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DUCTILE INTERMETALLIC TOUGHENED CARBIDE MATRIX COMPOSITES

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Ductile nickel aluminide (Ni_3Al) alloys have been used as a 'binder' phase for the fabrication of both titanium and tungsten carbide (TiC and WC) matrix composites. Ni_3Al alloys exhibit good resistance to aqueous acidic corrosion environments. These alloys are also unusual in that their yield strength increases with temperature, to a maximum at 700-800°C. These properties, combined with high tensile ductilities (up to 50 % strain), make Ni_3Al a potentially attractive replacement for Co in cemented carbide fabrication. Materials have been fabricated by both hot-pressing and vacuum-sintering, with Ni_3Al contents ranging from 15 to 95 vol. %. Vacuum-sintering cycles were generally similar to those used for the fabrication of WC/Co and TiC/Ni (i.e. T_{sint} ~1450-1600°C), resulting in sintered densities >95 % of theoretical. WC/Ni_3Al materials exhibited an order of magnitude improvement in corrosion resistance over WC/Co, during immersion tests in either sulfuric or nitric acid. These materials also demonstrated improved high temperature strength retention compared to WC/Co cermets, though the initial room temperature strengths were lower. Fracture toughness varied between 8 and 25 MPa.m$^{1/2}$, and depended primarily upon Ni_3Al content and composition.

INTRODUCTION

Cemented carbides, such as tungsten carbide/cobalt (WC/Co), exhibit a unique combination of properties that have led to their implementation in a large number of industrial applications, including; cutting tools, drilling bits, wire drawing dies, punch/die sets, spray and blast nozzles, aluminum/plastic extrusion dies etc. [1]. A summary of some of the mechanical properties of WC/Co cemented carbides is shown in Table I (from data collated by Ettmayer [2]). The fracture behavior of these materials is not fully understood, however, a number of recent studies have sought to gain further understanding of the fracture mechanisms involved [3-7].

There are several reasons for exploring alternative binders to Co, notably that Co is a rare, strategic material (and hence relatively expensive) and that it exhibits poor resistance to corrosion in aqueous and acidic environments. Several replacement binder systems have been investigated. These include Fe and/or Ni with small Co additions [8,9], which gave properties comparable to Co alone, and also ferro-alloys (i.e. stainless steel or Fe-Co-NiMoB) [10,11]. A mixed Ni-Al binder system was investigated by Viswanadham *et al* [12],with the aim of 'hardening' the binder phase by precipitation of the ordered γ' Ni_3Al intermetallic phase. In

the present study a range of cemented carbides have been investigated, which utilize ductile Ni_3Al binders as a replacement for Co [13-15]. Ni_3Al binders have been selected due to their improved corrosion resistance and high temperature strength retention relative to Co.

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

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

EXPERIMENTAL TECHNIQUES

Powder mixtures were prepared either by ball milling or attritor milling in non-aqueous medium (iso-propanol or hexane). Hot-pressing was performed in graphite dies, at various temperatures between 1150 and 1450°C, with uniaxial pressures of up to 34 MPa. Vacuum-sintering was performed in a conventional gas-pressure sintering furnace at temperatures from 1400 to 1600°C, for up to two hours at temperature. Some samples were also given a second stage low-pressure hot-isostatic pressing (LPHIP) treatment, with an applied argon gas pressure of 2 MPa. The densities of both hot-pressed and vacuum sintered were determined by immersion in distilled water. The microstructures of dense materials were assessed by optical and scanning electron microscopy. Fracture toughness has been measured using a number of different techniques, namely; indentation [16], indentation/strength [17] and applied moment double cantilever beam (AMDCB) [18]. Fracture strength was measured in four point bend, using inner/outer spans of either 20/40 mm or 6.35/19.05 mm. Vickers hardness was obtained using loads from 10 to 50 kg. The corrosion resistance of selected materials was determined by immersion in 10 % acid solutions for a period of 48 hours.

RESULTS AND DISCUSSION

(A) Hot-pressed cemented carbides

Theoretically dense WC/Ni_3Al cemented carbides are prepared by hot-pressing at temperatures of ~1350°C. Higher temperatures result in exudation of molten Ni_3Al from the sample and graphite die. Some mechanical properties of the hot-pressed cemented carbides are shown in Table II. Data for WC/Co is shown for comparison. The properties of the Ni_3Al bonded WC composites are generally similar to WC/Co, although the room temperature strengths are slightly lower. However, it is apparent that the Ni_3Al bonded materials retain a much higher proportion of their RT strength at elevated temperatures.

Table II. Summary of some of the mechanical properties of hot-pressed Ni_3Al bonded WC and TiC matrix composites.

