Microstructure and High-Temperature Oxidation Behavior of Dy-Doped Nb–Si-Based Alloys

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Abstract

Microstructures and oxidation behaviors of four Dy-doped Nb–Si-based alloys at 1250 °C were investigated. The nominal compositions of the four alloys are Nb–15Si–24Ti–4Cr–2Al–2Hf–*x*Dy (at.%), where *x* = 0, 0.05, 0.10 and 0.15, respectively. Results showed that the four alloys all consisted of Nbss, α Nb₅Si₃ and γ Nb₅Si₃, and the addition of Dy produced no obvious effect on the phase constitution and the microstructures of Nb–Si-based alloys. After oxidation at 1250 °C for 58 h, it was found that the addition of Dy accelerated the oxidation rate of Nb–Si-based alloys and caused a larger weight gain, accompanied by the formation of a more porous and less protective oxide scale. The oxides of Nb₂O₅, Ti₂Nb₁₀O₂₉, TiNb₂O₇, Ti_{0.4}Cr_{0.3}Nb_{0.3}O₂ and glassy SiO₂ were formed on Dy-doped Nb–Si-based alloys. The high-temperature oxidation mechanism of Dy-doped Nb–Si-based alloys was discussed.

Keywords Nb–Si alloy · Intermetallics · Directional solidification · Oxidation · Microstructure

1 Introduction

Both aircraft engines and land-based gas turbines are expected to run more efficiently at higher temperatures [1, 2]. The need for materials with higher temperature capability has driven the rapid development of Nb–Si-based ultrahigh-temperature alloys, with unparalleled advantages of high melting points, relatively low densities and outstanding high-temperature stiffness and strength

[3–5]. Based on the composite engineering approach, the development of Nb–Si-based alloys is oriented toward two-phase or three-phase systems, incorporating the metallic Nb solid solution (Nbss) phases and intermetallic compounds (Nb₃Si, α Nb₅Si₃, β Nb₅Si₃ and/or Cr₂Nb). Efforts to enhance the mechanical and environmental performance by modifying the alloy chemistry have achieved marginal improvement, and a Nb–Si–Ti–Cr–Al–Hf system has been recently developed [6, 7]. But the insufficient high-temperature oxidation resistance of Nb–Si-based alloys still restricts their practical applications as advanced turbine blade materials.

The poor oxidation resistance of Nb–Si-based alloys is due to the absence of protective oxide scales [3, 7]. The silicide phase is known to possess an excellent oxidation resistance, while Nbss phase has a larger oxygen solubility and faster oxygen diffusion rate, which is responsible for the insufficient oxidation resistance of Nb–Si-based alloys [8–10]. In addition to coating, alloying is a typical route to enhance the oxidation resistance of Nb–Si-based alloys and the beneficial elements of Ti, Cr, Al, B, Mo, Ge, Hf, Re have been confirmed [3, 11–15]. Dasary and Varma [14] presented that the addition of Re eliminated the pesting oxidation of Nb–Si-based alloys at lower temperatures and the spallation of oxidation scale at higher temperatures. Su et al. [15] found that the addition of Ge and B promoted the

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growth of protective SiO_2 phase and thus improved the oxidation resistance of Nb–Si-based alloys.

It has also been well established that small additions of rare earth elements, added in the form of elements or as oxide dispersions, can greatly improve the oxidation resistance of metals as well as coatings [16–19]. As one of the rare earth elements, Dy has been employed to improve the oxidation resistance of NiAl-based alloy [20] and coatings [18]. The improvement in the cyclic oxidation resistance of NiAl–30.9Cr–3Mo–0.1Dy alloy is due to the formation of continuous and compact Al_2O_3 external layer [20]. Besides, as reported by Tian et al. [21], the addition of Dy enhances the room-temperature and high-temperature compressive strength and room-temperature compressive ductility of Nb–Si-based alloys. However, the effect of Dy on the oxidation behavior of Nb–Si-based alloys has not been systematically explored.

Directional solidification (DS) has been employed to fabricate Nb–Si-based alloys recently, owing to its favorable effect on the mechanical property. In this work, the oxidation behavior of directionally solidified Nb–Si-based alloys doped with Dy was investigated, focusing on the role of Dy on the isothermal oxidation resistance.

