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The effects of Mo_2C additions on the microstructure and sliding wear of $TiC_{0.3}N_{0.7}$–Ni_3Al cermets

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ABSTRACT

Combining hard but brittle Ti(C,N) ceramic particles with the ductile Ni_3Al intermetallic produces a ceramic–metal composite, or cermet, with high wear resistance. However, for high N content Ti(C,N) cermets, the wettability of molten Ni_3Al is relatively poor, which leads to materials with residual porosity when a low binder volume fraction is used. Through a reaction sintering process, various amounts of Mo_2C (from 1.25 to 10 vol.%) were incorporated into $TiC_{0.3}N_{0.7}$–Ni_3Al cermets, with the aim of improving the densification behaviour. Materials were prepared with Ni_3Al binder contents from 20 to 40 vol.%, and were densified by vacuum sintering. Mo_2C was found to improve upon the wettability during sintering, thus enhancing the densification, especially for the lowest binder contents. The sliding wear and Vickers indentation behaviour of these cermets were assessed. It was found that Mo_2C additions had a positive effect on both the hardness and indentation fracture resistance of the samples, but had a detrimental effect on the sliding wear response of the cermets. This behaviour was attributed to increased microstructural inhomogeneity with Mo_2C additions.

1. Introduction

The properties of ceramic–metal composites, or cermets, are determined by several key factors of the ceramic phase, which include the grain size and shape, homogeneity, and connectivity. Additionally, both the amount and composition of the metallic binder help in determining the performance characteristics of the cermet [1]. In combination, these aspects play a crucial role relating to the physical response of the composite, such as hardness, toughness, strength, and wear resistance. As a consequence, the interactions between the ceramic and the metal binder phase must be taken into consideration in order to obtain a cermet with the desired properties. For example, there must ideally be a combination of both good wetting of the molten metal on the ceramic at the sintering temperature and some limited solubility of the ceramic phase in the metal [2]. If a system has poor wettability then the final structure will have a degraded densification response, resulting in a cermet with relatively poor physical properties [3]. For a given cermet system, alloying additions can be made that alter the interaction between the ceramic and metallic phases. Consequently, a poor wetting system can potentially be transformed into a system that densifies fully upon sintering.

With this in mind, titanium carbonitride Ti(C,N) based cermets are an attractive alternative to more conventional tungsten carbide–cobalt (WC–Co) cemented carbides for a variety of industrial applications [2]. Their relatively low densities make them more practical for use in structural applications, particularly when mass is a design factor. The high toughness, hardness, and wear resistance of Ti(C,N)-based cermets also make them promising for use as protective coatings on parts that are susceptible to high amounts of wear. Ti(C,N) cermets combine the high hardness properties generally associated with titanium carbide (TiC), with the beneficial toughness attributes of titanium nitride (TiN) [2]. However, they can suffer from poor wetting with some metallic binder systems as the fraction of TiN is increased [4,5]. This poor wettability can have a detrimental effect on sintering, leading to the retention of residual porosity. Ultimately, this has a negative impact on both the mechanical and tribological properties. One approach used to reduce the poor wettability of Ti(C,N) ceramics is through additions of Mo, in either its elemental or carbide form, as Mo_2C [5–7]. Improved wetting results in a reduction of microstructural defects, such as voids and micro-cracks, an increase in the interphase bond strength, and also improved phase homogeneity [8].

In the present study the intermetallic nickel aluminide (Ni_3Al) is used as the binder phase for a high nitrogen content Ti(C,N) system (i.e. $TiC_{0.3}N_{0.7}$). Ni_3Al has excellent physical properties at elevated temperatures, as well as a high oxidation resistance up to approximately 1100 °C [9]. Related TiC–Ni_3Al cermets have been shown to exhibit high strength retention to ~1000 °C [10], which is far in excess of WC–Co based materials [11]. However, while these materials show considerable promise, recent studies have shown that melt infiltration processed Ti(C,N)–Ni_3Al cermets with a high N:C ratio exhibit relatively poor sintering [12,13]. This response reduces the wear resistance, due to degraded wetting during processing and consequently retained porosity [13]. In order to alleviate this problem, the influence of Mo_2C additions

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to $TiC_{0.3}N_{0.7}$–Ni_3Al cermets is examined in the current study. The fabricated materials are assessed in terms of their microstructural development, Vickers indentation response, and dry sliding wear behaviour.

