TOWARD HIGH TEMPERATURE TOUGH CERAMICS

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Abstract

The study is aimed at development, fabrication and preliminary mechanical characterization of ZrC-based composites for high temperature applications. The improvement in densification was achieved through introduction of second phase (molybdenum, zirconia, and titanium carbide). ZrC powder was produced by cost-effective in situ reactive sintering of nano-sized zirconium dioxide and graphite. The powder mixtures were pressureless sintered in vacuum at temperatures lower than 2000 $^{\circ}$ C. The final densities of the composites varied between 96 – 98%. Materials obtained were quite hard (HV10 > 17 GPa) while relatively tough (IFT > 6.6 MPa m^{1/2}).

1 Introduction

Advanced engineering ceramics have many industrially attractive characteristics/properties such as high hardness and stiffness, excellent thermal and chemical stability, etc, while their brittleness often restricts them from many structural applications. In order to overcome the problem, incorporation of a second phase in the form of particulates, flakes or short/long fibers into a ceramics matrix has been an eminent practice for decades to produce tougher ceramic materials [1]. Thus, materials design approaches imparting a substantial degree of toughness to ceramics can obviously have a significant effect on in-service damage of the materials.

High temperature ceramics are a class of materials that can be used in environments that exhibit extremes in temperature, chemical reactivity, erosive attack, etc. Zirconium carbide (ZrC), except for cutting tools and far infrared applications, is known as a major ultra-high temperature ceramics [2, 3]. Zirconium carbide belongs to a class of ultra-high temperature ceramics, which possesses high melting point (\sim 3445 $^{\circ}$ C), decent refractory hardness (\sim 25

GPa), high modulus of elasticity (~440 MPa) and good corrosion and oxidation resistance [2-4]. In spite of the excellent properties, carbides have been hardly developed on an industrial scale due to the high cost of the raw materials, processing and sintering.

Carbides are typically used as nominally single-phase ceramics to maximize the melting temperatures by avoiding reactions, solution formation, or the formation of eutectics. The high melting temperatures combined with low self-diffusion coefficients makes densification of carbides difficult using conventional hot pressing of commercially available powders. While significant progress has been made in recent years in understanding fundamental microstructure-processing-property relationships in these materials, further work is needed to develop tough ceramics for high temperature applications.

So far, zirconium carbide has been sintered with pressure-assisted techniques, such as hot pressing, reactive hot pressing, spark plasma sintering, or by conventional sintering at temperatures higher than 2000 0 C [2, 5-6]. In [7] ZrC-based composites in the systems ZrC-MoSi₂, ZrC-HfC-MoSi₂, and ZrC-ZrB2-MoSi₂ were densified to 97% of the relative density by pressureless sintering at 1900 to 1950 °C. Various research attempts have signaled the use of molybdenum as a viable binder agent for liquid sintering in the effort to boost the mechanical properties of ZrC. Research into ZrC-Mo cermets synthesized in pressureless or non-carburizing environments have used temperatures in excess of 2000 °C [8-9].

The present work focuses on toughening of ceramics, which is a crucial issue that needs to be addressed for the structural application of ceramics. The purpose of this contribution is to develop ZrC-based composites that can be consolidated at temperatures lower than 2000 °C. Improvement in the mechanical endurance of the materials is aimed through the design of controlled technological processes and introducing a second or third phase into ZrC matrix. The means to improve the fracture toughness is explored by adding controlled amount of refractory metal molybdenum as a binder metal and/or toughening compounds such as tetragonal zirconia (t-ZrO₂) that undergoes phase transformation from its tetragonal polymorph into monoclinic one; and/or refractory titanium carbide, which is known to improve densification [7, 10]. Zirconium dioxide is one of the most versatile advanced materials commercially available today. It resists high temperatures, corrosion, wear and impact, is chemically inert in the presence of the most substances and one of the most intriguing oxide ceramics for investigation due to stress-induced tetragonal-to-monoclinic (martensitic) phase transformation resulting in increase in toughness of intrinsically brittle systems [11]. Densification, microstructure, and mechanical properties are presented and discussed for three binary compositions ZrC-Mo; ZrC- ZrO₂ and ZrC-TiC.