2 Experimental

Four types of Nb–Si-based alloys with different contents of Dy were prepared. The nominal compositions of the four alloys are Nb–15Si–24Ti–4Cr–2Al–2Hf– x Dy (at.%), where $x = 0, 0.05, 0.10$ and 0.15 , respectively. The Nb–15Si–24Ti–4Cr–2Al–2Hf alloy was designed for comparison and was denoted as base alloy, while the other three alloys were denoted as 0.05Dy alloy, 0.10Dy alloy and 0.15Dy alloy, respectively, based on the Dy concentration. The four alloys were firstly synthesized via vacuum non-consumable arc-melting (VCAM). The button ingots were melted for five times for the sake of chemical homogeneity. DS experiments were performed in a vertical Bridgman furnace at 1980 °C using liquid–metal–cooling method. The bars for DS were assembled in Y_2O_3 crucibles, and the withdrawn rate is 30 mm/min. The furnace chamber for DS was heated up when the vacuum level was higher than 1.0×10^{-3} Pa. All the samples for oxidation tests were chosen from the steady-state area [22].

The oxidation tests were performed in a tube furnace at 1250 °C in static air. All the Nb–Si-based alloy specimens (6 mm × 6 mm × 5 mm) were ground with SiC papers up to 800 grit, ultrasonically cleaned in the acetone medium to remove surficial contaminates and thoroughly dried gradually. All the alumina crucibles used for oxidation experiments were dried at 1250 °C for 2 h, and each Nb–Si-based alloy specimen was then placed in a separate alumina

crucible during the oxidation tests. The specimens were removed from the tube furnace after oxidation for different time and weighed together with the crucible using a precision analytical balance (Model CPA225D, Germany) with an accuracy of 0.00001 g.

The surface morphologies of the oxide scales were examined by scanning electron microscopy (SEM, Quanta 200F). The phases of the four alloys and the oxide products were determined by X-ray diffraction (XRD, D/max-2500, CuK_α). Metallographic examination was performed using SEM in the backscattered electron imaging (BEI) mode and an electron probe micro-analyzer (EPMA, JXA-8230) equipped with wave-dispersive spectroscopy (WDS). To observe their sections, the four oxidized Nb–Si-based alloys were mounted using liquid epoxy resins, followed by an overnight hardening. For metallographic examination, specimens were ground using successive grades of abrasive paper up to 1200# and finally mechanically polished on $\text{Fe}_2\text{O}_3/\text{CrO}_3$ -impregnated cloths. The distributions of O, Nb, Si, Ti, Al, Cr and Dy on the cross sections of the 0.15Dy alloy were obtained by EPMA using the X-ray mapping modes. The ZAF-corrected EPMA was calibrated by pure standards for different operating conditions and probe sizes. The oxide scales formed on the 0.15Dy alloy after oxidation for 58 h were further examined by transmission electron microscopy (TEM, JEM-2100). Samples for TEM were ground to 80 μm , dimpled to 10 μm and finally ion-milled. The Ellingham–Richardson diagram of Nb, Si, Ti, Cr, Al, Hf and Dy was calculated with software HSC Chemistry 6.0.

Fig. 1 XRD patterns of Dy-doped Nb–Si-based alloys

3 Results

Figure 1 shows the XRD patterns of Dy-doped Nb–Si-based alloys. The main phases of the base alloy, 0.05Dy alloy, 0.10Dy alloy and 0.15Dy alloy are body-centered cubic (bcc) Nbss and $\alpha\text{Nb}_5\text{Si}_3$ (D8₁, I4/mcm Cr₅B₃ type), suggesting the Dy addition up to 0.15 at.% does not alter the phase constitution of Nb–Si-based alloys. The microstructures of base alloy, 0.05Dy alloy, 0.10Dy alloy and 0.15Dy alloy are displayed in Fig. 2. The Nbss phases with light gray contrast and $\alpha\text{Nb}_5\text{Si}_3$ phases with dark gray contrast are observed in the four Nb–Si-based alloys, parallel to DS solidification. It is worth noting that the silicides with black contrast are also found in each alloy, which are considered to be hexagonal close-packed (hcp) $\gamma\text{Nb}_5\text{Si}_3$ phases [22]. The white particles are a mixture of Dy₂O₃ and HfO₂. No obvious difference is observed on either the vertical or the transversal microstructures of Nb–Si-based alloys with different Dy additions. The compositions of Nbss, $\alpha\text{Nb}_5\text{Si}_3$ and $\gamma\text{Nb}_5\text{Si}_3$ are listed in Table 1. It is observed that Dy is mainly partitioned in silicides, especially in $\gamma\text{Nb}_5\text{Si}_3$. Tian et al. [21] reported that the Dy addition remarkably refined the size of (Nb,Ti)₅Si₃ phase in Nb–23Ti–10Ta–2Cr–18Si alloy (at.%), as rare earth element of Dy had a high surface activity and tended to reduce the surface tension of liquid Nb–Si melt as well as the nucleation energy during solidification. However, for the Nb–15Si–24Ti–4Cr–2Al–2Hf alloy, the Dy addition produces no obvious effect on the microstructure fineness. In conclusion, the Dy addition up to 0.15 at.% does not significantly alter the phase constitution and microstructure fineness of Nb–15Si–24Ti–4Cr–2Al–2Hf alloy.

