Intermetallic Bonded Ceramic Matrix Composites


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ABSTRACT

A range of carbide- and oxide-based cermet materials have been developed utilizing ductile nickel aluminide (Ni₃Al) alloy binder phases. Some of these, notably materials based upon tungsten and titanium carbides (WC and TiC respectively), offer potential as alternatives to the cerments which use cobalt binders (i.e. WC/Co). Samples have been prepared by blending commercially available Ni₃Al alloy powders with the desired ceramic phases, followed by hot-pressing. Alumina (Al₂O₃) matrix materials have also been prepared by pressurized molten alloy infiltration. The microstructure, flexure strength and fracture toughness of selected materials will be discussed.

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INTRODUCTION

Hardmetal or cemented carbide materials such as tungsten carbide/cobalt (WC/Co) have reached a considerable degree of property refinement, achieved through continuous development for the last seventy years (1-3). These materials offer a unique combination of mechanical properties, as summarized in Table I, and consequently they have found a large number of applications. Examples of these include: cutting tools, drilling bits, wire drawing dies, punch/die sets, spray and blast nozzles, aluminum/plastic extrusion dies etc. (4). Although the mechanisms controlling the fracture behavior are not fully understood, several recent studies have addressed this problem more thoroughly (5-7).

Table I - Mechanical properties of WC/Co hard metals for three different Co contents (summarized from data presented in ref. 2).

<table>
<thead>
<tr>
<th>Co content, wt. % (vol. %)</th>
<th>5 (8.5)</th>
<th>15 (23.7)</th>
<th>25 (37)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vickers hardness</td>
<td>1400-1800</td>
<td>1100-1450</td>
<td>700-1100</td>
</tr>
<tr>
<td>Comp. strength (MPa)</td>
<td>5600-6100</td>
<td>4300-4900</td>
<td>3200-3700</td>
</tr>
<tr>
<td>Trans. rupture strength (MPa)</td>
<td>1800-2800</td>
<td>2600-3200</td>
<td>2900-3300</td>
</tr>
<tr>
<td>Fracture toughness (MPa.m^1/2)</td>
<td>8-10</td>
<td>15-17.5</td>
<td>18-22</td>
</tr>
</tbody>
</table>

The use of cobalt as the binder phase presents several problems. In particular cobalt is rare, and consequently expensive, and it also has poor resistance to corrosion in aqueous and acidic environments. Several examinations into alternative binder phases for WC cermet have been performed (8-12). Holleck (8) and Prakash et al (9) have demonstrated that iron and/or nickel, with small additions of cobalt, can be used as binders giving comparable properties to cobalt binders. A mixed Ni-Al binder system was examined by Viswanadham et al (10), where the Al content in the binder was varied between 4 and 12 wt.%. In this system attempts were made to 'harden' the binder phase by in-situ precipitation of the γ Ni$_3$Al phase, with mixed results (10). More recently, Farooq and Davies (11,12) have demonstrated that WC cemented with ferro-alloys (i.e. stainless steel or Fe-Co-NiMoB) also offer potential for replacement of WC/Co.

In the present study a range of carbide and oxide based hardmetal/cermet systems have been investigated, using ductile Ni$_3$Al binder phases as replacements for Co. Ni$_3$Al binders have been selected due their improved corrosion resistance relative to Co. They also exhibit good high temperature (i.e. up to 800°C) strength retention compared to Co. This initial report focuses upon materials densified by uniaxial hot-pressing, however the authors have recently demonstrated that carbide based systems can also be prepared to high sintered densities (>97% of theoretical) by conventional vacuum sintering techniques (13). In addition alumina (Al$_2$O$_3$) matrix cermets have been assessed, which were prepared by pressurized melt infiltration of Ni$_3$Al.

