

In-Situ Multi-layer Formation in the Oxidation of Ti₃Al-Nb

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The effect of niobium on the oxidation of a Ti₃Al alloy was studied in pure oxygen in the range of 850–1,100°C. The oxidation products for the Ti-30Al–2.7 Nb alloy were mainly TiO₂ (rutile) mixed with Al₂O₃ (alumina) and small amounts of niobium oxide. The oxidation resistance of Ti₃Al was improved by the addition of niobium. An in-situ multiple-layer structure comprising a mixture of rutile and alumina formed on the oxide scale of the alloy at temperatures 1,000°C and above. The number of layers increased as the temperature increased but the individual layer thickness decreased.

INTRODUCTION

Ti₃Al intermetallic alloys are candidates for applications in advanced aerospace engines and airframe components. However, the oxidation resistance of Ti₃Al is poor due to its inability to form a protective layer and the relatively high level of oxygen dissolution into the alloy, which results in oxygen embrittlement.^{1–3} Studies have reported that oxidation resistance improved when niobium was added to Ti₃Al^{4–6}, resulting in the formation of a dense, protective layer. Nonetheless, the formation and morphology of the oxide layer is still a subject of investigation. In this paper, the oxidation behavior in pure oxygen and characterization of the oxidation products of a Ti₃Al alloy of nominal composition Ti-30Al-2.7Nb at.% is reported.

The oxidation resistance of the alloy Ti-29.65Al-2.68Nb-0.20 at.% was much greater than its counterpart with no niobium addition. That improved resistance was evidenced during oxidation tests in pure oxygen at different temperatures, when the alloy niobium addition gained less weight per surface area. Data revealed a parabolic oxidation rate (k_p) that obeys an Arrhenius-type equation of the form

$$k_p = k_0 e^{-(Q/RT)}$$

where R is the universal gas constant, k_0 is the pre-exponential factor, T is the temperature in K, and Q is the effective activation energy. From the experimental data (plot of $\ln(k_p)$ vs $1/T$), an effective activation energy of 284 kJ/mol was deduced. This value is higher than that for binary alloy Ti-26Al,² but lower than Q values reported for Ti₃Al binary alloys with higher aluminum concentration.^{2,3}

CHARACTERIZATION RESULTS

The Ti-30Al-2.7Nb oxidized samples were characterized using scanning electron microscopy (SEM), energy-

dispersive x-ray (EDX), and x-ray diffraction (XRD) techniques. The XRD technique was used to identify the various phases present in the oxide scale. After XRD analysis, the samples were fractured into pieces, polished, and examined for the oxide morphology by SEM. Energy-dispersive x-ray spectra revealed the amounts of various elements present at different locations of the oxide scales on the oxidized samples. The products of oxidation of the alloy were mainly TiO₂ (rutile) and Al₂O₃ (alumina). Oxides of niobium were not identified in the oxide scales by XRD, possibly due to their very low content in the alloy. However, EDX spectra showed the presence of

Figure 1. A SEM micrograph of the Ti-30Al-2.7Nb alloy oxidized in pure oxygen at 850°C for 24 hours.

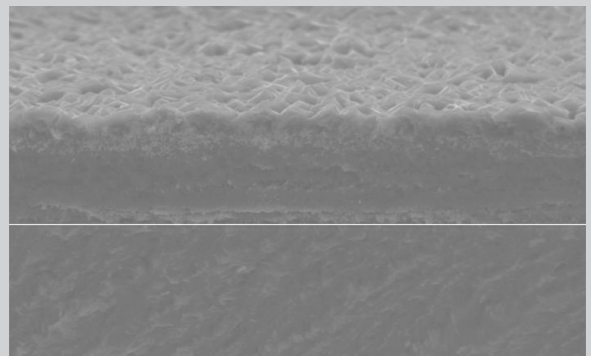
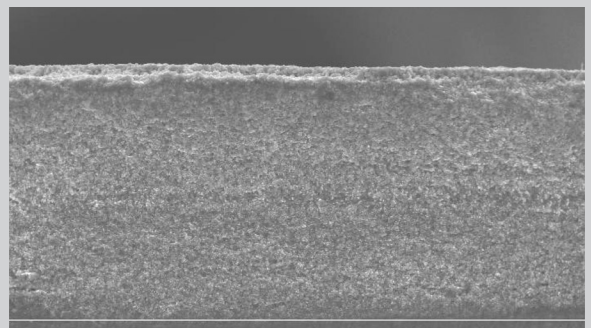


Figure 2. A SEM micrograph of the Ti-30Al-2.7Nb alloy oxidized in pure oxygen at 950°C for 24 hours.