2. Experimental procedures

2.1. Cermet raw materials and preparation

The raw powders used in the present study were: $TiC_{0.3}N_{0.7}$ (lot no. L25747; D_{50} = 1.72 μm) from Treibacher Industrie AG (Althofen, Austria); Mo_2C (lot no. PL71887718; 1.0–2.0 μm) from Pacific Particulate Materials (Vancouver, BC, Canada); Ni (lot no. L10W013; 2.2–3.0 μm) and Ni/Al 50/50 wt.% (lot no. D28X029; D_{50} = 38 μm), both obtained from Alfa Aesar (Ward Hill, MA, USA). The $TiC_{0.3}N_{0.7}$–Ni_3Al–Mo_2C cermets were manufactured using a simple in-situ reaction sintering process, based on the approach developed in prior studies [13,14]. The cermet compositions were prepared with a fixed Ni_3Al binder content of 20, 30 or 40 vol.%, with the Mo_2C additions made by substituting for $TiC_{0.3}N_{0.7}$ on a volume basis, with Mo_2C contents then varied from 1.25 to 10 vol.%. All of the compositions are therefore subsequently referred to by volume percentage for the Ni_3Al and Mo_2C contents, with the balance being $TiC_{0.3}N_{0.7}$. In addition, a '$TiC_{0.3}N_{0.7}$-free' cermet was produced, based on a matrix of 70 vol.% Mo_2C, with 30 vol.% Ni_3Al binder. Powders of each component were individually weighed with 0.5 wt.% polyvinyl butyral (PVB) resin and then ball milled in acetone for a period of 24 h, using yttria stabilized zirconia milling media at a ratio of 10:1 by mass to the powders; the PVB was added to improve dry compaction behaviour. The milled powder mixture was then left to evaporate in a fume hood for a period of 24 h before being sieved through a 75 μm stainless steel mesh. Sieved powders were then uniaxially pressed in to disc-shaped samples at 45 MPa (~31.75 mm diameter × ~4 mm thick), which were subsequently sealed in plastic bags and cold isostatically pressed (CIPed) at 207 MPa. During sintering, samples were placed on bubble alumina within an alumina crucible. Sintering was then performed at 1550 °C, for 1 h, under dynamic vacuum (~20 mTorr), with heating and (nominal) cooling rates of 10 °C/min and 25 °C/min, respectively (below ~800 °C a slower, natural furnace cool occurred). In addition to the materials prepared 'in-house', for comparative purposes a commercial WC–Co cermet was also evaluated. The material (grade SNR540-ZM18) was obtained from Ultra-met® (Urbana, OH, USA), and had a cobalt content of 18 wt.% (approximately 30 vol.%), and a mean grain size of approximately 5 μm (which is viewed as being a "coarse" grade from a commercial perspective).

2.2. Cermet characterisation

After sintering, the densities of the Ti(C,N)–Mo_2C–Ni_3Al cermets were determined by immersion in water, following Archimedes principle. They were then surface ground and polished to a finish of 0.25 μm for further evaluation. The microstructure of the polished cermets was assessed using field emission scanning electron microscopy (SEM; Model S-4700, Hitachi High Technologies, Tokyo, Japan). SEM observation was performed primarily using a purely back scattered electron (BSE) imaging mode, through application of a −50 V bias to the Hitachi ExB 'in-column' detector, in order to highlight atomic number related compositional contrast. Chemical analysis was conducted in the SEM using energy dispersive X-ray spectroscopy (EDS; Model X-Max^N (80 mm^2), Oxford Instruments, Concord, MA, USA). Quantitative analysis of grain size, contiguity and binder mean free path (MFP) were conducted on digital SEM images using the ImagePro software package, where the contiguity was measured by superimposing a series of lines upon a representative microstructure and counting the number of carbide/carbide and carbide/binder intercepts. In this instance grain size was determined using the lineal intercept method [15], while both contiguity and binder MFP were determined using the approach outlined by Gurland [16,17]. Selected samples were also examined using an electron probe micro-analyser (EPMA; Model JXA-8230 SuperProbe, JEOL, Tokyo, Japan), operating in wavelength dispersive X-ray spectroscopy (WDS) mode, with an applied operating voltage of 15 kV. The crystalline phase assemblage of both the starting powders and selected sintered samples were assessed using X-ray diffraction (XRD; Bruker D-8 Advance, Bruker Corp., Billerica, MA, USA), with a Cu Kα source.

