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High temperature compressive creep of spark plasma sintered zirconium (oxy-)carbide

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ABSTRACT

The effect of stoichiometry (*i.e.* carbon and oxygen contents) and microstructure (*i.e.* micro-sized grains) on creep mechanism of zirconium oxycarbide was considered. The synthesis of ZrC_xO_y powder of controlled stoichiometry and without impurity has been performed *via* the carboreduction route. Compressive creep experiments were conducted at 1500–1600 °C under applied stresses ranging from 60 to 140 MPa on fully dense zirconium oxycarbide specimens obtained by spark plasma sintering. The higher oxygen content composition (*i.e.* $ZrC_{0.79}O_{0.13}$) reveals low creep resistance in contrary to $ZrC_{0.94}O_{0.05}$ composition. The analysis of the creep data shows the existence of a linear creep limit (σ_t). At low stress (*i.e.* $\sigma \leq \sigma_t = 100$ MPa, $n \approx 1$, $m \approx 1$), the creep mechanism seems to be independent of the chemical composition, and is governed by zirconium volume diffusion. At high stress (*i.e.* $\sigma \geq \sigma_t = 100$ MPa, $n \approx 3$, $m \approx 0$), a power law regime of creep appears. However, the nature of the rate-determining step of creep process depends on stoichiometry. The limiting species for volume diffusion are (i) the metal atom for $ZrC_{0.94}O_{0.05}$; (ii) and the carbon atom for $ZrC_{0.79}O_{0.13}$ linked to a Rowcliffe dislocation diffusion mechanism.

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1. Introduction

Zirconium carbide is one of the transition metal carbides from the fourth and fifth groups. It has many of the general features exhibited by the monocarbides, *i.e.*, high melting temperature, elastic moduli, and hardness and relatively good thermal and electrical conductivities. These characteristics make it suitable for many applications such as furnace elements, plasma arc electrodes, or as fuels shielding materials for future nuclear reactors (because of its neutron transparency) [1]. Zirconium carbide has a rock salt-type fcc structure and also exists over a wide range of carbon-deficient compositions (*i.e.* ZrC_x with $0.55 \leq x \leq 0.98$) [2].

However, in these application areas, the working conditions can be associated to both high temperatures and stresses. So, the creep resistance is one of the critical working properties because it can control lifetime and thus the material choice.

The studies on the creep deformation and the rate controlling mechanisms of single crystal and polycrystal zirconium carbide were published during sixties and seventies and are limited to very high temperature (above 2000 °C) [3–15]. The creep behaviour at moderate temperature (*i.e.* about half of its melting temperature, 1500–1600 °C) has been poorly studied. Lee et al. [4] have worked on the characterization by transmission electron microscopy (TEM) of the active slip planes arising in a monocrystal of zirconium carbide submitted to compressive creep at temperatures ranging from 1400 to 2000 °C. The only study of the creep behaviour of zirconium carbides ceramics at about 1600 °C was performed on samples bearing numerous impurities (free carbon, oxygen and nitrogen) that led to unusual low creep resistance [3]. This temperature range of 1500–1600 °C is however of particular interest, since it could be associated to the accidental one which could be encountered for the fourth generation nuclear reactors (*e.g.* gas-cooled fast reactors). More particularly, the roles of the initial grain size of the ceramics as well as that of the stoichiometry on the creep resistance are not fully elucidated.

In addition, it is now well admitted that the carbon situated in the octahedral sites of the fcc zirconium lattice can be substituted by oxygen forming oxycarbides with ZrC_xO_y formulae. To our knowledge, all previous studies dealing with creep deformation report on ZrC_{1-x} carbides, and the creep behaviour of oxycarbides remains unstudied or not considered.

Finally, one of the main difficulties to get reliable and consequently interpretable data on this topic relies on the quality of the starting carbide or oxycarbide powders (*i.e.* purity, grain size distribution). The sintered specimens must show well-controlled microstructures as well as uniform stoichiometry. In addition, they must be free of impurities such as residual free carbon or zirconia. This point is important and the presence of free carbon in the

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starting powders ought to be avoided, since it should be related to the appearance of graphite intergranular inclusions after consolidation. As a matter of fact, few studies [16,17] have shown that their presence is detrimental to the mechanical performances of transition metal carbides whatever the creep mechanism involved. The well aligned intergranular graphite sheets make creep easier through (i) propagation of microcracks along the graphite planes; (ii) faster diffusion of species along the graphite planes, if the controlling mechanism is grain boundary sliding or diffusion [18]; and (iii) the formation of preferential sites for dislocation climb and/or dislocation source in the case of creep controlled by dislocation mobility [19]. At high stresses, high strain or high temperature, voids and cracks may form as a result of stress concentrations in the graphite phase [18].

In the present study, the effect of stoichiometry (*i.e.* carbon and oxygen contents) and microstructure (*i.e.* micro-sized grains) on creep mechanism of ZrC_xO_y ceramics has been considered, and a particular attention was paid on the influence of the oxygen amount on the creep resistance. This approach requires the elaboration of ZrC_xO_y ceramics with controlled composition and microstructure, and hence the mastering of the integrated approach of the ceramic process from the powder synthesis to the consolidation. In previous works, we defined the carboreduction route to synthesize ZrC_xO_y powders. This consisted of mixing zirconia and carbon powders under controlled atmosphere in order to produce carbide powders by promoting solid–solid reaction. We studied this reaction under flowing argon in order to define parameters that impact microstructure and composition of final solid solutions (*i.e.* ZrC_xO_y powder). Then, the extent of this solid solution has been studied [20]. These previous works allowed defining a carboreduction synthesis procedure to obtain ZrC_xO_y powder of controlled morphology and stoichiometry. Due to its poor sinterability inherent to the covalent character of the Zr–C bonding, spark plasma sintering has been implemented in order to synthesize fully dense ZrC_xO_y monoliths while maintaining fine microstructure (*i.e.* microsized) without sintering additives [21].

