

INFLUENCE OF OXIDE REINFORCEMENT MATERIALS ON HIGH-TEMPERATURE OXIDATION RESISTANCE OF  $\text{Ni}_3\text{Al}$  MATRIX COMPOSITES

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ABSTRACT

The oxidation resistance of  $\text{Ni}_3\text{Al}$ -based metal matrix composites was studied in high-temperature air under isothermal and thermal cycling conditions as a function of the composition and form of oxide reinforcement material. The incorporation of oxide fibers or particles into the  $\text{Ni}_3\text{Al}$  matrix led to oxidation rates significantly greater than that for the monolithic aluminide. The increase in susceptibility was primarily due to internal oxidation along the fiber- (or particle-) matrix interfaces and depended on the type of reinforcement material and its disposition in the matrix. The results suggest that the choice of reinforcement material and the method of materials processing will be important considerations in the design of oxidation-resistant  $\text{Ni}_3\text{Al}$  composites.

INTRODUCTION

The development of high strength, ductile  $\text{Ni}_3\text{Al}$  has generated considerable interest in its use as a matrix material for composites.<sup>1</sup> The potential for a strong, lower-density high-temperature composite based on  $\text{Ni}_3\text{Al}$  is quite attractive, particularly because, in many environments, the resistance of such materials to oxidation is excellent. However, there is some evidence that the presence of reinforcement material can increase high-temperature corrosion susceptibility,<sup>2</sup> and that this can occur even when a stable oxide ( $\text{Al}_2\text{O}_3$ ) is used to reinforce normally resistant  $\text{Ni}_3\text{Al}$ , as was shown in initial isothermal oxidation exposures.<sup>3</sup> This paper reports and analyzes data on the oxidation behavior of  $\text{Ni}_3\text{Al}$  composites reinforced with alumina and hafnia as part of a general effort to determine the influence of various reinforcement materials on oxidation and to develop alloy design approaches to more corrosion-resistant high-temperature metallic composites.

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## EXPERIMENTAL PROCEDURES

Composites consisting of  $\text{Ni}_3\text{Al}$  reinforced with  $\text{Al}_2\text{O}_3$  fibers or  $\text{HfO}_2$  particles were used in this study. The starting prealloyed powders were IC-218  $\text{Ni}_3\text{Al}$  (obtained from Homogeneous Metals) for the  $\text{Al}_2\text{O}_3$  fiber-reinforced materials and IC-396M (Ametek Specialty Metals) for the  $\text{HfO}_2$ - $\text{Ni}_3\text{Al}$  composite. IC-218 consisted of Ni-16.5Al-8Cr-0.4Zr-0.1B (at. %) while IC-396M was composed of Ni-16Al-8Cr-1.7Mo-0.5Zr-0.02B. Two different  $\text{Al}_2\text{O}_3$  fibers (from duPont) were used. The fibers were 20  $\mu\text{m}$  in diameter and chopped to 3 mm lengths. The FP Type I fibers contained less than 1 ppm Si, while the PRD-166  $\text{Al}_2\text{O}_3$  fibers contained 20 wt %  $\text{ZrO}_2$  ( $\text{Y}_2\text{O}_3$ -stabilized). The  $\text{HfO}_2$  particles were less than 6  $\mu\text{m}$  in diameter. The composites were prepared by mechanically mixing 10 or 20 vol % reinforcement material with the  $\text{Ni}_3\text{Al}$  powders (nominally 100  $\mu\text{m}$  in diameter), sealing in an evacuated stainless steel can, and hot extruding at 1100 to 1150°C using a 9:1 extrusion ratio. An extruded IC-396M product was also produced (in a similar manner) along with a hot pressed IC-218. The standard heat treatment sequence after processing was 1 h at 1000°C for recrystallization followed by 24 h at 800°C (both in a vacuum of less than  $10^{-2}$  Pa). The microstructures and mechanical properties of the composites are described elsewhere.<sup>4,5</sup>

The oxidation experiments were conducted using an automated Cahn 1000 microbalance system having a sensitivity of 0.05 mg. Small ( $\sim 18 \times 6 \times 1$  mm), mechanically abraded specimens were hung from the microbalance (using a platinum wire) in flowing (110 cc/min) dry air at 800°C. In selected experiments, the specimen temperature was cycled between 800 and approximately 1000°C over 3 to 4 h. Specimen weights were recorded at a frequency proportional to the rate at which they changed with time. Following exposure, selected specimens were examined by optical and scanning electron microscopy.

