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OXIDATION AND VOLATILIZATION OF SILICIDE COATINGS FOR REFRACTORY NIOBIUM ALLOYS

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ABSTRACT

Degradation mechanisms relevant to hypersonic environments have been investigated for silicide-coated niobium alloys. To assess the suitability of silicide coatings for possible leading edge, scramjet combustor, and vehicle acreage applications, tests were conducted over a range of oxygen and water vapor partial pressures. X-ray diffraction was used to characterize the composition of oxide phases. Chemical compositions of both the coatings and resulting oxides have been examined using energy dispersive x-ray analysis. Partial pressures of oxygen and water vapor have been found to influence the oxide composition, which may include silica, chromia, iron niobate, and chromium niobate phases. The formation of volatile oxide and hydroxide species also affects oxidation behavior and coating performance. Thermodynamic models of oxidation and volatilization are used to interpret experimental results.

INTRODUCTION

Since the 1960's, niobium alloys have generated intermittent interest as thermostructural materials. With liquidus temperatures well above 2000°C, niobium alloys suggest potential beyond current state-of-the-art nickel superalloys (melting temperatures around 1350°C)[1]; however, oxidation is a major obstacle.

Silicide coatings have been used to mitigate oxidation in Nb alloys in certain domains of temperature and oxygen partial pressure. For example, Hitemco R512E™, a standard silicide coating for niobium alloys, is applied as a slurry (nominally Si-20Fe-20Cr) to the refractory metal substrate. A subsequent heat-treatment fuses the coating and promotes the formation of various layers of intermetallics, most prominently MSi_2 and M_5Si_3 , where $M = (Nb, Fe, Cr)$ [2, 3]. The effectiveness of silicide coatings is generally attributed to the formation of a comparatively more adherent mixed-oxide; depending on the coating composition, temperature, and atmosphere,

combinations of SiO_2 , Nb_2O_5 , and mixed oxides of niobium along with various coating modifiers are reported[4, 5]

Silicide-coated niobium alloys are considered as candidate material systems for hypersonic vehicle acreage, scramjet combustors, and heat pipes, an emerging thermal management concept for high-heat flux environments, for example, leading edges of hypersonic vehicles[6, 7].

The effectiveness of silicide coatings largely depends upon their ability to maintain passive oxidation behavior in temperatures and environments where the underlying refractory metal would otherwise exhibit active oxidation. The oxides formed by silicide coatings on niobium substrates has been shown to depend on both coating composition and temperature[4]. Unalloyed coating slurries (i.e containing only silicon) form $NbSi_2$ after the coating diffusion treatment. Upon exposure to air, SiO_2 and Nb_2O_5 form, and the coating evolves into a mixture of $NbSi_2$ and Nb_5Si_3 . The unalloyed coating exhibits pest oxidation. Alloying the coating with chromium results in the formation of $NbSi_2$ and $(Nb, Cr)_5Si_3$ after the coating diffusion treatment. Oxidation results in the preferential removal of Cr from the $(Nb, Cr)_5Si_3$ phase, and oxide products include Nb_2O_5 , Cr_2O_3 , SiO_2 , and $CrNbO_4$. Pest oxidation is also observed for this composition[4]. R512E is additionally alloyed with iron, although the role of iron has not been elucidated. The absence of Nb_2O_5 in R512E silicide oxidation products, as well as the apparent lack of pest oxidation, suggests that iron is an important modifier.

Although silicide coatings for niobium alloys have been in use for decades, the mechanisms of microstructural evolution and oxidation are not well documented in literature. The motivation for this investigation is to provide insight into the microstructure, oxidation behavior, microstructural evolution, and degradation mechanisms relevant to silicide coatings in hypersonic environments.