EXPERIMENTAL TECHNIQUES

Several Ni$_3$Al alloys (supplied by Homogenous Metals, Clayville, N.Y.) have been utilized in the present study, and the compositions of those used for cermet fabrication are summarized in Table II. The Ni$_3$Al alloys were classified to -325 mesh (<44 μm). Various carbide and oxide powders have been used, and these are summarized in Table III. Powder mixtures have been prepared by ball milling in non aqueous medium (iso-propanol or hexane), for up to 24 hours. After milling the mixtures were dried, crushed and hot-pressed in graphite dies. Carbide based materials were hot-pressed between 1150 and 1450°C, whereas temperatures between 1300 and 1550°C were used for the oxide-based materials. Samples were hot-pressed at pressures up to 34 MPa, for between 15 and 120 minutes, in 0.1 MPa Argon. Wetting studies have been performed on hot-pressed or pressureless-sintered substrates of each of the 'pure' ceramics; several other Ni$_3$Al alloys have been used for the wetting studies. These were conducted using the sessile drop technique at 1450°C in vacuum (~10$^{-4}$ Pa), with samples held at temperature for 15 minutes. In addition to the hot-pressed materials, Al$_2$O$_3$/Ni$_3$Al cermets have been prepared by pressure infiltration of pre-sintered Al$_2$O$_3$ preforms at the Technische Universitat, Hamburg-Harburg, Germany. The infiltrated Al$_2$O$_3$/Ni$_3$Al cermets were prepared by immersing the preform into the molten alloy (at 1650°C), and subsequently pressurizing the furnace to ~17 MPa, after which the infiltrated body is extracted from the molten alloy and cooled (14).
Table II - The compositions (in wt. %) of Ni$_3$Al alloys used for cermet fabrication in the present work.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Aluminum</th>
<th>Boron</th>
<th>Zirconium</th>
<th>Chromium</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC-15</td>
<td>12.7</td>
<td>0.05</td>
<td>0</td>
<td>0</td>
<td>Balance</td>
</tr>
<tr>
<td>IC-50</td>
<td>11.3</td>
<td>0.02</td>
<td>0.6</td>
<td>0</td>
<td>Balance</td>
</tr>
<tr>
<td>IC-218</td>
<td>8.5</td>
<td>0.02</td>
<td>0.8</td>
<td>7.8</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table III - Ceramic powders used in the present study.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Supplier/Grade</th>
<th>Average Dia. (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten carbide (WC)</td>
<td>Kennametal/WCA-20</td>
<td>2.5</td>
</tr>
<tr>
<td>Titanium carbide (TiC)</td>
<td>Kennametal/TICA-3</td>
<td>1.3</td>
</tr>
<tr>
<td>Alumina</td>
<td>Sumitomo/AKP-30</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Densities have been determined by the Archimedes method, via immersion in distilled water. The microstructures of dense materials have been assessed by scanning and transmission electron microscopy (SEM and TEM respectively), both with energy dispersive X-ray (EDX) analysis capabilities. Flexural strength has been measured in four-point bend, with 20 mm inner and 40 mm outer spans, using test bars 3 x 4 x 50 mm. Fracture toughness has been assessed by both the indentation (15), indentation/fracture (16) and chevron notch techniques. Additionally, a few samples have been tested in-situ within the SEM to determine 'R'-curve behavior, using a four-point flexure straining stage. The corrosion resistance of selected materials has been measured by immersion in 10% acid solutions for a period of 48 h. Comparison has been made with data obtained at the same time on commercial grade WC/Co materials.

**RESULTS AND DISCUSSION**

The wetting angle for combinations of several ceramic substrates and Ni$_3$Al alloys are shown in Table IV. It is apparent that the wetting angles for Ni$_3$Al on various non-oxide substrates are low, typically less than 20°. Conversely, the wetting angle on the oxide substrates are high, generally greater than 70°, and often above 90°. It is important to note that for 'ease' of processing a low wetting angle is desirable. Figure 1a shows the cross section of an Ni$_3$Al (IC-50 alloy) sessile drop on TiC after heating to 1550°C. The low wetting angle previously noted is clearly shown. SEM examination of the interface between the Ni$_3$Al and TiC demonstrates the absence of any reaction phases, however grain boundary penetration by the molten Ni$_3$Al alloy is apparent (Figure 1b). The lack of interfacial reaction products in the Ni$_3$Al/TiC wetting studies confirms previous observations on this system (17). Conversely, interfacial reactions have been noted in the Ni$_3$Al/TiB$_2$ system (18,19). For the case of Ni$_3$Al and Al$_2$O$_3$ in combination, ZrO$_2$ precipitates have been noted to form at the interface between the two phases, for the cases where Zr is present in the Ni$_3$Al alloy (20-23).