Figure 3a shows the weight gain per unit area of Dy-doped Nb–Si-based alloys as a function of the exposure time at 1250 °C. After oxidation for 58 h, the weight gains of base alloy, 0.05Dy alloy, 0.10Dy alloy and 0.15Dy alloy are 136.02, 142.59, 147.76 and 168.55 mg/cm², respectively. The base alloy has the lowest weight gain after oxidation, while the 0.15Dy exhibits the highest weight gain. The weight gain after oxidation increases with the addition of Dy, and a higher amount of Dy addition results in a larger increase in the weight gain after oxidation. A lower weight gain after oxidation indicates a better oxidation resistance. Accordingly, it can be concluded that the Dy addition reduces the oxidation resistance of Nb–Si-based alloys, and when the larger amount of Dy is added, the Nb–Si-based alloy exhibits the worse oxidation resistance. As displayed in Fig. 3a, the thermogravimetric curves exhibit parabolic oxidation kinetics at the early stage of oxidation and then linear oxidation kinetics, i.e., the oxidation rate becomes constant at long times. The parabolic law tends to be obeyed when the oxidation rate is

determined by the diffusion through the oxide scale, and the linear law refers predominantly to oxidations whose rates are controlled by surface-reaction step [23]. Figure 3b shows the weight gains of Dy-doped Nb–Si-based alloys versus the square root of time up to 22 h, and linear patterns are observed. It further manifests the parabolic oxidation kinetics at the early stage of oxidation for Nb–Si-based alloys. For the parabolic law stage, the relationship of mass gain per unit area ($\Delta m/S$) and oxidation time (t) is given by Eq. (1) [24, 25].

$$\frac{\Delta m}{S} = \sqrt{\left(\frac{\Delta m}{S}\right)_{\max}^2 \times \frac{2K_O^{0\beta} D_O^{0\beta} (\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{\text{eq}}})}{v_m H_0^2} \exp\left(\frac{\Delta E_d}{RT}\right) t}, \quad (1)$$

where $\left(\frac{\Delta m}{S}\right)_{\max}$ is the theoretical maximum weight gain after complete oxidation and is consistent to a specific sample at a certain oxidation temperature, $K_O^{0\beta}$ and $D_O^{0\beta}$ are the temperature-independent constants, P_{O_2} and $P_{O_2}^{\text{eq}}$ are the oxygen partial pressure of oxidizing atmosphere and the oxygen partial pressure equilibrium with oxides, respectively, v_m is a coefficient related to the density of reactant and product, H_0 is the thickness of specimen, ΔE_d is the apparent diffusion activation energy, R is the gas constant, and T is the Kelvin temperature. In this paper, k_p is defined as Eq. (2).

$$k_p = \left(\frac{\Delta m}{S}\right)_{\max} \times \frac{2K_O^{0\beta} D_O^{0\beta} (\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{\text{eq}}})}{v_m H_0^2} \exp\left(\frac{\Delta E_d}{RT}\right). \quad (2)$$

Combining Eqs. (1) and (2) yields

$$\frac{\Delta m}{S} = \sqrt{k_p t}, \quad (3)$$

k_p is named as the parabolic constant of oxidation, whose value represents the oxidation resistance of alloys [9, 10, 26]. k_p (mg² mm^{−4} s^{−1}) can be determined by the slopes of the fitting lines in Fig. 3b, and the fitting equations representing the parabolic laws of the four Nb–Si-based alloys are thus shown as follows.