Composition	Hardness	Flexure strength (MPa)		Fracture Toughness
(Vol. %)	(GPa)	RT	800°C	($MPa.m^{1/2}$)
WC/17 Ni_3Al	14-18	1200-1350	1395	10-20
WC/68 Ni_3Al	7	1750	1640	25
TiC/17 Ni_3Al	16-20	750-900	745	8-14
WC/17 Co	12-14	~2000	N/A	17-18

The corrosion resistance of WC/Ni_3Al composites in three different acid solutions is shown in Fig. 1. A considerable improvement in resistance to corrosion in both nitric and sulfuric acid can be obtained via substitution of Ni_3Al for Co. This effect is further emphasized when noting the lower binder content of the two WC/Co materials, compared to the WC/Ni_3Al cermet. There is no significant difference in the corrosion behavior of Ni_3Al or Co binders in hydrochloric acid.

(B) Vacuum-sintered cemented carbides

Recent work has focused upon the development of vacuum-sintering techniques, in order to be able to fabricate materials to near-net shape (to improve the industrial viability of these materials). Sintered densities greater than 99 % of theoretical were achieved for the TiC cermets with the higher Ni_3Al contents (i.e. >25 vol. %). Densities greater than 95 % of theoretical were obtained for all the examined TiC based compositions, when sintering at temperatures between 1500 and 1600°C. Generally, WC based materials can also be vacuum sintered to high density, as shown in Table III. However, sintered densities are low for the fine (~0.8 μm) WC powder, presumably due to increased oxygen contamination.

Initial investigation of two-stage vacuum/low-pressure HIP (LPHIP) processing has produced mixed results, with the identification of an unusual de-sintering mechanism with the TiC based compositions, even for samples initially vacuum sintered to densities in excess of 99 % of theoretical. Large 'binder-free' regions were apparent in the LPHIP processed sample. High magnification SEM imaging demonstrated that the carbide grains in this region were clean, with no residual binder evident. It was also apparent that the binder/ carbide contact angle was approaching 90° at the edge of the 'binder-free' regions, significantly different from the contact angle of 'pure' Ni_3Al on TiC, which is ~20°. During sintering the binder composition is modified via incorporation of Ti and C (from dissolution of the TiC grains), and this appears to result in de-wetting. This effect is currently being assessed in more detail, in order to gain a better understanding of the de-wetting mechanism (via controlled alteration of the binder composition). De-wetting was not observed in any of the WC/Ni_3Al based systems, with density increases noted for nearly every composition (Table III).

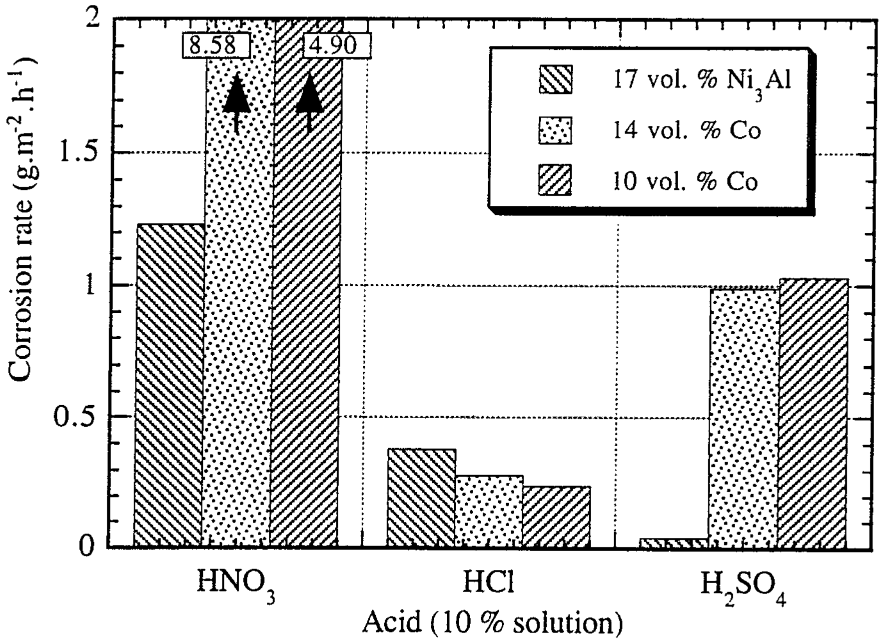

Figure 1. Corrosion rates, determined by weight loss, of a hot-pressed WC/ Ni_3Al cermet immersed in 10 % (by volume) acid solutions for 48 h (at 25°C). The WC/Co materials were commercial grade products.

Table III. Density values for vacuum sintered and low-pressure HIPed (1.7 MPa Ar) WC/Ni_3Al based cermets (average particle size of fine WC powder ~0.8 μm).