2 Materials and testing methods

2.1 Mechanically activated synthesis of ZrC

Mechanical activation by ball milling technology and reactive vacuum sintering are used to synthesize zirconium carbide (ZrC) nanopowders from zirconia (ZrO₂) and graphite as described elsewhere [12] according to the reaction:

$$ZrO_2 + 3C \rightarrow ZrC + 2CO$$

The precursors ZrO_2 and carbon were dispersed in ethanol by high energy ball milling (ballpowder ratio 12:1) for 10 h. Granules dried from the slurries were placed in graphite crucible undergoing reactive sintering at 1500 °C under a mild vacuum for at least 1 hour in a furnace (Red Devil, USA). In the standard state, the reaction is favorable above ~1700 °C (i.e., negative change in Gibbs' free energy) [13]. However, the reaction could be favorable at temperature as low as ~1500 0 C under vacuum due to the lower partial pressure of CO, which was assumed to be the nominal furnace pressure. The required threshold sintering temperature needed to reactively synthesize ZrC from ZrO₂ mixed with carbon is estimated to be 1500 $^{\circ}$ C [12].

2.2 ZrC – Mo cermets

With specific focus on ZrC-Mo composites, the goal was to improve the brittle, low fracture toughness starting material of ZrC as well as densification and hardness. Zirconium carbide powder was mixed with 20 wt% Mo powder (average particle size 2-3 μ m) and low energy ball milled for 72 h in WC-Co ball media. During milling ~1% binding agent, a mixture of 1:1 weight organic liquid rubber and paraffin wax were added to the powder. This would ensure quality mould pressing at 20 MPa for making green bulk samples. The green bodies were presintered at 1500°C for at least 1 hour under vacuum before a final sintering step. Compacted pre-sintered blocks were heated at 4 ^oC/min in a graphite crucible to temperatures of 1800 and 1900 ^oC. Final dwell time was 30 min for densification. Since solubility of Zr and C is limited in molybdenum [14], ductility of Mo can be retained even in molybdenum solid solution of the cermet.

2.3 $ZrC - ZrO_2$ ceramic composite

Zirconium dioxide ZrO_2 is one of the toughest ceramics known. It has a wide range of industrial applications because the excellent combination of flexural strength of about 1 GPa and good fracture toughness of about 10 MPa m^{1/2} coupled with stability at high temperatures. The promising properties of this ceramics are attributed to the stress induced phase transformation from tetragonal to monoclinic structures. The presumed successful incorporation of zirconia would be expected to increase fracture toughness of the ceramic composite as well as improve material performance. In the present study, 40 vol% of commercial 3 mol% yttria stabilized tetragonal zirconia powder (< 25 nm, 99.9 % purity, TOSOH, Japan) was used to fabricate the ZrC-based composite. The powder mixture comprising the yttria stabilized zirconia and zirconium carbide was multidirectionally attrited by ball milling in WC-Co milling media for 24 hours using conventional techniques to homogenize the final blend. The powdered mixture was then pressed into green forms suitable for sintering. The ZrC-40vol.% ZrO₂ composite was pressureless sintered in vacuum furnace at 1900°C for 30 minutes. Heating rate of the sintering cycle was 10 °C /min up to 1200 °C and then 7°C /min up to 1900°C.

2.4 ZrC – TiC composite

Titanium carbide (TiC) has a similar cubic structure to ZrC, yet it has a lower sintering temperature and significantly higher hardness. Furthermore, unlike molybdenum, TiC has no tendency to react with excess carbon or even the carbon from ZrC. The purpose is to use TiC as a reinforcing agent blended with ZrC to improve its hardness and fracture toughness. Zirconium carbide powder was mixed with 20%wt of TiC and low energy ball milled under the same conditions as with the ZrC-Mo experiments. The pellets were pressureless sintered under vacuum following the same protocols as for ZrC-Mo system.

2.5 Experimental procedure

The phases present in powders heating and sintering were analyzed by X-ray diffraction (XRD - a Siemens Bruker D5005 analyzer with CuK α -radiation with a scanning range 2 θ from 20° to 80° with a step size of 0.04°). X-ray diffraction analysis was performed on the each composition sintered. The bulk densities of sintered specimens were determined using Archimedes method with water as an immersing medium. Sintered specimens were ground,

polished and cleaned for scanning electron microscopy (SEM Leo Supra-35 equipped with energy dispersive spectroscopy (EDS)) analysis. Vickers hardness was determined from a minimum of 8 indents formed using a load of 10 kg and a dwell time of 10 s (Indentec 5030 SKV). The fracture toughness was determined by direct crack measurements under optical microscope using the following equation for Palmqvist crack system [15]:

$$K_c = 0.0515 \frac{P}{c^{3/2}} \tag{1}$$

Where *P* is a load (N) and *c* is a the crack half width (m).