It is apparent from SEM examination of the microstructures of the hot-pressed Ni$_3$Al containing cermets, that the wetting characteristics previously described have a strong influence upon the morphological evolution of the microstructure. Figure 2a demonstrates the formation of discrete islands of Ni$_3$Al in the Al$_2$O$_3$ based composites, indicating that densification is dominated by solid state sintering of the Al$_2$O$_3$ matrix (24). These materials were hot-pressed below the melting temperature of Ni$_3$Al, which is approximately 1390-1400°C, in order to prevent the non-wetting aluminate phase being exuded from the sample during hot-pressing.

Conversely the carbide matrix materials exhibited a semi-continuous Ni$_3$Al-based grain boundary phase (Figure 2b). The 'apparent' intergranular liquid volume is lower than the overall Ni$_3$Al content in these materials due to the retention of isolated large Ni$_3$Al regions after hot-pressing (Figure 2b). This indicates that the coarse Ni$_3$Al powders (-325 mesh, <44 μm) are not significantly reduced in size during wet milling. Recently a small batch of -10 μm Ni$_3$Al powder (IC-50 alloy) has been provided by X-form Ltd. (Cohoes, N.Y.), and the effects of substitution of this powder for the coarse Ni$_3$Al is the subject of
current investigations. The effective reduction in the Ni₃Al volume (due to the retention of isolated Ni₃Al islands) results in a high percentage of WC/WC grain boundaries, similar in appearance to low cobalt content WC/Co hardmetals. It is likely that these WC/WC boundaries undergo solid state sintering during hot-pressing, although high resolution electron microscopy would be required to confirm the absence of Ni₃Al at these grain boundaries. It was also apparent that a small volume of Al₂O₃ particles were formed during hot-pressing, presumably arising from oxygen 'pick-up' during wet milling (i.e. by partial oxidation of the Ni₃Al powder). These sub-micron Al₂O₃ grains were concentrated at the edge of the large Ni₃Al rich regions. EDX analysis of the Ni₃Al binder demonstrated that W dissolution into this phase had occurred during hot-pressing (and also Ti dissolution in the TiC-based materials). This is to be expected based upon the observations of Ochiai et al (25) and Liu and Stiegler (26). Ti is known to substitute primarily onto Al sites in Ni₃Al (25), unlike other metals such as Fe, Mo and W which substitute onto both Ni and Al sites in the Ni₃Al lattice (25,26). The solubility of W in Ni₃Al was observed to be lower than that of Ti, in accordance with previous work (25,26).

Table IV - The wetting behavior of several Ni₃Al alloy/ceramic substrate combinations.

<table>
<thead>
<tr>
<th>Alloy Composition (at. %)</th>
<th>Substrate Material</th>
<th>Wetting Angle (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-22Al-1Zr-0.1B</td>
<td>Al₂O₃</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>Ni-16Al-8Cr-1Zr-0.1B</td>
<td>Al₂O₃</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>Ni-23Al-1C-0.1B</td>
<td>Al₂O₃</td>
<td>76</td>
</tr>
<tr>
<td>Ni-22Al-1Zr-0.1C-0.1B</td>
<td>Al₂O₃</td>
<td>77</td>
</tr>
<tr>
<td>Ni-22Al-1Zr-0.1C-0.1B</td>
<td>Al₆Si₂O₁₃</td>
<td>90</td>
</tr>
<tr>
<td>Ni-22Al-1Zr-0.1C-0.1B</td>
<td>ZrO₂ (2.5 mol. Y₂O₃)</td>
<td>76</td>
</tr>
<tr>
<td>Ni-22Al-1Zr-0.1C-0.1B</td>
<td>TiC</td>
<td>10-20</td>
</tr>
<tr>
<td>Ni-22Al-1Zr-0.1C-0.1B</td>
<td>TiB₂</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 1 - (a) Optical micrograph demonstrating the wetting of TiC by a Ni₃Al alloy. (b) SEM micrograph of the interface between the TiC and Ni₃Al, showing grain boundary penetration.