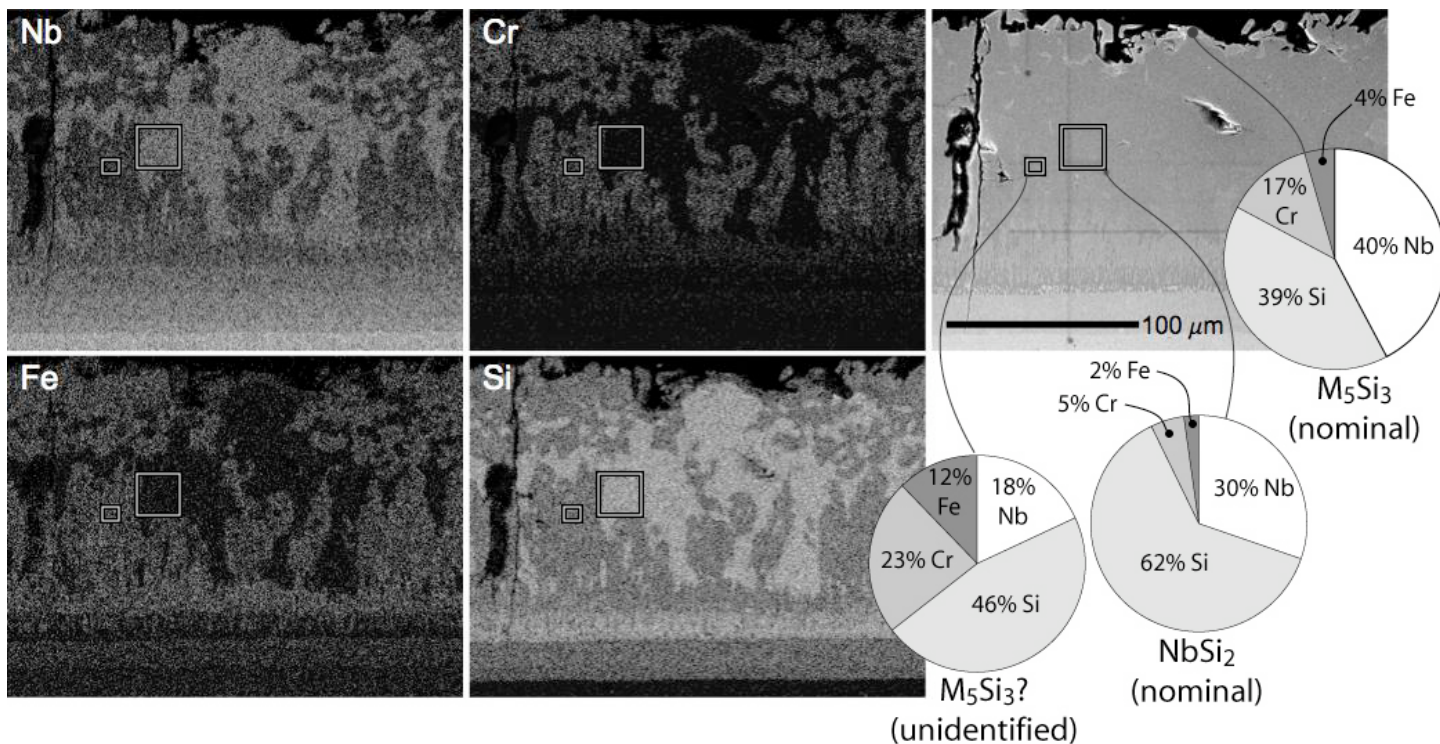


Figure 1: X-ray maps and SEM image (top right) of as-deposited R512E. Spot measurements and area scans (indicated by boxed areas in the micrographs) of NbSi₂ and M₅Si₃ phases provide chemical composition, shown in pie charts at right.

ANALYSIS OF R512E MICROSTRUCTURE

Prior to investigating high-temperature oxidation and microstructural evolution of fused-silicide coatings, it is useful to understand composition and microstructure in the as-deposited condition. To this end, a sample of R512E-coated C103 has been sectioned and analyzed. Figure 1 shows the R512E coating in cross section. Although Priceman and Sama describe the coating as six discrete layers[2], the x-ray maps in Figure 1 reveal significant interpenetration of various silicide phases.

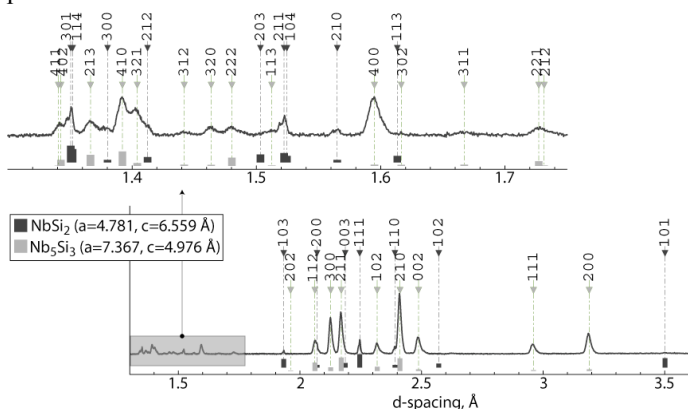


Figure 2: XRD spectrum of as-coated R512E and fit of adjusted lattice parameters.