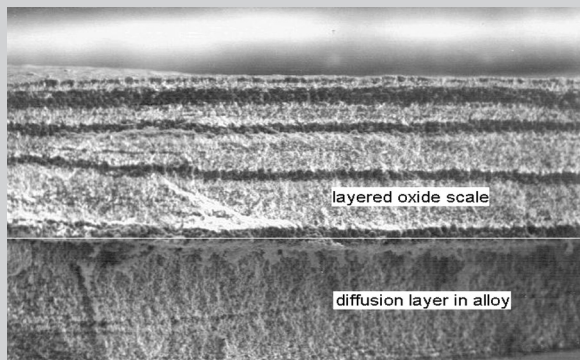


Figure 3. A SEM micrograph in-situ formed multiple-layer oxide structure of the Ti-30Al-2.7Nb alloy oxidized in pure oxygen at 1,000°C for 24 hours.

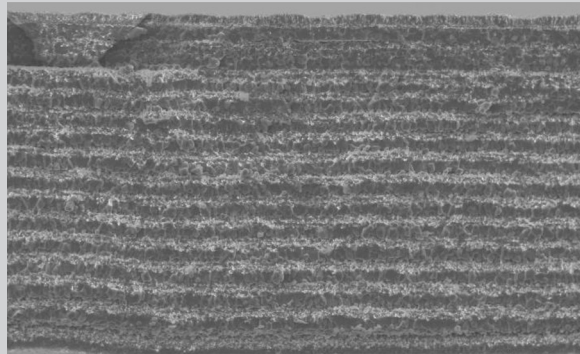


Figure 4. A SEM micrograph in-situ formed multiple-layer oxide structure of the Ti-30Al-2.7Nb alloy oxidized in pure oxygen at 1,100°C for 24 hours.

elemental niobium in the oxide scale.

Figure 1 shows the SEM micrograph of the fractured cross section of the alloy samples oxidized in pure dry oxygen at 850°C for 24 hours. The thickness of the oxide scale was about 15 μm. The composition of the interface region as obtained from EDX analysis was 66 at.% of oxygen, 32.5 at.% of titanium, 0.7 at.% of aluminum, and 0.8 at.% of niobium. This indicates that the interface was mostly composed of rutile. The outermost regions of the oxide scale consisted of rutile and alumina, while the rest of the scale was almost rutile. The oxide scale formed was thicker and adherent to the alloy matrix.

Figure 2 shows the SEM micrograph of the alloy sample oxidized at 950°C for 24 hours in pure oxygen. The oxide-scale thickness was more than 100 μm. The composition of the interface alloy/oxide interface was 79 at.% oxygen, 16 at.% titanium, 4.5 at.% aluminum, and 0.5 at.% niobium. The interface region consisted of mainly rutile and a small amount of alumina. No niobium oxide was detected by XRD in the oxide scale, although niobium could

have been present as a solid solution in the oxide mixture. The oxide scale appeared as a sintered compact of rutile and alumina with a uniform porosity along the direction perpendicular to the growth axis. The oxide scale on the alloy was thicker and adherent to the alloy matrix beneath.

Figure 3 shows a SEM micrograph of the fractured cross section of the alloy oxidized in pure oxygen at 1,000°C for 24 hours. An in-situ multiple-layer structure of the oxide scale was observed. The oxide layer was about 100 μm thick, while the diffusion-affected alloy surface layer ranged from 70–90 μm. The interface consisted mostly of rutile and alumina, with very small amounts of niobium. Some of the oxide scale spalled after the cool-down period in the form of several large pieces. The remnant oxide scale on the alloy was very thick (>100 μm) and layered with a mixture of rutile and alumina. The overall oxide scale was comprised of individual layers with varying thickness.

The interesting feature of the oxide scale on the alloy oxidized at 1,000°C

is the multiple-layer structure formed in-situ with alternate layers of rutile and a mixture of alumina with small amounts of niobium. The white layers composed of rutile mixed with alumina were typically 30 μm thick followed by 5–6 μm thick dark layers of rutile. The main component of the white layers was rutile, while the alumina particles were smaller in size compared to that of rutile. The multiple-layer oxide structure probably was formed due to the difference in the diffusion rates of aluminum, niobium, and titanium in rutile, coupled with the structure of rutile, which facilitates the easy diffusion paths for the transport of oxygen. Rutile structure has channels parallel to the c-axis, which can constitute the faster diffusion paths for oxygen. Since the diffusion rate is temperature dependent, this formation of multiple-layer oxide structure was predominantly observed on the alloys oxidized at temperatures 1,000°C and above. Such structure formation was not so obvious at lower temperatures as Table 1 shows.