Room temperature properties of some of the carbide and oxide matrix composites fabricated with Ni₃Al additions (IC-50 alloy) are shown in Table V. Although the observed properties are not as high as those observed for WC/Co cermets (Table I), it is important to note that those materials have benefited from over 70 years of continuous development. The WC/68 vol. % Ni₃Al cermets produced in the present study exhibit an impressive combination of high strength and toughness, with reasonable hardness (Table V). Both the WC and TiC cermets prepared with 17 vol. % Ni₃Al exhibit flexure strengths comparable to hardmetals prepared with Ni binders (27), while observed toughness values are similar to those for hardmetals prepared with Co binders (see Table I and references 2,3,5,6).
Table V - Summary of the mechanical properties of selected Ni$_3$Al containing cermets.

<table>
<thead>
<tr>
<th>Composition (Volume %)</th>
<th>Microhardness (GPa)</th>
<th>RT Flexure Strength (MPa)</th>
<th>RT Fracture Toughness (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$_3$-10 Ni$_3$Al</td>
<td>14</td>
<td>550</td>
<td>7-8</td>
</tr>
</tbody>
</table>

Figure 2 - (a) Optical image of isolated Ni$_3$Al islands within an Al$_2$O$_3$ matrix (24). (b) SEM image showing semi-continuous Ni$_3$Al grain boundary phase, with some isolated Ni$_3$Al regions (WC matrix).

Room and elevated temperature (800°C) fracture strengths of the cermets with an Ni$_3$Al-based binder phase are shown in Figure 3, with a typical WC/Co material shown for comparison. Excellent strength retention is apparent for the Ni$_3$Al containing materials, with flexure strengths being almost invariant with temperature up to 800°C. It is important to note that the yielding behavior of ordered Ni$_3$Al is somewhat unusual, with yield stress increasing with temperature up to ~800°C (28). In comparison the WC/Co material, with a binder content of ~17 vol. %, shows a decrease in flexure strength of ~32 % (29). This behavior is particularly important for cutting applications, when tool contact temperatures can approach 1000°C.

Figure 3 - Elevated flexure strengths for WC and TiC cermets prepared with an Ni$_3$Al binder phase (IC-50 alloy). Data for WC/Co is taken from reference 29.
The lack of wetting in the pure Al₂O₃/Ni₃Al system has led to the investigation of two revised processing routes for Al₂O₃ based matrices. The first utilizes the addition of 'wetting agents' to aid wetting during hot-pressing. Examples include Al₂O₃-TiC-Ni₃Al and Al₂O₃-TiB₂-Ni₃Al. The second approach involves pressurized infiltration of a molten Ni₃Al melt into a porous, pre-sintered Al₂O₃ preform (relative density ~60-65% of theoretical). An SEM micrograph of a Al₂O₃-TiC (25 vol. %)-Ni₃Al (10 vol. %) composite, hot-pressed at 1550°C for 90 minutes, is shown in Figure 4, which demonstrates the semi-continuous nature of the Ni₃Al phase. A distinct core-rim structure is apparent, with the core comprising solely of TiC and the outer rim containing additional W, which is due to 'pick-up' during ball milling with WC media. The properties of these composites were generally similar to the Al₂O₃/Ni₃Al (10 vol. %) materials, with slightly higher hardness (Microhardness, ~18 GPa; flexure strength 350-580 MPa; fracture toughness 7-8 MPa.m¹/²). These materials exhibit a rising 'R' curve behavior (Figure 5), due to combination of toughening mechanisms operating in the crack wake. It is apparent from Figure 5 that crack deflection, grain pull-out and ductile ligament bridging processes are occurring. Conversely, a fine grain sized Al₂O₃/TiC ceramic composite (which is shown for comparison) does not exhibit such toughening mechanisms (Figure 5).

Figure 4 - Secondary electron SEM image of a Al₂O₃-TiC (25 vol. %)-Ni₃Al (10 vol. %) cermet.