$$\left(\frac{\Delta m}{S}\right)_{\text{base}} = \sqrt{87.479t}, \quad (4)$$

$$\left(\frac{\Delta m}{S}\right)_{0.05\text{Dy}} = \sqrt{113.082t}, \quad (5)$$

$$\left(\frac{\Delta m}{S}\right)_{0.10\text{Dy}} = \sqrt{131.744t}, \quad (6)$$

$$\left(\frac{\Delta m}{S}\right)_{0.15\text{Dy}} = \sqrt{143.952t}. \quad (7)$$

Fig. 2 Microstructures of Dy-doped Nb–Si-based alloys: base alloy (**a**, **b**); 0.05Dy alloy (**c**, **d**); 0.10Dy alloy (**e**, **f**); 0.15Dy alloy (**g**, **h**). (**a**, **c**, **e**, **g**) are the vertical microstructures parallel to DS direction. (**b**, **d**, **f**, **h**) are the transversal microstructures perpendicular to DS direction

Accordingly, with the increase in amount of Dy addition, the parabolic oxidation rate constant grows significantly. It suggests that the addition of Dy mainly accelerates the parabolic oxidation rate. It can thus be concluded that the addition of Dy increases the oxidation

rate of Nb–Si-based alloys in the first 22 h, leading to a thicker oxide scale on Nb–Si-based alloys and a larger weight gain (Fig. 3a).

As shown in Fig. 4, Nb_2O_5 , $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, TiNb_2O_7 and $\text{CrNbO}_4/\text{TiO}_2$ are the dominant oxides grown on the base

Table 1 Compositions of the main phases in the base alloy and the 0.15Dy alloy (at.%)

Specimen	Nb	Si	Ti	Cr	Al	Hf	Dy
<i>Base alloy</i>							
Nbss	60.34	0.78	28.42	6.15	3.01	1.30	–
α Nb ₅ Si ₃	42.53	38.57	15.79	0.28	0.66	2.17	–
γ Nb ₅ Si ₃	28.35	37.38	27.94	0.72	1.43	4.18	–
<i>0.15Dy alloy</i>							
Nbss	60.28	0.49	28.52	6.48	2.96	1.27	–
α Nb ₅ Si ₃	42.77	38.67	15.50	0.22	0.66	2.18	0.01
γ Nb ₅ Si ₃	26.93	37.92	28.91	0.74	1.26	4.24	0.03

alloy, 0.05Dy alloy, 0.10Dy alloy and 0.15Dy alloy, after oxidation at 1250 °C for 58 h. No obvious difference is shown on the species of oxides grown on the four Nb–Si-based alloys. Either TiO₂ (rutile) or Nb₂O₅ has an octahedral structure [27], and Ti⁴⁺ (0.68×10^{-10} m) and Nb⁵⁺ (0.69×10^{-10} m) approximately equal the radii [28]. So Ti⁴⁺ tends to partly replace Nb⁵⁺ in Nb₂O₅ oxides during oxidation. Ti₂Nb₁₀O₂₉ is normally an intermediate oxide, resulting from the solid-state reaction between Nb₂O₅ and TiO₂, and it also can react with TiO₂ to generate TiNb₂O₇ oxides [29]. The XRD patterns of CrNbO₄ and TiO₂ are coincident, due to their identical crystal structures and similar lattice parameters [30]. So it is not able to distinguish the oxides of CrNbO₄ and TiO₂ by XRD, and then, they were investigated by SEM and TEM in Figs. 5 and 6. Figure 5 shows the surface morphologies of oxide scales grown on the four alloys after oxidation at 1250 °C for 58 h. It is observed that the oxide scale formed on the base alloy is more compact than those grown on Dy-doped Nb–Si-based alloys, with fewer pores and less spallation. The oxide scale on the Dy-doped alloys becomes less compact with a larger amount of Dy additions. A less compact oxide scale typically provides Nb–Si-based alloys with

Fig. 4 XRD patterns of the oxides grown on Dy-doped Nb–Si-based alloys after oxidation at 1250 °C for 58 h

insufficient protection, resulting in a higher weight gain after oxidation.