2. Experimental procedure

2.1. Preparation of samples

2.1.1. Synthesis of the zirconium oxycarbide powders

As previously mentioned, the zirconium oxycarbide powder has been synthesized using the carboreduction route, *i.e.* from the solid–gas reactions between commercially available carbon black (99.25%, Prolabo, France) and zirconia powders (monoclinic, 99.5%, Alfa Aesar, Germany). The detailed procedure of synthesis has been described in previous papers [21,22]. As mentioned above, this way of synthesis was developed to avoid the presence of impurities (*e.g.* free carbon) in the raw materials which are usually detected in commercial zirconium carbide powders [23].

The theoretical equation describing carburization of the zirconium oxide (ZrO_2) to reach the desired theoretical stoichiometry of oxycarbide (with x=C/Zr and y=O/Zr) can be written as

$$ZrO_{2(s)}+(2+x-y)C_{(s)}\rightarrow ZrC_xO_{y(s)}+(2-y)CO_{(g)} \quad (1)$$

Then, the sum of the two ratios x=C/Zr and y=O/Zr has been fixed to be equal to 1. In a first approach, that means the possible occurrence of carbon vacancies within the oxycarbide lattice is not considered. Under such hypothesis, the reaction of the zirconia carboreduction can be expressed as follows:

$$ZrO_{2(s)}+(1+2x)\ C_{(s)}\rightarrow ZrC_xO_{1-x(s)}+(1+x)\ CO_{(g)} \quad (2)$$

The coefficient x (x=C/Zr, $1-x$=O/Zr) has been fixed to reach different zirconium oxycarbide stoichiometries. In a previous paper dedicated to the study of sintering mechanisms involved during the SPS treatment of these oxycarbide powders [21], the limits of the solid solution of oxygen within the carbide powder were determined. It was shown that, under the retained synthesis conditions (*i.e.* temperature soaking, partial pressure of carbon monoxide), the limits of the solid solution in oxygen content would correspond to $ZrC_{0.95}O_{0.05}$ (the lowest oxygen content composition) and $ZrC_{0.80}O_{0.20}$ (the highest oxygen content composition). In the following, these two specific compositions were retained to emphasize the respective role of oxygen and carbon amounts on the creep resistance properties.

Carbon and zirconia initial powders were mixed in previously fixed stoichiometric proportions using a low speed planetary ball mill. The blending sequence was composed of 5 pulses of 1 min at 200 rpm interrupted by pauses of 2 min to prevent heating. Each mixture was then treated at 1750 °C for 8 h in a graphite furnace (V.A.S. furnace, Suresnes, France) under flowing argon (30 L h^{-1}). Finally, powders were sieved in dry way (40 μm) to remove the partially unreacted zirconia agglomerates detected after thermal treatment and whose average size largely exceeded 40 μm. It must be noticed that this residual content of zirconia agglomerates remains inferior to 0.2 wt%, as reported in a previous study [21].

2.1.2. Samples consolidation by SPS

SPS treatments (SPS-2080, SPS Syntex Inc., Kanagawa, Japan) have been performed thanks to the PNF² CNRS platform (University Paul Sabatier, Toulouse, France). The detailed procedure of sintering has been described in a previous paper [21]. These attempts were achieved under vacuum, using a 20 mm diameter graphite die lined with graphite paper (Papyer®, Carbone Lorraine, Genevilliers, France). The heating rate was fixed to 100 °C/min up to the targeted temperature. In order to obtain fully dense specimens, the soaking temperature was fixed at 2190 °C with a soaking time of 10 min and the applied macroscopic pressure was 50 and 100 MPa. It can be noted that these latter temperatures have been obtained by correcting the temperature measured by the IR pyrometer [23]. So, an empirical law has been used to estimate the actual temperature of the sample as follows: T_{sample} (K)= $T_{pyrometer}$ (K) × 1.22–254.

Final densities of sintered samples were measured using Archimedes's method with deionized water. At least five measurements were made for each sample. The final relative density (ρ_f) was determined as the ratio between the final density and the theoretical density computed from the crystallographic properties (*i.e.* chemical composition and lattice parameters).

Morphological observations were performed by scanning electron microscopy (SEM) with a XL30 microscope (Philips, Eindhoven, The Netherlands). The grain size was measured from SEM observations. The samples were previously thermally etched at 1800 °C for 10 min under flowing argon. The grain size distribution was determined by using image analysis software (Scion Image, Scion Corporation, MD, USA) considering at least 500 grains for each sample.

The cylindrical sintered specimens were cut using a diamond wire to obtain parallelepiped oxycarbide samples (3 mm × 3 mm × 8 mm). In order to prevent cracking during the creep test, the faces were “mirror” polished (up to 1 μm diamond paste) and their edges chamfered.

2.2. Obtained oxycarbide samples

In the previous work [20], the chemical composition of the sintered specimens was finally characterized, *i.e.* oxygen content, structural and free carbon content. To define accurately the chemical composition of ZrC_xO_y phase, powders and specimens

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