Fabrication of Al$_2$O$_3$-Reinforced Ni$_3$Al Composites by a Novel In Situ Route

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A novel in situ technique has been used to fabricate an Al$_2$O$_3$-reinforced Ni$_3$Al matrix composite. The composite was prepared by first incorporating a low volume fraction of continuous Al$_2$O$_3$ fibers in a Ni$_3$Al alloy containing 0.34 at. pct Zr. Pressure casting was used to embed the fibers. Casting resulted in partial reduction of the Al$_2$O$_3$ fiber by the Zr present in the matrix and the formation of a layer of ZrO$_2$ on the surface of the fibers. The final composite was then prepared by air annealing the precursor composite at 1100 °C for 10 days. Air annealing led to the formation of networks of Al$_2$O$_3$ around the fibers. The matrix in the immediate vicinity of the networks consisted of Ni$_3$Al particles in a matrix of disordered α-Ni(Al). The Al$_2$O$_3$ networks raised the yield and tensile strength of the material by 35 and 18 pct, respectively. The composite had a tensile ductility of 14 pct.

I. INTRODUCTION

NICKEL-BASED superalloys are already being used as load-bearing turbojet engine components at temperatures as high as 0.9 times their absolute melting temperature. Further progress in increasing operating temperature inevitably will be slow. Consequently, extensive attempts have been made to develop high-temperature structural materials with capabilities higher than those offered by nickel-based superalloys. Intermetallic compounds in general and aluminides in particular have received the most attention. Among the aluminides, the B-doped Cr-containing Ni$_3$Al-based alloys, because of their appreciable ductility from room to high temperatures, are the most attractive candidates. Although these alloys are noticeably stronger than the nickel-based alloys, they have an inferior creep resistance.

Reinforcing Ni$_3$Al-based alloys with a suitable material has the potential of not only increasing the strength and reducing the mass density but also of improving the creep resistance. Among the various reinforcing materials that were employed, Al$_2$O$_3$ appears to be the chemically most compatible material. However, recent investigation indicated that the interfacial bond strength between single-crystal Al$_2$O$_3$ fiber and binary Ni$_3$Al was weak, 19 MPa. Although alloying with 0.5 at. pct Cr increased the bond strength to 55 MPa, its addition resulted in a fiber/matrix reaction. The Weibull mean strength of the single-crystal Al$_2$O$_3$ fiber was 2.6 GPa, and its addition resulted in a fiber/matrix reaction. The Weibull mean strength of the single-crystal Al$_2$O$_3$ fiber was 2.6 GPa, and its addition resulted in a fiber/matrix reaction.

In a recent study, it was shown that when Ni$_3$Al composites unidirectionally reinforced with ZrO$_2$-toughened polycrystalline Al$_2$O$_3$ fiber were exposed to air at elevated temperatures, oxygen diffused rapidly along the grain boundaries of the Al$_2$O$_3$ fiber deep into the composite. This resulted in the oxidation of Al of the Ni$_3$Al matrix, which led to the formation of a layer of Al$_2$O$_3$ covering the surface of the fibers. When a Ni$_3$Al alloy containing small amounts of Zr, 0.34 at. pct was used as the matrix and the composite was subsequently annealed in air, the oxygen reacted with the Zr of the matrix and formed ZrO$_2$. In contrast to the behavior of Al$_2$O$_3$, the ZrO$_2$ did not precipitate as a layer on the surface of the fiber but rather as thin ribbons starting at the surface of the fiber and extending into the matrix. The diffusion of oxygen through the ZrO$_2$ ribbons and its subsequent reaction with the Al of the matrix resulted in the formation of Al$_2$O$_3$ covering the flat faces of the ZrO$_2$ ribbons. This process led to the formation of a rootlike Al$_2$O$_3$ network around the fiber.

This behavior offered the possibility of producing Ni$_3$Al composites reinforced with Al$_2$O$_3$ networks by an in situ technique in which relatively small amounts of Al$_2$O$_3$ fiber were incorporated. The aim of the study conducted was to fabricate a Ni$_3$Al-based composite by the in situ technique and to characterize its microstructure and mechanical properties. It is of interest to note that a similar behavior has also been observed in Zr containing NiAl and Fe$_3$Al composites reinforced with polycrystalline Al$_2$O$_3$ fiber. This suggests the possibility of producing Al$_2$O$_3$-reinforced composites using these two matrices.

II. EXPERIMENTAL PROCEDURE

The matrix alloy used in the investigation is known as IC50 (Ni-21.7Al-0.34Zr-0.1B, in at. pct). The alloy was provided by Armco Research Center (Middletown, OH). Single-crystal Al$_2$O$_3$ fibers were used as conduits for the diffusion of oxygen deep into the matrix. The single-crystal fibers, which had a diameter of 125 μm, were supplied by Saphikon (Milford, NH). The diffusion rate of oxygen through single-crystal Al$_2$O$_3$ is extremely low. The fiber, therefore, on its own does not allow significant oxygen diffusion to make it useful as a conduit for oxygen. It was mainly used because of its lower flexibility due to its larger
diameter as compared to the Al₂O₃-based fibers that are currently available, such as 20-µm-diameter FIBER FP* or PRD-166* or 10-µm-diameter ALMAX** fiber. As will be described later, the fiber had to be treated in order to accomplish the desired behavior.