Figure 5 - 'R' curve behavior of an Al₂O₃-TiC (25 vol. %)-Ni₃Al (10 vol. %) cermet, with data obtained for a fine grain size Al₂O₃ ceramic shown for comparison. Inset demonstrates the crack path in the Ni₃Al containing material (ductile bridging region arrowed).
The infiltrated Al₂O₃/Ni₃Al cermets possess a dual-phase interpenetrating microstructure (Figure 6), with approximately 35 vol. % Ni₃Al (14). These materials exhibit a rising 'R' curve behavior (Figure 7). The primary toughening mechanism in these materials is believed to be crack wake bridging by the ductile Ni₃Al ligaments, in a manner similar to that previously demonstrated for the Al₂O₃-TiC-Ni₃Al material (shown in Figure 5). The effects of temperature upon both toughness and strength of these composites are shown in Table VI. It is apparent that the observed strength retention is similar to the WC/Ni₃Al cermets, with negligible degradation at the higher test temperature.

One reason for the selection of Ni₃Al binders as potential replacements for Co-based binders, is the superior corrosion resistance of Ni₃Al over Co. A series of preliminary screening tests designed to assess the corrosion resistance of WC/Ni₃Al cermets has been performed, and comparison has been made to two commercial WC/Co materials (Figure 8). The Ni₃Al-based materials show excellent resistance to corrosion by both nitric and sulfuric acids, in comparison to the commercial WC/Co hardmetals. It is also important to note that the volume percentage of the Co binder is also lower for the two commercial materials, emphasizing the improvement in corrosion resistance that can be attained by substitution of Co binders by Ni₃Al. The effect of corrosion in hydrochloric acid appears to be similar for the two systems. A similar observation of improved resistance to corrosion has been noted when Ni is substituted for Co (4).
A range of carbide and oxide hardmetal/cermet materials have been prepared using ductile intermetallic binder phases based upon Ni$_3$Al. Dense materials can be prepared by uniaxial hot-pressing of powder mixtures or, in the case of Al$_2$O$_3$/Ni$_3$Al, by pressurized infiltration of a porous pre-sintered Al$_2$O$_3$ preform by molten Ni$_3$Al alloys. Based upon the present study, the following conclusions can be drawn:

- From initial studies it is clear that Ni$_3$Al wets carbides such as WC and TiC extremely well, with low wetting angles (<15°). Conversely, oxides such as Al$_2$O$_3$ are not wetted by Ni$_3$Al to any great extent, with wetting angles typically >70°. The lack of wetting in the 'pure' oxide systems results in the formation of isolated regions of Ni$_3$Al in hot pressed materials.

- High density WC cermets have been produced with varying amounts of Ni$_3$Al binder phase. These materials have been shown to exhibit four point bend fracture strengths approaching 2 GPa, with indent toughness values up to 25 MPa.m$^{1/2}$ and a hardness of 7 GPa, when high binder contents are used (i.e. ~68 vol. %). When the Ni$_3$Al binder content is similar to conventional WC/Co hardmetals (i.e. ~17 vol. %), the flexure strengths are between 1.2 to 1.4 GPa, with toughness values between 10-20 MPa.m$^{1/2}$ and hardnesses of the order of 14 to 18 GPa. Properties for the hot-pressed TiC/Ni$_3$Al cermets were generally inferior to the WC based materials, with the exception of hardness which was improved slightly.

- The WC/Ni$_3$Al based materials exhibited excellent property retention at temperatures up to 800°C, with flexure strength values similar to those obtained at room temperature. These observations compare
favorably to those for WC/Co, where flexure strength is typically reduced by 30-40% when testing at 800°C.

- The lack of wetting in the hot-pressed Al₂O₃/Ni₃Al system has led to two approaches to overcome this problem. The first has involved the addition of a 'wetting' phase, namely TiC, to the powder mixture. This leads to the retention of an interpenetrating microstructure after hot-pressing. However, to date the resulting properties of these composites are inferior to the simpler carbide/aluminide materials (i.e. WC/Ni₃Al). The second approach is based upon the use of pressure infiltration of a molten Ni₃Al melt into a pre-sintered Al₂O₃ preform. This results in a dual phase, interpenetrating microstructure, which exhibits a steeply rising 'R' curve behavior, and high toughness. Flexure strengths are relatively low however, due to a weak interface between the Al₂O₃ and Ni₃Al.

- WC cermets, based upon the use of Ni₃Al binder phases, show considerably improved resistance to corrosion in both nitric and sulfuric acid when compared to conventional materials prepared with Co. Resistance to corrosion by hydrochloric acid is similar for the two binder phases.

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