As shown in Figure 1, the outermost portion of the coating, approximately 50 microns thick, appears to consist of two different silicides, one rich in niobium, and the other containing significant amounts of iron and chromium. XRD analysis of the outer surface (Figure 2) suggests that these two phases are modifications of hexagonal NbSi₂ (space group P6₂22, ICDD reference pattern 00-008-0450, equivalent to a C40 Laves phase) and Nb₅Si₃ (space group P6₃/mcm, ICDD reference pattern 00-008-0422, equivalent to a D8₈ structure). It is worth noting that the hexagonal form of 5-3 niobium and chromium silicides are favored with the incorporation of ~1-2 atomic % of carbon, suggesting that the presence of iron or residual carbon may be responsible for structural modification. In the absence of carbon, the equilibrium 5-3 silicide phases of chromium and niobium are tetragonal, whereas the iron silicide is hexagonal. Lattice parameters were determined by numerical regression using measured peak locations in the spectrum along with {hkl} indices from the reference patterns. This analysis yields a=7.367 and c=4.976Å for Nb₅Si₃ (compared to a=7.536, c=5.248Å). Similarly, values of a=4.781 and c=6.559Å result for NbSi₂ (a=4.797, c=6.592Å). These lattice parameters correspond to a and c distortions of -2.2% and -5.3% for Nb₅Si₃, and distortions of -0.33% and -0.50% for NbSi₂.

Significant changes in the M₅Si₃ lattice parameters may be attributed to the incorporation of Fe and Cr. As demonstrated by x-ray analysis in Figure 1, the M₅Si₃ phase contains 40% Nb, 7% Cr, and 4% Fe. Assuming the lattice parameters *a* and

c vary linearly with metal composition, a rule-of-mixtures approach can be used to predict M_5Si_3 lattice parameters. This can be represented graphically by drawing a triangular surface (i.e. a Gibbs triangle) with z -values of vertices at pure component lattice parameters. The resulting surface provides the lattice parameter as a function of composition for any combination of Cr, Fe, and Nb on the metal site in M_5Si_3 . Using this approach with EDX data from Figure 1, lattice parameters of $a=7.334$ and $c=5.066\text{\AA}$ are predicted, shown by the vertical line in Figure 3. Conversely, the lattice parameters determined by XRD can be used estimate composition. The lines of $a=7.367$ and $c=4.976$ on the a and c surfaces are also shown in Figure 3. The lack of agreement between composition and lattice parameters, as well as the silicon-rich chemistry determined by EDX, suggest that the effect of silicon substitution on metal sites should also be considered.

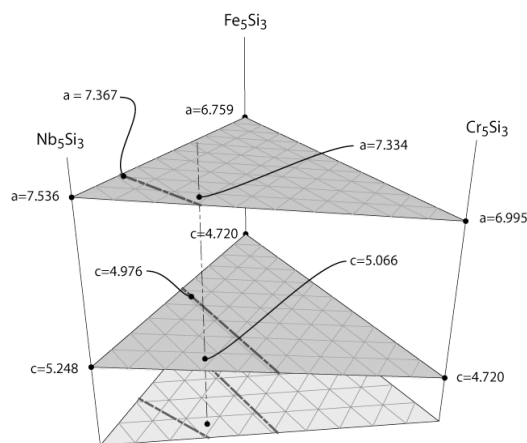


Figure 3: Rule of mixtures analysis for hexagonal M_5Si_3 lattice parameters.

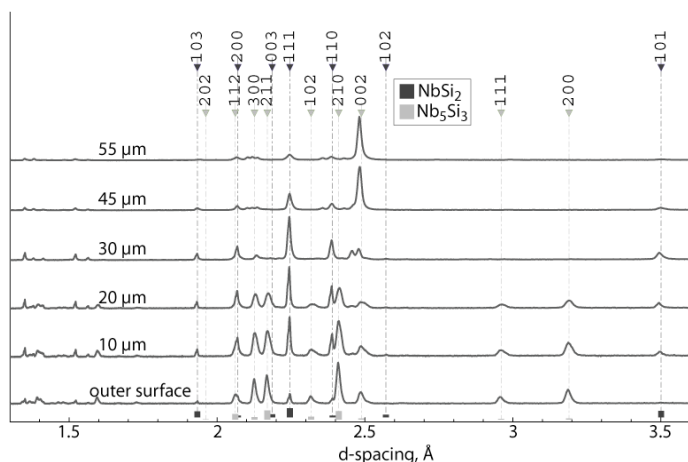


Figure 4: XRD spectra as a function of depth in R512E coating.

Sequential steps of grinding and x-ray diffraction were used to determine phase composition a function of depth in the R512E coating. A summary is provided in Figure 4. Based on peak intensities as a function of depth, it appears that the outer portion of the coating consists of M_5Si_3 and lesser amounts of $NbSi_2$. M_5Si_3 appears to extend to a depth of approximately 30

μm . $NbSi_2$ peak intensities increase from the surface up to about 30 μm , and then decrease. Phase composition beyond 50 μm remains to be investigated.

