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Balancing mechanical properties and oxidation resistance of Nb-based refractory alloys: The alloying effect of Hf, W and Ti

Xiaolong Li^a, Huahai Mao^b, Farid Akhtar^c, Sheng Guo^{a,*}

^a Department of Industrial and Materials Science, Chalmers University of Technology, SE-41296, Gothenburg, Sweden

^b Thermo-Calc Software AB, Råsundavägen 18A, SE-169 67, Stockholm, Sweden

^c Division of Materials Science, Luleå University of Technology, Luleå, 97187, Sweden

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ABSTRACT

Nb-based refractory alloys are among those available materials for ultrahigh-temperature applications, while the trade-off between mechanical properties and oxidation resistance is a long-standing scientific challenge. Two commercial Nb alloys, C103 (Nb_{92.5}Hf_{5.5}Ti₂, at.%) and WC3009 (Nb_{74.5}Hf₂₀W_{5.5}, at.%), both with good room-temperature ductility but with various high-temperature strength, were modified here in this work with the intention to simultaneously achieve high strength at high temperatures, reasonable ductility at room temperature, and decent oxidation resistance. Particularly, the contents of alloying elements Hf, W and Ti were varied with reference to C103 and WC3009, considering Hf is good for strength and not detrimental to room-temperature ductility, W is particularly useful for the high-temperature strength, and Ti helps to improve oxidation resistance. The mechanical properties of these modified Nb-based refractory alloys were measured at room temperature and 1200 °C, and their oxidation resistance at 800 °C, 1000 °C and 1200 °C was also evaluated. Among the newly developed Nb-based refractory alloys, Nb_{68.5}Hf₁₅Ti₁₀W_{6.5} (10Ti) and Nb_{55.5}Hf₂₀Ti₁₅W_{9.5} (15Ti) showed much improved oxidation resistance compared to C103 and WC3009, at a relatively small cost of reduced high-temperature strength compared to WC3009. The alloying effect of Hf, W and Ti on the mechanical properties at both room-temperature and high-temperatures, the oxidation resistance, and more importantly their balance was discussed, providing important insights into the further development of Nb-based refractory alloys targeting ultrahigh-temperature applications.

1. Introduction

Nb-based refractory alloys are well-known ultrahigh-temperature (above 1000 °C) structural materials, due to their inherent properties including low density of 8.57 g/cm³, high melting point of 2477 °C and low ductile-brittle transition temperature (DBTT) between −100 °C to −195 °C [1,2]. Nevertheless, they still suffer from the long-standing trade-off among materials requirements for ultrahigh-temperature applications, most importantly, high strength at high temperatures, reasonable ductility at room temperature [3–6], and decent oxidation resistance in the service temperature range [7–9]. Additionally, low density is preferred from the energy saving perspective, and microstructural and thermal stability are expected for them to function reliably at high temperatures [10,11]. Not surprisingly, it is demanding to identify materials that can satisfactorily meet all these requirements: satisfying one requirement could well be at the cost of jeopardizing

others, and that is also the case for Nb-based refractory alloys. They can either have high room-temperature ductility but not so good high-temperature strength (e.g. C103, Nb-10Hf-1Ti, wt.%, or Nb_{92.5}Hf_{5.5}Ti₂, at.%), or have decent high-temperature strength and also good room-temperature ductility but lacking oxidation resistance (e.g. WC3009, Nb-30Hf-9W, wt.%, or Nb_{74.5}Hf₂₀W_{5.5}, at.%). Depending on their properties, these Nb-based refractory alloys have been used for either long-term operations at 1000–1200 °C, or for short-term operations at 1200–1700 °C [1,12].

On the other hand, continuous efforts have been dedicated to simultaneously achieve high strength at high temperatures, reasonable ductility at room temperature, and decent oxidation resistance despite formidable challenges, and consequently the role of different alloying elements has been known better out of previous efforts [1,13–17]. For instance, the alloying of heavy elements Mo and/or W benefits the strength and particularly the strength at high temperatures by solid

* Corresponding author.

E-mail address: sheng.guo@chalmers.se (S. Guo).

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solution hardening, although at the expense of reduced ductility at room temperature and increased DBTT. The alloying of Ta (density of 16.65 g/cm³) with low Young's modulus [12] can be used as an alternative for Mo or W to bypass the strength-ductility tradeoff, but a much higher content than Mo/W is needed for the comparable strengthening effect, therefore undesirably increasing the density. Secondary phase dispersion strengthening (e.g. carbides, oxides and nitrides), where secondary phases are introduced via either solidification plus subsequent precipitation or the powder metallurgy route, could be an option for overcoming the trade-off between strength and ductility, although it is highly challenging to control the secondary phase dispersion and the associated thermal or thermal-mechanical treatments [18,19]. Regarding oxidation resistance, the heavy alloying of Al or Si, instead of the traditionally used Ti with a reasonable Pilling–Bedworth ratio of 1.73 [20], is efficient in reducing the oxidation weight gain [7] and forming dense and protective oxidation scales at elevated temperatures; their heavy alloying however could easily stimulate the formation of intermetallics and substantially jeopardize the ductility at room temperature [21,22].

The aim of the present work is to simultaneously achieve high strength at high temperatures, reasonable ductility at room temperature, and decent oxidation resistance in Nb-based refractory alloys. Here, we developed several new Nb-based refractory alloys by modifying the compositions of two commercial Nb alloys, i.e., C103 (Nb_{92.5}Hf_{5.5}Ti₂, at. %) and WC3009 (Nb_{74.5}Hf₂₀W_{5.5}, at. %), both with decent room-temperature ductility while the high-temperature strength of the latter is much higher than the former [12]. The rationale behind the alloy design is that: 1) an appropriate combination (from the alloying elements perspective) of C103 and WC3009 would maintain good room-temperature ductility and achieve reasonably good high-temperature strength; 2) by increasing the content of alloying elements that are beneficial for the oxidation resistance, without jeopardizing much the room-temperature ductility and high-temperature strength, a good balance of mechanical properties and oxidation resistance would be realized. Regarding the choice of alloying elements, Hf is good for solid solution hardening, and it does not negatively impact the DBTT of Nb; W is particularly useful for solid solution hardening at elevated temperatures; Ti helps to lower the density and at the same time to improve oxidation resistance, without increasing the DBTT of Nb. Naturally, the first modified composition is to mix 50 at. % of C103 and 50 at. % of WC3009 and one gets Nb_{83.5}Hf_{12.75}Ti₁W_{2.75} (at. %). Next, by fixing the ratio of Hf/Ti to 2.73, the Hf/Ti ratio in C103, while increasing the contents of both Hf and Ti, the second modified composition of C103 becomes Nb_{79.5}Hf₁₅Ti_{5.5}. Based on Nb_{79.5}Hf₁₅Ti_{5.5}, one now also adds W, using the ratio of Hf/W 3.6, the Hf/W ratio in WC3009, the composition evolves to Nb_{75.4}Hf₁₅Ti_{5.5}W_{4.1}; one now further increases the total Ti content to 10 at. % for the sake of improving oxidation resistance, and to compensate the softening at high-temperatures caused by this additional 4.5 at. % Ti, an extra 2.25 % at. % (half of additional Ti) of W is added [23] to make the total W content around 6.5 at. %. Thus, the third modified composition is Nb_{68.5}Hf₁₅Ti₁₀W_{6.5} (at. %). Similarly, one modifies WC3009 and by fixing the Hf/Ti and Hf/W ratio to 2.73 and 3.6, respectively, one gets Nb_{67.2}Hf₂₀Ti_{7.3}W_{5.5}; by further increasing the total Ti content to 15 at. % and compensating the additional 7.7 at. % Ti by 3.85 at. % W, the fourth modified composition Nb_{55.5}Hf₂₀Ti₁₅W_{9.5} is created. Finally, together with C103 and WC3009, the following six alloys were studied here in order of increasing Ti content: Nb_{74.5}Hf₂₀W_{5.5} (WC3009), Nb_{83.5}Hf_{12.75}Ti₁W_{2.75}, Nb_{92.5}Hf_{5.5}Ti₂ (C103), Nb_{79.5}Hf₁₅Ti_{5.5}, Nb_{68.5}Hf₁₅Ti₁₀W_{6.5}, and Nb_{55.5}Hf₂₀Ti₁₅W_{9.5} (all given in at. %).

