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Properties of Ni₃Al-bonded Titanium Carbide Ceramics

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Abstract

Cemented carbides are widely used in applications where resistance to abrasion and wear are important, particularly in combination with high strength and stiffness. In the present case, ductile nickel aluminide (Ni₃Al), was used as a binder phase to fabricate dense TiC cermets by either sintering of mixed powders or a melt-infiltration sintering process. The choice of an aluminide binder was based on the exceptional high temperature strength and chemical stability exhibited by these alloys. The resultant TiC–Ni₃Al composites exhibit improved oxidation resistance, Young's moduli > 375 GPa, high fracture strengths (> 1 GPa) that are retained to ≥ 900°C, and fracture toughness values 10 MPa√m. The thermal diffusivity at 200°C for the composites is ∼0·070 to 0·075 cm² s⁻¹ while the thermal expansion coefficient rises with Ni₃Al content from ∼8 to ∼11 × 10⁻⁶ K⁻¹ over the range of 8 to 40 vol% Ni₃Al. The oxidation and acidic corrosion resistances appear to be promising as well. Finally, they also exhibit good electrical conductivity allowing them to be sectioned and shaped by electrical discharge machining (EDM) processes. © 1998 Published by Elsevier Science Limited.

Introduction

Hard metal or cemented carbide materials based on tungsten and titanium carbides have reached a considerable degree of property refinement, due to continuous development over the last seventy years.[1–3] These materials offer a unique combination of mechanical properties, and consequently they have a large number of applications. Examples of these include; cutting tools, drill bits, wire drawing dies, punch and die sets, spray and blast nozzles, aluminum and 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]

Several reports have been published on the use of binder phases other than cobalt alloys for carbide cermets.[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. A mixed NiAl binder system was examined by Viswanadham *et al.*,[10] where the Al content in the binder phase was varied between 4 and 12 wt% to develop gamma prime phase. More recently, Farooq and Davies[11,12] have demonstrated that WC containing ferro-alloys (i.e. stainless steel or Fe-Co-NiMoB) offer potential for replacement of WC/Co. The present research effort is examining a range of cemented carbides that utilize ductile Ni₃Al[13–15] or iron aluminide[16] binder phases. The aluminides are of interest as they exhibit excellent mechanical properties that are retained to elevated temperatures and typically offer excellent oxidation and corrosion resistances.[17,18] In this paper, the influence of Ni₃Al binders on the properties of sintered TiC-based cermets is described.

Experimental Procedures

The initial process used to fabricate composite samples consisted of pressureless sintering of mixtures of TiC and Ni₃Al powders. More recently, a simple process, termed melt-infiltration sintering (MIS, Fig. 1), was developed and was used to fabricate most of the Ni₃Al-bonded TiC composites studied herein. In this process, TiC preforms were prepared by uniaxial cold pressing TiC powder[‡] at ∼40 MPa in a steel die, followed by cold isostatic pressing (CIPing) at 285 MPa. The particle size

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[†]Current address: Unilever Research, Bedfordshire MK44 1LQ, UK.
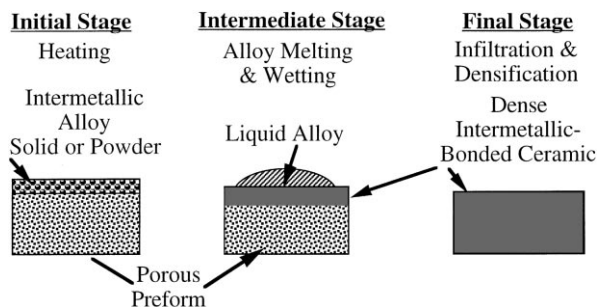[‡]TiC powder (1·0–1·4 μm), Kennametal, Latrobe, PA.

Fig. 1. Schematic representation of steps involved in the melt–infiltration sintering process.

analysis (centrifugal sedimentation) and SEM examination demonstrated that this powder is a mixture of coarse TiC particles (5–10 μm), and fine sub-micron TiC. This broad particle size range helps to give high green densities during compaction (i.e. ~63% of theoretical density when CIPing at 285 MPa). An appropriate amount of coarse (+ 325 mesh particle size) Ni_3Al powder* was placed on the top surface of the green TiC piece. The sample to be sintered was next placed in a covered alumina (99·99%) crucible that was then placed inside a covered graphite crucible set on the ram of a graphite resistance heated sintering furnace.[†] A dynamic vacuum (~1 Pa) was maintained in the furnace chamber to promote wetting and infiltration of the TiC preform by molten Ni_3Al. Melt infiltration has been performed at various temperatures from 1275° to 1450°C.