The oxide scale formed on the 0.15Dy alloy was further investigated by TEM, and the results are displayed in Fig. 6. The oxides of SiO₂, Nb₂O₅, Ti₂Nb₁₀O₂₉, TiNb₂O₇ and Ti_{0.4}Cr_{0.3}Nb_{0.3}O₂ are confirmed, and it can be inferred that these oxides grew on the base alloy, 0.05Dy alloy and 0.10Dy after oxidation at 1250 °C for 58 h. The composition of each kind of oxide obtained by TEM-EDS is listed in Table 2. The oxide with a tetragonal structure and a composition of 49.93O–14.90Nb–24.71Ti–10.46Cr (at.%) is not likely to be a single tetragonal oxide of either CrNbO₄ or TiO₂, as it has a considerably large content of Nb, Ti and Cr. Instead, the oxide is believed to be the complex oxide of tetragonal Ti_{0.4}Cr_{0.3}Nb_{0.3}O₂, which probably results from the reaction between CrNbO₄ and TiO₂, due to their identical crystal structures and similar lattice parameters [30]. As shown in Fig. 6c, it is worth noting that the glassy SiO₂ phase is generated in the oxide

Fig. 3 Weight gain versus time **a** and the square root of time **b** for Dy-doped Nb–Si-based alloys during oxidation at 1250 °C

Fig. 5 SEM morphologies of oxide scales grown on Dy-doped Nb–Si-based alloys after oxidation at 1250 °C for 58 h: **a** base alloy; **b** 0.05Dy alloy; **c** 0.10Dy alloy; **d** 0.15Dy alloy

scale on Nb–Si-based alloys with a composition of 66.76Si–33.24O (at.%). The fluid glassy SiO_2 phase normally fills the gaps among other oxides including Nb_2O_5 , $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, TiNb_2O_7 and $\text{Ti}_{0.4}\text{Cr}_{0.3}\text{Nb}_{0.3}\text{O}_2$, contributing to the healing of cracks and pores in the oxide scales. Yao et al. [10] presented that the oxide scale grown on the Nb–16Si–24Ti–6Cr–6Al–2Hf alloy included an outer oxide layer composed of TiNb_2O_7 , $\text{TiNb}_{10}\text{O}_{29}$, TiO_2 and Nb_2O_5 and an inner layer consisting SiO_2 , as well as an internal oxidation region filled with large amount of oxides. Combined with the results in this work, it can be concluded that the glassy SiO_2 phase exists in the whole oxide scale.

Figure 7 shows the oxide scales formed on oxidized 0.15Dy alloy after oxidation at 1250 °C for 58 h. The oxide scales are featured by a lamellar structure and have nearly spalled from the 0.15Dy alloy. As shown in Fig. 7b, the oxidized Nbss and silicide phases are observed, i.e., the Nbss and silicide phases have not completely oxidized to be Nb_2O_5 , SiO_2 , $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, TiNb_2O_7 and $\text{Ti}_{0.4}\text{Cr}_{0.3}\text{Nb}_{0.3}\text{O}_2$. It suggests that the oxide scale on Nb–Si-based alloy has fallen off before exhaustive oxidation. Measured by EPMA-WDS, the composition of the oxidized Nbss is 65.72O–19.29Nb–0.98Si–11.08Ti–1.52Cr–0.81Al–0.60Hf (at.%), and the composition of the oxidized silicide is

65.66O–14.30Nb–14.27–Si4.71–Ti0.15Cr–0.17Al–0.74Hf (at.%). Both Nbss and silicide have absorbed a huge amount of oxygen (> 60 at.%). Besides, the element of Dy is not detected in the oxidized Nbss and silicide phases.

Figure 8 shows the sectional microstructure of the four Nb–Si-based alloys after oxidation at 1250 °C for 58 h. The oxide scales grown on each alloy have fallen off, and bare alloys are exposed to the high-temperature environment. The outmost oxidized Nbss phases and silicides are observed to generate a porous oxide scale with insufficient adherence to the Nb–Si-based alloy. It can be inferred that these porous oxide scales would fall off during long exposure time, showing a lamellar structure eventually. In addition, the oxides of TiO_2 are formed, either at the interfaces between Nbss and silicide or inside the Nbss phases. The TiO_2 oxides at the interfaces are larger in size, in comparison with those inside the Nbss phases, suggesting the preferential oxidation of Ti at the interfaces between Nbss and silicide. Figure 9 shows the distributions of O, Nb, Si, Ti, Al, Cr and Dy on the cross sections of 0.15Dy alloy after oxidation at 1250 °C for 58 h. The porous oxide scale has a higher content of oxygen and a lower content of alloying element including Nb, Si, Ti, Al and Cr. Those phases richer in Si are silicides, and those

