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Mechanical properties of reactively processed W/Ta_2C-based composites

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Abstract

The mechanical properties of reactively processed W/Ta_2C cermet composites were studied. Dense W/Ta_2C cermets with a nominal composition of 40.4 vol% W(Ta)ss, 48.9 vol% Ta_2C and 10.6 vol% Ta_2WO_8 were fabricated using a pressureless reactive processing method. Four-point bend strength, fracture toughness, elastic modulus, and microhardness were measured at room temperature. The average flexure strength was 584 MPa which is lower than for pure W; however the strength of pure Ta_2C is unknown. The fracture toughness was 8.3 MPa $m^{1/2}$ which fits a rule of mixtures between literature values for the fracture toughness of the W and Ta_2C phases. The elastic modulus was 476 GPa, and the microhardness was 13.4 GPa. Both Young's modulus and hardness were higher than values reported for other W-based cermets.

Keywords: Composites; Mechanical properties; Cermets; Carbides

1. Introduction

Ultra high temperature materials are being investigated for a wide variety of aerospace applications. Propulsion applications, for example, require materials that are not only strong and durable at room temperature, but that can also maintain their properties in corrosive exhaust gases, at pressures in excess of 7 MPa and at temperatures in excess of 2500 °C.[1–3] In addition to these harsh conditions, for many applications, the materials must be able to survive temperature changes of hundreds of degrees per min without failing. One of the most demanding applications for these materials is nozzle throats of rocket engines.[4]

Currently, the most commonly used material for nozzle throats is tungsten (W) because of its high melting temperature (3422 °C), high room temperature strength (~800 MPa), high thermal conductivity at elevated temperature (105 ± 10 W (m K)$^{-1}$ at 2000 °C), and low thermal expansion (7.4×10^{-6} K^{-1} at 1500 °C).[5] Also, tungsten's ability to be formed into the complex geometries required for rocket engine components makes it the current material of choice.

A major drawback of tungsten is its high density (19.25 g/cm^3).[7] It is estimated that over the lifetime of a military plane the removal of each pound removed saves ~$1000. Weight savings becomes even more critical for orbital vehicles, with the removal of one pound of weight from the space shuttle saving ~$10,000.[8] Hence, lighter materials could significantly reduce the cost of rocket propulsion systems.

In addition to its high density, tungsten has been shown to suffer severe pitting corrosion in throat nozzle conditions, leading to a linear ablation rate 1.49×10^{-2} mm s^{-1} at 2500 °C in one test.[9,10] Another issue is that the strength of tungsten decreases rapidly as temperature increases. By 2000 °C the tensile strength of tungsten decreases to approximately 50 MPa.[7] Previous research has shown that alloying tungsten with various metals improves its mechanical strength at elevated temperature; however, no alloying technique has been effective at increasing the strength of tungsten above 2100 °C.[11]

Ultra high temperature ceramics (UHTCs) are currently being investigated for use in a variety of aerospace applications. UHTCs are a group of materials that are classified by having melting temperatures in excess of 3000 °C. The two main classes of UHTCs are the refractory diborides and carbides.[12,13] In particular, extensive work is being done on ZrB_2 and TaC to make them viable for aerospace applications. ZrB_2–SiC composites have found to have flexure strengths in excess of 1 GPa, while TaC was found to have a flexure strength of 680 MPa.[14,15] Materials in the Ta–C system with varying C/Ta ratios have been shown to exhibit unique combinations of strength and fracture toughness, with $TaC_{0.6}$ exhibiting the highest combination of fracture toughness (12.7 MPa $m^{1/2}$) and strength (672.7 MPa,) as a result of its phase composition and

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Table 1
Nominal batch composition for in situ reaction sintering.