Figure 4 shows the SEM micrograph of the fractured cross-section of the alloy oxidized at 1,100°C in pure dry oxygen for 24 hours. The oxide scale was more than 200 μm thick and the outermost layers spalled after the cool-down period. The in-situ multiple-layer structure of the oxide scale that was observed at this temperature was even more pronounced than that observed at 1,000°C. The oxide strata were also different from those observed at 1,000°C, the individual layer thickness was smaller, and more layers were formed. A magnified SEM micrograph of the multiple-layer oxide structure is shown in Figure 5, along with the EDX spectrum of a small particle marked by the arrow on the micrograph. The dark layered region was made up of large rutile particles and was 10 μm thick. The white layered region was made up of small particles, which were predominantly of alumina with small amounts of niobium and was less than 5 μm thick. The number of such alternate layers increased from that observed at 1,000°C and the layer thickness was decreased considerably. Further investigations are in progress to clarify this and model these layered structures.

Table I. Layered Structure Formation in Ti-Al-Nb Alloys

Temperature	Oxide Thickness (μm)	Oxide Layers
850°C	15	Not formed
950°C	100	Not formed
1,000°C	>100	Formed
1,100°C	>200	Formed

CONCLUSION

Although the oxidation resistance of the Ti_3Al alloy improved when niobium was added, a compact, dense, and continuous layer of alumina was not formed on the alloy. The oxide scale would render effective protection from further oxidation if there were a large amount of alumina in the overall scale. These layers had very little alumina, with rutile as the major oxide, and, hence, the expected protection from oxidation is not possible for the Ti_3Al alloy upon the addition of small amounts of niobium.⁴ The improved oxidation resistance of the Ti_3Al alloy upon the addition of niobium may be due to the increase in the c/a ratio of the alloy that decreases the oxygen solubility in the alloy. Doping of niobium into the TiO_2 lattice reduces the oxygen vacancy concentration, thereby decreasing the diffusivity of oxygen through the oxide layer.

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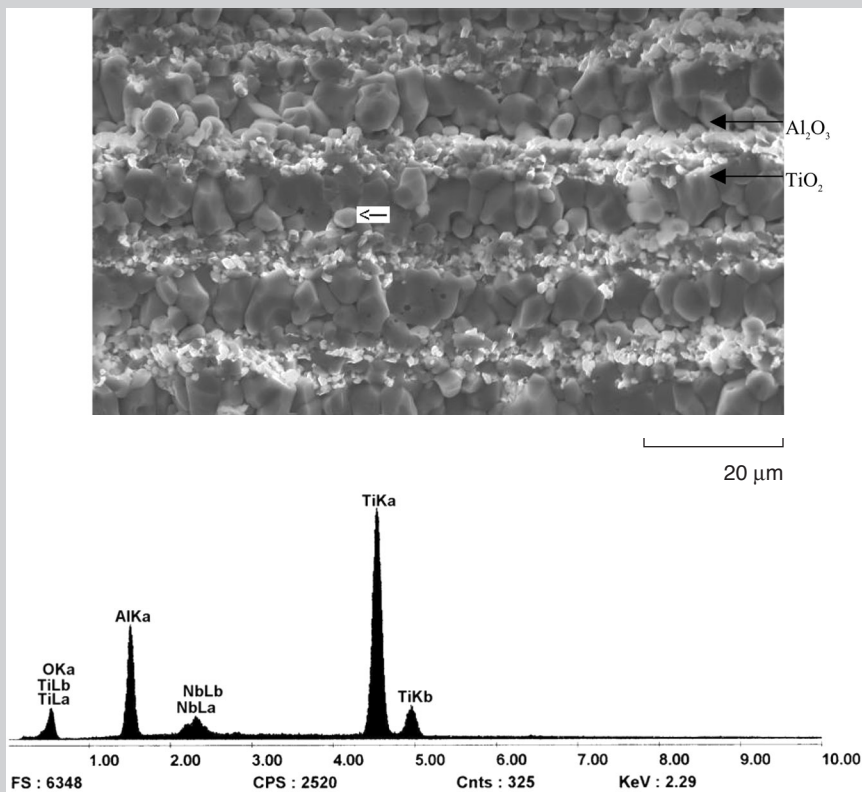


Figure 5. A magnified portion of the in-situ formed multiple-layer oxide structure of the Ti-30Al-2.7Nb alloy oxidized in pure oxygen at 1,100°C for 24 hours (shown in Figure 4). The EDX spectrum is for the particle in the oxide scale marked by the arrow on the micrograph.

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