Zirconium Carbide–Tungsten Cermets Prepared by In Situ Reaction Sintering

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Zirconium carbide–tungsten (ZrC–W) cermets were prepared by a novel *in situ* reaction sintering process. Compacted stoichiometric zirconium oxide (ZrO₂) and tungsten carbide (WC) powders were heated to 2100°C, which produced cermets with 35 vol% ZrC and 65 vol% W consisting of an interpenetratingtype microstructure with a relative density of ~95%. The cermets had an elastic modulus of 274 GPa, a fracture toughness of 8.3 MPa · m^{1/2}, and a flexural strength of 402 MPa. The ZrC content could be increased by adding excess ZrC or ZrO₂ and carbon to the precursors, which increased the density to >98%. The solid-state reaction between WC and ZrO₂ and W–ZrC solid solution were also studied thermodynamically and experimentally.

I. Introduction

TUNGSTEN (W) has the highest melting point (3422°C) of the refractory metals.¹ In addition, W has high strength (~800 MPa), high thermal conductivity $(105 \pm 10 \text{ W} \cdot (\text{m} \cdot \text{K})^{-1})$, and a low thermal expansion coefficient $(4.5 \times 10^{-6} \text{ K}^{-1})$ at room temperature.^{2,3} This combination of properties makes W attractive for aerospace applications, such as rocket nozzles, heat shields, combustion chamber liners, and re-entry components.^{4,5} However, the mechanical strength of pure W decreases rapidly as the temperature increases.^{4,6} Both alloying and particle reinforcement have been used to improve the strength of W at elevated temperatures.

Tungsten forms solid solutions with many metals. Rhenium (Re) is the most important alloying element for W in aerospace applications as it has a high melting temperature (3186°C) and reacts with W to form stable intermetallic phases.⁶ A W alloy containing 3.6 wt% Re has almost twice the tensile strength (230 MPa) of pure W (130 MPa) at 1400°C. Even so, the tensile strength of this alloy decreases as the temperature increases, reaching the same strength (50 MPa) as W at 2100°C and above, which are typical temperatures encountered in many of the aerospace applications. In addition, rhenium is expensive and markedly increases the cost of W–Re components.⁶

Fine ceramic particles including La₂O₃, ZrO₂, ThO₂, ZrC, TiN, TiC, and HfC have been used to enhance the elevated temperature strength of W^{3,5-9} by reducing grain growth and limit dislocation motion of W. Ceramic additions also improved the ablation resistance of the cermets compared with W alloys.⁵ Therefore, ceramic particle additions improve the high-temperature properties of W more effectively than alloying.^{6,5} Among ceramics, ZrC is attractive because of its high melting temperature properties.

ture (3540°C) and the similarity of its thermal and mechanical properties to W. For ceramic contents of 20 vol% or higher, W-based cermets are typically fabricated by hot pressing,^{4,9-11} which is limited to the formation of simple geometries and moderate sizes.

Recently, Breslin¹² and Sandhage and colleagues^{13–16} fabricated ZrC/W cermets using displacive compensation of porosity. In this process, a tungsten carbide (WC) preform was sintered to ~50% density at 1450°C and then infiltrated with a Zr₂Cu alloy at 1300°C. The resulting cermet contained W and ZrC as well as unreacted WC (>30 vol%) and a residual low melting point Curich phase (>5 vol%).¹⁵

The purpose of this paper is to describe an *in situ* reaction sintering process for preparing ZrC/W cermets.

II. Experimental Procedure

WC (<1 μ m, 99% purity, Cerac Inc. Milwaukee , WI) and ZrO₂ (-325 mesh, >99% purity, Alfa Aesar Chemical Co., Ward Hill, MA) were the starting materials. In addition, ZrC (<2 μ m Grade B, H.C. Starck, Karlsruhe, Germany) or ZrO₂ and carbon were added to some batches to increase the ZrC fraction in the final cermets. To reduce the particle size of the ZrO₂ and ZrC, the powders were attrition milled for 2 h using ZrO₂ or WC media, respectively. After milling, the average particle sizes were calculated from surface areas measured by nitrogen adsorption (NOVA 1000, Quantachrome, Boynton Beach, FL).

The precursors, WC, milled ZrO_2 , and ZrC were dispersed in methyl ethyl ketone by ball milling for 24 h with a dispersant (DISPERBYK-110, BYK-Chemie Co., Wesel, Germany). Next, 1 wt% binder (Qpac-40, Empower Materials, Newark, DE) was added and the mixture was milled for another 24 h. In batches with extra carbon, a soluble phenolic resin (GP 2074, Georgia Pacific Co., Atlanta, GA) was added at the same time as the binder. Granules dried from the slurries were used to form cylindrical pellets 1.9 cm (0.75 in.) in diameter by uniaxial pressing at 18.6 MPa (2.7 ksi), followed by cold iso-static pressing at 310 MPa (45 ksi). The compositions used in this study are summarized in Table I.