Fig. 6 TEM images of the oxide scale grown on 0.15Dy-doped Nb–Si-based alloy after oxidation at 1250 °C for 58 h **a, b** and the typical selected-area diffraction of $\text{Ti}_{0.4}\text{Cr}_{0.3}\text{Nb}_{0.3}\text{O}_2$ **c**, Nb_2O_5 **d**, TiNb_2O_7 **e** and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ **f**. The inset in **b** shows the typical selected-area diffraction pattern of SiO_2

Table 2 Compositions of the oxides grown on 0.15Dy after oxidation at 1250 °C for 58 h (at.%)

	Crystal structure	Composition					
		O	Nb	Si	Ti	Cr	Al
SiO_2	Amorphous	66.76	–	33.24	–	–	–
Nb_2O_5	Monoclinic	62.44	29.21	–	8.35	–	–
TiNb_2O_7	Monoclinic	72.45	18.94	–	8.61	–	–
$\text{Ti}_2\text{Nb}_{10}\text{O}_{25}$	Monoclinic	57.76	31.45	–	10.79	–	–
$\text{Ti}_{0.4}\text{Cr}_{0.3}\text{Nb}_{0.3}\text{O}_2$	Tetragonal	49.93	14.90	–	24.71	10.46	–

particles richer in Ti and O are the oxides of TiO_2 . It is worth noting that a homogeneous distribution of Dy is observed.

4 Discussion

Figure 10 shows the Ellingham–Richardson diagram of Nb, Si, Ti, Cr, Al, Hf and Dy, illustrating the thermodynamic stability of selected oxides. The Gibbs energies of

the oxides (ΔG^0) of these selected oxides are in order below:

$$\Delta G_{\text{Dy}_2\text{O}_3}^0 < \Delta G_{\text{HfO}_2}^0 < \Delta G_{\text{Al}_2\text{O}_3}^0 < \Delta G_{\text{TiO}_2}^0 < \Delta G_{\text{SiO}_2}^0 < \Delta G_{\text{SiO}_2}^0 < \Delta G_{\text{NbO}}^0 < \Delta G_{\text{Nb}_2\text{O}_5}^0 < \Delta G_{\text{Cr}_2\text{O}_3}^0$$

Due to the large content of Ti in the Nb–Si-based alloys (24 at.%) and its high oxygen affinity (lower Gibbs energy of the TiO_2 oxide), a number of TiO_2 oxides are formed both inside Nbss and at the interfaces between Nbss and silicide (Fig. 8). Cr_2O_3 and Nb_2O_5 have a similar Gibbs

Fig. 7 **a** Cross sections of the layer-structured oxide scale formed on 0.15Dy-doped Nb–Si-based alloy after oxidation at 1250 °C for 58 h. **b** The microstructure of the oxide scale at a high magnification

Fig. 8 Sectional microstructures of Dy-doped Nb–Si-based alloys after oxidation at 1250 °C for 58 h: **a** base alloy; **b** 0.05Dy alloy; **c** 0.10Dy alloy; **d** 0.15Dy alloy. **a** Displays the vertical microstructure parallel to DS direction. **b**, **c**, **d** show the transversal microstructures perpendicular to DS direction

energy, suggesting that their formations are almost simultaneous during high-temperature oxidation. Then, Cr_2O_3 and Nb_2O_5 react to form CrNbO_4 through the following reaction [31]:

CrNbO_4 has been found to improve the oxidation resistance of Nb–Si-based alloys, and a large amount of Cr added in the Nb–Si-based alloys produced a higher volume of CrNbO_4 and resultant a reduced oxidation rate [12, 13, 32].

The Gibbs energy of Dy_2O_3 is the lowest, suggesting the highest activity of the rare earth element of Dy. Apart from

Dy, it is now well established that small additions of reactive elements (typically 0.01–0.5 wt%), e.g., Y, Hf, La and Ce, generate pronounced effects on the oxidation resistance of alloys and coatings [33–36]. A number of investigations have reported small additions of reactive elements resulted in a better adherence and a reduced growth kinetics of protective alumina- and chromia-based surface scales, by strengthening the mechanical interlocking of the scale through the formation of oxide pegs at the scale/alloy interface [37–39] or changing growth mechanism of oxides resulting in reduced growth stresses [36, 40]. But it is a different case for the oxidation of Nb–

Fig. 9 Elemental X-ray mapping of 0.15Dy-doped Nb–Si-based alloy after oxidation at 1250 °C for 58 h obtained using WDS attached with EPMA

Fig. 10 Ellingham–Richardson diagram illustrating the thermodynamic stability of selected oxides (plotted with HSC Chemistry 6.0)