2. Experimental method

Nb-based refractory alloys with nominal compositions of Nb_{92.5}Hf_{5.5}Ti₂, Nb_{74.5}Hf₂₀W_{5.5}, Nb_{83.5}Hf_{12.75}Ti₁W_{2.75}, Nb_{79.5}Hf₁₅Ti_{5.5}, Nb_{68.5}Hf₁₅Ti₁₀W_{6.5}, and Nb_{55.5}Hf₂₀Ti₁₅W_{9.5} (all given in at. %, denoted

Table 1

EDS measured compositions (at. %) of the Nb-based refractory alloys.

Alloys	Nb	Hf	Ti	W
C103	92.3	5.8	1.9	–
WC3009	75.3	19.7	–	5.0
1Ti	83.8	13.0	1.1	2.0
5.5Ti	79.9	15.0	5.1	–
10Ti	68.5	15.7	10.0	5.8
15Ti	55.8	20.4	14.6	9.3

as C103, WC3009, 1Ti, 5.5Ti, 10Ti, and 15Ti afterwards) were produced by arc melting of high purity (>99.95 %) metals at least 5 times to ensure chemical homogeneity followed by drop casting with ingot dimensions of 10 mm × 10 mm × 40 mm. Microstructure and chemical compositions were examined by field emission gun scanning electron microscope (FEG-SEM, GeminiSEM 450) equipped with backscattered electron (BSE) detector, energy dispersive spectrometer (EDS) and electron backscatter diffractometer (EBSD). Vickers hardness at room temperature was tested under a load of 5 kgf for a duration of 15 s (Struers DuraScan-70 G5). The hardness value was averaged out from over 20 indentations. Compositional analysis from SEM-EDS is given in Table 1 below. The crystal structure was measured by X-ray diffractometer (XRD, Bruker D8 Advance), using Cu-K_{α1} radiation in the 2θ range of 20° to 100°. Specimens for compressive tests were electrical discharge machined (EDM) to a cylinder with a diameter of 6 mm and a height of 9 mm. Compressive tests at room temperature were done using a universal testing machine (Instron 5500R) with an initial strain rate of 10^{−3} s^{−1} and a maximum engineering strain of 60 %, showing a very good agreement among multiple tests. Compressive tests at 1200 °C were carried out under a vacuum of 3.0 × 10^{−3} mbar on a Gleeble 3800 thermal-mechanical physical simulation system with an initial strain rate of 10^{−3} s^{−1} and a maximum engineering strain of 30 %. Each composition was tested 3 times at both temperatures to guarantee the reproducibility of the results.

Oxidation tests for the target alloys were carried out in a tube furnace pre-heated to 800 °C, 1000 °C and 1200 °C, respectively, for 1h, 8h and 24h in static laboratory air. When the time was due, the specimens were removed from the furnace and cooled in air. The specimens for oxidation tests were in the form of cubic blocks with approximate dimensions of 4 mm × 4 mm × 4 mm. Before the oxidation tests, the surfaces of each specimen were ground to 800-grid finish, ultrasonically cleaned in the ethanol and air dried. The surface area (including all six faces) was accurately calculated by carefully measuring the dimensions of each specimen. The specimen was loaded in a crucible with dimensions of 20 mm × 20 mm × 20 mm and the crucible with the specimen inside was weighed together before and after the oxidation tests, using a highly sensitive balance (to the precision of 10^{−6} g) to evaluate the weight change. To prevent any loss of oxidation products during the oxidation tests and/or cooling in the air, an alumina lid was placed to cover the crucible throughout the oxidation and weighing process. Finally, the specific mass change was determined, dividing the measured mass change by the initial surface area of the specimen.

3. Results and discussion

3.1. Microstructure

EBSD results for six studied Nb-based refractory alloys are shown in Fig. 1, from which average grain size and grain size distribution can be seen. The examined areas were taken near the center of the cross-section slice with dimensions of 10 mm × 10 mm × 2 mm, perpendicular to the length direction of the cast ingot. The grain size of C103 is the largest, with an average diameter of 85.91 μm, while that of WC3009 is the smallest with an average diameter of 30.64 μm. Grain sizes of the four newly developed Nb-based refractory alloys have an average diameter

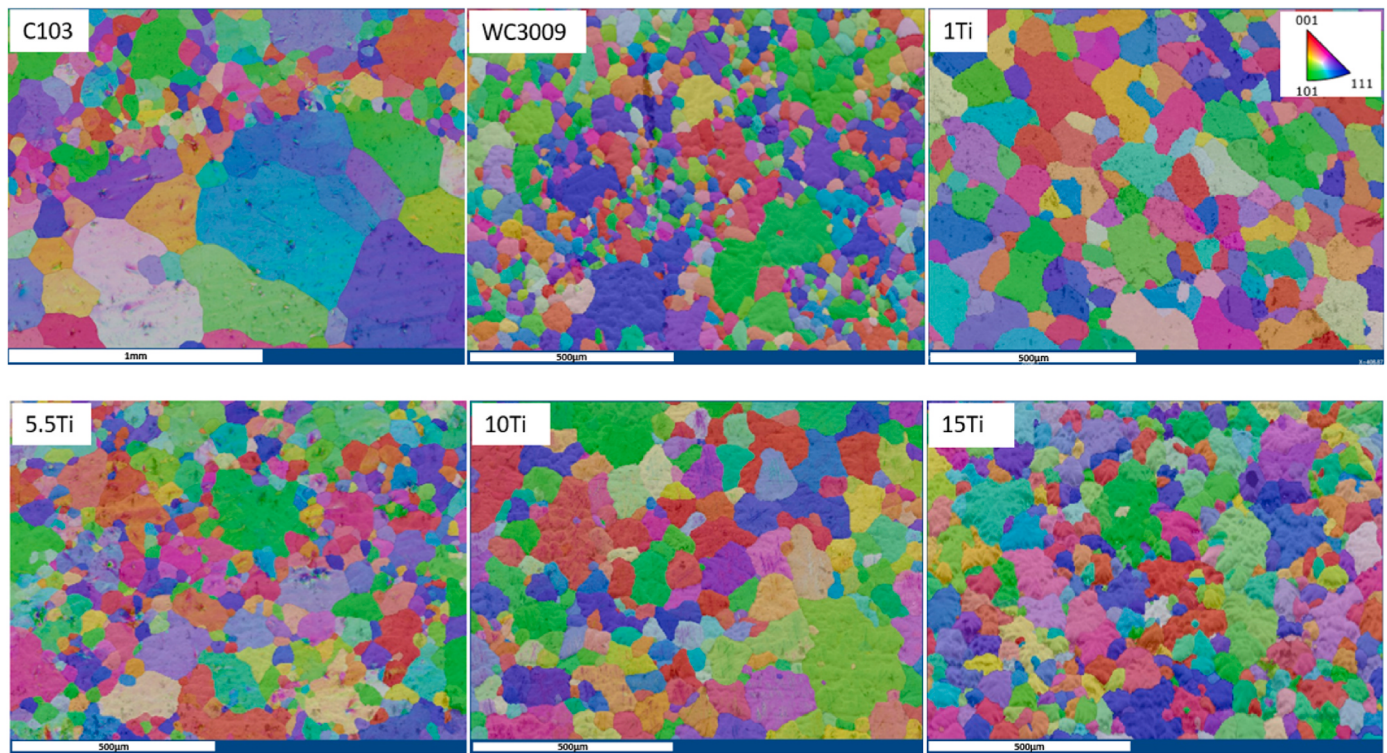


Fig. 1. Microstructure of the Nb-based refractory alloys based on EBSD analysis.

