Ceramic Composites With A Ductile Ni$_3$Al Binder Phase


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Introduction

Hardmetals composites, based on WC-Co combinations, have been used and studied for a number of years.$^{1,2}$ The replacement of the cobalt binder phase by nickel alloys for improved corrosion resistance has been the subject of many investigations. Early work showed a significant decrease in the transverse rupture strength for the nickel alloys compared to the cobalt-based counterparts.$^{1,2}$ To overcome this deficiency, strengthening of the Ni-W-C alloys by using precipitation hardening with the formation of coherent Ni$_3$Al ($g'$) precipitates was studied.$^3$ It showed no significant improvement in strength and a decrease in the fracture toughness. Other research looked at solid solution strengthening of nickel alloy binder systems and it showed it was possible to use combinations of Cr, Mo, Al and Co to produce WC-based hardmetals with mechanical properties equivalent to WC-Co materials.$^4$

Nickel aluminide, Ni$_3$Al, is an attractive material for structural applications at elevated temperatures.$^5$ The reason is because, unlike conventional metallic alloys, the yield stress of Ni$_3$Al increases substantially with increasing temperature due to extremely rapid work hardening of the alloy.$^6$ Nickel aluminide is also capable of being strengthened by solid solution techniques because it can dissolve substantial alloying additions without losing the advantage of long-range order.$^7$ In addition, the alloys also exhibit good oxidation and corrosion resistance.$^8$ Normally, the application of polycrystalline Ni$_3$Al materials is limited due to the brittleness of the alloy, however, with the addition of small amounts of boron, the ductility is greatly improved.$^9,10$ The beneficial effect of boron has been attributed to an increase in the intrinsic strength or cohesion of the grain boundary and enhancement and facilitation of slip transmission across grain boundaries. Several Ni$_3$Al alloys have been developed in recent years using additions of other alloying agents, such as zirconium, chromium and molybdenum.$^5,8$

In the present study, composites using B-doped ductile Ni$_3$Al alloys were produced with both non-oxide (WC, TiC) and oxide (Al$_2$O$_3$) ceramic powders. Earlier work had shown these materials to have mechanical properties appropriate for industrial applications.$^{11}$ The purpose of this study was to establish a framework for the development of metallic reinforced ceramic matrix composites with improved mechanical properties and high reliability.
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Experimental Procedure

Characteristics of the raw materials used are shown in Tables 1 and 2. Note the large size difference between the ceramic components and the inert gas atomized Ni$_3$Al powder. The test materials were fabricated by ball milling powders of the ceramic and Ni$_3$Al particles together in non-aqueous liquids (isopropanol or hexane) using conventional powder processing techniques. The mixtures were then dried, screened and hot-pressed in graphite dies at 1150-1450°C for the non-oxide based materials or 1300-1550°C for the oxide based materials. The pressing conditions were ≤34 MPa (5 ksi) for 15-120 minutes in 0.1 MPa argon. Hot-pressing in graphite dies was used to consolidate the initial samples to determine the range of properties possible with these types of composites. Compositions with ceramic contents from 0-95 vol. % were fabricated in this fashion. Further work has shown fabrication to high density is also possible by pressureless sintering and melt infiltration of sintered ceramic preforms.$^{12,13}$ However, the data presented will be limited to the results on the hot-pressed materials.

Densities were determined by the Archimedes' method. Selected samples of high density were machined into bend bar specimens with nominal dimensions of 3 mm x 4 mm x 50 mm. Flexural strength testing was done in four point bending with inner and outer spans of 20 mm and 40 mm, respectively. Fracture toughness was determined by both an indentation and indentation/fracture methods.$^{14,15}$ The corrosion resistance was determined by measuring the weight loss during immersion in an acid solution at ambient temperature during a period of 48 h.

Table 1. Ni$_3$Al alloy compositions.