Material	Source	Average particle size (μm)	Weight (%)
Ta_2O_5	AEE	0.5	32.84
WC	Cerac	0.64	33.54
TaC	AEE	1–5	28.32
Phenolic resin	Georgia Pacific	–	5.7

layered microstructure.[16] Ditantalum carbide, Ta_2C, is another promising material for these applications due to its high fracture toughness (9.3 MPa m$^{1/2}$) and its low thermal expansion coefficient (7.2×10^{-6} K^{-1} at 1500 °C).[17,18] However, no flexure strength data have been published for Ta_2C in the open technical literature. To date, the only successful method for producing dense Ta_2C is hot isostatic pressing (HIP). Ta_2C, with a relative density of 98%, was produced by HIPing at 1630 °C and 195 MPa for 2 h.[19] Despite their high strength and melting temperatures, it has been conceded by most that monolithic ceramics are not viable options for high speed propulsion applications due to their poor oxidation and thermal shock resistances.[4]

Recent research has focused on metal–ceramic composites or cermets as potential materials for next generation aerospace applications.[1–3] Several researchers have focused on various ceramic additions to W to produce composites. The advantage of combining a refractory metal and a ceramic is that the high thermal conductivity and ductility of the metal phase may mitigate the thermal shock problems suffered by monolithic ceramics, while the ceramics may improve elevated temperature strength retention and lower the ablation rate as compared to the pure metal. Several ceramics, including ZrO_2, ThO_2, ZrC, TiN, TiC, and HfC, have been added to tungsten to form cermets. Normally, the ceramic is the minor phase, which is dispersed in a continuous metal matrix.[20–23] The addition of 30 vol% ZrC to tungsten increased the strength at 1000 °C to ∼800 MPa, compared to 140 MPa for pure tungsten.[5] The increase in elevated temperature strength was accompanied by a decrease in the linear ablation rate to 3.28×10^{-3} mm s^{-1} at 2500 °C.[9] The addition of 30 vol% ZrC was also found to increase the fracture toughness (K_{IC}) of tungsten from 7.6 to 9.3 MPa m$^{1/2}$.[22] Ta_2C is also an attractive reinforcement for tungsten cermets due to the close match of their thermal expansion coefficients (7.2×10^{-6} K^{-1} for Ta_2C vs. 7.4×10^{-6} K^{-1} for W at 1500 °C).[7,18]

This study focuses on the determination of the mechanical properties of W/Ta_2C cermets produced by pressureless reactive sintering.

2. Experimental procedure

2.1. Sintering conditions

The precursor powders were prepared in 100 g batches according to the composition listed in Table 1. After mixing, the powders were uniaxially and isostatically pressed into 35 mm by 20 mm by 8 mm billets. The billets were then placed in a boron nitride crucible and heated in a graphite furnace (3060-FP20, Thermal Technology Inc., Santa Rosa, CA) at 1450 °C for 4 h for reaction and then densified at 1850 °C for 1 h under vacuum (∼26 Pa). The powder processing, sintering process, and chemistry of the reactions have been described in more detail previously.[24] The samples produced from the reactive processing were nominally 28 mm by 18 mm by 5 mm.

2.2. Characterization

The Archimedes' technique was used to measure the bulk density of the specimens after sintering. Water was used as the immersion medium for the Archimedes' measurements. Scanning electron microscopy (SEM; S570, Hitachi, Pleasanton, CA) was used to characterize the microstructures. Details regarding phase identification and microstructure characterization were reported in a previous paper.[24]

Specimens for mechanical testing were sectioned from the as-processed billets by surface grinding and cutting. Twenty bars were fabricated (ASTM C1162 type "A" bars with nominal dimensions of 1.5 mm by 2.0 mm by 25 mm) for mechanical testing. The tensile sides of the test bars were polished to a 1 μm finish using successively finer diamond slurries. Flexural strength was determined using four-point bending (5881, Instron, Norwood, MA) in accordance with ASTM C1161-02. The test specimens were tested in a fully articulated fixture having an outer span of 20 mm with loading at the quarter points. The elastic modulus was determined from load deflection curves obtained during flexure testing. Modulus and flexure strength were determined as the average from 10 test bars.

Hardness measurements were conducted according to ASTM C 1327-03 using Vickers' diamond indentation (Duramin 5, Struers, Ballerup, Denmark) with a load of 1 kg and a hold of 15 s. The measured hardness value was taken as the average of 10 indents.