3 Results and discussion

3.1 Precursor materials

Analysis of XRD patterns indicated that the reaction initiated at 1500 0 C under vacuum resulted in the formation of ZrC as the major phase, Figure 1. The zirconium carbide can be presented in a wide range of non-stoichiometry in carbon. The lattice constant of 0.4698 nm is given for ZrC₁ composition (JSPDS 00-035-0784). Figure 1a depicts a single-phased XRD pattern that can be indexed with the usual zirconium carbide database. The oxygen can either be incorporated in the remaining vacant sites or be partially substituted to carbon in ZrC unit cell. Lattice parameter is modified with the presence of the oxygen; in our case the lattice constant was found to be 0.4695 nm pointing to the ZrC_{0.9}O_{0.1} phase. No residual zirconia or free carbon is detected in the powder.



Figure 1. (a) XRD pattern of the precursor powder; (b) SEM image of the powder after mechanical milling

After reactive sintering powder was subjected to high energy milling in ethanol to reduce the particle size to sub-micron and break agglomerates presented after thermal treatment. Figure 1b shows the powder after re-milling.

Samples of the precursor ZrC made from zirconia are pressed into green blocks and then vacuum sintered at 1800 and 1900 0 C. The obtained densification of 86.5% (material hardness: 12.7 GPa) and 87.8% (hardness: 13.9 GPa), respectively, indicates high residual porosity due to low sintering temperature. Therefore, the aim of this contribution is to develop ZrC-based materials that can be consolidated by pressureless sintering at temperatures lower than 2000 0 C.

3.2 ZrC – Mo cermet

The pressureless sintering of ZrC-Mo mixture in vacuum results in formation of a composite consisting of at least 3-phases. XRD analysis reveals noticeably shifted ZrC peaks in the

pattern, Figure 2a, probably attributed to the substitution of Mo into Zr cites of oxycarbide phase having a lattice parameter of 0.46258 nm. No metallic Mo is found in the composite due to the carburization properties of free molybdenum in the formation of molybdenum carbide. The entire Mo reacted to form two major phases: MoC and Mo₂C. However, the Mo₂C peaks exhibited decreasing intensity with increasing temperature while peaks of molybdenum monoxide increase. As all of the metal in the system was carburized, quantitative XRD analysis was not performed. The fact that no metal persisted led to the conclusion that ZrC–Mo processing could not be performed in furnaces with graphite heating elements.



Figure 2. (a) XRD patterns of the cermets; and (b) SEM image of the cermet produced at sintering temperature of 1900 ⁰C.

For the procedure mentioned the densification has reached >94% when sintering at 1800 0 C and >96% after sintering at 1900 0 C. The composites have a satisfactory hardness of 13.6 and 17 GPa, respectively, and quite low fracture toughness of around 3 and 6.6 MPa m^{1/2}, respectively, that is a characteristic of ceramic composites.

$3.3 ZrC - ZrO_2$ ceramic composite

Dense specimen without significant change in composition was obtained after vacuum sintering. X-ray diffraction analysis revealed zirconia and zirconium carbide grains after sintering, Figure 3a. At least one-fifth of the stabilized zirconia has retained in its tetragonal polymorph. Dissolved oxygen is known to lower the lattice parameter in Group IV carbides and ZrC tends to gather oxygen up to several percent when heated. The Zr-C system contains one cubic compound, ZrC; its lattice parameter varies with oxygen contamination noticeably decreasing from a = 0.4698 nm for $ZrC_{0.97}$ down to a = 0.4673 nm for $ZrC_{0.69}O_{0.15}$ [16]. Slight decrease in lattice parameter (or the displacement of the diffraction peaks toward higher diffraction angles) of ZrC after sintering suggests the formation of Zr-C-O compound with $ZrC_{0.9}O_{0.1}$ stoichiometry.

Microstructure of the composite is shown in Figure 3b. The presence of zirconia improves the sinterability of the material as compared to pure ZrC probably due to formation of defect oxy-carbides responsible for enhanced diffusion and densification of ZrC matrix in a presence of ZrO₂ as an oxygen source. Traces of tungsten are seen as white inclusions; W presence in the structure is due to WC ball media used for milling. The final density of 98 % was achieved at the temperature of 1900 0 C. The composite exhibits a high hardness of around 19 GPa as can

be expected from the rule of mixtures and a good fracture toughness of 10.2 MPa m^{1/2}. Toughening effect of tetragonal zirconia (*t*-ZrO2) is masked by insufficient energy of crack propagation under actions of 10 kg indentation that hardly can cause the transformation from tetragonal to monoclinic phase.



