Synthesis of nanosized zirconium carbide by a sol–gel route

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Abstract

Nanosized zirconium carbide was synthesized by a new simple sol–gel method using zirconium *n*-propoxide, acetic acid as chemical modifier, and saccharose as carbon source. When heat-treated at 900 °C under flowing argon, gels transformed into intimately mixed amorphous carbon and nanosized tetragonal ZrO_2. Further heat treatments above 1200 °C led to the formation of zirconium carbide with some dissolved oxygen in the lattice. Oxygen content could be reduced by increasing the heat treatment temperature from 1400 to 1600 °C, which unfortunately also induced a mean crystallites size increase from 90 to 150 nm. Short heat treatments above 1600 °C were carried out to further purify the samples and to limit the particles growth. A compromise between purity and average crystallite's size could then be found. Powders were assessed using X-ray diffraction, thermal analysis and scanning electron microscopy.
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1. Introduction

The development of a new generation of nuclear reactors (Gen-IV project),[1,2] with improved thermodynamic yield and a drastic reduction of waste production, requires new materials able to withstand very high temperatures (1000–1200 °C in normal conditions, up to 1500 °C in incidental ones) without performances loss. Metal alloys can no longer meet these specifications and highly refractory compounds such as graphite or silicon carbide, monolithic or composites must be considered. Moreover, in the case of fast-neutron reactors required for efficient nuclear waste burning, low-Z materials are not suitable due to their high neutron slowing-down efficiency. Other compounds are more appropriate, in particular, transition metal carbides like ZrC and TiC. These materials are highly refractory,[3] have a good thermal conductivity,[4] a low neutron absorption and a small absorption cross sections, a weak damage sensitivity under irradiation.[5,6] Unfortunately, they are characterized by brittle mechanical behaviour.[7]

Over last years, nanosized grain materials have shown increasing interests due to new properties, which arise for example from the absence of extended defects in these particles.[8] In fact, unusual mechanical properties are expected in such materials, where the usual characteristic distance between two defects (e.g. dislocations) is larger than the grain-size; moreover the fraction of atoms at the grain boundaries is no longer negligible when it is compared to the bulk material. The increased effect of grain boundaries can be responsible for the onset of new properties such as superplasticity[9] or toughening even in the case of brittle (matrix) materials. In ceramics, few results were published, showing a remarkable improvement of the mechanical properties in some systems such as YSZ.[10] In the case of transition metals nitrides and carbides, diphasic systems such as TiC–TiN or SiC–Si_3N_4[11] were also studied, but no accurate data exists concerning the mechanical properties of pure nanosized carbide ceramics.

Therefore, we have focused our attention on the elaboration of nanosized ZrC powders in order to test the potentialities of this material against two different directions; improving of their mechanical properties (toughness and yield) and analysing their behaviour under irradiation (defect clustering and swelling). The crucial point is to study these properties in compounds as pure

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as possible, easily and cheaply prepared in large quantities by a simple process scalable at an industrial level. The current commercial method for producing MC carbide powders consists of direct reaction of M metal with carbon or by carbothermal reduction of the M_xO_y oxide. Recent studies suggest carbides can be obtained by carbothermal reduction of a precursor, generally prepared by sol–gel process.[12,13] The advantage of using a gel instead of a physical mixture of the solid compounds is the high intimacy at a molecular or colloidal scale. The shorter diffusion distance helps to decrease the heat treatment (dwell temperature and duration) resulting in smaller particles sizes.[14] Sol–gel processing involves the use of molecular precursors, mainly alkoxides, as starting materials. However, most alkoxides are known to react spontaneously with water to form a viscous precipitate; therefore, they require to be chemically modified in order to control their hydrolysis and condensation.[15] In the case of ZrC, gel precursors were obtained by hydrolysis of zirconium alkoxides chemically modified by acetylacetone.[14,16] However, both papers pointed out the formation of oxycarbides with relatively high oxygen content, highly detrimental for mechanical application. Another way to control the alkoxides hydrolysis is to use acetic acid as chemical modifier.[15,17] Such sol–gel process was already investigated for TiC synthesis using saccharose as carbon source[13] and TiC formation with low oxygen content was reported. Surprisingly, this process was not investigated yet for ZrC synthesis. This paper deals with the discussion of a new sol–gel route, using acetic acid as modifier, to obtain nanosized ZrC.

