TEM study of the reaction mechanisms involved in the carbothermal reduction of zirconia

J. David, G. Trolliard [*], M. Gendre, A. Maître

Laboratoire Science des Procédés Céramiques et de Traitements de Surface – UMR CNRS 7315, Centre Européen de la Céramique - 12, rue Atlantis - 87068 LIMOGES, France

Abstract

The carbothermal reduction of zirconia has been studied by TEM. The starting reactants consist in carbon black and monoclinic zirconia. Two successive steps are involved in the formation of the oxycarbide. The first one leads to the formation of an oxygen rich oxycarbide compound surrounded by an amorphous covering layer that regulates the achievement of species between gas and oxycarbide. The growth is controlled by three solid–gas partial reactions corresponding either to the destabilisation of the two products or to the nucleation and growth of the oxycarbide. The oxycarbide nucleation site is strictly located within the amorphous carbon. During the second step of the process, one of the initial constituents is missing (zirconia) and the previous solid–gas equilibriums are broken. The maturation of the oxycarbide into nearly stoichiometric carbide begins. The surrounding amorphous covering layer crystallises in carbon rich secondary carbide which progressively equilibrates in composition within the inner primary one.

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1. Introduction

Ultrarefractory carbides are really suitable for ultra-high temperature applications, thanks to their high properties: high hardness, good wear resistance and high decomposition temperature. These properties allow them to be used for example as barriers retaining the fission products in nuclear reactors, or as wear-resistant coatings. Nowadays, most of these industrial applications involve the silicon carbide (SiC) but owing to its higher melting point,[1,2] the zirconium carbide (ZrC) knows a regain of interest and is planned to replace SiC in many specific applications[2,3] or to elaborate fuel shielding materials in the core of the future nuclear reactors (*e.g.* Gas Fast Reactors – GFR[4]) because of its neutronic transparency.

Many routes were developed to synthesize powders – Self-propagated High-temperature Synthesis (SHS) reaction,[5–8] laser pyrolysis,[9–13] fusion synthesis by arc-melting,[14] mechanosynthesis[15–17] or thin films by Chemical Vapour Deposition (CVD[18,19]). Each of these synthesis routes presents both advantages and drawbacks, but they are generally used to produce limited quantities of carbides.

The most commonly employed route is certainly the carbothermal reduction. This method, which is industrially used for its good reproducibility is indeed very suitable to produce a large amount of powder. It rests on the reduction of a metal oxide by carbon, to form the carbide together with the release of carbon monoxide following:

$$MO_{x(s)} + (x+1)C_{(s)} = MC_{(s)} + xCO_{(g)} \qquad (1)$$
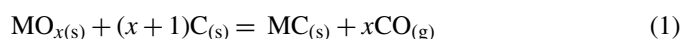
As an example, the carboreduction of silica called Acheson process[20] is certainly the process the most used to synthesize silicon carbide.

From a structural viewpoint, the zirconium carbide ZrC_x is known as sub-stoichiometric in carbon with $0.7 < x < 0.98$.[21,22] However, in the case of carbothermal reduction of metal oxides, most of the recent studies agreed on the fact that the reaction product obtained is rather an oxycarbide phase with ZrC_xO_y composition. In such compounds it is generally admitted that the oxygen atoms are located in octahedral position of the fcc zirconium sublattice and are then substituted to carbon.[23,24] It was

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* Corresponding author. Tel.: +33 5 87 50 23 81.
E-mail address: gilles.trolliard@unilim.fr (G. Trolliard).

also shown that the oxycarbide composition may vary depending on the encountered experimental conditions[14,25] and in a recent paper,[3] we synthesized zirconium oxycarbide powders with controlled stoichiometry (*i.e.* carbon and oxygen contents) and microstructure (*i.e.* microsized grains). In the synthesis conditions retained, the stability domain of ZrC_xO_y phase is shown to range from $ZrC_{0.94}O_{0.05}\square_{0.01}$ to $ZrC_{0.80}O_{0.20}\square_{0.10}$, were the $\square$ symbol stands for the vacancies amount, so that the increase of O/Zr ratio leads to the stabilization of a significant amount of vacancies in the zirconium oxycarbide crystal lattice.[3]

A good understanding of the reaction mechanisms involved in these carbothermal reactions is a major issue to control the characteristics of the obtained oxycarbide powders, mainly their grain size and chemical compositions. A rigorous control of such parameters is mandatory for subsequent studying of the elementary processes arising during further sintering, shaping or other ceramic processing.