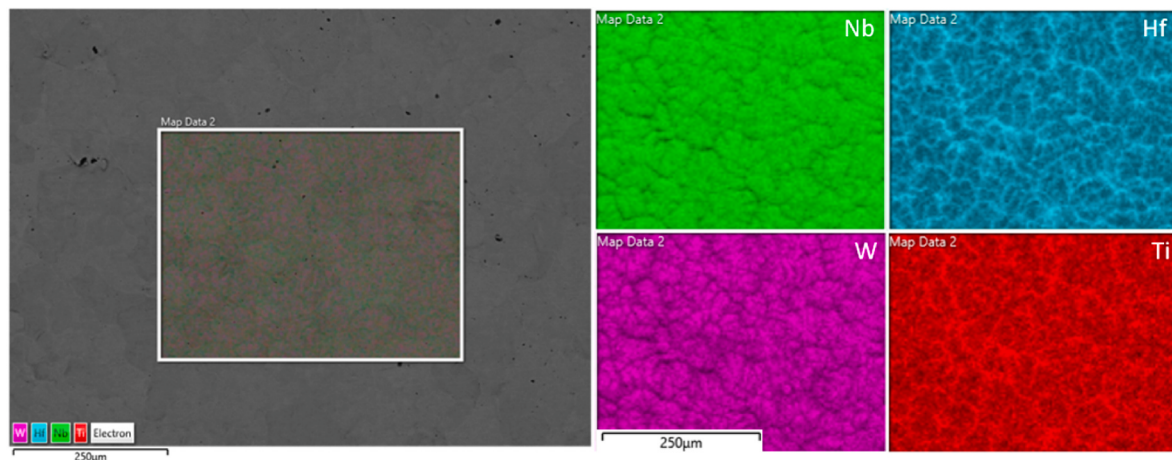


Fig. 2. EDS elemental mapping of the 10Ti alloy.

range between 37.74 μm and 61.59 μm .

EDS elemental mapping of the 10Ti alloy is shown in Fig. 2, giving a typical example of the dendritic microstructure seen in these Nb-based refractory alloys, with enrichment of Nb and W having high melting points in the dendritic region, while enrichment of Hf and Ti with relatively lower melting points in the inter-dendritic region. Similar patterns are seen in all other alloys studied here, and they are not shown for simplicity. The XRD results shown in Fig. 3 confirm the single-phase bcc crystal structure in all the Nb-based refractory alloys that were studied here.

3.2. Mechanical properties

Hardness of the Nb-based refractory alloys at room temperature is shown in Table 2, where C103 exhibits the lowest hardness, 148 HV5,

while the 15Ti alloy exhibits the highest hardness, 314 HV5, and the other benchmark alloy WC3009 has the second highest hardness of 278 HV5. As expected, hardness in general shows a positive correlation with solute concentration in that the higher solute concentration the higher hardness, evidencing the solid solution strengthening in these single-phase Nb-based refractory alloys. In addition, hardness indeed has a better correlation to the solute concentration of Hf+W (Fig. 4(b)), than the total solute concentration of Hf+W+Ti (Fig. 4(a)), further indicating Hf and W contribute to hardness more significantly than Ti, in agreement with the known alloying effects.

Fig. 5 shows the compressive true strain-stress curves for all six alloys at room temperature (RT) and 1200 °C. It is noted that all the alloys that were tested here did not show any sign of fracture when reaching the maximum engineering strain limited by the testing facility. Therefore, the compressive strain is not discussed, and the peak stress at RT could

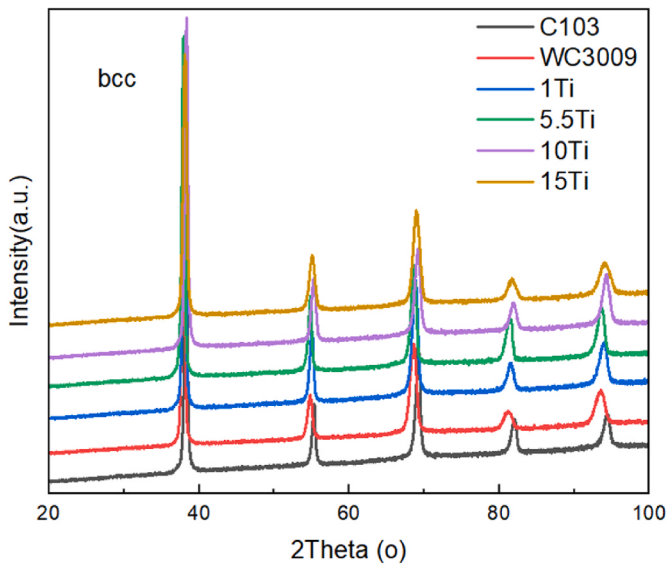


Fig. 3. XRD pattern of the Nb-based refractory alloys in the as-cast condition.

Table 2
Room temperature Vickers hardness with the actual solute concentration.

Alloys	Hardness (HV5)	Solute concentration (Hf+W+Ti, at.%)	Solute concentration (Hf+W, at.%)
C103	148 ± 3	7.7	5.8
WC3009	278 ± 5	24.7	24.7
1Ti	220 ± 3	16.1	15
5.5Ti	202 ± 3	20.1	15
10Ti	270 ± 2	31.5	21.5
15Ti	314 ± 4	44.3	29.7

unfortunately not be determined. As such, we focus here more on yield strength and its variation with composition and temperature, which are summarized in Table 3. One generic feature of compressive curves at RT is that they all show the work hardening behavior. In order of increasing yield strength, C103 has the lowest one of 367 MPa, followed by 1Ti and 5.5Ti which have the same yield strength of 566 MPa, then WC3009 and 10Ti with a yield strength of 762 MPa and 811 MPa, respectively. Finally, the 15Ti alloy has the highest yield strength of 949 MPa. The trend of yield strength at RT is rather consistent with that of hardness (although 10Ti has a slightly lower hardness, but a higher yield strength than WC3009), again indicating that the strengthening or hardening at

RT is generally proportional to the solute concentration and governed by the solid solution strengthening/hardening mechanism.

By contrast, compressive curves at 1200 °C show a general softening behavior after yielding, suggesting dynamic recovery and recrystallization dominate during the high-temperature deformation. The yield strength at 1200 °C does not follow the same trend of hardness (comparing Figs. 6(a) and 4(a)), although C103 still has the lowest yield strength of 170 MPa. In order of increasing yield strength, C103 is followed by 5.5Ti, with the yield strength of 228 MPa, then 15Ti, 10Ti and 1Ti, with a similar yield strength around 260 MPa. WC3009, the benchmark alloy with known good high-temperature strength, has the highest yield strength of 343 MPa. By analyzing the correlation between yield strength at 1200 °C and the solute concentration, it seems that the Ti and W content plays a critical role: C103 and 5.5Ti with the lowest yield strength have the Ti content of about 2 at.% and 5 at.%, respectively, and no W addition; WC3009 with the highest yield strength has no Ti addition and 5 at.% W; 15Ti, 10Ti and 1Ti, with the intermediate yield strength, have the W addition of 9.3 at.%, 5.8 at.% and 2 at.%, respectively. One could clearly see that W addition is beneficial for the high-temperature strength, while Ti addition is detrimental for that. To compensate for the detrimental effect caused by Ti addition, more W is needed than what was added here, which of course will bring adverse effect on density. Roughly, yield strength at 1200 °C has a positive correlation with the solute concentration of Hf+W–Ti (Fig. 6(b)), although the compensation effect between Ti and W at high Ti contents complicates the correlation (1Ti, 5Ti and 10Ti exhibit a similar yield strength around 260 MPa).

We now look at the ratio of yield strength at 1200 °C to yield strength at RT, the temperature dependence of the yield stress [24–26], which could be used to evaluate the ability of the alloys to withhold the yield strength from RT up to 1200 °C. The ratios are given in Tables 3 and it is seen from the table that C103, 1Ti and WC3009 have a high ratio of 0.46, 0.46 and 0.45, respectively, while 5.5Ti, 10Ti and 15Ti have a relatively low ratio of 0.40, 0.32 and 0.27, respectively. The adverse effect of Ti addition in achieving a more gradual degradation of yield strength with increasing temperature, is again revealed.