EXPERIMENTAL SETUPS

In order to accurately characterize materials performance in air-breathing hypersonic flight environments, laboratory test conditions must capture relevant features of pressure and temperature. Unlike turbine engines, which reach maximum altitudes of 10km, hypersonic vehicles are anticipated to fly at altitudes up to 30 km. This altitude corresponds to a total free stream pressure of about 0.01 atmospheres, and an oxygen partial pressure of 0.002 atmospheres. To simulate oxidation in a low- P_{O_2} environment, a tube furnace with mass flow controllers provided a mixture of argon and oxygen (Figure 5). The low- P_{O_2} oxidation test in this study was performed at an oxygen partial pressure of 0.02 atmospheres, corresponding to an altitude of 15 km.

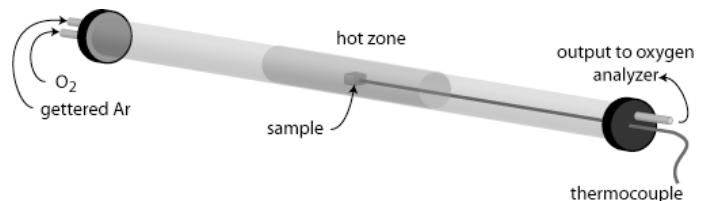


Figure 5: Schematic of low- P_{O_2} tube furnace setup

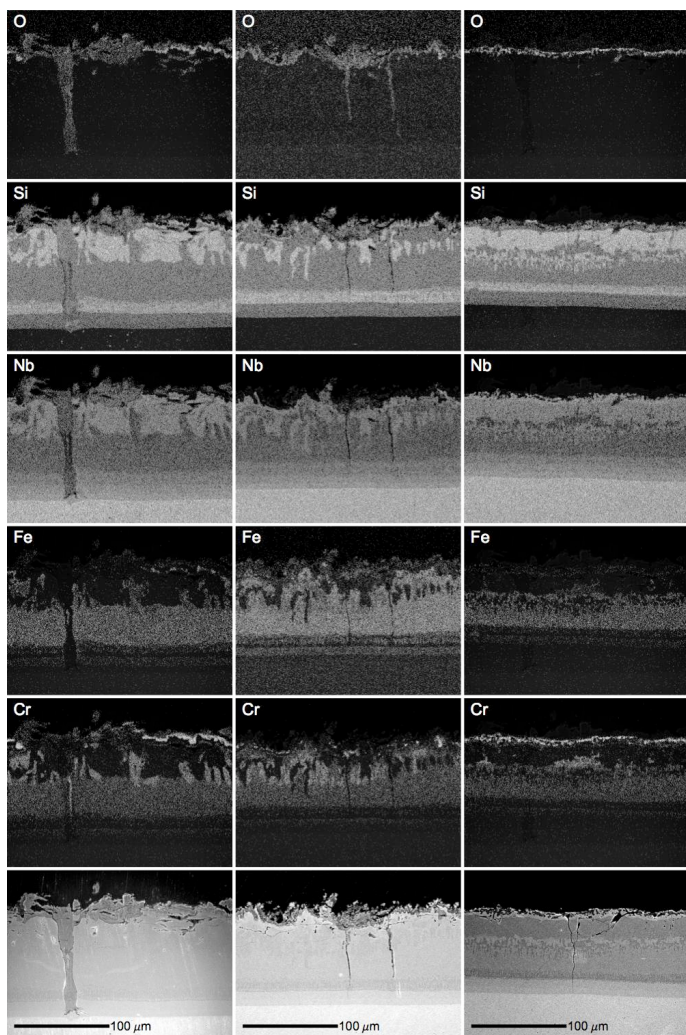


Figure 6: R512E-coated C103 in H_2+O_2 torch setup

In combustion environments, the effects of high-velocity high-temperature water vapor must be considered. Water-vapor concentration in a scramjet combustor is reported to be approximately 0.2 mass fraction at 4 atmospheres total pressure, equivalent to a partial pressure of 1.1 atmospheres[8]. A $H_2 + O_2$ torch setup has been developed that produces a test environment of approximately 1 atmosphere of water vapor (Figure 6).

OXIDATION STUDIES

R512E-coated C103 oxidation experiments have been performed in air, low- P_{O_2} , and high-velocity water vapor environments. To provide a baseline comparison, a sample was isothermally oxidized in air for 20h at 1200°C. Additionally, a sample was thermally cycled in air for the same equivalent hot time (20x1h at 1200°C). The low- P_{O_2} test consisted of a 20h isothermal hold at 1200°C with an oxygen partial pressure of 0.02 atmospheres. The high velocity water vapor test consisted of a 10h soak at 1230°C in a water vapor partial pressure of 1 atmosphere and a gas stream velocity of approximately 20 m/s.



1200°C, 20x1h air 1230°C, 10h torch 1200°C, 20h $P_{O_2}=0.02$ atm.

Figure 7: X-ray maps of R512E cross-sections after high temperature exposure. Thermally-cycled (left), torch (center), and low- P_{O_2} (right). The bottom-most image in each set is a secondary electron image.