<table>
<thead>
<tr>
<th>Alloy ID</th>
<th>Al</th>
<th>B</th>
<th>Zr</th>
<th>Cr</th>
<th>Ni</th>
</tr>
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<tbody>
<tr>
<td>IC-15</td>
<td>12.7</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IC-50</td>
<td>11.3</td>
<td>0.02</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IC-218</td>
<td>8.5</td>
<td>0.02</td>
<td>0.8</td>
<td>7.8</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Characteristics of powders.

<table>
<thead>
<tr>
<th>Powder Type</th>
<th>Supplier/Grade</th>
<th>Ave. Particle Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Al</td>
<td>Homogeneous Metals</td>
<td>≤44</td>
</tr>
<tr>
<td>WC</td>
<td>Kennametal/WCA-20</td>
<td>2.5</td>
</tr>
<tr>
<td>TiC</td>
<td>Kennametal/TICA3</td>
<td>1.3</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Sumitomo/AKP-50</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Results and Discussion

The microstructural morphology of the composites developed during densification depends primarily on the wetting behavior between the alloys and the ceramic powders. The non-oxide ceramic powders are wet well by Ni$_3$Al, with typical wetting angles of <15° as measured on dense substrates.$^{12,16}$ Consequently, densification occurs by typical liquid phase sintering mechanisms with particle rearrangement and solution-reprecipitation taking place. In the final microstructure, the Ni$_3$Al alloys form a semi-continuous intergranular second phase with some remnant Ni$_3$Al-rich areas due to the relatively large size of the starting alloy powders (Fig. 1). The apparent lack of wetting
of some of the WC grain boundaries is related to the large starting Ni$_3$Al particle size and the hot-press conditions that resulted in some solid state sintering of the WC particles to occur. Some oxygen pickup occurs during the powder processing and this results in the formation of discrete Al$_2$O$_3$ particles as shown in Fig. 2. Analysis of the Ni$_3$Al areas by energy dispersive x-ray shows a small amount of W remaining in the binder phase alloy.

In contrast to the non-oxides, the Ni$_3$Al alloys do not wet the Al$_2$O$_3$ powders well, with wetting angles measured on dense substrates ranging from 60-120°. Only Ni$_3$Al alloys containing zirconium were observed to be adherent to an Al$_2$O$_3$ substrate. Therefore, in the Al$_2$O$_3$-Ni$_3$Al system, densification is dominated by solid state processes within the Al$_2$O$_3$ phase. Since Ni$_3$Al alloys melt at approximately 1390°C, hot-pressing had to be performed with an Al$_2$O$_3$ powder which could readily sinter at temperatures below the melting point. Materials made in this manner had a morphology where the Ni$_3$Al tended to form discrete "islands" within the Al$_2$O$_3$ matrix phase (Fig. 3). Hot-pressing above the melting point resulted in Ni$_3$Al being exuded from the composite. Wetting in these oxide materials can be improved by the addition of non-oxide particles, such as TiC.

The range of mechanical properties observed for the hot-pressed composites is summarized in Table 3.

Table 3. Summary of mechanical properties of Ni$_3$Al-bonded ceramic composites.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Microhardness (GPa)</th>
<th>Flexural Strength, 25°C (MPa)</th>
<th>Fracture Toughness, 25°C (MPa m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-17 Ni$_3$Al</td>
<td>14-18</td>
<td>1200-1350</td>
<td>10-20</td>
</tr>
<tr>
<td>WC-68 Ni$_3$Al</td>
<td>7</td>
<td>1750</td>
<td>25</td>
</tr>
<tr>
<td>TiC-17 Ni$_3$Al</td>
<td>16-20</td>
<td>750-900</td>
<td>8-14</td>
</tr>
<tr>
<td>Al$_2$O$_3$-25 TiC-10 Ni$_3$Al</td>
<td>18</td>
<td>350-580</td>
<td>7-8</td>
</tr>
<tr>
<td>Al$_2$O$_3$-10 Ni$_3$Al</td>
<td>14</td>
<td>550</td>
<td>7-8</td>
</tr>
</tbody>
</table>