Fracture toughness was tested using a method modified from that outlined in ASTM C1421-01 for the surface crack in flexure test. The fracture toughness was calculated using Eq. (1):

$$K_{IC} = 0.59\left(\frac{E}{H}\right)^{1/8}(\sigma_m P^{1/3})^{3/4} \qquad (1)$$

where E is Young's modulus, H the Vickers' microhardness, σ_m the measured four-point bend strength after indentation, and P is the indentation load. This modified method did not include grinding the surface after indentation as required by the standard because of the potential for corrosion of the W. In addition, a Vickers' indenter, instead of a Knoop indenter, was used for flaw symmetry with respect to loading.[25] Compensation for the lack of a ground surface was achieved using a large load (50 kg) on the indenter. This was designed to drive the surface crack deeper and mitigate any surface effects.[25] The specimens were 1.5 mm by 2 mm by 25 mm with the indentation placed on the 2 mm wide surface that was the tensile surface when loaded in four-point bending. The fracture toughness was determined as the average of 10 test bars.

Table 2
Physical and mechanical properties of W/Ta_2C cermet and constituent phases.

Mechanical property	W	Ta_2C	W/Ta_2C
Flexure strength (MPa)	787[22]	–	584
Young's modulus (GPa)	403[23]	–	476
K_{IC} (MPa m$^{1/2}$)	7.6[22]	9.3[27,a]	8.3
Vickers hardness (GPa)	3[7]	18[26,b]	13.4
Density (g/cm^3)	19.3	15.1	15.8

[a] Tested on 3 bars.
[b] Tested on thin film of Ta_2C.

3. Results and discussion

The overall composition of the W/Ta_2C cermets was previously determined to be 40.4 vol% W(Ta)$_{ss}$, 48.9 vol% Ta_2C and 10.6 vol% Ta_2WO_8.[24] The tungsten was found to contain 31.2 at% Ta in solid solution, while the Ta_2C was found to contain 13.4 at% W in solid solution.[24] The measured bulk density of the W/Ta_2C cermets was thus calculated to be 99.5% of its theoretical density after sintering at 1850 °C.

The results for flexure strength, elastic modulus, fracture toughness, and hardness of the W/Ta_2C cermets are summarized in Table 2. The microstructure of the cermets contains two interpenetrating phases (W and Ta_2C) with isolated Ta_2WO_8 grains (Fig. 2). The Ta_2C grains were found to be ∼3 μm in diameter, while the tungsten grains were found to be ∼1–2 μm in diameter. Average grain sizes were difficult to measure due to an inability to thermally or chemically etch the samples. As a result, transmission electron microscopy (TEM) was used to observe individual grains, which afforded only a limited number of grains that could be measured (Fig. 3). The flexure strength of the W/Ta_2C cermets was 584 ± 73 MPa with a low of 487 MPa and a high of 676 MPa. The flexure strength for nominally pure tungsten at room temperature has been reported to be around 800 MPa.[5] Since the flexure strength of Ta_2C has not been reported; it is difficult to conclude, or calculate, what the ultimate strength of the W/Ta_2C composite might be.

The Young's modulus of the W/Ta_2C cermets was 476 ± 37 GPa compared to a value of 403 GPa reported for pure W.[7] Again, no modulus value is available from the technical literature for Ta_2C. However, using a rule of mixture calculation based on a W modulus of 403 GPa and the composite modulus of ∼476 GPa, the modulus of Ta_2C was estimated to be ∼530 GPa. Using this same rule of mixtures approach to calculate the hardness for the Ta_2C in the W/Ta_2C cermet, the hardness of Ta_2C was determined to be 18.3 GPa, which agrees well with the only published value for Ta_2C (∼18 GPa).[26] Since the hardness appears to follow a traditional rule of mixtures approach, it is expected that the modulus would also follow the rule of mixtures, as a first approximation, so the calculated modulus of ∼530 GPa for Ta_2C should be a good approximation of its true elastic modulus. Further, it is believed that this is the first report of a W-based cermet with an elastic modulus that is higher than that of pure W. The reported values for W/transition metal carbide cermets range from 274 to 380 GPa, with all values below that of pure tungsten.[21,22,27] As with modulus, the hardness of the W/Ta_2C cermets was higher than that of pure W. The composite hardness was 13.4 ± 0.5 GPa, which is in higher than that of W (3 GPa), but lower than the value of 18 GPa that has been reported for Ta_2C. The value of hardness measured for the W/Ta_2C cermet prepared in the present study is twice the hardness value reported for any other tungsten based cermet (5.7–6.2 GPa).[6,12,13,17,27] This difference in elastic behavior might be explained by the increased bonding and interpenetrating nature of the W and Ta_2C in the material developed in this study compared to the more common, dispersed particulate microstructure found in other W cermets. The high hardness of the W/Ta_2C cermet is an indication that it may be more resistant to recession (ablation) than pure or alloyed tungsten in the proposed applications.