Compacted pellets were heated at 10° C/min in a graphite crucible to temperatures ranging from 1450° to 2150° C in a

 Table I.
 Batch Compositions Used to Study Reaction and Densification

	Compositions (moles)				
Sample code	WC	ZrO ₂	ZrC	Carbon	Highest sintered density (%)
ZrC/W-1	3	1	0	0	94.5
ZrC/W-4	3	1	0.8	0	94
ZrC/W-6	3	1.8	0	2.4	>98

WC, tungsten carbide; ZrC, zirconium carbide; ZrC/W, zirconium carbidetungsten; ZrO₂, zirconium oxide.

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graphite element furnace (3060-FP20, Thermal Technology, Santa Rosa, CA). The furnace atmosphere was a mild vacuum $(\sim 20 \text{ Pa})$ for temperatures of 1850°C or below, but was switched to flowing argon (~ 10^5 Pa) for temperatures above 1850°C. Hold times were 1 h for powder reactions and 4 h for sintering. The phases present after heating were analyzed by X-ray diffraction (XRD) (XDS 2000, Scintag Inc., Cupertino, CA). The bulk densities of sintered specimens were determined using Archimedes method. Relative densities were calculated by dividing the measured bulk densities by the theoretical densities, which were calculated for each composition based on the amounts of W and ZrC predicted in the final composites. Some sintered specimens were surface ground, polished, and thermally etched for scanning electron microscopy (SEM, S-570, Hitachi, Tokyo, Japan) analysis. The flexure strength was measured according to ASTM C1161-02a for type A bars using a screw-driven test frame (Model 5881, Instron, Norwood, MA). The elastic constants were measured according to ASTM Standard C1259-01 for impulse excitation of cylindrical disks (Grindosonic, J.W. Lemmens, St. Louis, MO). Vickers hardness was determined from a minimum of 10 indents formed using a load of 200 g and a dwell time of 15 s (Duramin 5, Struers, Westlake, OH). The fracture toughness was determined by direct crack measurements¹⁷ using indents produced with a load of 75 kg and a dwell time of 15 s.

III. Results and Discussion

(1) The WC– ZrO_2 Reaction

Previous research on the pressureless sintering of ZrB_2^{18} revealed that ZrO_2 present as an impurity on the particle surfaces of ZrB_2 particles reacted with WC according to Reaction 1:

$$ZrO_2 + 3WC \rightarrow ZrC + 3W + 2CO(g)$$
(1)

In the standard state, the reaction is favorable above $\sim 1950^{\circ}$ C (i.e., negative ΔG°) as shown by the solid line in Fig. 1. However, the reaction could be favorable at temperatures as low as $\sim 1300^{\circ}$ C under vacuum due to the lower partial pressure of CO, which was assumed to be the nominal furnace pressure (20 Pa). To verify the predictions, pellets batched with the stoichiometry of Reaction 1 (ZrC/W-1 from Table I) were heated to 1250°, 1450°, 1650°, 1850°, and 1950°C and held for 1 h under mild vacuum (~ 20 Pa). Analysis of XRD patterns in a previous study¹⁸ indicated that the reaction initiated at 1450°C under vacuum, which was $\sim 150^{\circ}$ C higher than predicted. Reaction at 1850°C and higher resulted in the formation of ZrC and W as the major phases (not shown). In addition, pellets



Fig. 1. Change in Gibbs' free energy as a function of temperature for Reactions 1 and 3. Data for the calculations come from Chase.²¹



Fig. 2. X-ray diffraction patterns showing a shift in the (311) peak of zirconium carbide (ZrC), suggesting the formation of a ZrC-based solid solution.

heated to 1850° C for 1 h had a uniform distribution of ZrC in a W matrix.

To characterize densification behavior, pellets (ZrC/W-1) were sintered at 1900° , 2100° , and 2150° C for 4 h. Pellets had a relative density of 94.5% when sintered at 2100° C for 4 h. Both the XRD analysis and microstructure suggested that Reaction 1 can be used to fabricate ZrC/W cermets.

(2) ZrC/W Solid Solution Formation

ZrC peaks in the XRD patterns of fully reacted ZrC/W (ZrC/W-1) were shifted compared with the reported positions (JCPDS card 35-0784 for ZrC) and the peak positions observed for commercial ZrC powder. For example, Fig. 2 shows that the (311) peak for ZrC was shifted from 65.97° (commercial powder and JCPDS card) to 66.475° for ZrC/W, which is also higher than the corresponding (622) peak position (66.023°) reported for carbon-deficient ZrC_{0.7}. The increase in angle indicates a decrease in the corresponding *d*-spacing, and, therefore, the lattice parameter of ZrC. The covalent radius of W (1.38 Å) is ~12% smaller than that of Zr (1.57 Å),¹⁹ which indicates that W is likely to have some solid solubility in Zr compounds as has been demonstrated by Song *et al.*¹⁰ and as shown in the Zr–W–C phase diagram.²⁰ As the position of the (311) peak is shifted to higher 2 θ values than the reported position of the (311) peak in ZrC or the (622) peak in ZrC_{0.7}, it seems likely that the ZrC was sub-stoichiometric in addition to containing some W. The formation of a (W,Zr)C_x solid solution may be beneficial for densification of the ZrC/W cermet.