The microstructures of dense materials were assessed by optical and scanning electron microscopy. Fracture toughness has been measured with the applied moment double cantilever beam (AMDCB).[19] Fracture strengths were measured in air at temperatures from room temperature to 1100°C in four point flexure (typical loading rate of ~300 MPa s^{-1}), using inner/outer spans of either 20/40 mm or 6·35/19·05 mm. Test samples were cut from the as-sintered pieces using electrical discharge machining and then surface finished with diamond abrasive wheels to remove the surface layers. Flexure test bars had 3 × 4 mm cross-sections with diamond (400 grit) ground (grinding direction parallel to tensile axis) surfaces. The Young's moduli were obtained employing standard piezoelectric techniques.[‡] The thermal expansion coefficients of the composites were measured

*Ni_3Al alloy (IC 50), Homogeneous Metals, Inc., Clayville, NY.
[†]Sintering furnace, Thermal Technology Inc., Concord, NH.
[‡]Measurements performed by W. A. Simpson, ORNL, Oak Ridge, TN.
[§]Theta Industries (Port Washington, NY) modified at ORNL with PC interfacing for control and data acquisition and analysis.
[¶]R. B. Dinnwiddie, ORNL, Oak Ridge, TN.

against a N. I. S. T. sapphire standard in a nitrogen atmosphere using a dual rod dilatometer[§] operating at a heating-cooling rate of 2°C min^{-1}. Thermal diffusivities were obtained by laser flash calorimetry.[¶] Finally, oxidation rates were assessed by measuring weight changes on samples exposed to flowing air at 900°C for 24 h. Corrosion response was determined at 22 and 95°C in 1 N sulfuric, hydrochloric, and nitric acids measuring weight loss after 200 h immersion test.

Results and Discussion

Densification by melt-infiltration sintering

After heating the preforms to 1275°C and holding for 1 h, only partial infiltration of the Ni_3Al had occurred, with most retained on top of the sample. However, melt infiltration and densification reached completion when the processing temperature was raised to 1300°C (Fig. 2). Further increases in the processing temperature had little effect on the density of the composites except in samples with low (< 12 vol%) Ni_3Al contents. These experiments reveal that full density can be readily achieved with Ni_3Al contents of ≥ 12 vol% at temperatures as low as 1300°C for hold times of ≤ 1 h.

It is possible, using the sintered density of the 'pure' TiC sintered at 1300°C (Fig. 2), to estimate the final density that would be obtained if only infiltration of the TiC by a known amount of Ni_3Al occurred (i.e. there is no particle rearrangement). This reveals that with Ni_3Al contents between ~5 and ~15 vol% there would be insufficient intermetallic to totally infiltrate the whole piece if it retains its original dimensions. In addi-
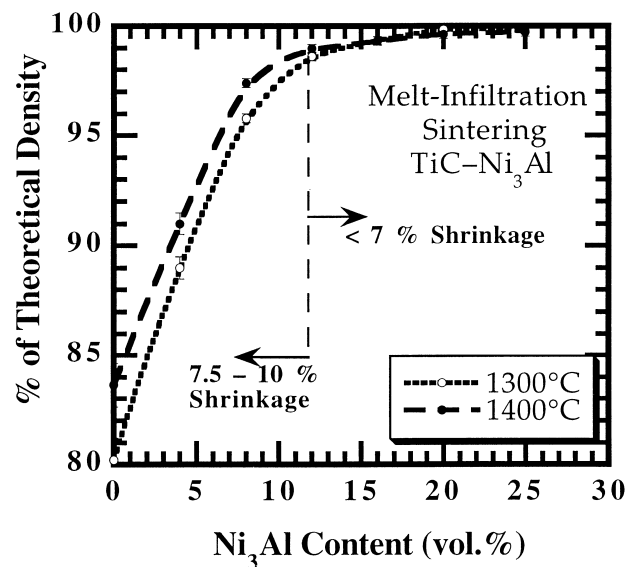

Fig. 2. Final density is as a function of Ni_3Al content at both 1300 and 1400°C; however, an increase in density with temperature is only seen with aluminide contents < 12 vol%.

tion, the measured densities are much greater than those predicted for infiltration alone. Therefore, densification must be aided by particle rearrangement within the TiC preform as the liquid intermetallic infiltrates the preform. When the infiltration process dominates the densification (by increasing either the aluminide content, $\geq$ 12 vol%, or the density of the carbide preform), the linear shrinkage during the densification cycle is $< 7\%$, Fig. 2. This approach has the benefit of near-net shape capability; thus, composites with a wide range of Ni₃Al contents can be produced with the present technique.