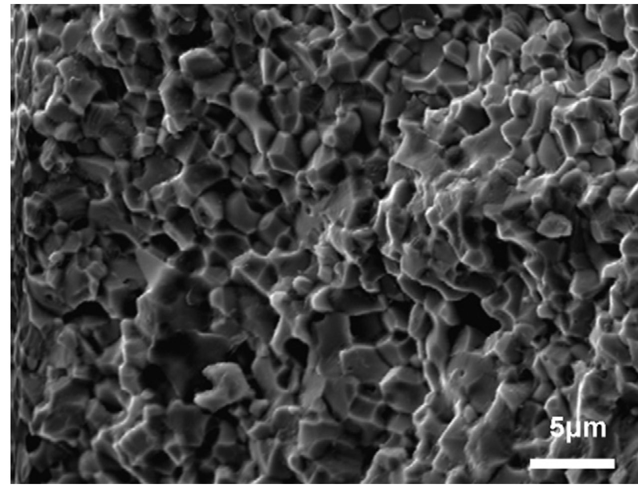

Fig. 1. Fracture surface of a W/Ta_2C cermet.

The fracture toughness of the W/Ta_2C cermet was 8.3 ± 0.4 MPa m$^{1/2}$, again between values that have been reported for W and Ta_2C (7.6 and 9.3 MPa m$^{1/2}$).[17,22] It is thought that Ta_2C has such a high fracture toughness due to the fact that it forms elongated grains under the processing conditions used.[17] It has been shown that acicular grains can increase the apparent fracture toughness of a material by 2–3 times over the value for the same material with equiaxed grains depending on whether crack tilting or crack twisting around high aspect ratio rod-shaped grains occurs during crack propagation.[28] The researchers did not go into depth about the crack deflecting mechanisms that may have been active for Ta_2C. However, it is reasonable to expect that the fracture toughness for Ta_2C with equiaxed grains would be significantly lower than the reported 9.3 MPa m$^{1/2}$. Examination of the fracture surface of the cermets from the present study (Fig. 1) revealed a predominantly intergranular fracture pattern, which is to be expected based on the clean interface observed between the grains.[24] Other researchers have similarly reported a correlation between the clean interface between the ceramic particles and tungsten and a resultant intergranular fracture mode.[22] In W/ZrC and W/TiC cermets containing 30 vol% ceramic phase, the fracture surface was found to be primarily intergranular with some transgranular rupture in the tungsten grains.[21,22] Song et al. found that crack deflection was the primary toughening mechanism in both W/ZrC and W/TiC cermets.[21,22] The W/ZrC and W/TiC

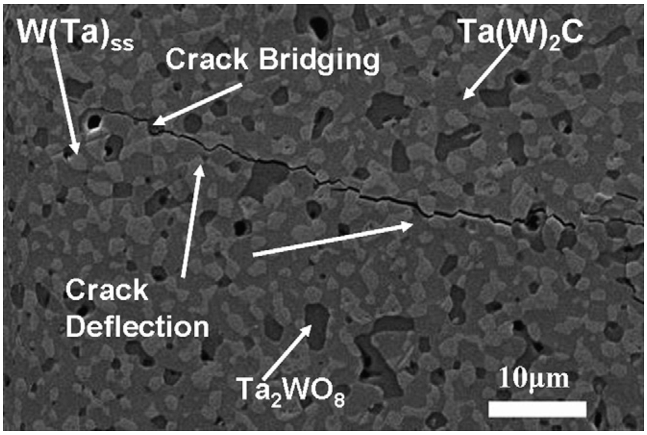

Fig. 2. Crack deflection (white arrow) in a W/Ta_2C cermet. The crack was produced using a load of 50 kg and dwell time of 15 s.