The dependence of oxide species on environment is qualitatively shown in Figure 8. Oxidation in air produces a dark gray scale. Oxidation in $P_{O_2} \approx 0.02$ atmospheres yields a nearly black scale, and oxidation in water vapor produces a yellow-orange oxide.

The various samples have been cross-sectioned to provide a comparison of microstructural evolution during oxidation. SEM images of these cross sections are shown in Figure 9. Isothermal oxidation in air produces a continuous oxide scale that is several microns thick. Thermal cycling results in a much thicker, spalling scale; cracks in the coating also show noticeably more oxidation compared to isothermal exposure. Comparatively thinner scales form on the samples tested in low- P_{O_2} and high-velocity water vapor environments. X-ray

elemental maps of the thermally cycled, low- P_{O_2} and high-velocity water vapor samples are shown in Figure 7.

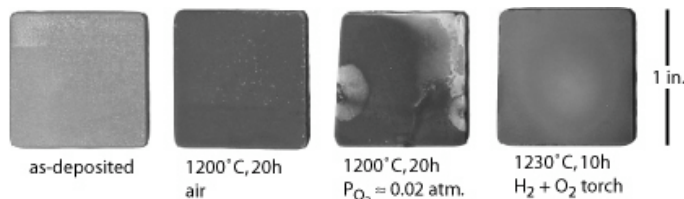


Figure 8: Photographs of R512E/C103 coupons

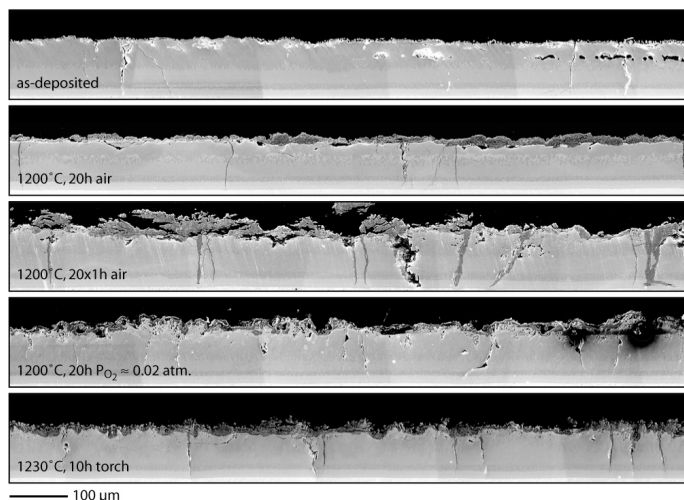


Figure 9: SEM cross sections of R512E coatings

When compared to the as-deposited coating (Figure 1), the thermally cycled sample shows coarsening of the silicon-rich region. This change in coating microstructure can be seen by comparing the silicon x-ray maps of the as-deposited and thermally-cycled coatings. In the as-deposited condition, silicon-rich areas are visible through the coating thickness. Moreover, these silicon rich features exhibit a wide range in size and aspect ratio in the as-deposited coating. After thermal cycling, the silicon rich areas appear to have concentrated near the surface of the coating, and finer-scale structures are not as prevalent. Additional microstructural changes upon thermal cycling include the concentration of iron in the middle of the coating, and incorporation of niobium, chromium, and silicon in the oxide. The infill of cracks by oxidation products is clearly shown in Figures 7 and 9.

In the low- P_{O_2} test, the coarsening of silicon-rich areas and concentration of iron towards the center of the coating are again visible. The oxide appears to have a much stronger chromium signal, which is supported by the presence of larger Cr_2O_3 peaks in the XRD spectrum. Crack infill is not observed. The greater $Cr_2O_3:CrNbO_4$ ratio in the low- P_{O_2} test suggests that the incorporation of niobium into the scale at higher oxygen partial pressures may be governed by chromium diffusion from the coating interior to the coating surface.

The sample tested in the H_2+O_2 torch shows less coarsening of the coating microstructure, which may be attributed to the shorter duration of the test (~10h compared to

