

PHASE TRANSFORMATIONS AND OXIDATION RESISTANCE OF Nb-Ti-Si-BASED ALLOYS

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Abstract

Multiphase Niobium-Silicon alloys offer great potential as a new generation of refractory material system that could meet the high-temperature capability envisaged to exceed the application temperatures of Ni base superalloys. One of the serious concerns in the application of Nb based alloys is their poor oxidation resistance at elevated temperatures. However, alloying of the Nb solid solution phase can be quite effective in obtaining remarkably improved high-temperature oxidation resistance without compromising other high-temperature mechanical properties. Several researchers have investigated microstructures and properties of Nb-Ti alloys containing Si as one of the main alloying additions, together with other elements such as Cr, Al, Mo and Hf. Alloy systems containing high volume fractions of high-melting intermetallic silicide phase together with the ductile refractory solid-solution phase have been studied in detail in the past. In this paper an overview of the high temperature oxidation resistance of these multiphase alloys will be provided. Calculated phase diagrams will be examined with a view to exploring a variety of possible invariant reactions in these systems and the effect of alloying elements on the stability and distribution of silicides, mainly Nb₃Si and Nb₅Si₃ will be illustrated. The effect of microstructural distribution on high temperature oxidation resistance of multiphase alloys will be discussed. In addition, the overall kinetics of the oxidation reaction, the nature of the reaction products and the development of the oxidation products as well as the mechanism of oxidation are discussed.

Introduction

The demand for improved performance of gas turbines used in several applications have prompted scientists to look for high temperature materials that can be used for structural applications. Alloying of Nb with Ti and other elements has been found to be an effective method to greatly improve its oxidation resistance at high temperatures where these alloys offer great potential [1-7]. Nb-Si alloys containing a variety of other alloying elements, principally Ti offer a good combination of mechanical properties at elevated temperatures. Detailed reviews of recent studies are available [1-14] and here aspects of high temperature oxidation resistance of multiphase Nb alloys containing Si will be discussed. Extensive investigations aimed at achieving oxidation-resistant Nb alloys have indeed been carried out in the past and serve as useful guidelines in the recent alloy-development studies [15-17]. Many of these efforts were based on the development of Nb-Al alloys, and the formation of marginally protective alumina scales at high-temperatures was reported for some complex alloys [18-20]. The recent alloy-development efforts have focused on the promising potential of silicide-

bearing multicomponent Nb alloys, and this study was initiated to examine the oxidation behavior of this class of Nb alloys. Silica can provide a stable surface oxide to higher temperatures than alumina and the lower activation energy for oxygen diffusion in silica may make it more effective than alumina at higher temperatures [18]. Other major alloying additions in promising Nb alloys include Ti, Al and Hf, all of which form oxides that are even more thermodynamically stable than silica, and since SiO_2 and Nb_2O_5 have virtually no solubility in the solid state, complex oxide scale formation is expected to occur during oxidation of the multicomponent Nb alloys. A crucial drawback is the fact that the binary phase diagrams for these oxides with Nb_2O_5 (melting point $\sim 1550^\circ\text{C}$) indicate eutectic formation [20, 21] and hence the maximum useful or safe temperatures before catastrophic melting of the oxide scales may be further lowered.

Thus, it is important that a fundamental understanding of the influence of chemistry and microstructure on the nature, sequences and mechanisms of oxidation at various temperatures be gathered. We have recently examined the kinetics of oxidation of advanced Nb-Ti-Si based alloys [22] and thus, in this paper only some of the results of current efforts on microstructural effects on oxidation resistance of Nb alloys will be emphasized. An understanding of the nature of phase transformations and microstructural stability of multicomponent alloys will be provided initially to form a background for understanding the high temperature behavior of these alloys.

Phase Transformations and Microstructures

Binary Nb-Si alloys have been studied in detail though various phase transformations occurring in alloys of interest are not well understood. The binary Nb-Si and the ternary Nb-Si-Ti systems have been well characterized in the composition regimes of interest to the Nb and the high temperature materials community and modeling studies of these phase diagrams have clearly provided a greater understanding of these alloys [23-25]. The equilibrium diagrams Nb-Si and Ti-Si show eutectic reactions of the form $L \rightarrow \beta + \text{Nb}_3\text{Si}$ and $L \rightarrow \beta + \text{Ti}_5\text{Si}_3$ and consequently the ternary diagram exhibits eutectic groves nearly parallel to the Nb-Ti binary and terminate in a Class II invariant reaction, $L + (\text{Nb,Ti})_3\text{Si} \rightarrow \beta + (\text{Ti,Nb})_5\text{Si}_3$. A peritectic ridge from the reaction, $L + (\text{Nb,Ti})_5\text{Si}_3 \rightarrow (\text{Nb,Ti})_3\text{Si}$ also exists at Si contents slightly higher than the eutectic grove at higher Nb compositions and these reactions control the microstructures resulting from solidification of alloys of interest to the present discussion. The binary Ti_3Si phase forms from the peritectoid reaction, $\beta + \text{Ti}_5\text{Si}_3 \rightarrow \text{Ti}_3\text{Si}$ while the binary Nb_3Si phase undergoes the eutectoid reaction, $\text{Nb}_3\text{Si} \rightarrow \beta + \text{Nb}_5\text{Si}_3$.