3.3. Oxidation behavior

Optical images of oxidized specimens at different oxidation conditions are shown in Fig. 7. Pesting, or disintegration into powder upon oxidation, appears at almost all conditions and it generally gets worse with increased exposure time and increased temperature. Nevertheless, the beneficial effect from high Ti addition on the improved oxidation resistance is obvious, seen in the 10Ti and 15Ti alloys. A color change of

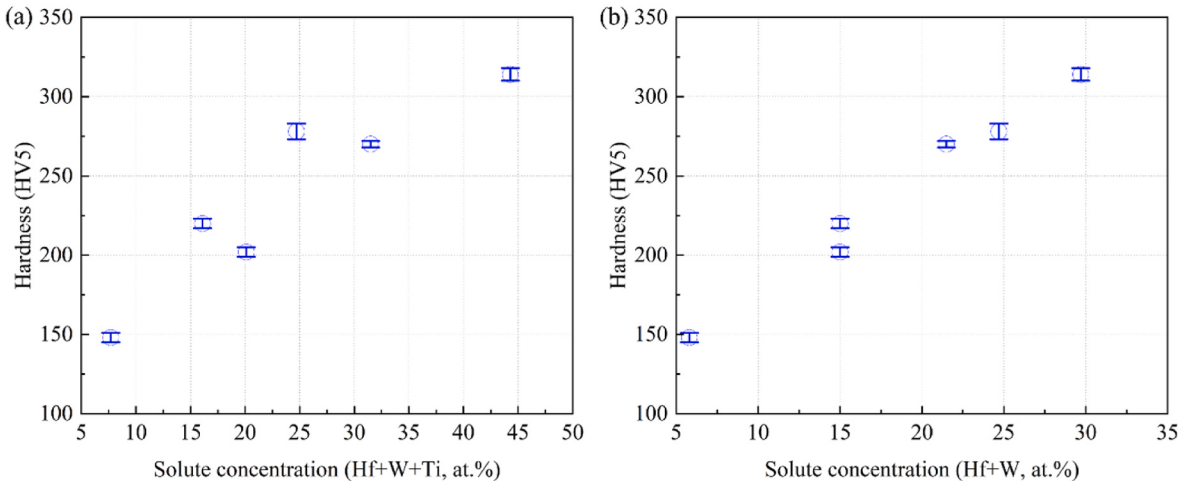


Fig. 4. Vickers hardness with the actual solute concentration (from Table 1): (a) Hf+Ti+W, (b) Hf+W.

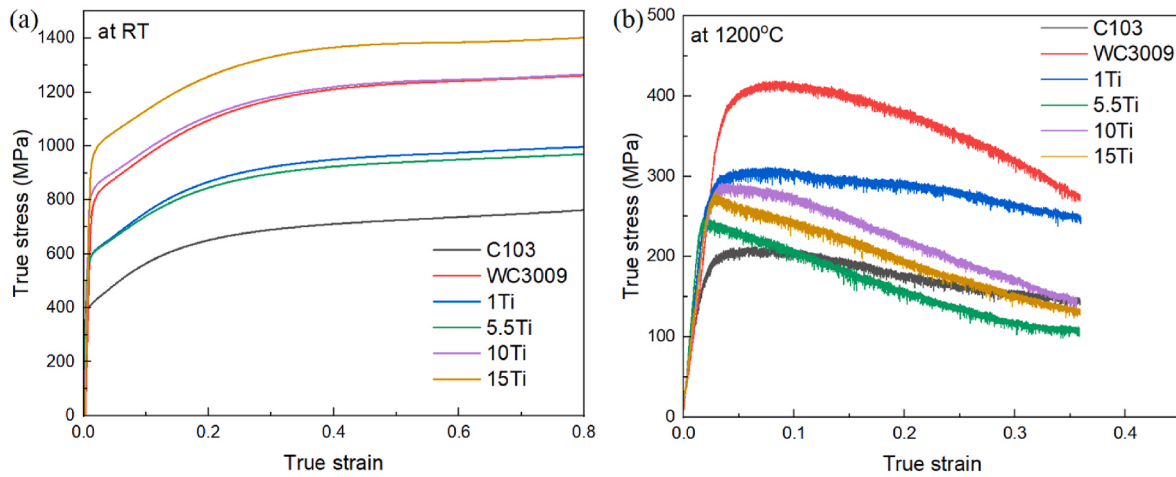


Fig. 5. Compressive true strain-stress curves for the Nb-based refractory alloys at (a) RT and (b) 1200 °C.

Table 3

Yield strength at RT and 1200 °C and the ratio between these two, for the Nb-based refractory alloys.

Alloy ID	C103	WC3009	1Ti	5.5Ti	10Ti	15Ti
σ_y^{RT}	367	762	566	566	811	949
$\sigma_y^{1200^\circ C}$	170 ± 9	343 ± 11	262 ± 5	228 ± 6	259 ± 9	254 ± 17
$\sigma_y^{1200^\circ C} / \sigma_y^{RT}$	0.46	0.45	0.46	0.40	0.32	0.27

oxidation products is also observed for different alloys: for the C103 and the 5.5Ti alloys without any W additions, oxides first look yellowish for C103 and blackish for 5.5Ti at 800 °C, then turn into yellowish for both alloys at 1000 °C and 1200 °C; for the other four alloys with W additions, oxides first look blackish at 800 °C, transit to greenish at 1000 °C, and finally turn to yellowish at 1200 °C.

The oxidation kinetics curves of specimens oxidized at 800 °C, 1000 °C and 1000 °C are shown in Fig. 8. The oxidation kinetics were quantified, using the growth rate law expressed in Eq. (1) [27]:

$$\frac{\Delta m}{SA} = kt^n \quad (1)$$

Here, Δm and SA are the mass change in mg and the initial surface area in cm^2 , $\frac{\Delta m}{SA}$ is the specific mass change with the unit of mg/cm^2 , k is

the rate constant, t is the oxidation exposure time, n is the time exponent. Fitting curves are shown in Fig. 8 and the fitting parameters are summarized in Table 4 where R^2 indicates the quality of the fitting. k is dependent on n , and k cannot be compared directly with different n values; n , however, can be compared directly and it indicates different active oxidation mechanism. For C103, fitting was done up to 8h at all three oxidation temperatures, since with the exposure time longer than 8h, the specimens almost completely disintegrated into powders, which can be seen from the optical images shown in Fig. 7; the weight change was however measured at all temperatures. Overall, C103 has the highest weight gain, 10Ti and 15Ti have the lowest weight gain (with one exception for WC3009 at 1200 °C, where the weight gain for WC3009 is higher than 10Ti, but lower than 15Ti), while 1Ti, 5.5Ti and WC3009 have the intermediate weight gain, which is consistent with the observation from the optical images shown in Fig. 7.

Fitting curves at 800 °C show a nearly linear behavior for alloys with low Ti contents, C103, WC3009 and 1Ti, with fitted n close to 1, suggesting that oxidation is controlled by the interface reaction between oxygen and the base alloy. With the linear oxidation behavior, the oxides formed cannot effectively block the further attack from oxygen and they kept spalling off. This is unsurprising since it is known that the dominating $4\text{Nb} + 5\text{O}_2 \rightarrow 2\text{Nb}_2\text{O}_5$ reaction will result in a high oxide-metal volume ratio (Pilling-Bedworth ratio) of 2.69 [7], providing no protection to the base alloy. The fitted n is however <1 for 10Ti, which also has the lowest weight gain among all 6 alloys. Due to the beneficial Ti additions, the weight gain after is lowered from $251 \text{ mg}/\text{cm}^2$ for C103

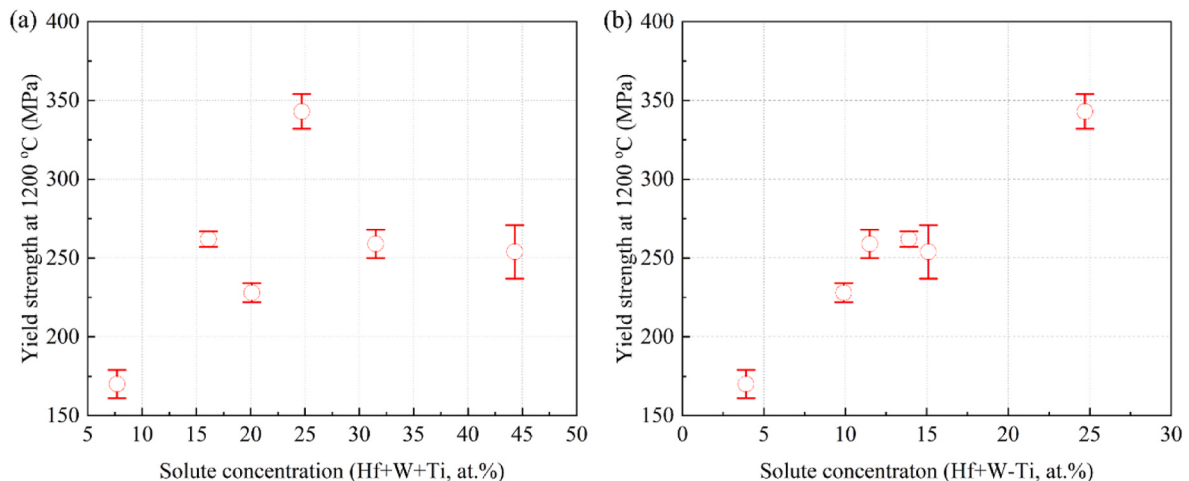


Fig. 6. Yield strength at 1200 °C with the actual solute concentration: (a) Hf+Ti+W, (b) Hf+W-Ti.