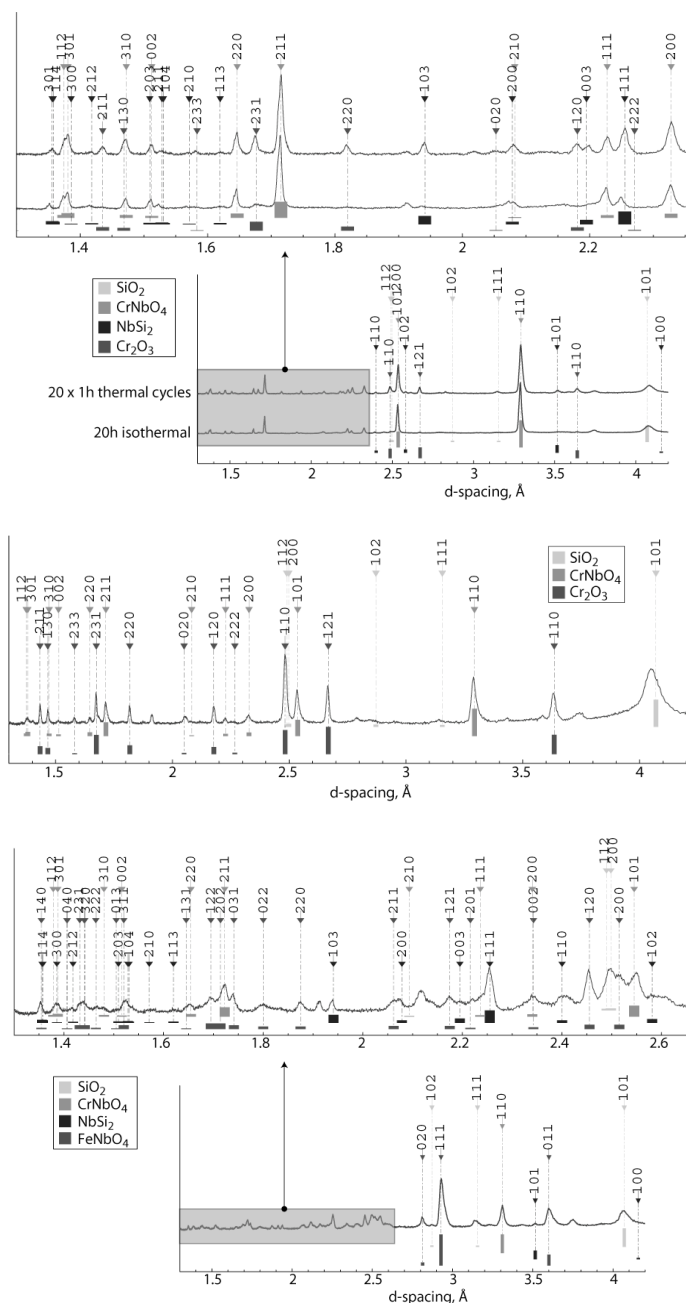


Figure 11: XRD spectra of oxidized samples. Isothermal and thermally-cycled in air (top), low- P_{O_2} (middle), and torch (bottom). Peak locations from ICDD reference spectra are represented by bars.

20h). The through-thickness thermal gradient should also be considered. Although the oxide surface temperature was measured around 1230°C for the duration of the test, a thermocouple on the backside of the sample recorded 1000°C, corresponding to a thermal gradient of $\sim 0.2^\circ\text{C}/\mu\text{m}$. The oxide composition is noticeably different; the iron signal is much stronger, and chromium seems to be absent from the scale. The silicon-rich regions appear reduced in volume, indicating the

depletion of silicon as well as chromium. Because the substrate is comparatively cooler (on account of the thermal gradient), and considering that the duration of this torch test was half the time of the other oxidation tests, it is likely that silicon and chromium have been depleted through volatilization reactions.

EDX area scans of the outer coating surfaces have been used to provide a more quantitative assessment of scale compositions. The ratios of major coating constituents in the as-coated condition and in the oxide scales are shown in Figure 10. This analysis supplements the XRD and SEM observations: The scales of the thermally cycled and low- P_{O_2} samples contain more chromium, whereas the sample tested in the torch contains more iron, but only a trace amount of chromium.

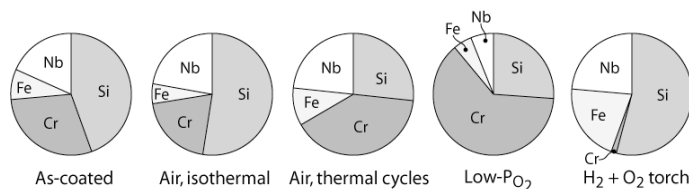


Figure 10: EDX characterization of scale compositions.

The various scales have been characterized by XRD to determine phase composition. In air at 1 atmosphere, CrNbO_4 and SiO_2 are formed (Figure 11). Thermal cycling appears to promote the formation of Cr_2O_3 in addition to CrNbO_4 and SiO_2 . In the low- P_{O_2} environment, SiO_2 and Cr_2O_3 form, with comparatively less CrNbO_4 than oxidation in air. High-velocity water vapor results in the formation of CrNbO_4 , FeNbO_4 , SiO_2 ; Cr_2O_3 peaks are absent from the x-ray spectrum. NbSi_2 peaks in the thermally-cycled, low- P_{O_2} , and water vapor tests suggest thin or spalled scales; additionally, the absence of M_5Si_3 peaks, a predominant phase in the as-coated surface, suggests its preferential oxidation.