The as cast microstructure (back-scattered electron image in the SEM) of a hypereutectic binary alloy shows the presence of three phases, Nb_3Si (gray), Nb_5Si_3 (dark) and β (bright). The Nb_5Si_3 phase formed first during solidification, followed by the Nb_3Si phase and the remaining liquid undergoes the eutectic reaction that produced the finer distribution of the β and the Nb_3Si phases seen in Figure 1(a). The solid-state decomposition of the Nb_3Si phase was not observed in the as-cast microstructure at all. In fact, as can be seen from Figure 1(b), even after prolonged ageing at 1200°C , the eutectoid decomposition was observed only in isolated areas indicating that this invariant reaction is kinetically not favorable. The lamellar product of the eutectoid reaction, $\text{Nb}_3\text{Si} \rightarrow \beta + \text{Nb}_5\text{Si}_3$, can be seen near the center in Figure 1(b) and apparently originated at the $\text{Nb}_3\text{Si} / \text{Nb}_5\text{Si}_3$ interface. Figure 1(c) illustrates the microstructure of the as-cast Nb-Ti-Si ternary alloy and shows a distribution of the β and the Nb_3Si phases. A heat treatment identical to that of the binary alloy led to a complete decomposition of the Nb_3Si phase through the eutectoid reaction. The eutectoid reaction product was lamellar as can be seen from Figure 1(c). The Nb_3Si phase was found to be stable

in this ternary alloy after aging at 1500°C for 100 hours suggesting that the eutectoid decomposition temperature in this alloy is between 1500°C and 1200°C.

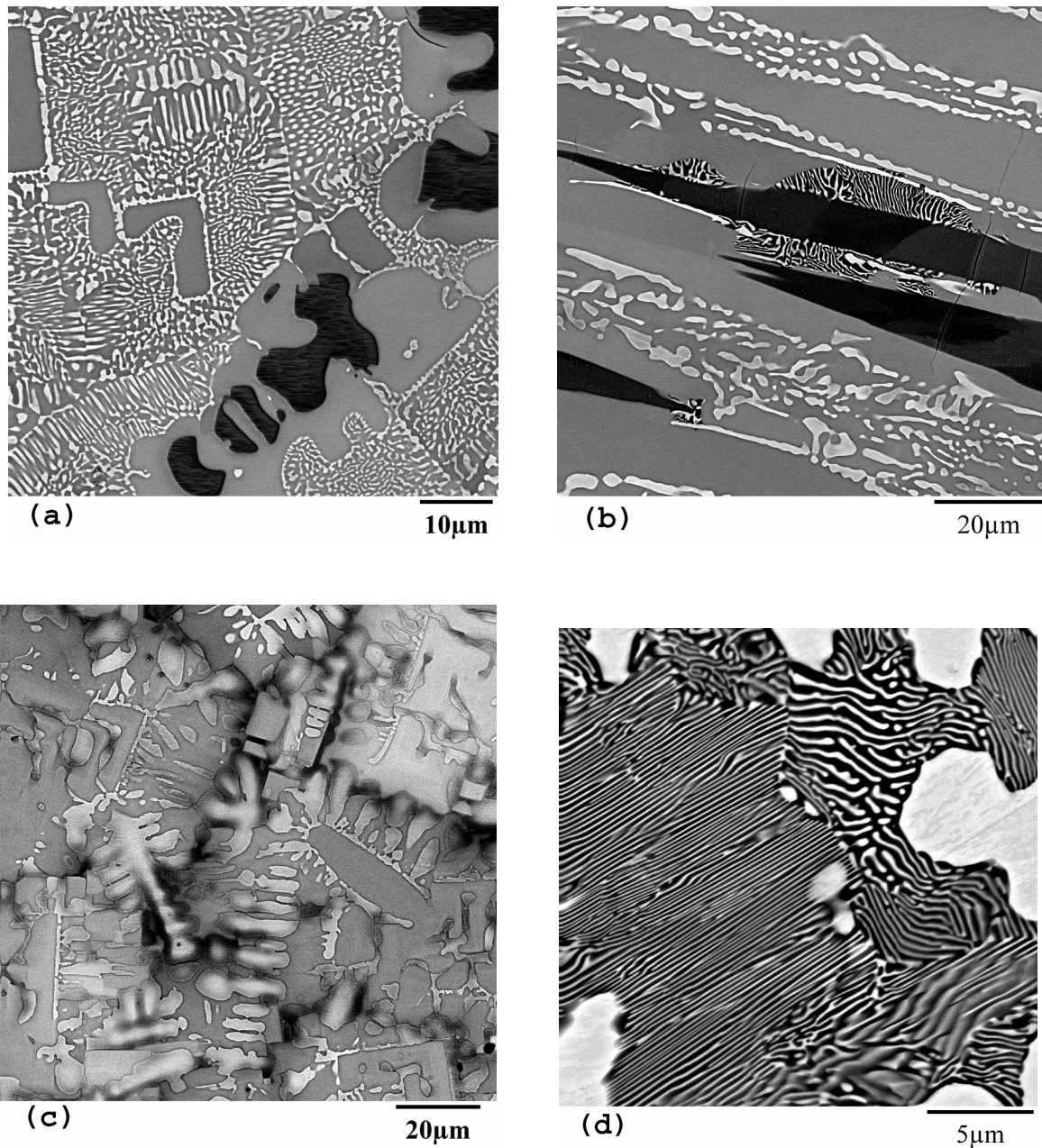


Figure 1: (a) & (b) are from Nb-17.2 Si, and (c) & (d) are from Nb-15Si-12.5Ti. (a) & (c) are obtained in the as-cast condition while (b) & (d) are from alloys that were aged at 1200°C for 120hrs.

