-sectional microstructures of the Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho addition after oxidation have been characterized. As shown in Fig. 9, the Ho addition has really restrained the extending of oxidation in matrix. For the Nb-Si-Ti-Cr-Al-Ta-Hf alloy without Ho addition, the depth of inner oxidation zone is about 60 μm, as shown in Fig. 9(a). Moreover, the inner diffusion of oxygen has resulted in the oxidation

Fig. 7. X-ray diffraction patterns of Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho addition oxidized at 1373 K for 60 hours: (a) 0 Ho, (b) 0.1 Ho, (c) 0.2 Ho
along the Nbss/Nb5Si3 phase interface. With the addition of Ho, the depth of inner oxidation zone has been decreased, as shown in Fig. 9(b) and (c). The depth of inner oxidation zone of the Nb-Si-Ti-Cr-Al-Ta-Hf alloy with 0.1 and 0.2 at.% Ho addition is about 30 μm and 40 μm, respectively.

According to the recent researches [28-30], the mechanical properties are closely related with microstructure. Especially for the alloy with intermetallic phase, the ductile phase could play an important role [31,32]. In the present research, the Nbss acts as the ductile phase to improve the room-temperature deformation behavior of the NbSi based alloy. The original multi-phase structure in Nb-Si-Ti-Cr-Al-Ta-Hf alloy could use the Nb5Si3 phase to enhance the strength, but it could not take full use of the Nbss phase to improve the ductility. Due to the coarse microstructure, the propagation of microcracks initiated in Nb5Si3 would be accelerated inside and difficult to be bridged or reversed by the Nbss phase [33]. The Ho addition refines the microstructure and suppresses the rapid propagation of crack along linear direction, which contributes to the compressive ductility. Therefore, the Nb-Si-Ti-Cr-Al-Ta-Hf alloy with Ho addition has better compressive strength and strain simultaneously. Due to the high activity of RE, the doped Ho could induce the selective oxidation along phase interface and restrain the inner diffusion of oxygen. Therefore, the 0.1 at.% Ho doped Nb-Si-Ti-Cr-Al-Ta-Hf alloy possesses the best oxidation resistance. If more Ho is added, it would accelerate the oxidation and begin to extend the inner oxidation, which is detrimental to the oxidation resistance. Then, the appropriate Ho addition is helpful to regulate the microstructure of the Nb-Si-Ti-Cr-Al-Ta-Hf alloy and improve its properties.

4. Conclusions

In the present research, the Nb-Si-Ti-Cr-Al-Ta-Hf alloys with different Ho addition were prepared. Their microstructure, compressive properties and oxidation behaviors were studied preliminarily. Some conclusions can be drawn as following.

(1) The Nb-Si-Ti-Cr-Al-Ta-Hf alloy prepared by vacuum arc smelting possesses coarse microstructure which is mainly composed of Nb solid solution, Nb5Si3 and Ti5Si3 phases. The minor Ho addition could refine the microstructure and suppress the precipitation of Ti5Si3 phase. Moreover, the Ho addition also results in the formation of Ho2Hf2O7, which prefers to precipitate along the Nbss/Nb5Si3 phase interface.

(2) Compared with the Nb-Si-Ti-Cr-Al-Ta-Hf alloy, the minor Ho addition improves the room-temperature and high-temperature compressive properties. Its room-temperature compressive strength and ductility obtain the maximum value of 1825 MPa and 16.5% when the Ho content is 0.1 at.%. Moreover, the alloy with 0.1 at.% Ho has the best compressive strength at 873 K, 1273 K and 1473K with value of 1495 MPa, 765 MPa and 380 MPa, respectively.

(3) The oxidation behavior of the Nb-Si-Ti-Cr-Al-Ta-Hf alloy is diversified with the Ho addition. The oxidation rate of the alloy with 0.1 at.% Ho addition is the lowest while the alloy with 0.2 at.% Ho addition is the highest. Therefore, the 0.1 at.% Ho would be the appropriate content for the Nb-Si-Ti-Cr-Al-Ta-Hf alloy.

Acknowledgments

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