The as-received continuous fiber was cut into 50-mm-long pieces. These fibers were placed inside an alumina jig (Figure 1). The fibers in the jig were held at their ends. The function of the jig was to keep the fibers apart and to prevent fiber movement during casting. The small-diameter fibers, because of their high flexibility, could not be held rigidly in the jig and, therefore, were not used. The jig was then placed inside a 55-mm-internal diameter alumina mold. The experimental setup and procedure used to fabricate the composites were described in some detail elsewhere.11 In brief, the IC50 alloy was placed inside a bottom poured alumina crucible positioned on top of the alumina mold containing the fibers. Both the alloy and fibers were concurrently but individually heated by induction heating under vacuum to preselected temperatures. On reaching the desired temperatures, approximately 200 °C above the melting temperature of the alloy, the molten metal was poured into the mold containing the fibers. In order to prevent fiber damage, the molten metal was not poured directly onto the fibers but rather onto a 50-mm-diameter alumina disk placed over the jig containing the fibers. The molten alloy was then forced to infiltrate the interstitial spaces between the fibers by pressurizing the casting chamber with 2.7 MPa argon gas pressure. The cast composite was allowed to cool to a temperature approximately 150 °C below the melting temperature of the matrix before the gas pressure was released. Further cooling to ambient temperature was carried out under vacuum.

The cast composite was removed from the Al₂O₃ jig and machined into a rod with fibers unidirectionally aligned parallel to the length of the rod. It was ensured that both ends of the fibers were exposed. A total of four composite rods were cast. Two rods were air annealed for 10 days at 1100 °C. One air-annealed rod and one as-cast rod were cut into two pieces. These pieces were machined into cylindrical specimens and were used for compression testing. The specimens were 10-mm long and had a diameter of 6.35 mm. The other two rods were machined into dog-boned tensile specimens by electrodischarge machining. The tensile specimens had a gage length and diameter of 22 and 6.35 mm, respectively. All the samples had a fiber volume fraction of 2.5 pct. Tensile and compression testing were performed in an MTS servohydraulic testing machine at an initial strain rate of 10⁻³ mm/s⁻¹.

For transmission electron microscopy (TEM) examination, 0.5-mm-thick slices taken perpendicular to the fibers were cut into 3-mm-diameter disks using an ultrasonic disk cutter. The disks were then dimpled on both sides by a dimple grinder and subsequently ion milled under a voltage of 5 kV at an angle of 12 deg to perforation. Examination of the samples was conducted in a Hitachi (San Jose, CA) H-800, a 200 kV scanning TEM equipped with an energy dispersive spectroscopy (EDS) detector.

III. RESULTS AND DISCUSSION

A. Processing

The diffusivity of oxygen in single-crystal Al₂O₃ is too low to make the Al₂O₃ fiber an efficient oxygen conductor. In contrast, the diffusivity of oxygen in ZrO₂ is many orders of magnitude larger than that in Al₂O₃.12 In order to enhance ingress of oxygen into the composite and produce the desired microstructure, the Al₂O₃ fiber had to be coated with a continuous layer of ZrO₂. Initially, a binary Ni₃Al alloy containing less than 0.1 at. pct Zr was employed. The Zr in the Ni₃Al reduced the Al₂O₃ fiber and formed ZrO₂ on the surface of the fiber. Figure 2 is a scanning electron micrograph (SEM) showing the surface of a single-crystal Al₂O₃ fiber extracted from the binary Ni₃Al composite containing very small amounts of Zr (<0.1). The fiber was extracted by dissolving the matrix in an acid, 75 pct HCl + 25 pct HNO₃. As can be seen, the ZrO₂ particles have dendritic morphology. The lack of uniform coverage of the fiber surface by ZrO₂ implied that the ZrO₂ had difficulty in nucleating but, once formed, could grow with relative ease. In order to obtain a continuous layer of ZrO₂, and, therefore, to provide an easy path for the ingress of oxygen into the composite, a Ni₃Al alloy that contained 0.34 pct Zr, IC50, was employed. Figure 3 reveals the surface of a single-crystal fiber extracted from a Saphikon fiber-reinforced IC50 matrix composite. The entire surface of the fiber is coated with ZrO₂.

Figure 4 is an optical micrograph taken from the cross section of one of the as-cast Saphikon fiber-reinforced composites. The fibers in the jig were arranged in groups of four fibers. The fibers in each group were located at the corners of a square. The distortion of the squares was due to movement of the fibers during liquid-metal infiltration and solidification of the matrix. The extent of fiber deflection, halfway along the length of the fiber, during liquid metal pressurization can be obtained by using the following relationships:13

\[ \Delta_{\text{max}}(\text{center}) = \frac{5FL^4}{384EI} \]

where \( I \) is the second moment of area, \( F \) is the applied force.