Examination of ternary Nb-Ti-Si alloys showed that the eutectoid reaction was considerably accelerated and a lamellar product of $\beta + (\text{Nb,Ti})_5\text{Si}_3$ formed during lower temperature heat treatments as seen from a comparison of Figures 1(b) & 1(d). Microstructures resembling that of hypo-eutectoid steels constituting pearlite and proeutectoid ferrite could be produced in ternary alloys as illustrated in Figure 1(d). Increasing Ti contents of ternary alloys to about 20at% resulted in completely stabilizing the Nb_3Si phase even after prolonged aging as shown in Figure 2(a). Interestingly, addition of quaternary alloying elements such as Al, Cr or C was

found to completely suppress the formation of the Nb_3Si phase, instead leading to formation of the Nb_5Si_3 phase from the liquid phase itself. In fact addition of Al to Ti-free Nb-Si alloy lead to eutectic solidification resulting in a fine microstructure composed of β and Nb_5Si_3 . Figure 2 illustrates some examples of microstructures that result from different alloying additions to Nb-Si alloys. From these micrographs it is clear that a wide variety of microstructures can indeed be generated in Nb alloys with careful alloying and suitable heat treatments.

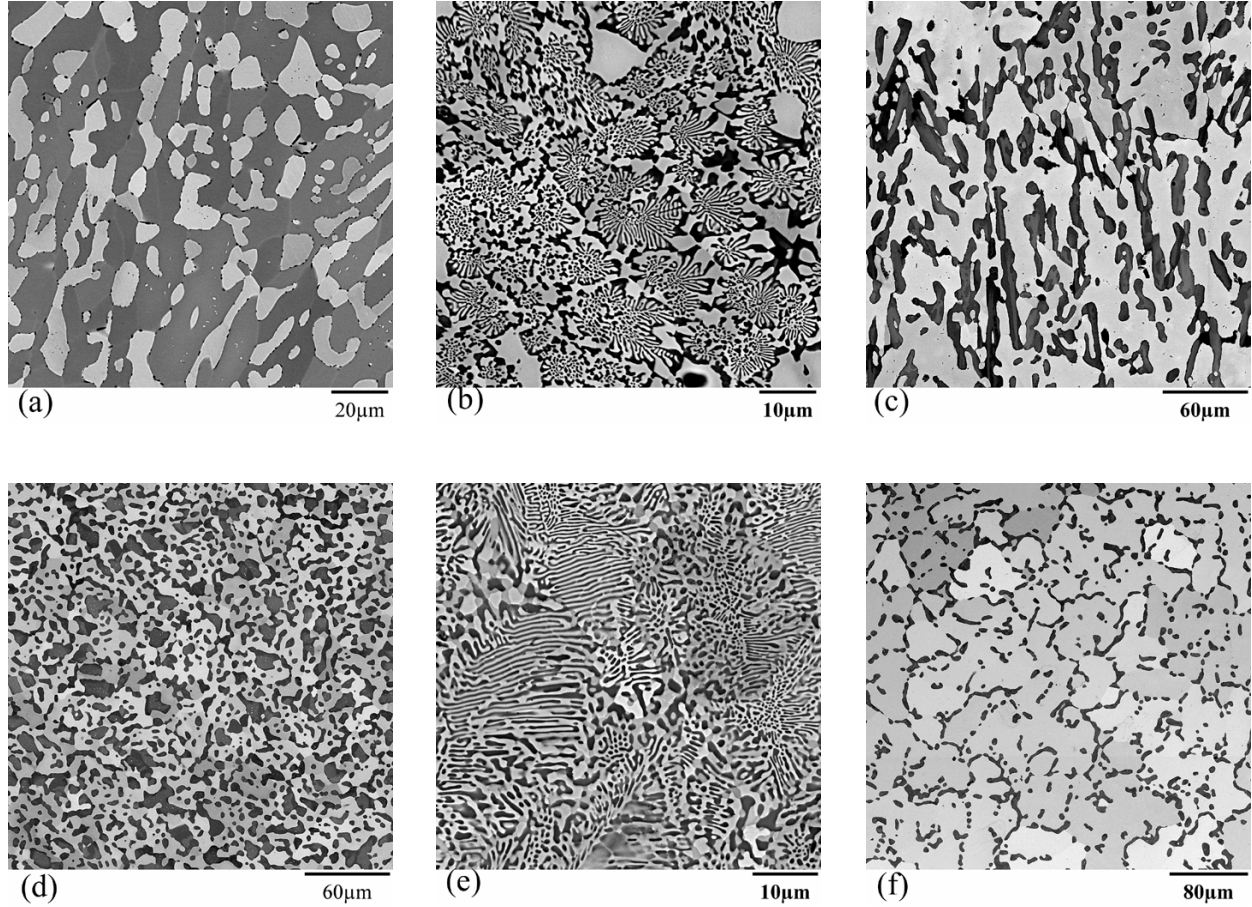


Figure 2: (a) Nb-20.8Ti-15.8Si (b) Nb-12.6Ti-14.0Si-2.3C (c) Nb-12.0Ti-13.6Si-9.81Cr (d) Nb-20.8Ti-15.7Si-4.3Al (e) Nb-16.1Si-4.9Al (f) Nb-20.5Ti-7.6Si-4.54Al.