Properties of the composites

Thermal–mechanical

As expected, the properties of the intermetallic-bonded carbide can be tailored by controlling the binder phase content. For example, the linear thermal expansion coefficient can be increased with Ni₃Al content, as expected from simple rule-of-mixtures (ROM) calculations (Fig. 3). Thus one can match the expansion coefficients of other materials (e.g. metallic alloys) whose values lie in between those of the carbide and the intermetallic.

In the TiC–Ni₃Al composites, the Young's modulus and hardness values decrease and the density increases with aluminide content, Table 1, again consistent with ROM estimates. On the other hand, there are only slight changes in the thermal diffusivity values when the Ni₃Al content is $\leq$ 25 vol%.

Fracture strengths and fracture toughness at 22°C

The room temperature fracture strengths of fully dense composites generally increase with Ni₃Al content but greater strengths are also achieved
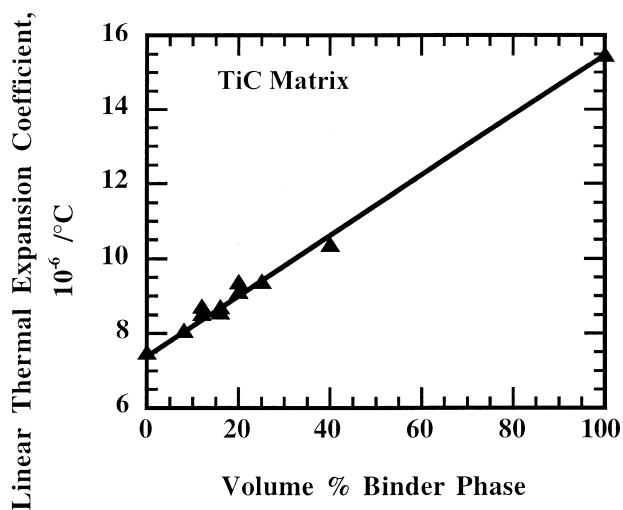
Table 1. Thermal–mechanical properties of TiC-based composites with nickel aluminide (Ni₃Al) binder phase

Volume % Ni3Al	Density (g cm⁻³)	Thermal diffusivity (@ 200°C cm² s⁻¹)	Vickers diamond pyramid hardness (GPa @ 1 kg)	Young's modulus (GPa)
0	4·94	0·0658	21	455
8	5·13	0·0703	17·2	—
12	5·23	—	15·3	430
15	5·31	—	—	—
16	5·33	—	16	—
20	5·43	0·0755	14·6	410
25	5·55	—	—	370
40	5·92	—	—	—
100	7·39	0·0343	3	185

when the minimum processing temperature is used (Fig. 4). The decrease in strengths with increase in processing temperature can, in part, be attributed to the increase in TiC grain size observed at the higher processing temperature (Fig. 5). Keeping this in mind, fracture strengths of over 1 GPa are routinely obtained in samples containing > 12 vol% Ni₃Al and processed at the lower sintering temperature. The steady-state (or long crack) fracture toughness values rise above 10 MPa√m when the Ni₃Al content is > 12 vol% (Fig. 6). In fact, the toughness values for the Ni₃Al-bonded TiC composites are comparable to those measured in our facilities for commercial cobalt-bonded WC materials.

Strengths at elevated temperatures

As noted earlier, the aluminides can exhibit exceptional retention of their mechanical properties with

Fig. 3. The measured thermal expansion coefficients increase with Ni₃Al content; the solid line is the projection based on rule-of-mixtures calculations
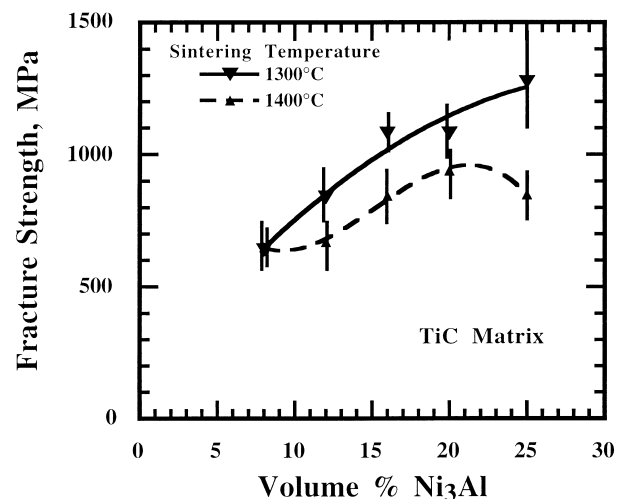

