Ceramics International 42 (2016) 10985–10991

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Influence of surface roughness and temperature on the oxidation behavior of ZrC/SiC samples

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ARTICLE INFO

Article history:
Received 22 February 2016
Received in revised form
25 March 2016
Accepted 30 March 2016
Available online 31 March 2016

Keywords:
C. Corrosion
C. Hardness
B. Composites
B. Electron microscopy

ABSTRACT

New composites were elaborated using ZrC and SiC powders and the Spark Plasma Sintering process. The samples were polished at 4 different levels in order to compare the influence of surface roughness and temperature (1400 and 1600 K) on the characteristics of the oxide layers. By XRD analysis, it was confirmed that polishing and temperature level provoked changes in the crystalline structure. SEM imaging coupled to EDS microanalysis showed that the oxide layer was made of zirconia grains with silica at the grain boundaries. Nano-indentation was used to analyze the influence of the initial surface roughness and temperature on the hardness of the oxide layer. At 1400 K, the initial polishing has favored the growth of a hard oxide layer, which could be probably correlated to the higher crystallinity of the oxide. At 1600 K, it seems that a rougher initial surface favors the hardness of the oxide layer, which could be correlated to a better adherence between the oxide layer and the substrate. Both phenomena (crystallinity and adherence) would be in competition to reduce the fragility of the oxide layer.

1. Introduction

Ultra-High Temperature Ceramics (UHTCs) are promising materials for high-temperature applications such as sharp leading edges of future generation of hypersonic vehicles, solar receivers of concentrating solar power plants, or elements of combustion chambers. This is due to their unique combination of properties, such as melting temperature above 2000 K, good hardness, high electrical and thermal conductivities, as well as chemical inertness against molten metals. ZrC has attracted a lot of attention because of its melting point around 3500 K, relatively low density, good strength at high temperatures, and high elastic modulus [1].

The main weakness of ZrC is its poor high temperature chemical stability in an oxidizing atmosphere, which significantly limits its actual application. The incorporation of Si-containing compounds could change the structure and the composition of the oxide layer, and therefore would improve its oxidation resistance by forming a SiO_2 phase that could reduce the diffusion of oxidizing species [2]. Such behavior would require a homogenous microstructure in terms of chemical composition and grain size distribution.

The Polymer Derived Ceramics (PDCs) route could achieve a hybrid material in which a mineral ZrC powder would be coated by a Si-based precursor, and this route could lead to a ZrC–SiC composite with a homogeneous microstructure after pyrolysis [3–6]. Besides, Spark Plasma Sintering (SPS) allows the densification of ZrB_2/ZrC/SiC composites at a lower temperature and in a shorter time compared to conventional techniques [7–9]. So, the combination of PDCs and SPS could be a promising way to reach oxidation-resistant composites in the Zr–Si–C system.

First investigations on ZrC/SiC composites produced by SPS and oxidized in air using a solar furnace at temperatures ranging from 1600 to 2400 K have illustrated that the oxide layers may peel off the samples due to fissuring and low adherence [10]. This peeling would accelerate the oxidation of the material as the access of the oxidizing species to the carbide would be easier whereas a harder and more adherent layer would reduce the diffusion kinetics of these species to the carbides.

This paper presents therefore the continuation of our investigation in a lower temperature range (1400–1600 K), with four different surface roughnesses in order to check the influence of the roughness on the mechanical properties of the oxide layer, and therefore to improve its hardness.

2. Material and methods

2.1. Material

Samples of ZrC/SiC composites were elaborated with 20 wt% SiC. The powders were ball-milled (planetary mono mill, Fritsch,

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http://dx.doi.org/10.1016/j.ceramint.2016.03.236
0272-8842/

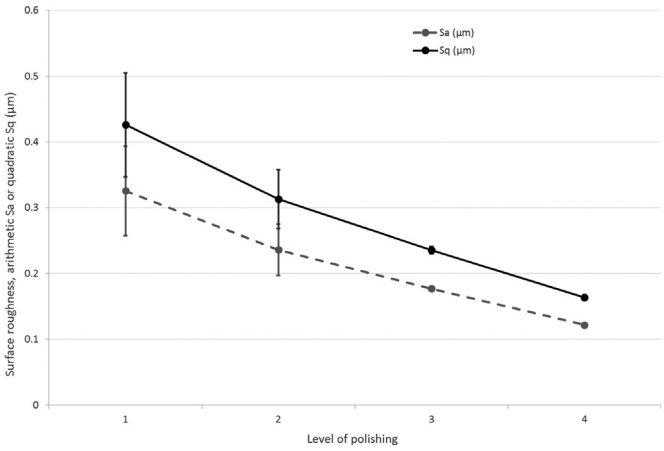

Fig. 1. Average surface roughness of the ZrC/SiC samples according to the polishing level, measured using an optical profilometer scanning at magn. × 50.

