An Examination of the Mechanisms Involved in the Oxidation of the Aligned Eutectic Alloy Ni₃Al–Ni₃Nb

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The aligned eutectic alloy Ni₃Al–Ni₃Nb at 1155°C exhibits an initial very rapid rate of oxidation which rate eventually decreases to a very significantly lower level. This decrease in the rate of oxidation has been shown to be associated with the formation of an aluminum oxide layer. The work reported here was conducted to determine both how such a layer forms in oxidation at 1155°C as a function of time and which elements are the active diffusing species in the oxidation process.

KEY WORDS: eutectic alloy oxidation; refractory metals; oxidation mechanism.

INTRODUCTION

In the course of a recent investigation of the oxidation behavior of the directionally aligned lamellar eutectic alloy Ni₃Al–Ni₃Nb, a coherent and apparently compact aluminum oxide layer was observed to eventually form around the alloy surface at 1155°C in air.¹ The appearance of this layer was associated with a very dramatic concomitant decrease in the oxidation rate of the alloy. The aluminum oxide layer was not observed on samples oxidized at lower temperatures (600, 800 and 990°C), even after 12 days at 990°C. A plausible mechanism to account for the formation of such an oxide layer could only be suggested as a result of that work. Therefore, a detailed study of the oxidation behavior of this alloy at 1155°C has been made to


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determine mechanistically how such an aluminum oxide layer forms as a function of time in the course of oxidation.

Additionally, to help understand the process of oxidation in this lamellar eutectic, it was decided to use inert Pt markers to determine, if possible, the nature of the most important diffusion species in the oxidation process. Arbuzov and Chuprina\textsuperscript{2,3} reported the results of using Pt markers in an oxidation investigation of the cast two-phase Ni\textsubscript{3}Al–Ni\textsubscript{3}Nb alloys. Their results indicated the Pt markers were to be found after oxidation at the base of an outer layer of NiO and above a layer of more complex oxides. However, both the structures of the oxide layers in the case of the cast alloys and their thermogravimetric behavior during oxidation differ substantially from the behavior observed in the case of the aligned alloys. Therefore, in view of the fact that the mechanism of oxidation could be substantially different for the two different microstructures of the alloy (cast and directionally aligned), inert (Pt) markers were used in this study of the oxidation behavior of the aligned alloys.

**EXPERIMENTAL**

The Ni\textsubscript{3}Al–Ni\textsubscript{3}Nb alloy samples were prepared and directionally solidified at 1 in./h as described elsewhere.\textsuperscript{1} The chemical composition of this alloy as determined by wet chemical methods was 73.0 (±0.2) wt.% Ni, 22.1 (±0.2) wt.% Nb, and 4.9 (±0.1) wt.% Al. The interlamellar spacing between the Ni\textsubscript{3}Nb and Ni\textsubscript{3}Al phases was 1.7 μ. The coupons used in this investigation were circularly shaped, approximately 1.25 cm in diameter, and 0.10 cm thick with a small hole, 0.10 cm in diameter, for support during the oxidation. The Ni\textsubscript{3}Al–Ni\textsubscript{3}Nb lamellae were perpendicular to the circular surface. The Pt markers, 2 and/or 5 mil Pt (99.999 % Pt), were affixed to the surface by spot welding techniques. After washing and degreasing, the samples were then oxidized in an apparatus and by a technique described elsewhere.\textsuperscript{1} The atmosphere used was 20 % O\textsubscript{2}–80 % N\textsubscript{2} artificially blended by and purchased from Linde Div., Union Carbide. The minimum amount of time needed to reliably arrive at the oxidizing temperature for this experimental configuration was found to be less than 10 min. Accordingly the minimum time for which a sample was oxidized was 10 min. Based on the results of the thermogravimetric data and metallography of earlier oxidation experiments involving this alloy, the aluminum oxide layer was expected to be established after about 16 h at 1155 °C. Accordingly the maximum duration of oxidation was 65 h, a time sufficiently greater than 16 h so as to ensure that the aluminum oxide film had indeed formed.

The phase identifications referred to in the text are based on information acquired by x-ray crystallography and electron microprobe examination of