Figure 3. (a) XRD pattern; and (b) SEM image of the ZrC – ZrO₂ ceramic composite

Toughening by thermal residual stresses is also one of the effective toughening mechanisms in ceramic composites provided that the coefficient of thermal expansion of the second phase particles ($CTE_{ZrO2} \approx 11 \times 10^{-6} \,^{0}C$) is larger than that of the matrix grains ($CTE_{ZrC} \approx 4.7 \div 6 \times 10^{-6} \,^{0}C$). As zirconia phase is expected to be in tension and no transgranular cracking is observed, the crack deflection mechanism may be an appropriate one.

3.4 ZrC – TiC composite

Mixing ZrC with TiC eliminates the issue of carburization affecting ZrC. Peaks from two carbide phases are present in the diffraction patterns, Figure 4a. ZrC is presented with a 0.468 nm cubic lattice structure corresponding to formation of $ZrC_{0.8}O_{0.2}$ compound, while cubic TiC exists with the 0.435 nm lattice constant. It has been documented in literature that using ZrO_2 as a precursor substrate to synthesis ZrC could yield carbide with some remaining ZrO_2 and thus can lead to the presence of residual oxygen in the carbide lattice, resulting in the stabilization of a zirconium oxycarbide composition ZrC_xO_y [17]. Increase in lattice parameter of TiC may correlate with large lattice strains introduced by thermal mismatch of two phases ($CTE_{TiC} \approx 7.5 \times 10^{-6}$ °C).

Ab-initio calculations provided in [18] predict ZrC-TiC system to be nearly insoluble; the system forms a miscibility gap below 2000 ⁰C. SEM images of Figure 4b show only 2 visible phases in the microstructure, thus indicative of the relative stability of the two carbides during sintering.

Mechanically however, using 20% wt TiC as a ZrC reinforcing agent produces near perfect densification (>98%) and give the composite nearly 19.2 GPa in mechanical hardness after pressureless sintering at 1900 0 C, an improvement of 2.5% over 1800 0 C sintering results. The slight increase in densification at the highest sintering temperature also enhances the fracture toughness by 37% from 1800 0 C results to 6.63 MPa m^{1/2}.

The compositions and properties of the composites densified are summarized in Table 1.

Grade	Final composition	Densification, %	Measured hardness, HV10	Measured IFT (Palmqvist approach), MPa m ^{1/2}
ZrC	ZrC	87.8	13.9 ± 1.3	-
ZrC-Mo	$(Zr,Mo)C_xO_y$ -	96	17 ± 2.1	6.6 ± 1.9
	Mo ₂ C-MoC			
ZrC-ZrO ₂	$ZrC-cZrO_2-tZrO_2$	98	19 ± 1.8	10.2 ± 2.5
ZrC-TiC	ZrC(O)-TiC	98	19.2 ± 2.0	6.63 ± 3.0

Table 1. Composition and properties of the materials.



Figure 4. (a) XRD pattern of the ZrC-TiC ceramic composite; and (b) SEM image of the ZrC-TiC composite

Conclusions

Based on the study within this work on vacuum sintering of ZrC – based composites, the following conclusions can be drawn:

- 1. Synthesising ZrC from ZrO₂ and graphite can be done using high-energy milling and reactive sintering using parameters of 12:1 ball-powder ratio, 10 hours milling time, and 1500 °C.
- 2. Synthesising ZrC-Mo by using low-energy milling and sintering at 1900 ^oC improves densification, hardness, and fracture toughness by 2%, 40%, and 20%, respectively, as compared with sintering at 1800 ^oC. Attempts to make ZrC:Mo cermets showed a homogenous structure largely composed of double oxy-carbides and Mo₂C.
- 3. Addition of yttria stabilized zirconia enhances the sintering of ZrC; final composite has quite high hardness combined with sufficient fracture toughness (~ 10 MPa m^{1/2}) and low porosity. Tetragonal polymorph of ZrO₂ has been retained (to some amount) in the material after sintering at 1900 $^{\circ}$ C that may contribute into dynamic toughness of the material.
- 4. Doping with TiC and pressureless sintering at 1900 0 C results in a dense ZrC-TiC composite of homogeneous microstructure and high hardness while of relatively good fracture toughness (~ 6.6 MPa m^{1/2}).

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