The powders obtained after heat treatments at different temperatures under argon flow were characterized by X-ray diffraction (XRD) to determine the cell parameters and the crystallites size evolution, and by scanning electron microscopy (SEM) to describe the powders morphology. Thermal analyses were carried out to follow the oxidation behaviour under air of the successive powders (precursors and carbides). The heat treatment effect on the lattice parameter and the crystallites size was then determined and these results were used to assess the phase purity (free carbon and oxygen contents).

2. Experimental procedure

The starting chemicals were zirconium *n*-propoxide $Zr(OPr)_4$ (70% in propanol, Fluka), acetic acid AcOH (100% RP Normapur, VWR) and saccharose (Rectapur, VWR).

The preparation of the precursor for ZrC consists of progressively dissolving saccharose (S) in acetic acid kept at 80 °C. Then, the solution is cooled down to room temperature and zirconium *n*-propoxide (ZP) is added under continuous stirring. Immediately, a brown solution is obtained and gelling begins. After 3 h, the solution viscosity has increased; heating at 80 °C evaporates the residual acetic acid and the generated acetates. The so-formed gel is then dried to powder at 120 °C. This dried powder was ground in a vibrating grinder for 1 h before being placed in a graphite boat to undergo the carbothermal reduction. The reduction was performed between 1400 and 1800 °C under flowing argon atmosphere for 3 h in a Pyrox furnace equipped with graphite resistor and matrix.

XRD patterns were recorded using an Inel diffractometer equipped with a curved position sensitive detector (CPSD) using monochromatic Cu $K\alpha_1$ radiation ($\lambda = 1.54052$ Å). Rietveld refinements were carried out at room temperature using the XND program[18] to determine the structural information, the crystallites size and the microstrain.

Sample weight losses during oxidative combustion were monitored by simultaneous thermal gravimetric analysis and differential scanning calorimetry TGA/DSC (Calvet TG-DSC111 using the B111 symmetrical microbalance–Setaram, France).

The morphological information of the different samples were determined by scanning electron microscopy using a FEI Quanta 200.

3. Results and discussion

3.1. Chemistry of gel formation

In sol–gel processing, inorganic metal salts or metal organic compounds such as metal alkoxides are combined with a mixture of solvents (mostly water) to form a sol or a gel. The metal precursors are partially, or completely, hydrolysed and condensed after mixing. The amount of water in the mixture must be precisely controlled to form a sol, with a proper viscosity, or a gel. However, metal alkoxides are well known to react spontaneously with water and to form precipitates resulting from successive hydrolysis and condensation reactions. In order to obtain a sol or a gel, zirconium *n*-propoxide must then be chemically modified by a complexing agent to decrease the alkoxide reactivity with water. Several works have shown that metal alkoxides can be modified by acetic acid, which acts as bridging and chelating ligands[19,20] with the formation of acetates by substitution of (OPr) by (OAc) groups.[17]

Basically, the general reactions occurring during the precursor preparation are metal chelate formation, transesterification and hydrolysis—condensation. The first reaction taking place when zirconium *n*-propoxide is added into acetic acid is the formation of zirconium propoxide diacetate $Zr(OAc)_2(OPr)_2$.[17] This carboxylatoalkoxide can then react following different competitive reactions. The first one is the transesterification of alkoxy groups in $Zr(OAc)_2(OPr)_2$, which react with the saccharose OH groups according to Eq. (1):

$$PrO–Zr(OAc)_2(OPr) + HO–X–(OH)_7$$
$$\rightarrow PrO–Zr(OAc)_2–O–X–(OH)_7 + PrOH \tag{1}$$
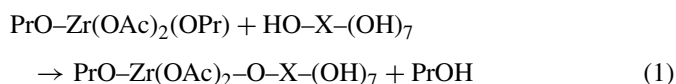
where X is a simplified notation for $C_{12}H_{14}O_3$.

The second reaction occurs between the unreacted acetic acid and the propanol (solvent and product of reaction (1)) to form water and propyl acetate (Eq. (2)):

$$AcOH + PrOH \rightleftharpoons PrOAc + H_2O \tag{2}$$
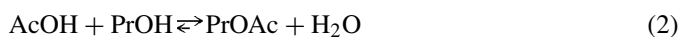
The so generated water and the zirconium propoxide diacetate react spontaneously in a substitution reaction (Eq. (3)), in which