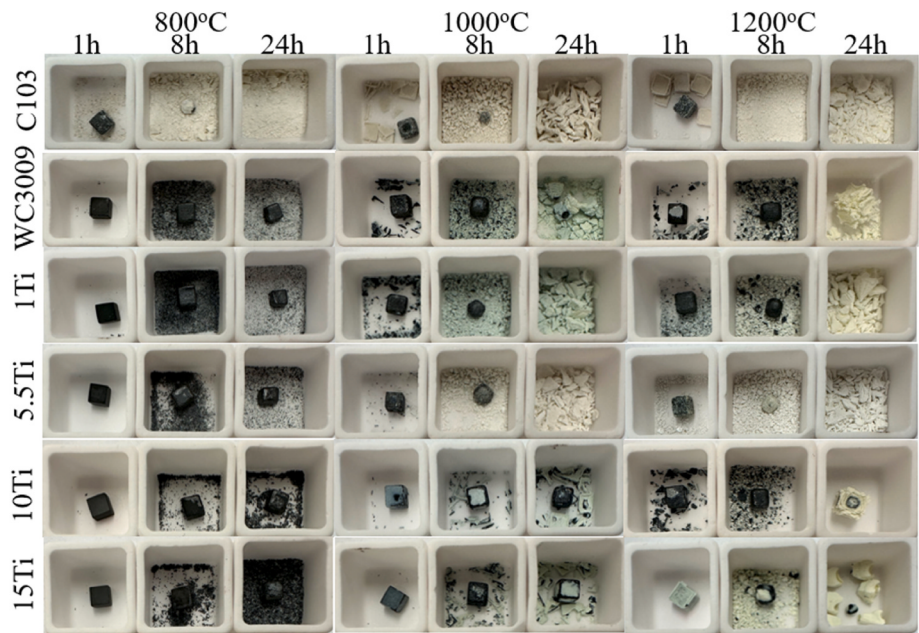


Fig. 7. Optical images of the oxidative specimens of the Nb-based refractory alloys at 800 °C, 1000 °C and 1200 °C after 1h, 8h and 24h of exposure, with the crucible dimensions of 20 mm × 20 mm × 20 mm.

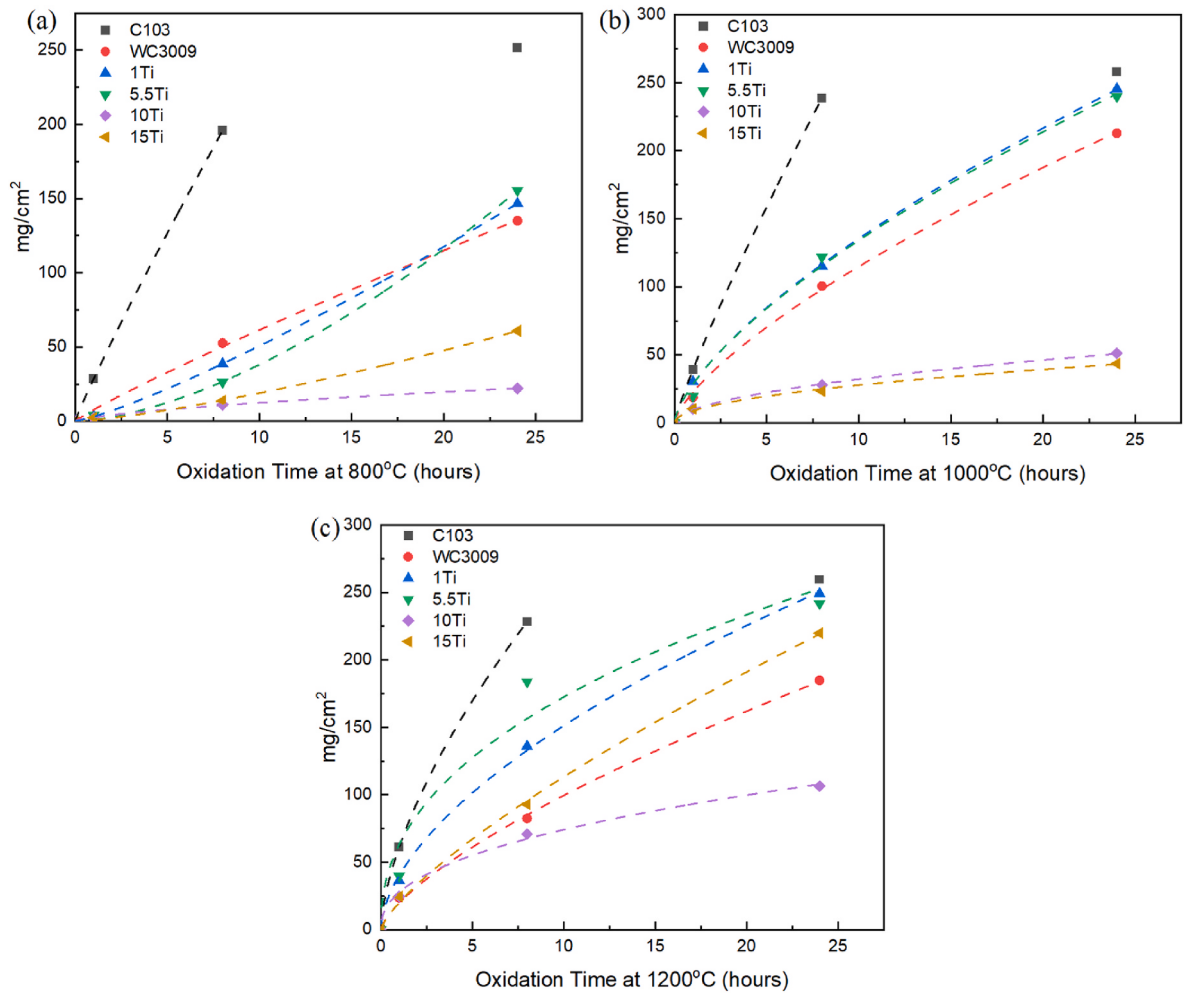


Fig. 8. Oxidation kinetics of the Nb-based refractory alloys at (a) 800 °C, (b) 1000 °C and (c) 1200 °C. The fitting curves follow Eq. (1) with the fitting parameters given in Table 4.

Table 4
Fitting parameters for oxidation kinetics curves shown in Fig. 8.

Alloys	k [mg cm ⁻² h ⁻ⁿ]	n	R ²
T = 800 °C			
C103 (0–8h)	28.53417 ± 0	0.92626 ± 0	1
WC3009	7.70065 ± 2.41644	0.90243 ± 0.10249	0.99621
1Ti	3.11551 ± 0.03144	1.21197 ± 0.00324	1
5.5Ti	0.95109 ± 0.30489	1.60376 ± 0.10171	0.99935
10Ti	2.66603 ± 0.44933	0.66829 ± 0.05645	0.99726
15Ti	0.89036 ± 0.27070	1.32905 ± 0.09711	0.99884
T = 1000 °C			
C103 (0–8h)	39.11504 ± 0	0.86956 ± 0	1
WC3009	22.45372 ± 2.5203	0.70864 ± 0.03739	0.99897
1Ti	28.41957 ± 1.30852	0.67797 ± 0.01540	0.99979
5.5Ti	28.40544 ± 6.62406	0.67383 ± 0.07804	0.99495
10Ti	9.62749 ± 0.84299	0.52345 ± 0.03007	0.99835
15Ti	8.78844 ± 1.58250	0.49963 ± 0.06216	0.99185
T = 1200 °C			
C103 (0–8h)	61.20487 ± 0	0.63323 ± 0	1
WC3009	19.75921 ± 2.68517	0.70222 ± 0.04530	0.99836
1Ti	40.13634 ± 3.34450	0.5761 ± 0.02832	0.99893
5.5Ti	63.15385 ± 29.5115	0.43644 ± 0.16386	0.93439
10Ti	27.70647 ± 3.88879	0.42771 ± 0.04934	0.99277
15Ti	19.97263 ± 2.89838	0.75371 ± 0.04808	0.99849

to 147 mg/cm² for 1Ti, to 22 mg/cm² for 10Ti after 24h of oxidation. Interestingly, the fitted *n* is > 1 for 5.5Ti and 15Ti, probably indicating breakaway oxidation, where an initially protective oxide layer becomes unstable and fails, leading to rapid oxidation. The complicated

contribution of Ti addition to the oxidation kinetics at 800 °C needs more attention in the following work, although the high Ti addition (10Ti and 15Ti) does help to lower the weight gain.