Fig. 4. The room temperature fracture strengths increase with Ni₃Al content; however, the strengths are reduced as the processing temperature is increased from 1300 to 1400°C. While increasing the processing temperature results in decreased porosity for Ni₃Al contents < 12 vol%, an increase in TiC grain size also occurs for all compositions
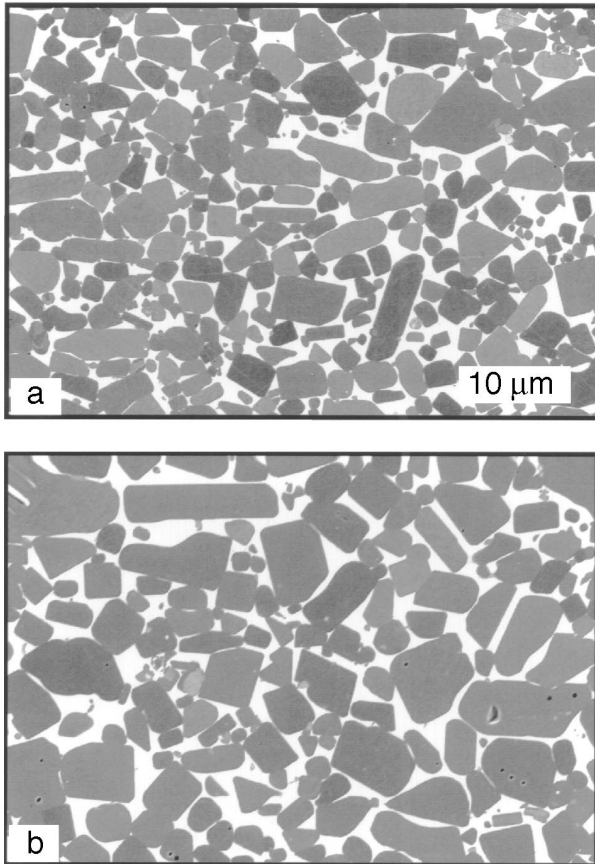
Fig. 5. Growth of TiC grains evident in TiC–20 vol% Ni₃Al composite when the melt–infiltration sintering temperature increased from (a) 1300°C to (b) 1400°C with 1 h hold time at peak temperature in each case.
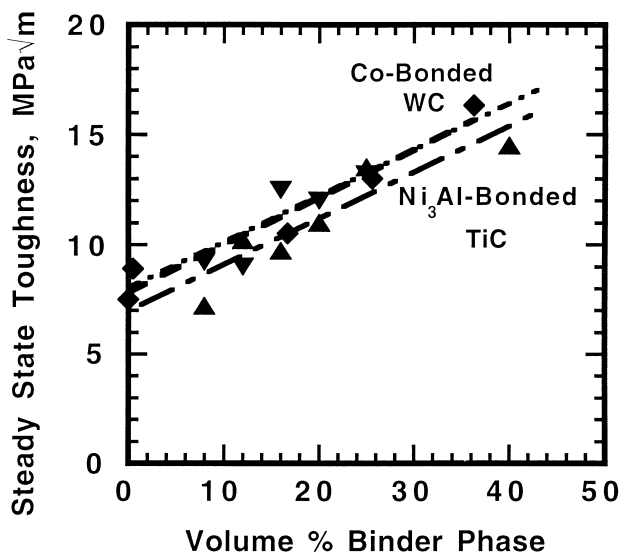

Fig. 6. The room temperature toughness values of Ni₃Al-bonded TiC composites (▲) increase with binder content and are comparable to cobalt-bonded WC cermets (◆). Note that data for TiC-based composites includes samples fabricated by normal sintering and by melt–infiltrate sintering; no effect of processing route is apparent. Note that data was obtained for each material using the same precracked double cantilever beam test method.

increase in temperature. To assess the upper limit for the composites, one composition was subjected to additional testing in air. As seen in Table 2, the TiC–20 vol% Ni₃Al composite exhibits an increase in fracture strength (e.g. from 1·1 to 1·3 GPa with temperature up to 950°C. The temperature (950°C) for the maximum in fracture strength for the composite is well above that (~600°C) for the maximum in the yield (and ultimate) strength observed for the commercial Ni₃Al alloy used to fabricate the composite.[18] As noted in Table 2, the tests of the composites were conducted at quite high stressing rates. Thus this must be considered as a factor in the shift in strength maximum between of the composite versus the alloy. At the same time, deformation of the aluminide phase will be constrained by surrounding stiff TiC matrix which can also contribute to the shift in the temperature for maximum composite strength where plastic deformation of the aluminide is a controlling factor. Indeed at 1100°C, extensive plastic deformation was observed, even at the high stressing rates. As expected, the yield strength of the composite also decreases as the stressing rate is reduced.