Si-based alloys, due to the absence of adherent and protective oxide scales of Cr_2O_3 or Al_2O_3 on the surface. The

protectiveness provided by glassy SiO_2 resulting from the decomposition of silicides is limited, due to its insufficient

volume, unless these elements that can promote the formation of SiO_2 are added, such as Ge and B. Previous investigations [9, 15, 41] have reported that the lack of protective oxide scales allows the continuous adsorption, dissolution and diffusion of oxygen through the Nbss phases, because of the quite high oxygen solubility of oxygen inside Nbss phases. Grain boundary and phase interface are typically the short-cuts for the diffusion of oxygen. Thus, the oxidation of Dy, Hf and Ti, which have a higher affinity for oxygen than Nb (Fig. 10), preferentially takes place at grain boundary and phase interfaces. The reactive elements tend to promote the selective oxidation of Al and Cr [35, 39, 42], but the protective Cr_2O_3 or Al_2O_3 oxide scale still cannot be produced on Dy-doped Nb–Si-based alloys due to the limited concentrations of Al and Cr in the alloys and the high permeability of Nbss for oxygen. Unlike the reactive element dopants in β -NiAl alloys acting as vacancy sinks to suppress void formation at the alloy/oxide interfaces [39], the continuation of the accelerated oxidation of Al and Cr as well as other alloying elements typically leads to the development of voids triggered by the Kirkendall effect. These voids are covered with discontinuous oxide particles, and the glassy SiO_2 phase is not capable of healing all the voids. According to the results in Fig. 3, the thermogravimetric curves of the four Nb–Si-based alloys display parabolic oxidation kinetics at the early stage during oxidation; namely, the transport of ions across the scale is the oxidation rate-controlling process. The oxide scale with more voids therefore increases the oxidation rate of Nb–Si-based alloys. After oxidation at 1250 °C for 58 h, these voids aggregate to generate a multitude of pores in the oxide scale. It can thus be concluded that the addition of Dy results in the formation of a more loose and less compact oxide scale. The porous oxide scale fails to protect Nb–Si-based alloys from severe oxidation, leading to a higher weight gain after oxidation.

The insufficient oxidation resistance of Nb–Si-based alloys is due to the large amount of the Nb_2O_5 products. The formation of Nb_2O_5 normally causes considerable volume expansion (about 169%) [43]. Resultantly, extensive compressive stress is created in the oxide scale, leading to the cracking of oxide scales, and this may explain the loose oxidation products grown on Nb–Si-based alloys (Fig. 8). In addition, thermal stress tends to be generated during cooling, due to the difference in thermal-expansion coefficient of the Nb–Si-based alloys and oxides. Especially, the exposure to the cyclic temperature generates more stresses than isothermal exposure. Both growth stresses and thermal stresses induce the spalling of oxides and the cracking of oxide scales on Nb–Si-based alloys. Unfortunately, according to Fig. 8, the addition of Dy does not significantly reduce stress generation in the oxide scales and enhance their adherence to Nb–Si-based

alloys. It may even produce an adverse effect on the scale adherence, as the oxide scales grown on Dy-doped Nb–Si-based alloys have more porous than the Dy-free alloys.

5 Conclusions

1. The main phases of the base alloy, 0.05Dy alloy, 0.10Dy alloy and 0.15Dy alloy were Nbss, $\alpha\text{Nb}_5\text{Si}_3$ and $\gamma\text{Nb}_5\text{Si}_3$. The Dy addition has no obvious effect on the phase constitution and the microstructures of Nb–Si-based alloys.
2. The addition of Dy caused a larger weight gain of Nb–Si-based alloys after oxidation at 1250 °C for 58 h, and a higher amount of Dy addition resulted in a larger weight gain. The thermogravimetric curves of Dy-doped Nb–Si-based alloys showed parabolic oxidation kinetics firstly and then linear oxidation kinetics. It was found that the addition of Dy significantly accelerated the parabolic oxidation rate.
3. The oxides scales formed on Dy-doped Nb–Si-based alloys primarily consisted of Nb_2O_5 , $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, TiNb_2O_7 , $\text{Ti}_{0.4}\text{Cr}_{0.3}\text{Nb}_{0.3}\text{O}_2$ and glassy SiO_2 . Compared with the base alloy, a more porous and less protective oxide scale was grown on the Dy-doped Nb–Si-based alloys.

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