Except for C103, which still shows nearly linear behavior (*n* ~ 0.87), the fitting curves at 1000 °C seem to follow the nearly parabolic behavior (*n* 0.50–0.71). The weight gain is much lowered from 258 mg/cm² for C103, to 240 mg/cm² for 5.5Ti, and to 51 mg/cm² for 10Ti and 44 mg/cm² of 15Ti, clearly evidencing the beneficial effect from Ti addition on the improved oxidation resistance. The nearly parabolic behavior suggests that oxides formed at this temperature can partially adhere to the base alloy, slowing down further oxygen/base alloy reaction that occurs at the interface. Nevertheless, these oxides still spall off, as seen from the optical images given in Fig. 7, due to the high oxide-metal volume ratio. With comparable *n* values, *k* values for 10Ti and 15Ti specimens are much lower than those for 1Ti and 5.5Ti alloys, again indicating the slower oxide growth kinetics and the improved oxidation resistance.

Fitting curves at 1200 °C seem to also follow the parabolic behavior, but there is quite some difference among alloys. The weight gain is lowered from 260 mg/cm² for C103 to 242 mg/cm² for 5.5Ti, and to 106 mg/cm² for 10Ti. The fitted *n* values are 0.44 for 5.5Ti and 0.43 for 10Ti, indicating a parabolic behavior and the connected diffusion-controlled mechanism, with a much-lowered oxidation rate. The *k* value for 10Ti is however much lower than that of 5.5Ti, with comparable *n* values, suggesting a relatively higher activation barrier for oxidation in the former; while for 1Ti, C103, 15Ti and WC3009, the

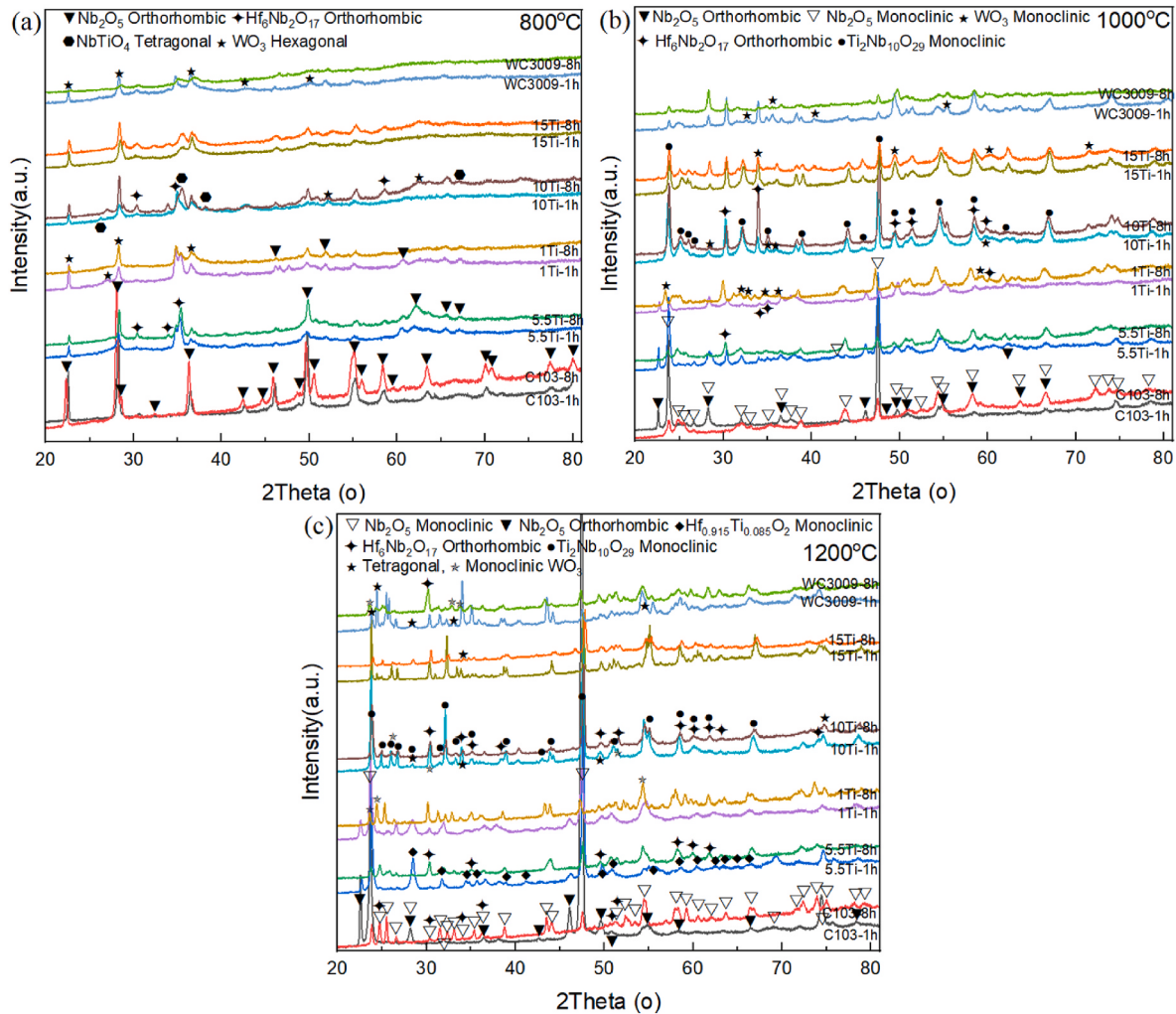


Fig. 9. XRD pattens of oxidation products for the Nb-based refractory alloys after 1h and 8h of oxidation exposure at (a) 800 °C, (b) 1000 °C and (c) 1200 °C.

Table 5
Summarized oxidation products for the Nb-based refractory alloys after 1h and 8h of exposure at 800 °C, 1000 °C and 1200 °C.

Alloys	Oxidation products		
C103	800 °C	1h	Nb ₂ O ₅ (orthorhombic)
		8h	
	1000 °C	1h	Nb ₂ O ₅ (orthorhombic), Nb ₂ O ₅ (monoclinic)
		8h	Nb ₂ O ₅ (monoclinic)
	1200 °C	1h	Nb ₂ O ₅ (monoclinic), Nb ₂ O ₅ (orthorhombic)
		8h	Nb ₂ O ₅ (monoclinic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic)
WC3009	800 °C	1h	Nb ₂ O ₅ (orthorhombic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic),
		8h	WO ₃ (hexagonal)
	1000 °C	1h	Nb ₂ O ₅ (monoclinic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic), WO ₃
		8h	(monoclinic)
	1200 °C	1h	Nb ₂ O ₅ (monoclinic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic), WO ₃
		8h	(tetragonal, monoclinic)
1Ti	800 °C	1h	Nb ₂ O ₅ (orthorhombic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic),
		8h	WO ₃ (hexagonal)
	1000 °C	1h	Nb ₂ O ₅ (orthorhombic), Nb ₂ O ₅ (monoclinic),
		8h	Hf ₆ Nb ₂ O ₁₇ (orthorhombic)
	1200 °C	1h	Nb ₂ O ₅ (monoclinic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic), WO ₃
		8h	(monoclinic)
5.5Ti	800 °C	1h	Nb ₂ O ₅ (orthorhombic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic)
		8h	
	1000 °C	1h	Nb ₂ O ₅ (orthorhombic), Nb ₂ O ₅ (monoclinic),
		8h	Hf ₆ Nb ₂ O ₁₇ (orthorhombic), Ti ₂ Nb ₁₀ O ₂₉ (monoclinic)
	1200 °C	1h	Nb ₂ O ₅ (monoclinic), Nb ₂ O ₅ (orthorhombic),
		8h	Hf ₆ Nb ₂ O ₁₇ (orthorhombic), Ti ₂ Nb ₁₀ O ₂₉ (monoclinic)
10Ti	800 °C	1h	Nb ₂ O ₅ (orthorhombic), NbTiO ₄ (tetragonal),
		8h	Hf ₆ Nb ₂ O ₁₇ (orthorhombic), WO ₃ (hexagonal)
	1000 °C	1h	Nb ₂ O ₅ (monoclinic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic),
		8h	Ti ₂ Nb ₁₀ O ₂₉ (monoclinic), WO ₃ (monoclinic)
	1200 °C	1h	Nb ₂ O ₅ (monoclinic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic),
		8h	Ti ₂ Nb ₁₀ O ₂₉ (monoclinic), WO ₃ (tetragonal, monoclinic)
15Ti	800 °C	1h	Nb ₂ O ₅ (orthorhombic), NbTiO ₄ (tetragonal),
		8h	Hf ₆ Nb ₂ O ₁₇ (orthorhombic), WO ₃ (hexagonal)
	1000 °C	1h	Nb ₂ O ₅ (monoclinic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic),
		8h	Ti ₂ Nb ₁₀ O ₂₉ (monoclinic), WO ₃ (monoclinic)
	1200 °C	1h	Nb ₂ O ₅ (monoclinic), Hf ₆ Nb ₂ O ₁₇ (orthorhombic),
		8h	Ti ₂ Nb ₁₀ O ₂₉ (monoclinic), WO ₃ (tetragonal, monoclinic)