The microstructures associated with most alloys studied and characterized in detail is similar to that shown in Figure 3 and is constituted of a distribution of large grains of Nb_5Si_3 in β matrix and depending upon exact alloy composition and heat treatment, smaller volume fractions of other phases like Ti_5Si_3 and Cr_2Nb may also be present. Indeed, it has very recently become clear that alloys that are expected to combine excellent high temperature properties and

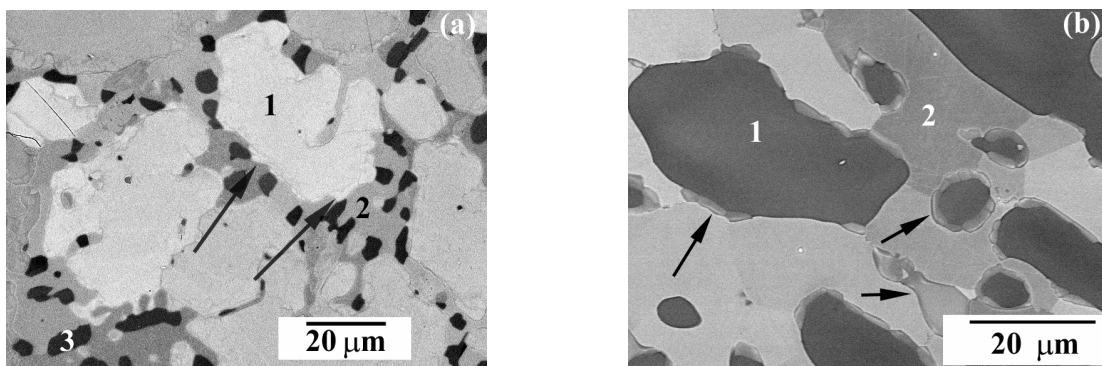


Figure 3: Microstructure of two alloys homogenized and heat-treated at 1200°C (a) Nb-19.86Ti-19.74Si-4.21Ge-3.26Al-4.21Hf-9.90Cr and (b) Nb-25.99Ti-12.61Si-4.94Ge-1.92Al-1.90Hf-6.73Cr-0.43Sn. In these micrographs 1 denotes the Nb_5Si_3 – type phase, 2 the β phase and the arrows point to the Ti_5Si_3 – type phase. The dark phase denoted as 3 in (a) is the Cr rich Laves phase.

reasonable oxidation resistance possessing a fine distribution of silicides can be produced by judicious alloying. Microstructures of some of these alloys are shown in Figure 4 and the detailed evaluations of various properties are under way in our laboratory now. In these alloys, the formation of large primary Nb_5Si_3 phase is nearly eliminated and the formation of finer silicides by eutectic solidification encouraged.

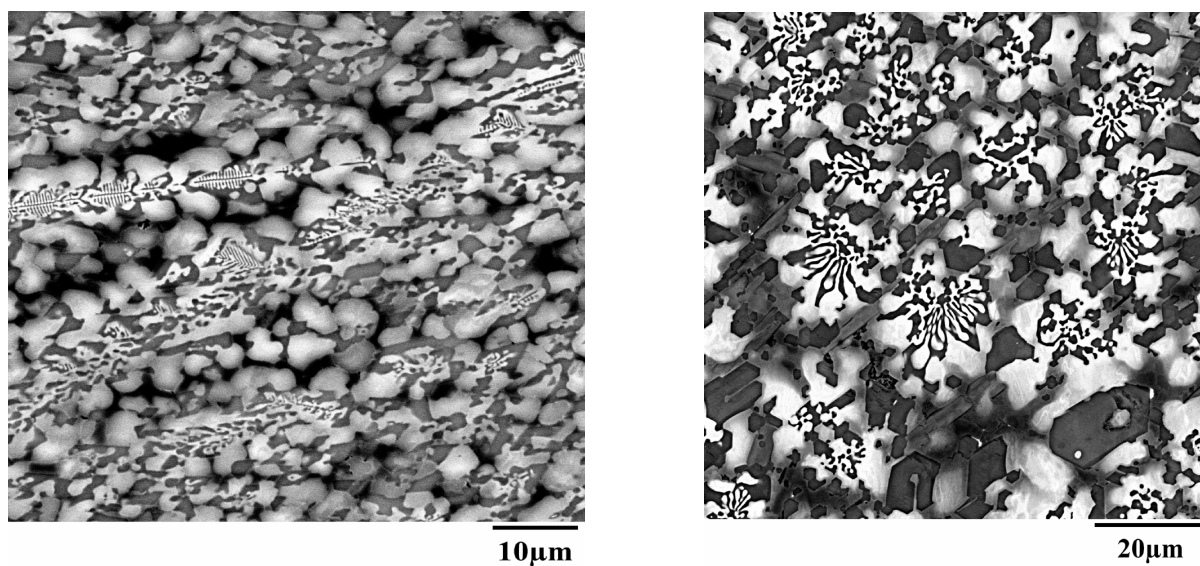


Figure 4: Silicide distribution in two as cast Nb-Ti-Si-Cr-Mo-Hf-Al-Sn alloys showing eutectic solidification microstructures.

Oxidation Resistance

Cyclic oxidation experiments conducted on a large number of alloys can be classified together and Figures 5 and 6 illustrates some examples. As can be seen in Figure 5(a), oxidation behavior of Nb can be substantially improved by alloying the bcc phase. The oxidation resistance of alloys is very sensitive to alloying contents and the oxidation resistance can be