The Vickers hardness and indentation fracture resistance (IFR) were determined using applied loads of 5 and 30 kg, respectively. In this instance the IFR was calculated using the equation of Niihara [18], with the assumption of Palmqvist cracking in all of the cermets. The dry sliding wear response was assessed against a WC–Co counter face sphere (6.35 mm diameter, grade C2), with 6 wt.% Co (designated WC–6Co). A reciprocating sliding distance of 5.03 mm was employed, at a frequency of 20 Hz (Model Universal Micro Tribometer (UMT), Bruker, Billerica, MA, USA), giving a total sliding distance of ~1.45 km after 2 h. The reciprocating conditions used relate to a total sliding distance of ~1.45 km, over a two hour period. Wear tests were conducted under applied loads between 20 and 60 N. The UMT system monitors the dynamic sliding coefficient of friction (COF) during the wear tests. The surfaces of the commercially procured WC–Co cermets were prepared in a similar manner to the Ti(C,N) materials, and they were tested against the same WC–Co spheres described previously, with applied loads between 20 and 60 N. Three repeat tests were conducted for selected samples, and the maximum standard deviation error in that instance was ±25%.

Wear track volumes were subsequently determined using an optical profilometer (Model PS50 Optical Profilometer, Nanovea, CA, USA), and these data were then used to calculate specific wear rates following the Lancaster approach [19]. After wear testing, the associated damage was assessed using SEM and EDS. The tribolayers formed during wear tests were also examined using focused ion beam microscopy (FIB; Model F-2000A, Hitachi High Technologies, Tokyo, Japan). FIB involved deposition of a tungsten protective strip prior to site specific Ga^+ ion milling to reveal the tribolayer through thickness structure, which was then examined using SEM. Further details regarding the characterisation procedures used can be found in prior publications [13,20].

3. Results and discussion

3.1. Densification behaviour and microstructure development

In cermet systems the wettability of a carbide by a molten metal is determined in part by its stability, in the sense that the lower the negative heat of formation a carbide has, the smaller the wetting angle is between the two phases [2]. Amongst the carbides that are composed of elements from groups IV, V, and VI of the periodic table, Mo_2C has the lowest heat of formation and therefore the lowest contact angle with liquid metals. As a consequence, Mo_2C is generally an excellent addition to systems with poor melt wettability [2]. From Fig. 1 it can be seen that, in the absence of Mo_2C additions, samples with the lowest amount of Ni_3Al binder show relatively poor densification, achieving less than 95% of theoretical density following liquid phase sintering. However, with an addition of only 1.25 vol.% Mo_2C the final sintered density increases to ~99% of theoretical density, highlighting the positive effect the carbide has upon the sintering response of Ti(C,N) cermets with high N:C ratios. In general, the sintered densities of the samples all increased as the amounts of Mo_2C and percentage of Ni_3Al were increased, and essentially all Mo_2C containing cermets were sintered to in excess of 99% of theoretical density.

During liquid phase sintering carbide grain coarsening occurs, due to partial dissolution of the $TiC_{0.3}N_{0.7}$ into the binder phase, and subsequent re-precipitation. The reduction of surface energy of the solid particles is the primary driving force for small grains to dissolve and large grains to grow. It has been shown that the addition of Mo_2C acts as a grain refiner in the Ti(C,N) systems [2,7]. It was suggested that the addition of Mo improves the wettability between the ceramic and metallic phases, which actually decreases the solubility of Ti(C,N) in the binder,