fitted *n* values are 0.58, 0.63, 0.75 and 0.71, respectively, suggesting that they follow semi-parabolic behavior. Seen from Fig. 7, only oxides formed on the 10Ti specimen are still intact, while spalling off happens on the other five alloys. This could possibly be due to the unique smaller *k* and *n* values for the 10Ti alloy. Interestingly, the WC3009 alloy, with no Ti addition, shows a relatively good oxidation resistance at 1200 °C. The reason could be attributed to the high Hf content in this alloy and the formation of Hf-oxide helping to better adhere Nb₂O₅ to the base alloy [28,29].

XRD patterns of the oxidation products for Nb-base refractory alloys at 800 °C, 1000 °C and 1200 °C, after 1h and 8h of exposure, are shown in Fig. 9 and summarized in Table 5. The main oxide is Nb₂O₅ in all alloys, which is kinetically favored in Nb-based alloys and known to be with non-protective nature. Taking C103 as an example here, Nb₂O₅ is formed at three temperatures with only a small amount of Hf-oxide forming upon oxidation at 1200 °C. The formation of non-protective Nb₂O₅ is responsible for the catastrophic failure of oxide scales, known as pesting. It experiences a crystal structure change from orthorhombic at 800 °C, to a mixture of orthorhombic and monoclinic at 1000 °C, finally to monoclinic at 1200 °C. This change may correlate to the color change of oxides shown in Fig. 7, from blackish at 800 °C to yellowish at 1200 °C. An orthorhombic Hf₆Nb₂O₁₇ forms at 1200 °C,

which itself can be synthesized by solid-state reactions (e.g., annealing at high temperature) between HfO₂ and Nb₂O₅ (6HfO₂·Nb₂O₅) [30,32]. This complex oxide Hf₆Nb₂O₁₇ is more protective than the exclusive formation of HfO₂ and Nb₂O₅, and once it forms it slows down the oxidation rate [30,31]. Hf₆Nb₂O₁₇ appears in all oxidation conditions except for the C103 alloy with the least Hf content (5.5 at%) at 800 °C and 1000 °C. However, it shows at 1200 °C for C103, suggesting its formation requires a high thermal energy with low Hf contents. Monoclinic Hf_{0.915}Ti_{0.085}O₂, as another type of Hf oxide, appears only in 5.5Ti upon oxidation at 1200 °C for 1h, which is formed by partial Ti substitution of Hf in HfO₂, given the low Ti content. WO₃ forms in all W containing specimens. WO₃ could combine with Nb₂O₅ to form different complex oxides also via solid-state reactions, such as Nb₁₂WO₃₃ (monoclinic), Nb₁₆W₅O₅₅ (monoclinic), and Nb₆₀WO₁₅₃ (monoclinic), especially at 1200 °C here. WO₃ also experiences a change of crystal structure with temperatures, changing from hexagonal at 800 °C to monoclinic at 1000 °C and a mixture of monoclinic and tetragonal at 1200 °C. Due to the quick take-out of the specimen, the stable phase at high temperatures, i.e., the tetragonal WO₃ is preserved to room temperature in the 10Ti, 15Ti and WC3009 specimens, with W content of 6.5 at.%, 9.5 at.% and 5.5 at.%, respectively. This crystal structure change of WO₃ may also correspond to the color change in oxides as shown in Fig. 7. Regarding Ti containing oxides or complex oxides, monoclinic Ti₂Nb₁₀O₂₉ forms as the main Ti oxide, which itself can be synthesized by solid-state reactions between TiO₂ and Nb₂O₅ (2TiO₂·5Nb₂O₅) [33], and could well be the case seen in this work. The formation of Hf₆Nb₂O₁₇ and Ti₂Nb₁₀O₂₉ could be the reason for the much-improved oxidation resistance for the 10Ti and 15Ti alloys with actual Hf + Ti concentration of 25.7 at. % and 35.0 at.%, respectively.

Fig. 10 shows the backscattered electron images of cross-sections of Nb-based refractory alloys after 1h of oxidation at 800 °C, 1000 °C and 1200 °C. Generally, the outer oxide scales get thicker with the increase of temperature for all alloys, and the thickness is within the range of several hundreds of μm. There is a transition layer sitting between the outer oxide scale and the base alloy in the 10Ti, 15Ti and WC3009 alloys at 1000 °C, and only for the 10Ti alloy at 1200 °C; such a transition layer is not seen in alloys that were oxidized at 800 °C. Cracks mainly occur in the outer oxide scale due to the growth stress of oxides and the thermal stress during air cooling to room temperature, which are directly related to the oxide-metal volume ratio (Pilling–Bedworth ratio) for different metals and their coefficients of thermal expansion, respectively. Although there are several types of oxide formed simultaneously, Nb₂O₅ is the one kinetically favored, and it basically plays the dominant role in the stress distribution during growing oxides at high temperatures and the thermal expansion mismatch during the fast-cooling process to room temperature. With a high Nb₂O₅/Nb volume ratio of 2.69, growth of Nb₂O₅ will create a volume that is 2.69 times larger than the base metal Nb, causing crushing of oxides into one another due to the significant compressive stress within them. When the oxidized specimens were taken out from the furnace and cooled directly to room temperature, the volume shrinkage mismatch between the base alloy and the oxides formed, due to the difference in their coefficients of thermal expansion, induces cracks and leads to the spalling-off of the oxides.

Now we have a closer look at the oxidation fronts, with backscattered electron images for the 10Ti, 15Ti and WC3009 alloys shown in Fig. 11. For these alloys after 1h of oxidation at 1000 °C, the features are in general similar in that cracking with varying degrees seen in both the oxide scale and the transition layer. The stress generated is significant enough to cause the sort of self-sabotage in the outer oxide scale. Formation of the transition layer helps stress relaxation and prevents the direct contact between oxygen and the base alloy. As mentioned before, when it comes to the oxides formed at 1200 °C after 1h of oxidation, the transition layer is only seen in the 10Ti alloy. It can be concluded that the best oxidation resistance is achieved in the 10Ti alloy up to 1200 °C, when compared to the 15Ti and WC3009 alloys where the protective transition layer is not seen at 1200 °C.