Composition	Density after vacuum sintering (% T.D.)		Density after low pressure HIP (% T.D.)	
	1550°C	1600°C	1550°C	1600°C
WC-20 vol. % Ni_3Al	96.8	96.9	98.6	98.3
WC-20 vol. % Ni_3Al (5 % Fe)	96.0	98.3	98.9	99.5
WC-20 vol. % Ni_3Al (5 % W)	96.0	97.1	98.2	98.3
WC-20 vol. % Ni_3Al (5 % Ti)	92.0	92.9	95.7	95.4
WC (Fine)-20 vol. % Ni_3Al	84.3	85.6	83.7	85.7
WC-30 vol. % Ni_3Al	98.4	97.9	98.7	98.1

(C) Mechanical behavior of vacuum-sinter/LPHIP processed TiC/Ni_3Al cermets.

An initial mechanical property survey has been performed upon a series of vacuum-sinter/LPHIP processed TiC/Ni_3Al cermets. As previously noted, these materials contain regions of coarse porosity. However, it was felt that these materials would provide a property baseline for the assessment of future vacuum-sintered materials. Flexure strength has been obtained in four-point loading, with typically 20 plus tests for each composition. The effects of Ni_3Al content upon the room temperature flexure strength are shown in Fig. 2. High strengths are obtained, despite the retained porosity in these materials. Weibull moduli plots for cermets prepared with 15 and 40 vol. % Ni_3Al binder are shown in Fig. 3. Even though coarse porosity is present, the materials show reasonable reliability (damage tolerance), particularly at the higher binder content.

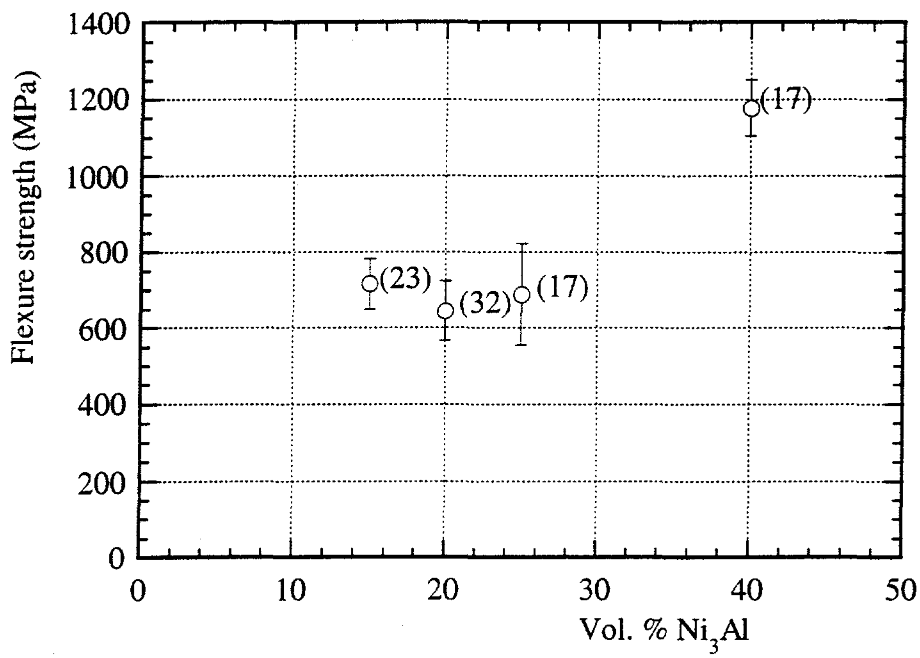

Figure 2. The effects of Ni_3Al binder volume on the flexure strength of TiC based cermets (vacuum-sinter plus LPHIP processed samples). Number of tests indicated in parenthesis.

In addition to flexure testing, preliminary measurement of the 'R' curve behavior of these materials has been performed. Plateau fracture toughness values for cermets with 25 and 40 vol. % binder were 9-10 and 11-12 $MPa.m^{1/2}$ respectively. The 'R' curves for two specimens with 40 vol. % binder, and retained coarse porosity, are shown in Fig. 4. A pronounced 'R' curve is apparent. Toughening mechanisms in these materials are currently being assessed further, with high density compositions.