significantly increased over pure Nb by judicious choice of alloying. Figure 5(b) shows the role of silicide phase in improving the oxidation resistance of complex alloys. All alloys show a two-stage oxidation reaction with an initial slow oxidation region followed by a rapid linear oxidation region. The second stage can be described as a breakaway oxidation reaction where rapid oxidation and oxide spallation occurs. Alloys containing ~10at%Mo were found to be more spallation-resistant in comparison to other alloys. The onset of the breakaway oxidation is strongly temperature dependent and occurs earlier in time as the temperature is raised as illustrated in Figure 6. Role of different alloying elements upon oxidation kinetics have been discussed in earlier papers [10,22]. Results of weight change data such as those in Figure 5 and 6 can be analyzed by using the equation, $\Delta w = Kt^n$, where Δw is the weight change per unit area, t is the reaction time; K and n are constants. The oxidation reaction kinetics is then characterized as linear, parabolic, cubic, etc. depending upon the value of the exponent n . Wagner showed that the kinetics of oxidation can be treated as a diffusion problem and a simple parabolic law (i.e. $n = 0.5$ in equation above) derived to explain the kinetics of the reaction [26,27]. The oxidation of pure Nb in oxygen (at partial pressures high enough to form Nb_2O_5), as well as static air, follows a parabolic law at short times (i.e. $n = 0.5$) and becomes linear at longer exposure times. The oxidation kinetics of Si-containing, multicomponent Nb alloys appear to be somewhat different from those of Nb-Ti-Al base where the value of n was found to be usually very close to unity [16,17] indicating much faster oxidation kinetics. This is best seen in Figure 4 where the values of the kinetic law exponent, n , of Nb-Ti-Al alloys are compared with those of Nb-Ti-Si alloys. It must be cautioned that in the cyclic-oxidation experiments performed here, weight changes reported do not account for any weight losses due to spallation and thus the value of the exponent n in the kinetic law deduced from these data may actually be somewhat less than the true parameter.

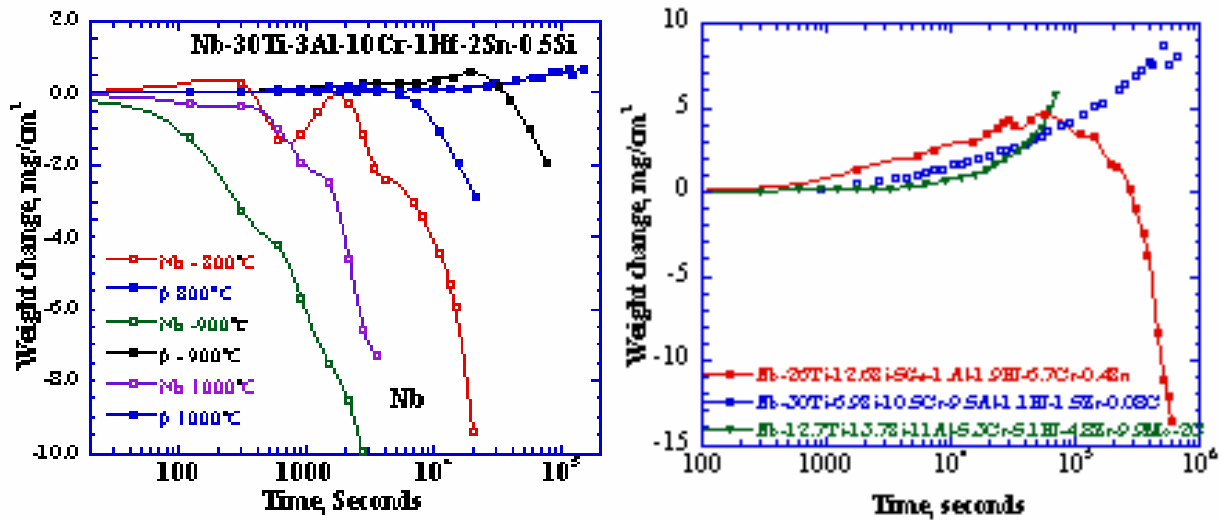


Figure 5: (a) Comparison of cyclic oxidation (in static air) behavior of Nb and a solid solution alloy at different temperatures. (b) Oxidation of silicide bearing alloys.

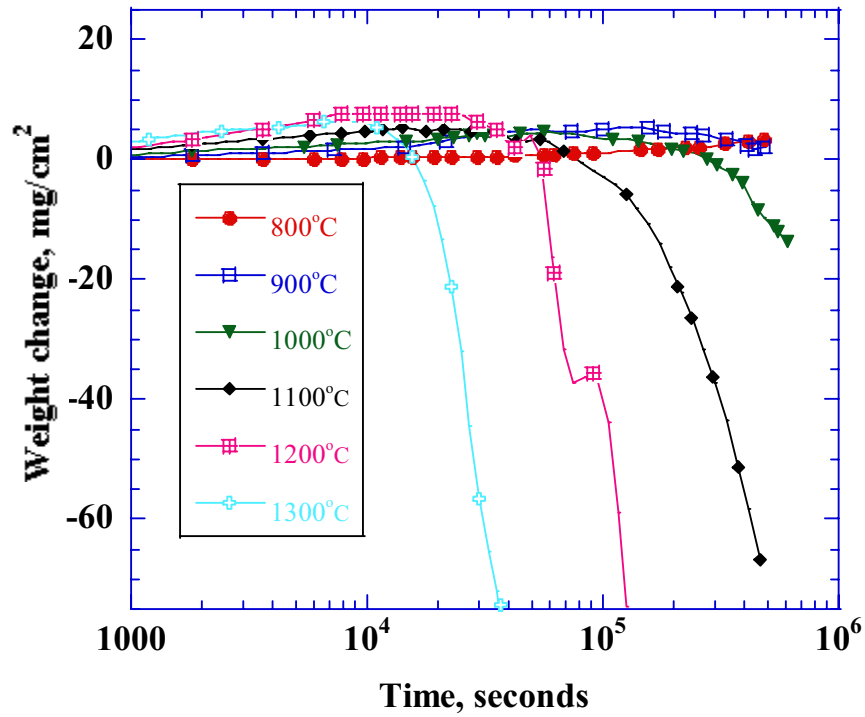


Figure 6: Influence of temperature on the kinetics of cyclic oxidation of an Nb-26Ti-12.6Si-5Ge-1.Al-1.9Hf-6.7Cr-0.4Sn alloy.