## RESULTS

Figure 1 shows weight gains as a function of time for several fiber-reinforced  $\text{Al}_2\text{O}_3$ - $\text{Ni}_3\text{Al}$  composites. In all cases, the presence of the  $\text{Al}_2\text{O}_3$  reinforcement material increased the measured weight gain for a given time, but there was a large variation in the magnitude of the effect. The PRD-166 fibers were more deleterious to oxidation resistance than the FP type. As also shown in Fig. 1, specimens with 10 vol % FP fibers actually oxidized faster than those containing 20 vol %. Examination of polished cross sections of the oxidized  $\text{Ni}_3\text{Al}$ - $\text{Al}_2\text{O}_3$  specimens revealed that the relationship between the fiber alignment (parallel to the extrusion direction) and the specimen faces differed between the 10 and 20 vol % FP  $\text{Al}_2\text{O}_3$ . The fibers in the 10 vol %  $\text{Al}_2\text{O}_3$  material tended to be aligned such that their axes were perpendicular to the principal exposed faces of the specimen (see Fig. 2), while in the 20 vol % composite, the fiber axes were predominantly parallel to these surfaces.

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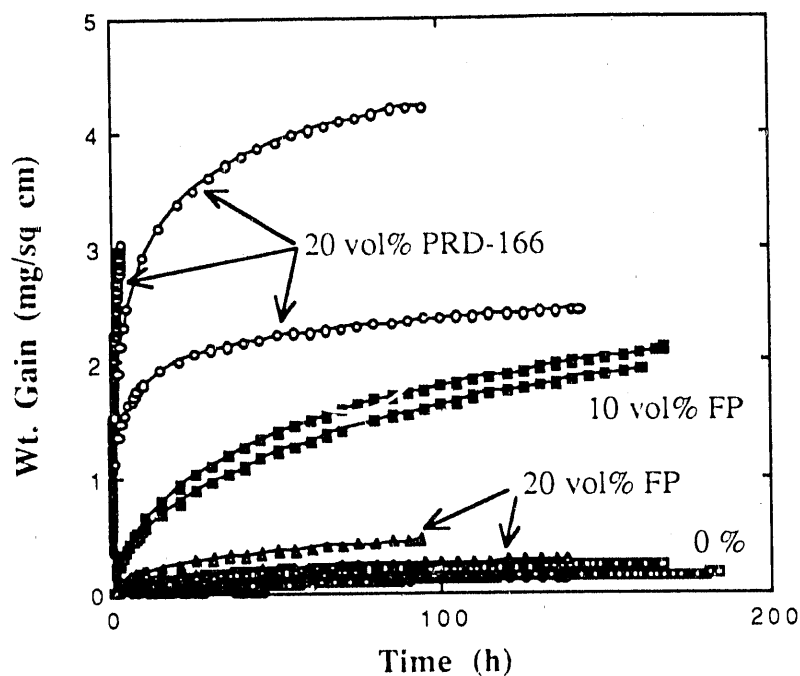


Fig. 1. Weight gain versus time for  $\text{Al}_2\text{O}_3\text{-Ni}_3\text{Al}$  exposed to air at  $800^\circ\text{C}$ .

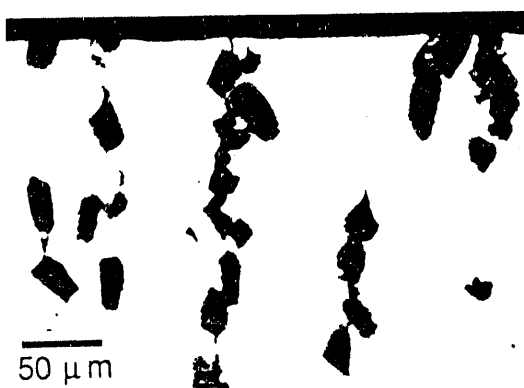


Fig. 2. Polished cross section of  $\text{Ni}_3\text{Al-10\% FP Al}_2\text{O}_3$  exposed to dry air at  $800^\circ\text{C}$  for 168 h.



Fig. 3. Polished cross section of  $\text{Ni}_3\text{Al-10\% HfO}_2$  exposed to dry air at  $800^\circ\text{C}$  for 171 h.

As shown in Fig. 3, the  $\text{HfO}_2$  particles in the  $\text{Ni}_3\text{Al}$  matrix tended to clump during processing and were aligned in the extrusion direction, which was perpendicular to the major exposed surfaces (as were the fibers in the 10 vol % FP specimens, see Fig. 2). The presence of the hafnia particles increased weight gains relative to the associated monolithic P/M product (Fig. 4). As also shown in Fig. 4, the weight gains were of the same order as those measured for  $\text{Ni}_3\text{Al-10 vol \% FP}$

$\text{Al}_2\text{O}_3$ , although there was some difference in the actual shape of the weight-versus-time curves. There were no differences in the oxidation kinetics of the monolithic IC-218 and -396M materials.