THERMODYNAMIC MODELING

Thermodynamic characterization of R512E oxidation requires thermodynamic models of NbSi_2 and M_5Si_3 phases along with the oxidation products. Free energy data is not available for CrNbO_4 . Although thermodynamic properties of hexagonal Fe_5Si_3 are available in the Thermocalc TCFE4 database, the thermodynamic descriptions used in this database do not allow for Nb solubility in this phase. Additionally, Cr solubility in Fe_5Si_3 is limited to ~ 20 atomic percent, whereas the composition of the D8_8 silicide in R512E coatings appears to have a Cr:Fe ratio of $\sim 2:1$. Insufficient thermodynamic models and data obscure the thermodynamic analysis of R512E silicide oxidation; nevertheless, a few observations and inferences can be made with the available thermodynamic information.

An Ellingham diagram was constructed to compare the driving force for oxidation of chromium, niobium, silicon, and iron over temperature and oxygen partial pressure. A comparison of pure metals may be used as a qualitative assessment of the tendency for individual coating constituents to oxidize, shown by the dashed lines in Figure 12. Ranking

the simple oxides by free energy of reaction results in silica being most thermodynamically favorable followed by Nb_2O_5 and Cr_2O_3 (approximately equivalent), and finally Fe_2O_3 . A somewhat more representative description of oxidation may be formulated by considering the activities of these elements when present as silicide phases observed in the R512E coating: M_5Si_3 and MSi_2 , shown by the solid lines in Figure 12. Silicon activity is equivalent in Cr_5Si_3 - CrSi_2 and Nb_5Si_3 - NbSi_2 mixtures. Activity data for iron and silicon in Fe_5Si_3 - FeSi_2 is not available. The reduced activities of chromium, niobium, and silicon in silicides reduce the driving force for oxidation; however, oxides are thermodynamically preferred to silicides even at low oxygen partial pressures. For example, at 1250 °C, an oxygen partial pressure below 10^{-15} bar is required for chromium to remain in a Cr_5Si_3 - CrSi_2 mixture. This highlights the importance of tailoring coating chemistry in order to develop protective oxides.

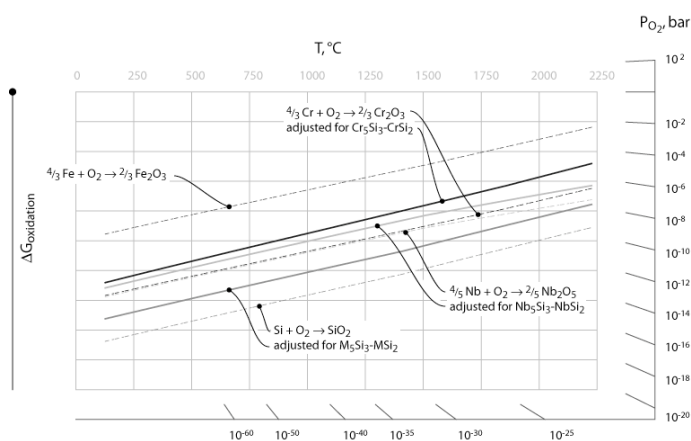


Figure 12: Ellingham diagram for oxidation of Cr and Nb silicides.

Beyond oxidation, the thermodynamics of water-vapor-mediated volatilization have been investigated for oxides and hydroxides of silicon and chromium. For reactions involving two gas species (e.g. oxygen and a volatile metal oxide or hydroxide), volatility diagrams are often used to visualize thermodynamics of the system. In general, a volatility diagram is an isothermal plot of reaction equilibria as a function of the partial pressures. Volatility diagrams have been used to elucidate thermodynamics of high temperature oxidation and decomposition in non-oxide ceramics and silica formers as a function of oxygen partial pressure[9-11]. Thermodynamic data is available for numerous volatile silicon and chromium oxide and hydroxide species[12-15]. This data may be used to determine equilibrium partial pressures as a function of temperature and environment in order to identify dominant volatilization reactions. Figure 13 shows the equilibrium partial pressures of various silicon and chromium species (over SiO_2 and Cr_2O_3 respectively) at 1500 K. Silica volatilization is dominated by three species at this temperature. High partial pressures of water vapor drive the formation of $\text{Si}(\text{OH})_4$. Low partial pressures of oxygen favor the formation of SiO . At high partial pressures of oxygen and low partial pressures of water vapor, $\text{SiO}(\text{OH})_2$ may be the dominant volatile species.

Chromia volatilization involves several hydroxides ($\text{CrO}(\text{OH})_2$, CrO_2OH , $\text{CrO}_2(\text{OH})_2$, $\text{CrO}(\text{OH})$), as well as the oxides CrO_2 and CrO_3 .