cermets had fracture toughness values ranging from 7.8 to 9.3 MPa $m^{1/2}$.[21,22] The high fracture toughness measured for the W/Ta_2C cermets prepared in the present study can be attributed to an active crack deflection and crack bridging toughening mechanisms (Fig. 2). Similarly, Zhang et al. found that crack bridging along with crack deflection was present in reaction processed W/ZrC cermets.[27] The W and Ta_2C are interpenetrating phases and due to their close match in thermal expansion can be considered to be the matrix with the Ta_2WO_8 acting as a dispersed particulate phase. The significantly lower CTE for the Ta_2WO_8 phase (-2.0×10^{-6}/°C) would suggest that it is in compression, while the matrix is in tension, after cooling from the sintering temperature.[29] The crack path in these cermets seems to be attracted to the Ta_2WO_8 phase despite the compressive force. This can be explained by the fact that the highest tensile stresses would be in the matrix nearest to the Ta_2WO_8 phase. Further, poor bonding has been demonstrated between oxides and both metals and carbides, the lack of bonding allows for the crack bridging observed for the W/Ta_2C cermets (Fig. 2).[30] In comparison to other tungsten cermets the W/Ta_2C cermets show similar toughness and toughening mechanisms (Fig. 3).

The primary difference in microstructure between the reaction processed W/Ta_2C cermets, and similar reaction processed W/ZrC cermets,[27] was that the ZrC formed isolated islands within the tungsten matrix. Also the W/ZrC cermets contained ~5 vol% porosity and had feature sizes on the order of 5–8 µm. The reactively processed W/ZrC cermets had a flexural strength of 402 MPa. The microstructure of previously reported W cermets that were produced by hot pressing consisted of a continuous tungsten matrix with a uniform distribution of equiaxed ceramic grains. The feature size of these composites was in the range of 2–4 µm. The composites had flexure strengths of 700–780 MPa.[21,22] The similarity in fracture behavior between the various W cermets, despite their significantly lower ceramic content, shows that the ceramic dominates the fracture mechanics. The room temperature flexure strength may be improved in the W/Ta_2C cermets by tailoring the structure to form isolated, equiaxed ceramic grains. However, the lower ceramic content may decrease the elevated temperature strength. Further research is needed to optimize the volume fraction, size, and shape of the ceramic phase to maximize the strength and fracture toughness of this cermet.

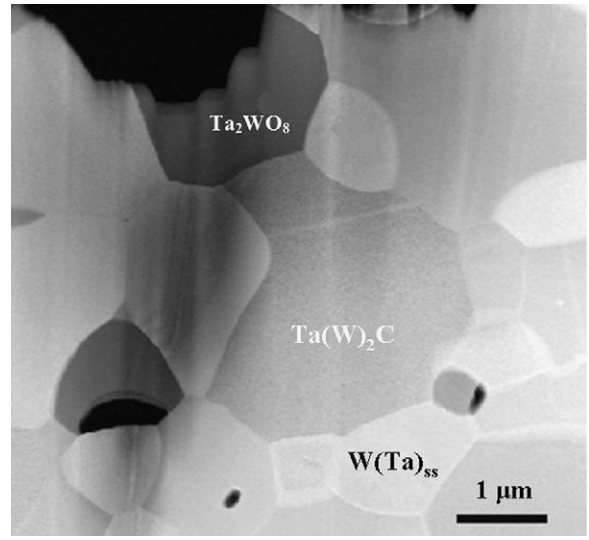

Fig. 3. Bright field TEM image taken at 200 keV of a W/Ta_2C cermet.

4. Conclusions

Dense W/Ta_2C cermets were produced by pressureless reactive sintering. The cermets had a nominal composition of 47.5 wt% $W(Ta)_{ss}$, 47.2 wt% Ta_2C and 5.2 wt% Ta_2WO_8. Microstructural analysis found that $W(Ta)_{ss}$ and Ta_2C formed a two phase, interpenetrating microstructure that contained isolated grains of Ta_2WO_8. The Ta_2C grains were found to be ~3 µm in diameter, while the W grains were found to be ~1–2 µm in size. Dense W/Ta_2C cermets exhibited ambient temperature mechanical properties that make them promising materials for rocket propulsion applications. The cermets had a flexure strength of 584 MPa, a Young's modulus of 476 GPa, a Vickers' hardness of 13.4 GPa, and a fracture toughness of 8.3 MPa $m^{1/2}$. The hardness, modulus and fracture toughness were higher than nominally pure tungsten.

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