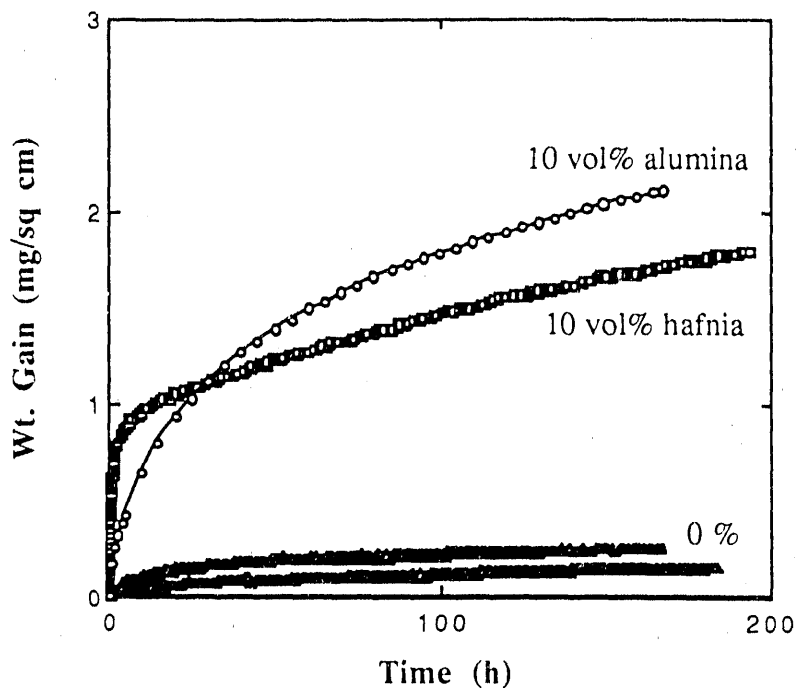


Fig. 4. Weight gain versus time for  $\text{HfO}_2$ - and FP  $\text{Al}_2\text{O}_3$ - $\text{Ni}_3\text{Al}$  exposed to dry air at  $800^\circ\text{C}$ .

A few experiments with the alumina-reinforced  $\text{Ni}_3\text{Al}$  composites were conducted under thermal cycling conditions. In these, weight was monitored while a specimen was first held isothermally at  $800^\circ\text{C}$  for at least 24 h, cooled to about  $100^\circ\text{C}$  over several hours, and then heated again to the same maximum temperature in less than 1 h. In all cases, no significant weight losses were observed during cooling nor was there any appreciable change in the oxidation rate after a thermal cycle. Total weight gains under isothermal and thermal cycling conditions were similar for equivalent exposure times.

## DISCUSSION

While the presence of a potentially reactive reinforcement material, such as  $\text{TiC}$ ,  $\text{TiN}$ , or  $\text{SiC}$ , could be expected to lead to degradation of an otherwise oxidation resistant material (see, for example, ref. 3), the above results showed that the presence of stable oxides also can deleteriously influence corrosion when used to reinforce  $\text{Ni}_3\text{Al}$ . With respect to the fiber-reinforced composites, the bulk of the pure  $\text{Al}_2\text{O}_3$  appeared to be relatively unaffected by the exposures (see, for example, Fig. 2 and ref. 6) and only a thin alumina scale, typical of the oxidation of monolithic  $\text{Ni}_3\text{Al}$ , formed on the metallic material. However, as shown in Fig. 1, a

significant acceleration of weight gain was measured when the fiber-reinforced composites were exposed to high-temperature air. In view of these observations and the finding that the weight gains are sensitive to disposition of the fibers in the matrix, it would appear that localized internal oxidation along fiber-matrix interfaces was the cause of the degradation of the high-temperature corrosion resistance of these composites. Indeed, a concurrent study using an  $O^{18}$  tracer technique has definitely shown internal oxidation of this  $Ni_3Al-Al_2O_3$  system along these interfaces<sup>6</sup> and such an influence of fibers on oxidation behavior of composites has been previously reported for superalloy matrices.<sup>2</sup>