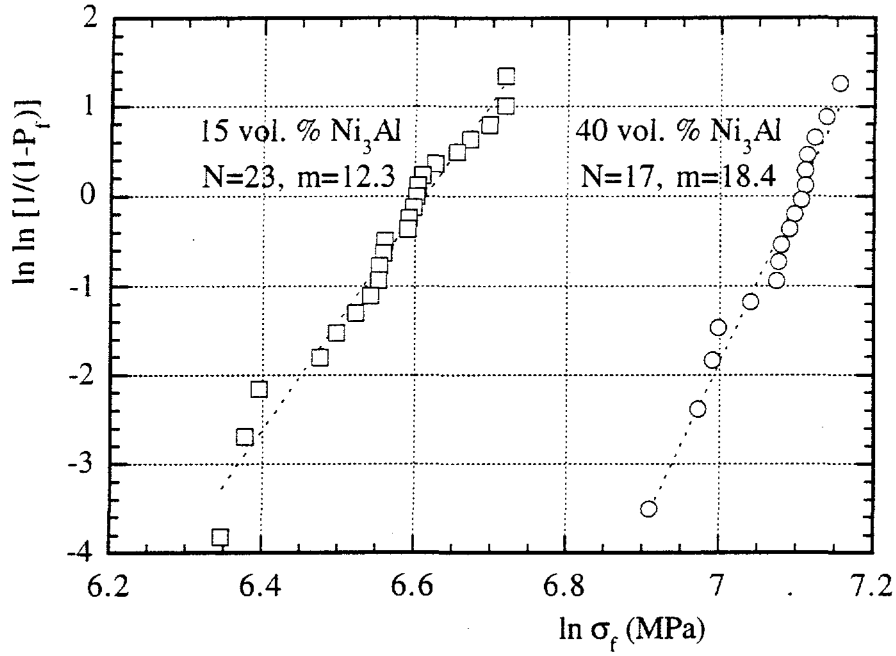

Figure 3. Weibull plots for vacuum-sintered/LPHIP processed TiC/Ni_3Al composites prepared with 15 and 40 vol. % binder. Samples tested in four point bend.

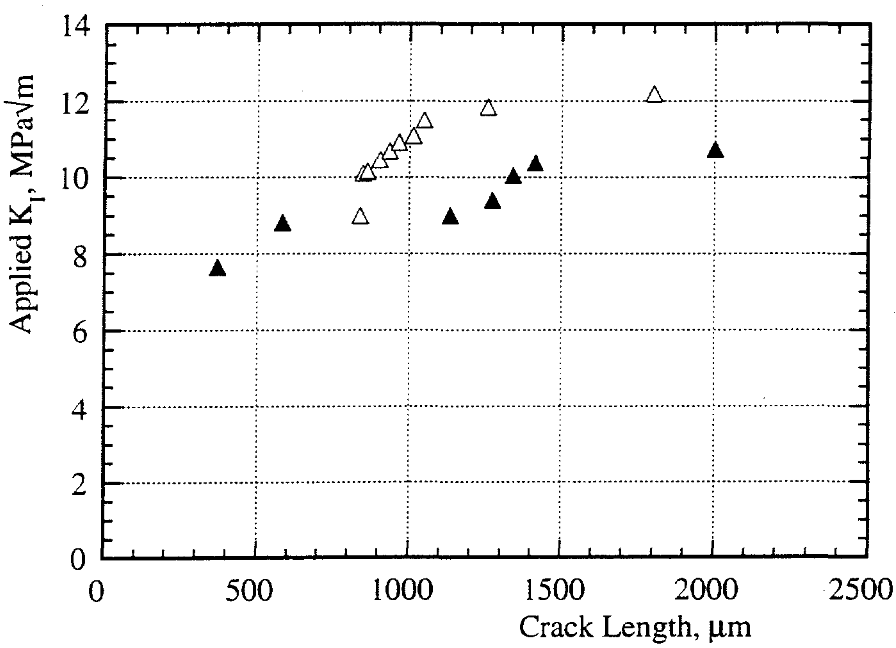

Figure 4. 'R' curves for two TiC based cermet samples prepared with 40 vol. % Ni_3Al binder. AMDCB sample geometry.

CONCLUSIONS

A range of carbide based cermets have been developed, utilizing a ductile nickel aluminide binder phase. High density materials have been fabricated by both hot-pressing and vacuum-sintering. The densities of vacuum-sintered materials (with 15 to 40 vol. % nickel aluminide binder) ranged from ~95 % T.D., for the low binder content samples, to >99 % T.D. for the highest binder contents. An unusual de-wetting phenomenon was noted for TiC/Ni_3Al cermets when a post-vacuum-sinter low-pressure HIP treatment was employed. The cause of this effect is currently being assessed.

The corrosion resistance of hot-pressed WC/Ni_3Al materials was found to be an order of magnitude better than that of comparable WC/Co hardmetals in both nitric and sulfuric acid environments.

Although an initial property assessment was performed with samples containing regions of coarse porosity, these materials have been found to exhibit a good combination of strength, reliability and fracture toughness. The fracture behavior of high density cermets is currently being assessed via the use of *in-situ* fracture studies within a scanning electron microscope, using an AMDCB specimen geometry. This work will be discussed in a future publication.

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