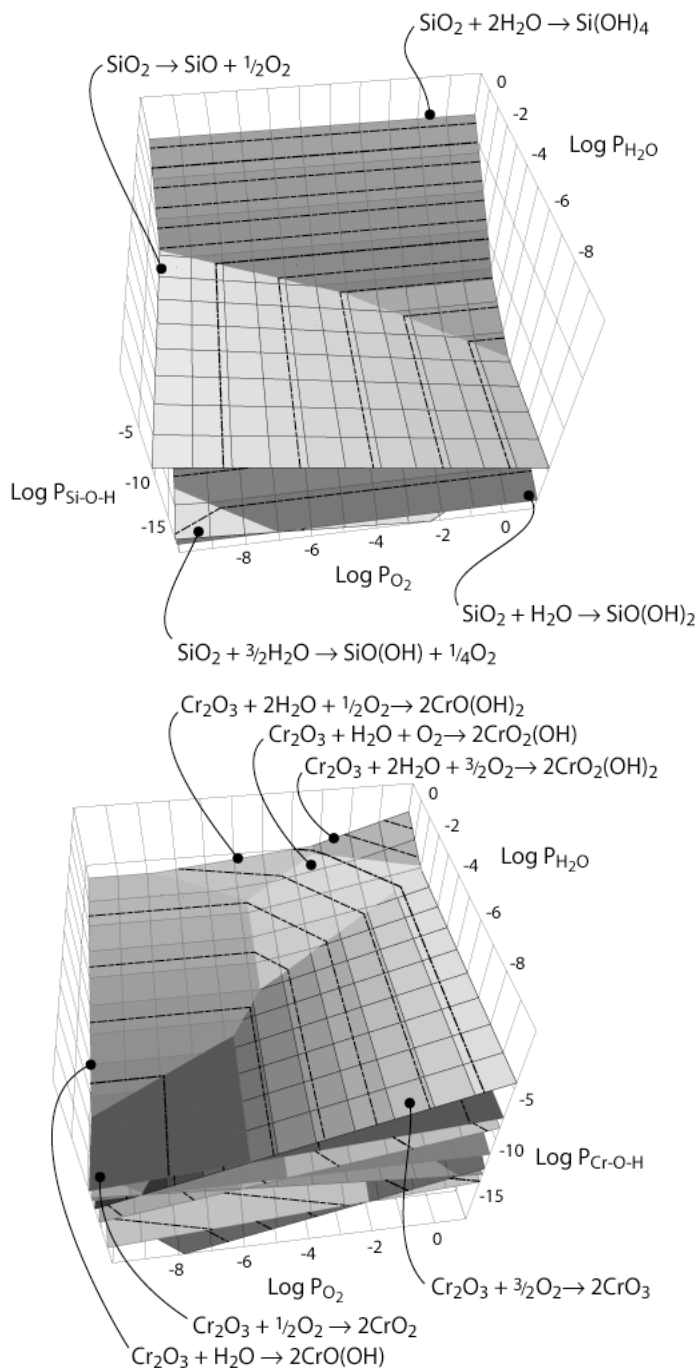


Figure 13: Volatility diagrams at 1500 K for SiO_2 (top) and Cr_2O_3 (bottom)

Both SiO_2 and Cr_2O_3 exhibit high equilibrium partial pressures of volatile species (i.e. $\text{Si}(\text{OH})_4$ and $\text{CrO}_2(\text{OH})_2$) in high $P_{\text{H}_2\text{O}}$ environments. In environments where equilibrium vapor pressures cannot be achieved due to continuous removal of volatile species (e.g. combustion environments), recession of

silica and chromia scales will affect oxidation behavior. This is experimentally supported by the lack of Cr_2O_3 in the scale formed in the torch test, as well as the depletion of Si from the R512E coating interior as shown in the x-ray map (Figure 9).

From the perspective of volatilization thermodynamics, the incorporation of iron in the silicide coating may provide a nonvolatile oxide (FeNbO_4) in environments where chromium-bearing oxides are not stable.

CONCLUSIONS

Microstructural characterization of R512E coatings on C103 has shown that the outermost portion of the coating contains NbSi_2 and $(\text{Cr}, \text{Nb}, \text{Fe})_5\text{Si}_3$ phases. High-temperature oxidation tests have shown that oxide species formed from these phases include SiO_2 , Cr_2O_3 , CrNbO_4 , and, in high velocity water vapor, FeNbO_4 . A thermodynamic analysis of oxidation demonstrates that oxides are more stable than silicides in temperatures pressures relevant to hypersonic flight. Similarly, an analysis of volatilization has shown that oxide stability, in particular the stability of SiO_2 and Cr_2O_3 , should be considered in the design and selection of coatings for use in combustion environments.

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