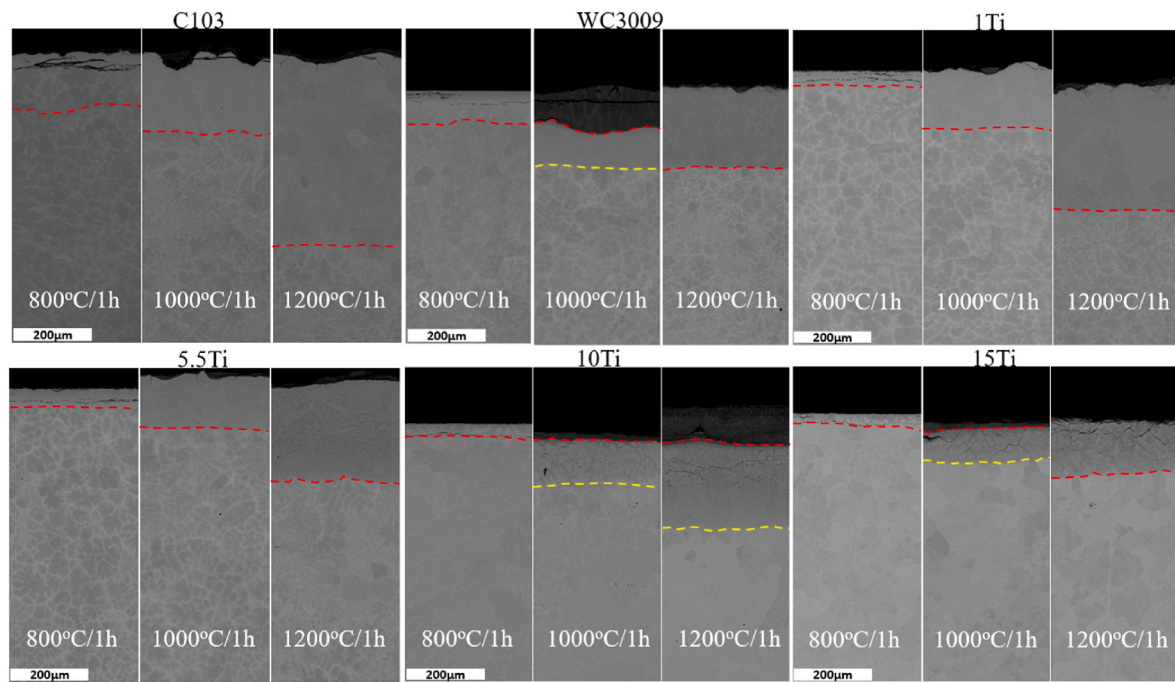


Fig. 10. Backscattered electron images of cross-sections of the Nb-based refractory alloys after 1h of oxidation at 800 °C, 1000 °C and 1200 °C. Oxide scales are at the top, separated from the base refractory alloy or the transition layer by red dashed lines, and transition layers are located between the base refractory alloy and the oxide scale, separated from the base alloy by yellow dashed lines.

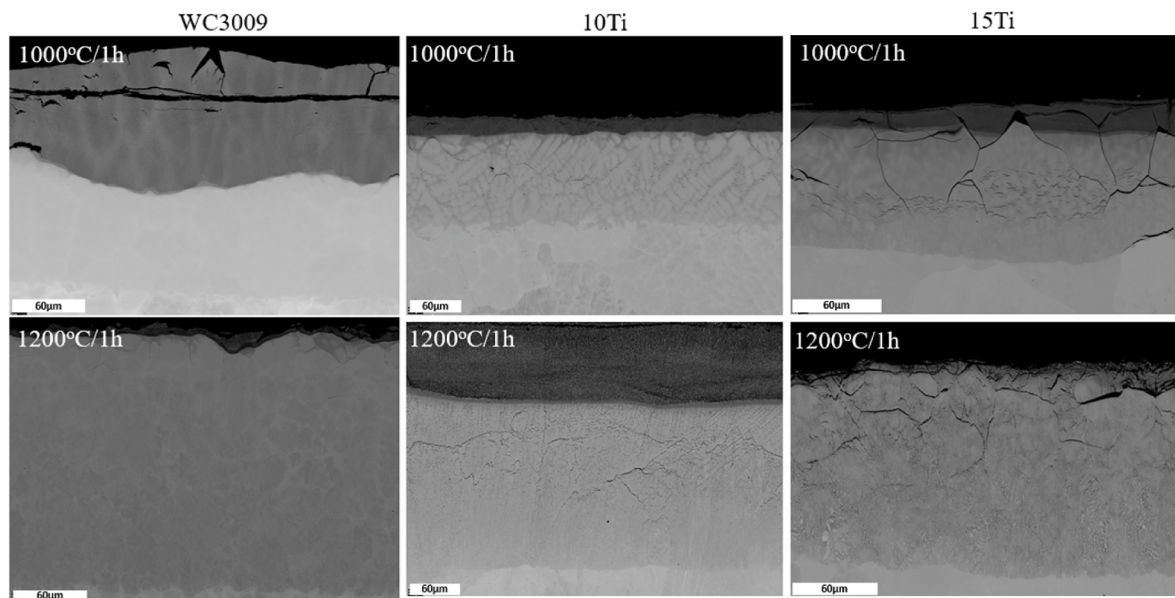


Fig. 11. Backscattered electron images focusing on oxidation fronts for 10Ti, 15Ti and WC3009 alloys at 1000 °C and 1200 °C, after 1h of oxidation.

4. Conclusions

Four new Nb-based refractory alloys, $\text{Nb}_{83.5}\text{Hf}_{12.75}\text{Ti}_1\text{W}_{2.75}$ (1Ti), $\text{Nb}_{79.5}\text{Hf}_{15}\text{Ti}_{5.5}$ (5.5Ti), $\text{Nb}_{68.5}\text{Hf}_{15}\text{Ti}_{10}\text{W}_{6.5}$ (10Ti), and $\text{Nb}_{55.5}\text{Hf}_{20}\text{Ti}_{15}\text{W}_{9.5}$ (15Ti) (all in at.%), were developed here in this work by modifying and benchmarking two commercial Nb alloys, C103 ($\text{Nb}_{92.5}\text{Hf}_{5.5}\text{Ti}_2$, at.%) and WC3009 ($\text{Nb}_{74.5}\text{Hf}_{20}\text{W}_{5.5}$, at.%), both with good room-temperature ductility but with various high-temperature strength. The main intention was to simultaneously achieve high strength at high temperatures, reasonable ductility at room temperature, and decent oxidation resistance. The following conclusions can be drawn from this work.

- 1) All six alloys that were studied here possess a single-phase bcc structure, and they all exhibit a typical dendritic structure where the dendrites are enriched with elements with high melting point like Nb and W, while the inter-dendrites are enriched with elements with relatively low melting point like Hf and Ti. The grain size of C103 is the largest with an average diameter of 85.91 μm , while that of WC3009 is the smallest with an average diameter of 30.64 μm ; grain sizes of the four newly developed alloys are in the range between 37.74 μm and 61.59 μm .
- 2) Vickers hardness (HV5) at room temperature of the Nb-based refractory alloys that were studied here basically shows a strong correlation to the actual solute concentrations and in particular the

concentrations of Hf and W, evidencing the solid solution strengthening effect, which is consistent with the trend of yield strength determined from room-temperature compression tests. Yield strength at 1200 °C clearly reveals the significant weakening effect due to heavy Ti additions, which cannot be compensated by the amount of intentionally added W additions here in this work. Comparatively, alloys with less Ti additions retain a higher yield strength to elevated temperatures.

- 3) Ti additions effectively reduce weight gain and enhance oxidation resistance of the Nb-based refractory alloys. The oxidation products differ in different alloy systems and differ upon oxidation at different temperatures. Nb₂O₅, as the main oxidation product in Nb-based alloys, shows a crystal structure change from orthorhombic at 800 °C, to a mixture of orthorhombic and monoclinic at 1000 °C, finally to monoclinic at 1200 °C. Complex oxides like orthorhombic Hf₆Nb₂O₁₇ (6HfO₂·Nb₂O₅) and monoclinic Ti₂Nb₁₀O₂₉ (2TiO₂·5Nb₂O₅) are more protective than their simpler forms including HfO₂, TiO₂ and Nb₂O₅, thus helping to slow down the oxidation rate. WO₃ that is formed in W-containing alloys, also experiences a crystal structure change from hexagonal at 800 °C to monoclinic at 1000 °C and a mixture of monoclinic and tetragonal at 1200 °C. After 1h of exposure, oxide scales with better adhesion to the substrate alloy are formed only in the 10Ti alloy, contributing to the much-improved oxidation resistance.
- 4) Although 10–15 at.% of Ti addition lowers the high-temperature strength at 1200 °C, a reasonably high yield strength of 259 MPa and 254 MPa, respectively, are achieved in the 10Ti and 15Ti alloys, compared to 343 MPa for the benchmark WC3009 alloy. Meanwhile, the oxidation resistance of the 10Ti and 15Ti alloys is much improved compared to that of C103 and WC3009.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sheng Guo reports financial support was provided by Swedish Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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