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Thermomechanical properties of a spark plasma sintered ZrC–SiC composite obtained by a precursor derived ceramic route

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ABSTRACT

The thermomechanical behaviour of a spark plasma sintered ZrC-30 wt% SiC composite, made with a ceramic precursor, are characterised and compared with monolithic ZrC. At room temperature, the composite and monolith materials exhibit similar elastic properties. The fine microstructure of the composite leads to an improvement of fracture toughness and flexural strength. During sintering of composite, the overall strain associated to the applied load is preferentially accommodated by the plastic deformation of ZrC and to a more restricted degree by the formation of stacking faults through $\beta \rightarrow \alpha$ phase transition operating within SiC. As evidenced in the ZrC monolith, the plastic deformation in the ZrC grains of the composite corresponds to dislocation motion and formation of dislocation walls defining cells. The composites and monolithic material show similar compressive creep strain rates, at temperatures from 1500 to 1600 °C and stresses between 60 and 100 MPa. As suggested by the identified creep parameters and structural observations, it appears that the main deformation mechanism of the composite is preferentially accommodated by the SiC phase through dislocation motion in the crystal core that is rate-controlled by lattice diffusion of Si.

1. Introduction

Ceramics based on the carbides of the Group 4 transition metals are of great interest for applications at high temperatures in both aerospace and nuclear applications [1]. However, they are limited by their oxidation resistance. One approach has been to incorporate SiC into the ZrC matrix [2,3], so that a protective surface layer of SiO_2 or $ZrSiO_4$ is formed. Various methods have been developed including chemical vapour deposition (CVD) [4], polymer infiltration and pyrolysis [5], and pyrolysis of hybrid liquid precursors [6]. In our previous studies, it has been shown that the SiC can be introduced by mixing the ZrC powder with a SiC polymer precursor following the precursor derived ceramic (PDC) route [7,8]. In this way, the ZrC–SiC composites, made by densified by spark plasma sintering (SPS), have good oxidation resistance [9]. Indeed, the amount of SiC and the temperature were found to be critical parameters for the oxidation behaviour of such ZrC–SiC composites in ambient air. The addition of SiC clearly improved the oxidation resistance, and particularly, two main ranges of stability in temperature were identified for two compositions: ZrC-10 wt% SiC and ZrC-30 wt% SiC.

In many industrial applications, the material is subjected to high mechanical and thermal stresses in a thermal gradient, so the knowledge of the mechanical strength and of high temperature mechanical properties of the composite material is crucial.

In the literature, several ZrC–SiC composites with various amount of SiC have been sintered by solid state or reactive pressure-assisted sintering (*i.e.* SPS or Hot Pressing – HP). Table 1 gives an overview of the main mechanical properties of dense ZrC monolith and ZrC–SiC composite materials elaborated in previous works. On the one hand, Sciti et al. [13] have produced by SPS dense ZrC monolith with mean grain size of 13 μm, which exhibits a Vickers hardness of 18 ± 1 GPa, a Young's modulus of 464 ± 22 MPa and a bending strength of 407 ± 38 MPa. Gendre et al. [14] have also sintered ZrC ceramics with mean grain size of 5 μm and Young's modulus around 420 GPa depending on stoichiometry. On the other hand by addition of SiC, Zhao et al. [10] have obtained by reactive SPS a ZrC-18.4 wt% SiC composite with mean grain size of 1 μm. The measured Vickers hardness of 19 ± 1 GPa is similar to that of ZrC monolith [13,15]. The Young's modulus of 390 ± 7 GPa is relatively lower than that of monolith [13], and seems to be related to the finer grain size and to the remained Si and graphite in the composite. However, higher bending strength of 523 ± 20 MPa and enhanced toughness of 4.0 ± 0.3 MPa $m^{1/2}$ are shown. Similarly, Wang et al. [11] have

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obtained by reactive HP a ZrC-7.5 wt% SiC composite with improved bending strength of 819 ± 102 MPa and toughness of 3.3 ± 0.1 MPa $m^{1/2}$. Therefore, it appears that the addition of SiC increases significantly the mechanical strength and toughness with no substantial effect on hardness and elastic properties. However, the creep behaviour of such ZrC–SiC composite material and the role of SiC on the deformation mechanism at high temperature have not yet been reported in the literature.

This work deals with the characterisation of the thermomechanical properties of a ZrC-30 wt% SiC composite and its comparison with a ZrC monolith. This ZrC-30 wt% SiC composite has been selected since it exhibits a good oxidation resistance up to 1550 °C [9], and hence its application as structural material can be considered up to such a high temperature. More particularly, the main objective is to study the effect of SiC on elastic properties, mechanical strength, and in particular on deformation mechanism induced during compressive creep tests at high temperature (at temperatures ranging from 1500 to 1600 °C). These ceramics are sintered by SPS starting from ZrC powders and a commercial polycarbosilane as SiC precursor for the composite. The sintering and creep mechanisms are discussed as well as the role of SiC adding by means of Transmission Electron Microscopy (TEM) investigations.