Oxidation and corrosion resistances

The weight change in two Ni₃Al-bonded TiC composites, resulting from oxidation at 900°C for 24 h, is compared to that of a commercial Co-bonded WC in Fig. 7. Notice that increasing the Ni₃Al binder content diminishes the weight loss. The oxidation of Ni₃Al involves the formation of a stable aluminum oxide scale;[17] thus, the incorporation of the aluminide binder offers considerable potential for oxidation protection at elevated temperatures. From the immersion tests, it is apparent that the composites are more resistant to sulfuric acid corrosion than to nitric acid (Fig. 8). The resistance to hydrochloric acid is intermediate to the other two acids with the resistance decreasing for each acidic solution with increase in temperature.

Table 2. Temperature dependence of the strength of TiC–20 vol% Ni₃Al composite in air

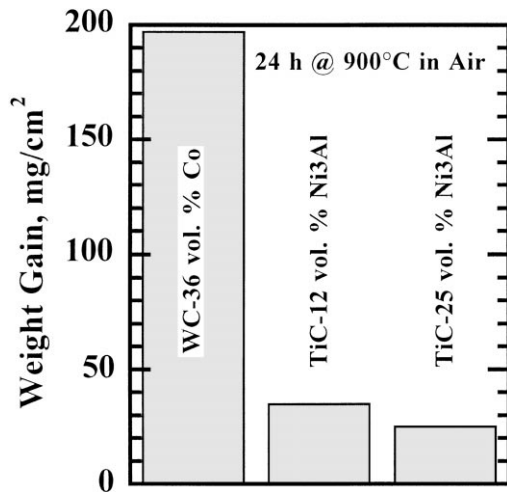| Temperature (°C)	Strength (MPa @ stressing rate of ~300 MPa s⁻¹)	
22	1080	Fracture Strength
800	1235	Fracture Strength
950	1330	Fracture Strength
1025	1030	Fracture Strength
1100	690	Yield Strength
1100	540	Yield Strength @ 105 MPa s⁻¹
1100	380	Yield Strength @ 15 MPa s⁻¹

Fig. 7. The weight change associated with oxidation at 900°C in air is reduced in the Ni₃Al-bonded TiC as compared to Co-bond WC.
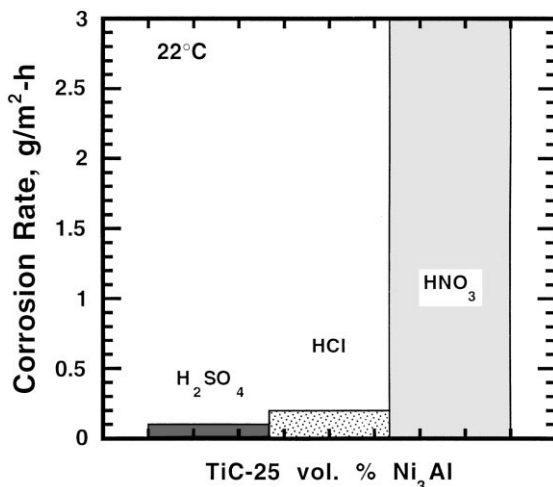

Fig. 8. Corrosion resistance of Ni₃Al-bonded TiC composite in acid solutions (1 normal) at 22°C varies with specific acid being most resistant to hydrochloric and sulfuric acids.

Summary

Recent efforts have succeeded in the development of a low cost, industrially viable fabrication method by melt infiltration sintering (MIS) to form dense TiC–Ni₃Al composites with excellent properties. The process has proven very versatile as a wider range of compositions can be produced and the aluminide powder size range is not critical. In addition, the equipment requirements and processing conditions are identical to those presently used in the 'hard-metal' industry. Both the thermal and mechanical properties can be tailored by adjusting the Ni₃Al content and the processing temperature.

For example, fracture strengths and toughness values of more than 1 GPa and 10 MPa√m, respectively, are achieved at room temperature.

The aluminide binder results in the retention of the mechanical properties to 1000°C. Increasing the aluminide content raises the thermal expansion coefficient (e.g. $\sim 11 \times 10^{-6}$ °C^{-1} at 40 vol% Ni₃Al) to approach values of metallic alloys and greatly improves the oxidation and corrosion resistances.

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