Although there is evidence for preferential oxidation along the FP fiber-matrix interfaces, the reason(s) for the occurrence and rapidity of this type of corrosion process have not been definitely established. However, the unique structure of internal solid-state interfaces can provide preferential paths for both cation and anion (oxygen) diffusion and therefore can accelerate oxidation kinetics.<sup>7,8</sup> The presence of reactive impurities at such sites can also lead to localized oxidation (such as the role of grain boundary Zr in the internal oxidation of wrought  $Ni_3Al$ <sup>9</sup>) and, for the present case, enriched concentrations of these type of elements (Cr, Zr, and  $ZrO_2$ ) at  $Ni_3Al-Al_2O_3$  fiber interfaces have been reported.<sup>4,10</sup> Additionally, any voids or extended cracks at the fiber-matrix interface arising from thermal expansion mismatches between the metallic and ceramic materials can provide a means for gas phase transport of the oxidizing species into the bulk of the composite. Therefore, in the present case, the internal fiber-matrix interfaces can degrade oxidation resistance by providing structural fast paths, sites of localized concentrations of reactive elements, and/or gaps that facilitate delivery of oxygen along the interfacial region. Similar arguments can be made for the  $HfO_2$ -reinforced material in view of its comparable weight gains to that of the FP  $Al_2O_3-Ni_3Al$  and the observation that, as with the 10 vol % FP fibers, the particles tended to be aligned so that a significantly greater proportion of them intersected the surfaces exposed to the oxidizing gas. The difference in the oxidation curves (Fig. 4) between the FP  $Al_2O_3-Ni_3Al$  and the  $HfO_2$ -reinforced composite may be related to the respective shapes of the reinforcement materials. For a given volume density of reinforcement material, there should be more particles than fibers intersecting an arbitrary plane surface (ignoring particle clumping and assuming similar spatial distributions). Because internal oxidation can initiate at such sites and proceed along the interfacial regions, the particle-reinforced composite should have a higher initial oxidation rate and, as shown in Fig. 4, this is what is observed. However, in view of the length of the fibers, weight gains for the  $Al_2O_3-Ni_3Al$  should be greater at extended times due to the longer effective path lengths for internal oxidation. This is also in agreement with the data of Fig. 4.

As noted in the Experimental Procedures section, the PRD-166 fibers are composed of  $Al_2O_3$  and yttria-stabilized  $ZrO_2$ . While the  $ZrO_2$  itself should be quite stable, its presence in the  $Al_2O_3$  provides interfaces that could serve as additional paths for localized, directed oxidation, as discussed above. Therefore, the greater susceptibility of the composites reinforced with the PRD fibers (Fig. 1) may be ascribed to a higher density of available pathways for internal oxidation. However, the oxidation of many stable ceramics is strongly influenced by their impurities and

a contribution from preferential oxidation of such possible species in the PRD-166 may also have an influence. (FP  $\text{Al}_2\text{O}_3$  has an extremely low impurity content.)

The important role of internal oxidation of oxide-reinforced  $\text{Ni}_3\text{Al}$  is also illustrated by the negligible influence of thermal cycling on weight gain kinetic behavior. Thermal cycling should have little, if any, effect on weight gain from internal oxidation. For the  $\text{Al}_2\text{O}_3$ -reinforced  $\text{Ni}_3\text{Al}$  composites, no significant effects on weight change behavior with time were observed during thermal cycling and subsequent exposures at  $800^\circ\text{C}$ .

The discontinuous nature of the reinforcement materials dispersed in the  $\text{Ni}_3\text{Al}$  would suggest that the effect of these fibers and particles on oxidation should be transitory; their deleterious influence should eventually decrease to negligible levels as the interfacial paths are exhausted. The thermogravimetric curves indicate that there may be a decreasing effect with time. In several cases, a very high initial oxidation rate is followed by a lower one, but, with very few exceptions, rates of weight gain for the composites at extended times ( $>100$  h) were still greater than those associated with the monolithic  $\text{Ni}_3\text{Al}$  (see Figs. 1 and 4). However, even if the oxidation rates ultimately decrease to that of  $\text{Ni}_3\text{Al}$ , the properties of the composites may have already been compromised (particularly with respect to corrosion fatigue); oxidation along the interfacial regions of the composites provide a very efficient means for significant environmental degradation of these materials over short periods of time. Therefore, methods in which the influence of these particles and fibers on corrosion can be mitigated must be considered. Possible ways to improve the basic oxidation resistance of the composites would be to choose the shape (surface-to-volume ratio) of the reinforcement material to minimize the length of interfacial paths and to process the composite in a way that the extent of continuous reinforcement material is reduced (shorter fibers, smaller particles, better consolidation). Additionally, the extrusion direction should be parallel to the large external surfaces of the composite component. However, such approaches may severely impact attainment of the desired mechanical properties. This caveat would also apply to efforts to control fiber-(particle-) matrix reactions (by compositional modifications or coating of the reinforcement material) to reduce the susceptibility of interfacial regions to oxidation.

## SUMMARY

$\text{Ni}_3\text{Al}$  composites suffered degradation of their oxidation resistance when reinforced with  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\text{-ZrO}_2$ , and  $\text{HfO}_2$  despite the inherent stability of these materials in oxidizing environments. Corrosion was accelerated by internal oxidation along interfaces between the matrix and reinforcement material. Such ingress of oxygen into the bulk via the interfacial regions can possibly compromise the mechanical properties of the composite. The influence of a particular reinforcement material on oxidation behavior depended on its composition, shape and disposition in the matrix. The choice of reinforcement material for a given matrix and the method of materials processing will be important considerations in the design of oxidation-resistant  $\text{Ni}_3\text{Al}$  composites.

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