The flexural strengths for the WC and TiC-based composites are similar to comparable hardmetal materials made with nickel as the binder phase. On the other hand, the fracture toughness values for the WC and TiC-based composites are similar to hardmetal materials made with a cobalt binder phase. In the case of the Al$_2$O$_3$-based composites, the fracture toughness values are significantly improved over comparable materials without any Ni$_3$Al second phase. In addition, the fracture toughness of these types of composites has been observed to increase with increasing crack extension. A rising fracture resistance is required for improving mechanical reliability and damage tolerance.

Of particular interest for this general class of composites is the high temperature behavior. The elevated temperature flexural strength and microhardness are shown in Figs. 4 and 5, respectively. As shown in Fig. 4, the strength of the WC-17 vol. % Ni$_3$Al composite actually increases from room temperature to 800°C. For comparison, data for a WC-Co material with a comparable binder content from the literature is also shown. In that case, the strength is observed to decrease over the same temperature range. The good strength retention is also observed for WC-based composites containing significantly higher binder contents as shown in Fig. 6. The elevated temperature hardness measurements show good retention comparable to values of WC-Co materials.
Preliminary screening tests for corrosion resistance in various acid solutions are summarized in Fig. 7. The Ni$_3$Al bonded material shows excellent resistance to nitric and sulfuric acids. The corrosion resistance in hydrochloric acid appears to be comparable to the WC-Co hardmetals. Similar results have been observed previously with Ni-bonded WC materials.$^{20}$

Conclusions

Composites using B-doped ductile Ni$_3$Al alloys were produced with both non-oxide (WC, TiC) and oxide (Al$_2$O$_3$) ceramic powders. Typical powder processing techniques were used to fabricate materials with ceramic contents from 0-95 vol. %. The microstructural morphology of the composites depends primarily on the wetting behavior between the alloys and the ceramic powders. The non-oxide ceramic powders wet well and the Ni$_3$Al alloys form a semi-continuous intergranular phase. On the other hand, the Ni$_3$Al alloys do not wet the oxide powders well and tend to form discrete "islands" of the metallic phase. Wetting in these materials can be improved by the addition of non-oxide particles, such as TiC. The results on the mechanical properties showed ambient temperature flexural strength similar to other Ni-based hardmetals. In contrast to the WC-Co materials, the flexural strength is retained to temperatures of at least 800°C. The fracture toughness and hardness were found to be equal or higher than comparable Co-based hardmetal systems. Initial corrosion tests showed excellent resistance to acid solutions.

References


Acknowledgments


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Fig. 1. Microstructure of WC-17 vol. % Ni$_3$Al composite showing a semi-continuous intergranular second phase with some remnant Ni$_3$Al-rich areas.

Fig. 2. Al$_2$O$_3$ particles near a Ni$_3$Al rich area resulting from some oxygen pickup during the powder processing.
Fig. 3. Microstructure of an alumina-10 vol. % Ni₃Al composite showing formation of discrete Ni₃Al "islands" within the Al₂O₃ matrix phase.

Fig. 4. Elevated temperature flexural strength for both WC and TiC composites containing 17 vol. % Ni₃Al (IC-50). Data for WC-Co taken from reference 18 for a comparable binder content.
Fig. 5. Elevated temperature hardness for a WC-17 vol. % Ni$_3$Al composites containing different Ni$_3$Al alloys. Data for WC-Co taken from reference 19.

![Hardness vs. Temperature Graph](image)

Fig. 6. Elevated temperature flexural strength for both WC composites containing various volume contents of Ni$_3$Al (IC-50).

![Flexural Strength vs. Temperature Graph](image)
Fig. 7. Corrosion rates of a WC-17 vol. % Ni$_3$Al composite immersed in 10 % acid solutions for 48 hours at 25°C. The WC-Co materials were commercial grade products.