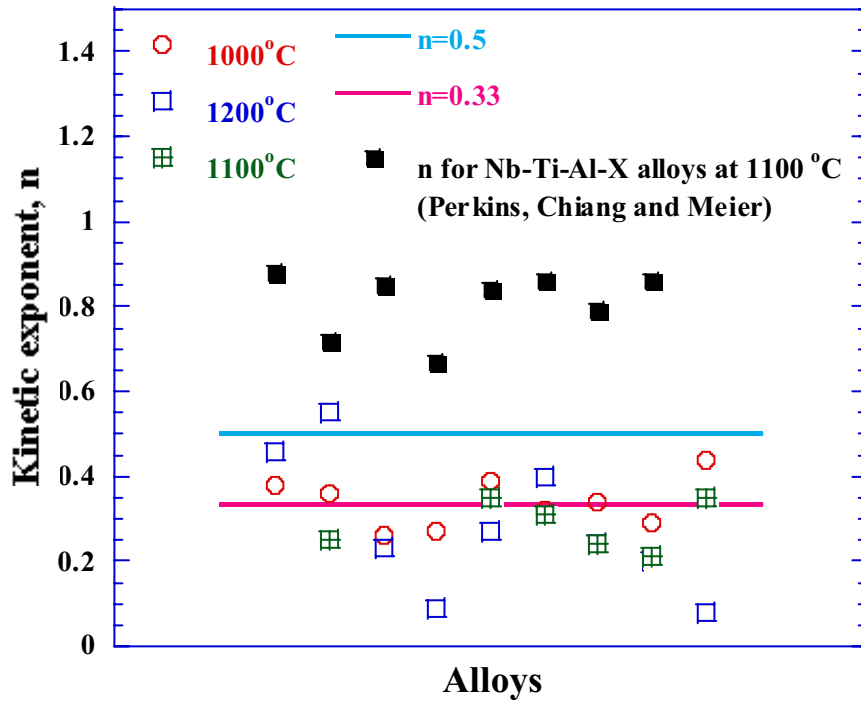


Figure 7: Comparison of experimentally determined values of the kinetic exponent, n , for a number of multicomponent Nb alloys. Data from Perkins, Chiang and Meier [17] is shown with filled square symbols whereas our data is shown using open symbols. Perkins, Chiang and Meier study [17] used several alloys having the composition (25-40) at% Nb- (23-32) at% Ti – (22-44) at% Al with other additions. Data for Si-bearing alloys show $n \sim \frac{1}{3}$ while for the Al-rich alloys $n \sim 1$.

Figure 7 indicates that the time dependence of oxidation (or the rate of oxidation) for high Si-bearing Nb alloys is less than that of Al-rich Nb-base alloys. While analyzing the oxidation kinetics data in the light of Wagner theory for high-temperature oxidation, one must bear in mind that the assumption of thermodynamic equilibrium at the metal / oxide interface is not realized. This is especially true during oxidation of transition elements belonging to groups IVA (Ti, Zr, Hf) and group VA (V, Nb and Ta) since the solubility of oxygen in these metals is high at high-temperatures [28]. Oxygen solubility in Nb is substantial at these temperatures and may be influential in determining the oxidation resistance of multicomponent Nb alloys as well. Thus, in reality, the reaction-rate constant, K , represents the sum of reaction rates associated with the dissolution of oxygen in the alloy and the growth of an oxide on the surface of the alloy. One must also bear in mind that the derivation of the parabolic law for oxide growth is based on volume diffusion of oxygen through the oxide while it is certainly possible that short-circuit diffusion could play a significant role in cases like the one in this study. For these the microstructure of the oxide film offers sufficient heterogeneities and oxide cracking as well as spallation occurs, such that oxygen may be transported to the metal-oxide interface at much higher rates than that afforded by volume diffusion alone. Further, if oxygen diffusion in the alloy occurs to appreciable levels, internal oxidation is likely to occur since elements like Hf, Al, Cr that have high affinity for oxygen are also present in the alloy. Microstructural examination of oxidized samples revealed that at high temperatures, adherent oxide layer formed quickly and upon prolonged oxidation, spallation of the oxide occurred. Detailed description of these can be found in ref. 10 and 22. It was always found that the β phase as well as the β /Nb₅Si₃ interface was preferentially oxidized while the silicide phase resisted oxidation till much longer oxygen exposure. Microstructures of internally oxidized samples are shown in Figure 8. Clearly, the finer microstructure (figure 8(b)) is associated with relatively reduced internal oxidation. This indicated that the finer microstructure obtained in the powder-processed material may be advantageous in terms of improving the oxidation resistance of Nb alloys. Several component as well as complex oxide phases formed in these samples as described elsewhere [10].