2. Experimental procedure

2.1. Raw chemicals and powders

The ZrC powders (ZrC grade AX, Starck, Germany) had a purity of 98.5% and a mean diameter of 10.8 μm. The size distribution of the powders was determined by laser granulometry (AccuPyc II 1340, Micrometrics France S.A. Verneuil Halatte, France). SiC was derived from the polycarbomethylsilane (PCMS) (Aldrich), a polymer with a theoretical molecular formula [Si(H)(CH3)CH2]n and an average molecular weight of 800 g mol^{-1}. It is a white solid with a melting point around 84 °C and was used in the as-received form.

2.2. Preparation of the powders and densification

2.2.1. Powder synthesis

This process was already described in a previous paper [16]. The first step was to crosslink the PCMS by heating in air for 10 h at 250 °C. This gave a ceramic yield of 55% [8]. The resulting powder was then mixed with ZrC powders to give a ZrC–SiC mixture with 30 wt% SiC, i.e. ~45 vol% of SiC. Afterwards, the mixture was pyrolysed under argon at 600 °C for 5 h. The pyrolysed powder was then ball milled in air (Planetary mono mill, Fritsch, Germany) before spark plasma sintering.

2.2.2. Procedure for the densification of ZrC monoliths and ZrC–SiC composites by SPS

The ZrC–SiC mixed powders were handled in air and were poured into a graphite die with an inner diameter of 20.4 mm. They were densified without sintering additives by spark plasma sintering (Syntex, Dr. Sinter 825, Japan) at 1950 °C for $t = 15$ min under vacuum, under a pressure of 50 MPa. They were heated to 1900 °C at 100 °C min^{-1} up, then at 50 °C min^{-1} up to 1950 °C, with a dwell of 15 min. The samples were then cooled, under pressure, at 25 °C min^{-1} to 1200 °C in order to reduce any quenching stresses. The ZrC samples were sintered in the same way.

2.3. Microstructural and structural analysis

Powder samples as well as sintered ceramics were investigated with a D500 Siemens (Munich, Germany) X-ray diffractometer (40 kV, 30 mA, $CuK_{\alpha 1}$ radiation). A 2θ scanning step of 0.02° and a measuring time between each step of 10 s was used in the range of $20° < (2\theta) < 120°$.

Densities were determined using the Archimedes method with deionized water. At least five measurements were made for each sample.

Scanning electron microscopy (SEM) was used to measure the grain size in sintered and crept samples (XL30, Philips the Netherlands). The monolithic zirconium oxycarbide samples were thermally etched at 1800 °C for 10 min under flowing argon. However, thermal etching was not effective for the ZrC–SiC composites. Their grain size was therefore determined from fracture surfaces, using both coupling back scattered and secondary electron imaging. The grain size distribution was determined by using image analysis software (Scion Image, Scion Corporation, MD, USA) from at least 200 grains in fractography and 1300 grains for thermal etched samples.

Slip patterns in deformed samples were studied using transmission electron microscopy (JEOL 2100, Tokyo, Japan) with an accelerating voltage of 200 kV. Thin foils were prepared by cutting thin slices with diamond wire (2×2 mm^2 section). These slices were then ground, dimpled and finally thinned down to perforation by Ar-milling with a 4 kV accelerating voltage with PIPS 691 apparatus (GATAN Inc., Pleasanton, USA).

2.4. Mechanical characterisation

2.4.1. Mechanical properties at room temperature

Dynamic nanoindentation measurements were made on mirror polished samples using a XP diamond nanoindenter (MTS Nano Instruments, Santa Clara, USA) equipped with a Berkovich type indentor and carrying out oscillations of 45 Hz and of 2 nm amplitude. Multiple indentations (*i.e.*, about 20) were made on selected samples at different peak loads in the range of 0.5–600 mN on polished cross-sections. The Young's modulus and the Berkovich hardness were then calculated from Oliver–Pharr model [17] and the results averaged.

Apparent elastic constants (Young's modulus, shear modulus) were determined by ultrasonic method using 10 MHz transductors working in reflexion mode (WC37-10 and SW37-10, Ultran, State College, USA) on 4 mm thick samples.

Flexural strength (σ_r) was tested on a universal testing machine (LLOYD E-Z 20, Lloyd Materials Testing, West Sussex, UK) in three-point bending on 3 mm × 4 mm × 14 mm bars, using a 12 mm span and a crosshead speed of 0.2 mm min^{-1}. The faces were polished to 1 μm diamond finish and their edges chamfered in order to limit premature cracking during the test. The reported flexural strength was the average of three measurements for each sample.

The fracture toughness, K_{Ic}, was measured by the direct crack measurement (DCM) method, using loads of 19.6 and 49.1 N and a dwell time of 15 s, with a Vickers indentor. The value was estimated from the equation of Anstis et al. [18], since the ratio of the lengths of edge cracks to indentation diagonals was higher than 2.5, characteristic of a semi-circular crack system. Ten tests were performed in each sample.

2.4.2. Compressive creep tests

Compressive creep tests were carried out on fully dense samples at temperatures from 1500 to 1600 °C and at stresses of 60 to 100 MPa under flowing argon, using a screw-driven test machine (INSTRON 8652, France SAS, Elancourt, France) equipped with silicon carbide pistons. The sample strain was measured by a linear