Table 1
Mass variation of the samples according to temperature and polishing level after oxidation, for the composition ZrC/20 wt% SiC.

Polishing level	T (K)	Mass variation (mg cm^{-2} min^{-1})
1	1400	3.54
	1600	3.41
2	1400	2.93
	1600	3.31
3	1400	3.50
	1600	3.73
4	1400	3.52
	1600	3.84

Germany). The ZrC/SiC mixed powders were then sintered by Spark Plasma Sintering (Syntex, Dr. Sinter 825, Japan) at 2223 K for 15 min in vacuum, with heating rates of 100 K min^{-1} up to 2173 K, then of 50 K min^{-1} up to 2223 K, with a dwell of 15 min. A controlled cooling rate of 25 K min^{-1} was used down to 1500 K in order to reduce quenching stresses. A uniaxial pressure of 50 MPa was applied to the samples during the heat treatment.

ZrC/SiC samples were polished using a Struers polisher with MD-Piano disks (the surface is made of diamonds grains into a resin matrix) at PROMES-CNRS according to 4 levels:

- Level 1: no polishing, the sample has only supported a pre-polishing in order to remove the Papyex carbon surrounding the sample previously used for the SPS experiment,
- Level 2: the sample was polished during 15 min using a 68 µm-grain size disk (MD-piano 220),
- Level 3: Level 2+5 min. polishing using a 30 µm-grain size disk (MD-piano 500),
- Level 4: Level 3+5 min. polishing using a 15 µm-grain size disk (MD-Piano 1200).

Fig. 1 presents the evolution of the surface roughness versus the polishing level. The roughness analysis was performed using an optical profilometer Leica DCM 3D with a magnification of 50. We observed that polishing both reduced the quadratic (Sq) and arithmetic (Sa) roughnesses and the standard deviation around their average values.

2.2. Experimental set-up

The oxidation tests were performed using the REHPTS (REacteur Hautes Pression et Température Solaire) facility implemented at the focus of the 6 kW Odeillo solar furnace [11]. The samples were placed 25 mm above the focus, and irradiated over their entire surface by the concentrated solar flux with a homogeneous zone of 10 mm in the center. The temperature was measured at the center of the sample – on a 6 mm diameter circle – using a monochromatic (5 µm) optical pyrometer Ircon Modline 7 and the temperature level can be adjusted by playing on the opening of a shutter placed between the concentrator and the reactor. For these experiments, the sample was quickly covered by an oxide layer mainly composed of zirconia/silica, therefore the value taken for its normal spectral (5 µm) emissivity was 0.75. The reactor was open to the surrounding air at a total pressure of 87 kPa (lower than the pressure at sea level as the solar furnace is located in Odeillo, at an altitude of 1500 m). Such a set-up enabled fast heating of samples (with rates up to 100 K s^{-1}) and the samples were maintained during 20 min. at the desired temperature plateau. Each experiment was filmed using a video camera, and the mass variation rate was determined by weighing the sample before and after experiment, then by reporting the mass variation to the initial surface and the duration of the temperature plateau, in order to obtain a rate expressed in mg cm^{-2} min^{-1}.

2.3. Post experimental analyses

XRD analysis was performed using a PANanalytical X'Pert Pro diffractometer (MPD) operating at 40 kV and 20 mA (Cu Kα radiation, λ=0.15418 nm). The X-ray diffraction measurement of θ–θ symmetrical scans was made in the range 10–100°. The indexations were achieved after oxidation using the ICDD reference file 83-0944 for monoclinic ZrO_2. 3D profilometry was performed after oxidation and image treatments were applied to remove the parasite oscillations (planarity, artefacts…). Especially, as the measured quadratic roughnesses were in between 2 and 10 µm, the samples were analyzed on a 5 × 5 mm^2 in order to apply a Gaussian filter on a large enough surface (2.5 × 2.5 mm^2) to remove these oscillations. SEM (Hitachi S-4500) on surfaces was performed in secondary electron imaging at a magnification of 2000. Some cross-sections of ZrC/SiC were analyzed using SEM coupled with EDS microanalysis. Hardness measurement of the oxide layers was performed by nano-indentation (Nanoindenter® II manufactured by Nano Instruments) using a Berkovich indenter. The hardness values were derived from Oliver and Pharr model [12], based on the analysis of the initial unloading data. The hardness value was averaged over a minimum of 8 indentations. A load of 600 mN was applied to minimize the effect of the layer roughness on the measurement.

3. Results and discussion

Table 1 reports the experimental results with the mass variation according to the temperature and the polishing level. It can be observed that except for sample 1, the mass variation is increasing with temperature and with the level of surface polishing. Increasing temperature improves the oxidation kinetics and the polishing may eliminate a strained layer and favor the oxidation kinetics by reducing the interfacial tensions between the oxide and the substrate.