(3) Microstructure and Control of Composition

The *in situ* reaction process used to fabricate ZrC/W cermets is based on the reaction between WC and ZrO_2 . From the stoichiometry of Reaction 1, the ZrC–W cermet should contain 65 vol% W and 35 vol% ZrC. Figure 3(a) shows the microstructure of ZrC/W-1 sintered at 2100°C for 4 h in argon. From the image and EDS analysis (not shown), the W grains (light gray) form an interconnected network with embedded ZrC grains (dark). The composition of the starting powders was modified by adding ZrC (Reaction 2), or ZrO₂ and C (Reaction 3), to increase the ZrC content of the cermet.

$$ZrO_2 + 3WC + xZrC \rightarrow (1+x)ZrC + 3W + 2CO(g) \quad (2)$$

$$(1+x)\operatorname{ZrO}_2 + 3WC + 2xC \rightarrow (1+x)\operatorname{ZrC} + 3W + 2(1+x)\operatorname{CO}(g)$$
(3)

Attrition-milled ZrC with an average particle size of 0.16 μ m was used to form cermets with additional ZrC (x = 0.8 moles in



Fig. 3. Microstructures of zirconium carbide–tungsten (ZrC/W) cermets produced by (a) Reaction (1), (b) Reaction (2), and (c) Reaction (3), sintered at 2100°C for 4 h in Ar.

Reaction 2), which resulted in 50 vol% ZrC. Pellets sintered at 2100° C for 4 h had a relative density of >94% and the ZrC inclusions were smaller (Fig. 3(b)) than in pellets produced by Reaction 1.

Carbon and excess ZrO_2 were also used to increase the ZrC content (Reaction 3). A soluble phenolic resin was used as the carbon source. Pellets containing the resin were charred at 600°C for 4 h in a flowing 90% Ar+10% H₂ atmosphere to convert the resin to carbon (yield 40% by weight). The addition of carbon and ZrO₂ increased the ZrC content of the cermet to ~50 vol% and resulted in a high density (>98%) and a finer microstructure (Fig. 3(c)) with features on the order of 1–3 μ m.

Crack Deflection Crack Bridging

Fig. 4. Crack deflection (white arrow) and crack bridging (black arrow) in zirconium carbide–tungsten (ZrC/W) cermets produced by Reaction (1) under a load of 75 kg and a dwell time of 15 s.

(4) Properties

Sintered ZrC/W-1 disks, having relative densities of $\sim 95\%$, were used to investigate mechanical properties. The elastic modulus was 274 GPa, the hardness was 6.2 GPa, the flexure strength was 402 MPa, and the fracture toughness was 8.3 MPa m^{1/2}. The elastic modulus, hardness, and fracture toughness were comparable with values of 383, 5.77 GPa, and 9.23 MPa \cdot m^{1/2} reported for 30 vol% ZrC/W material produced by hot pressing.⁶ Analysis of the indentation crack path by SEM (Fig. 4) indicates that both crack deflection and crack bridging contributed to toughening. The strength measured for the sintered cermets was lower than the value of 705 MPa reported for a hot-pressed W cermet containing 30 vol% ZrC.³ The lower strength of the sintered material (ZrC/W-1) can be attributed to the small fraction of porosity (~ 5 vol%) present and the relatively large grain size in this material. Higher strengths are expected with a higher density and a smaller grain size, such as sample ZrC/W-6.

IV. Conclusions

A solid-state reaction between ZrO_2 and WC was used to fabricate ZrC/W cermets using an *in situ* reaction sintering process. The reaction was thermodynamically favorable at temperatures as low as ~1300°C in vacuum. The reaction between 3 moles of WC and 1 mole of ZrO_2 (Reaction 1) could be driven to completion at 1850°C or higher under vacuum. The resulting cermets with >95% relative density and 35 vol% ZrC and 65 vol% W had an elastic modulus of 274 GPa, a fracture toughness of 8.3 MPa · m^{1/2}, and a flexural strength of 402 MPa. The sintered density and ZrC content of the cermet were increased to >98% and 50 vol% by adding ZrO_2 and carbon, respectively. The (W,Zr)C_x solid solution formation in the cermets was observed by X-ray analysis.

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