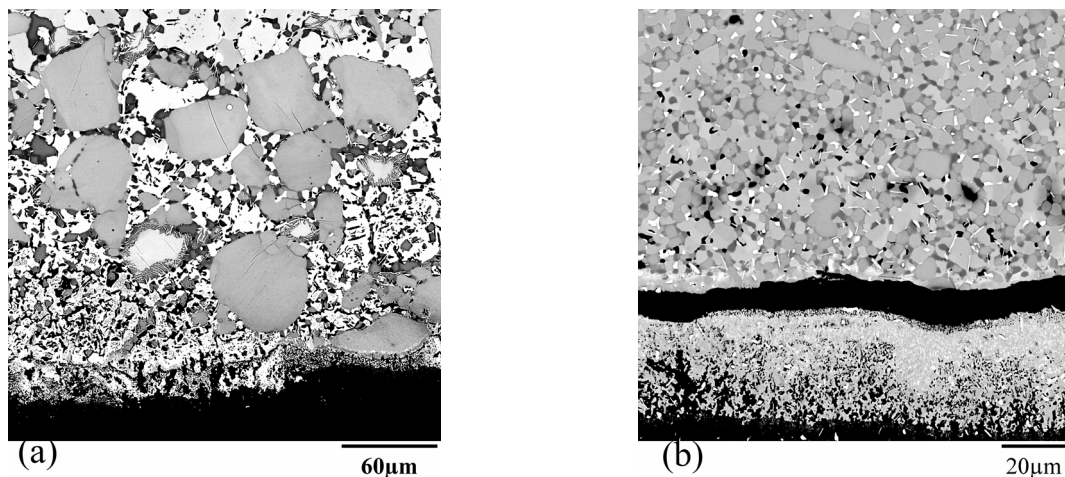


Figure 8: Internal oxidation after oxidation at 1200°C in Nb-20Ti-11Si-5Ge-6Cr-3Fe-2.5Al-2Hf-1.3Sn in (a) cast and heat-treated alloy and (b) in P/M processed alloy. Notice the preferential oxidation of β and the interface in relation to the Nb₅Si₃ phase clear in (a). Oxide layer thickness in (a) was > 100μm and was lost during polishing.

Oxidation at Low Temperatures

Weight-change data for most of the alloys at temperatures below 900°C did not show a breakaway oxidation period at least till about 150 hours. However, a common microstructural observation made in all the alloys that were oxidized at temperatures of 900°C or less was that the surfaces of all the alloys were characterized by cracks parallel to the surfaces just below the oxide layer as illustrated in Figure 9(a). Cracks form just below the surface oxide layer (see figure 9(a)) and these cracks appear mostly in the silicide phase, though one can see them in the β phase as well to a lesser extent. This observation has been made in a wide variety of Nb alloys in our study. Internal cracking of the silicide phase could be controlled to a remarkable extent by a finely distributed microstructure as can be seen in figure 9(b). However the cracks appear along the $\beta/\text{Nb}_5\text{Si}_3$ interfaces in this sample.

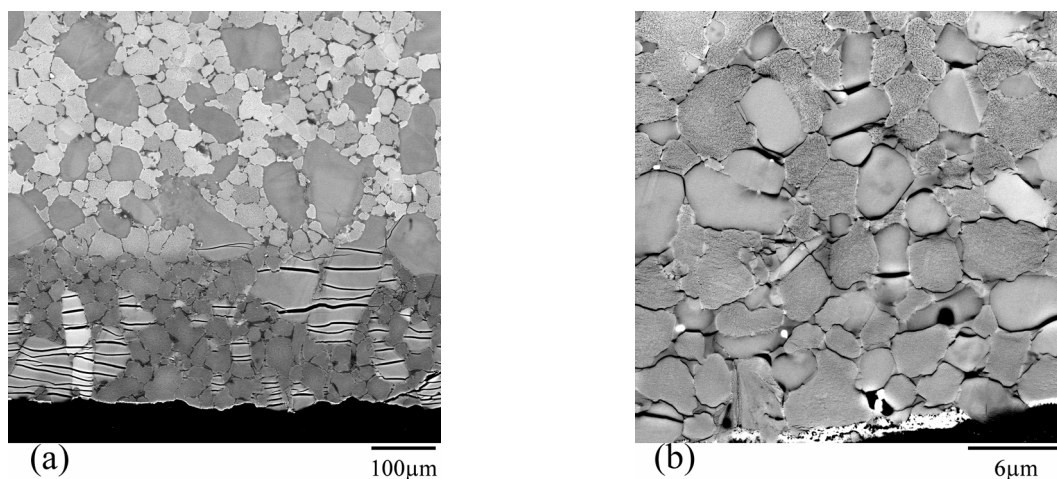


Figure 9: Internal oxidation after oxidation at 800°C in Nb-20Ti-11Si-5Ge-6Cr-3Fe-2.5Al-2Hf-1.3Sn in (a) cast and heat-treated alloy and (b) in P/M processed alloy. Notice the cracks in silicide phase in (a) and mostly at the β /silicide interface in (b).

The surface cracks forming in the alloy appear to follow the sample geometry, or in other words the oxygen concentration profile and were absent in Ar- or vacuum encapsulated samples heat-treated at the same temperature. Cooling rates from the heat treatment temperature also had no influence as far as surface cracking was concerned ensuring that these cracks did not result from thermal stresses. It appears that high residual stresses are being developed in the β phase during oxidation, and the silicide that is presumably brittle even at these temperatures fractures under these stresses. Precipitation of Nb_2O_5 can be observed in oxygen-enriched areas where the oxygen solubility has been exceeded as illustrated in Figure 10. Nb_2O_5 has a negative thermal expansion coefficient and fine-scale precipitation of the oxide such as that shown in figure 10 may lead to generation of residual stresses in the β phase at these temperatures. The monoclinic to orthorhombic allotropic transformation reported in Nb_2O_5 at ~830°C – 900°C also may contribute to residual stresses. At higher temperatures, lower thermal-expansion coefficient, together with the ability of the silicide phase to sustain plastic flow prevents fracture of the silicide phase. To test this hypothesis, residual stresses generated during oxidation of polished samples at 800°C were measured from X-ray diffraction experiments. Figure 11 shows the plot of residual stresses as oxidation progresses, demonstrating that compressive stresses are quickly developed within the β phase during the initial stages of oxidation. Further, it appears that once the stresses reach a critical value,

fracture of the brittle phase (silicide) occurs, thus relieving the stresses. SEM examination of the surface of these samples showed that oxide whiskers grew in the β phase very early during oxidation and as oxygen diffuses deeper in to the sample with longer exposure, oxide precipitation occurs and consequently, β regions inside the sample are stressed to a point when fracture of the silicide phase becomes inevitable.

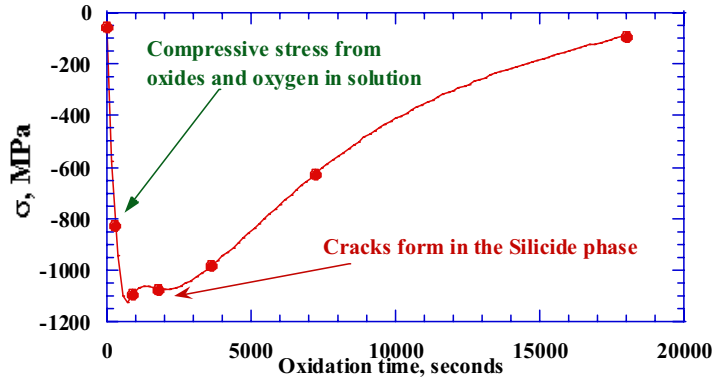
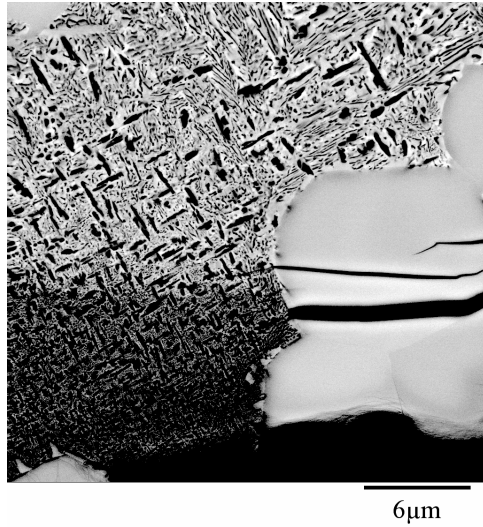


Figure 10: Nb-30Ti-7Si-10.5Cr-9.5Al - 1.1Hf-1.5Zr-0.08C, oxidized at 900°C for 16 hours showing oxide precipitates in the β phase regions. Figure 11: Residual stresses as determined by XRD in Nb-25Ti-13Si-5Ge-6Cr-2Al-2Hf alloy oxidized at 800°C.

Oxidation of ternary Nb-Ti-Si alloys possessing eutectoid microstructures like those in Figure 1(d) also lead to cracking of the fine Nb_5Si_3 phase, as illustrated in Figure 12(a). In alloys containing Nb_3Si also the silicide phase was found to undergo similar effects of cracking as shown in Figure 12 (b). It may be noticed that the lamellar type microstructure leads to much finer cracks since the silicide size is small. However, the oxidation resistance of Nb-Ti-Si ternary alloys is insufficient to be of practical use and as discussed earlier, more complex alloying invariably suppressed the formation of Nb_3Si phase and thus the eutectoid reaction.

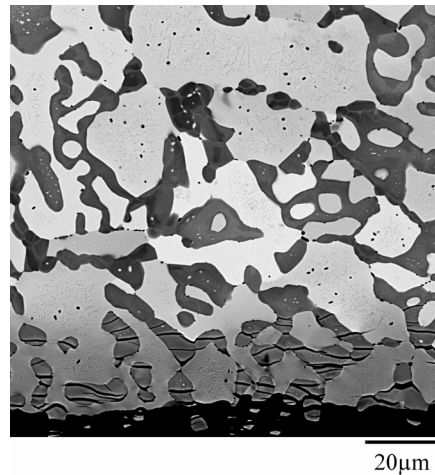
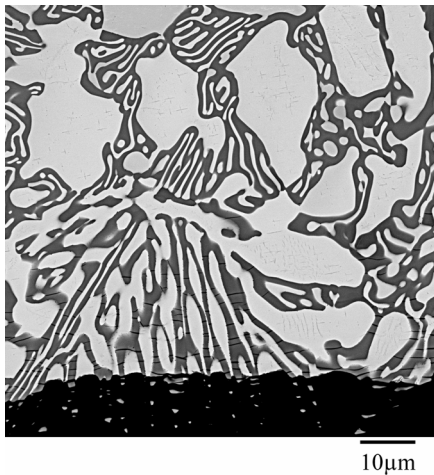


Figure 12: Internal oxidation after oxidation for 4 hours at 800°C in (a) Nb-10.5Ti-16.2Si (b) Nb-20.8Ti-15.8Si. The dark phase is Nb_3Si and the bright phase is β solid solution.

Summary

A wide variety of microstructures can be obtained by suitable alloying in Nb alloys and the oxidation resistance of Nb alloys can be dramatically improved by alloying. It is important to investigate the microstructural aspects associated with oxidation in order to establish the high temperature behavior of these alloys. Here an overview of the effects of alloying on microstructural development was illustrated and their effects on oxidation examined. At lower temperatures, oxidation is accompanied by high residual stress build-up and the brittle silicide phase undergoes cracking.

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