This work reconsiders the reaction mechanism involved in the carbothermal reduction of zirconia by a TEM study of zirconium oxycarbide powders taken at various advancing steps of the carbothermal reaction. In order to further elaborate ceramic bodies with optimal mechanical properties,[26] the syntheses parameters (*e.g.* T, P_{CO}) were adjusted to obtain the final compound with the most stoichiometric composition,[3] *i.e.* $ZrC_{0.94}O_{0.05}\square_{0.01}$.

This structural approach allows to discuss the mechanisms by which the products are destabilized or to identify the nucleation sites and growth mechanisms involved in the oxycarbide formation. In particular, it will be interesting to check if the oxycarbide grows in epitaxy onto the zirconia grains in order to preserve their common fcc sublattice of zirconium during the carbothermal reduction.

2. Previous results of thermodynamic and kinetic approaches in the Zr-C-O system

In the beginning of 1950s, the hypothesis of a complex reaction of formation of the zirconium oxycarbide, based on successive partial reactions, merges from the literature.[27–29] In particular Kutsev et al.[29] have proposed that the carbothermal reduction is in fact achieved by a two steps process: first, the formation of an oxycarbide $ZrC_{0.71}O_{0.08}$ which is characterized by a well defined composition and can be considered as an intermediate phase; then the second step which corresponds to the reaction between the so formed oxycarbide and the remaining carbon to produce the final oxycarbide.

More recently, in the 1990s, some comprehensive studies essentially based on thermodynamic and kinetic approaches were performed[30–33] to decipher the fine reaction mechanisms involved in the two step reaction process first proposed by Kutsev et al.[29] Maître et al.[30] confirmed the formation of an intermediate oxycarbide with the $ZrC_{0.84}O_{0.06}$ composition and also concluded that the second step of the reaction corresponds to its slow maturation giving rise to the final stoichiometric oxycarbide. According to these authors,[30] the most probable scenario accounting for the formation of the intermediate oxycarbide phase during the first step of the reaction relies on the following reaction:

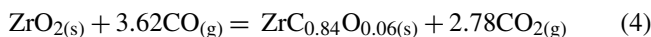$$ZrO_{2(s)} + 2.78C_{(s)} = ZrC_{0.84}O_{0.06(s)} + 1.94CO_{(g)} \qquad (2)$$
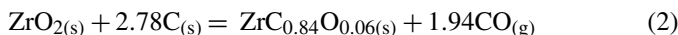
This overall reaction corresponds to the sum of two reactions because carbon and zirconia parent phases are invoked to be two distinct reaction sites:

- the carbon reaction site with:

$$2.78C_{(s)} + 2.78CO_{2(g)} \rightarrow 5.56CO_{(g)} \qquad (3)$$
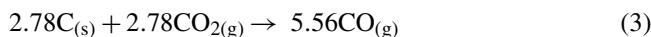
- the zirconia reaction site with:

$$ZrO_{2(s)} + 3.62CO_{(g)} = ZrC_{0.84}O_{0.06(s)} + 2.78CO_{2(g)} \qquad (4)$$

The same set of equations was also retained in a more recent study.[34] According to the same authors,[30] the solid–gas reaction (Eq. (4)) could occur since the main gas phase detected in the furnace remains carbon monoxide. Indeed, some experiments that have been conducted to analyse the outflowing gas phases by using an infrared analyser[32] attested that the furnace atmosphere is mainly composed of carbon monoxide with corresponding partial pressure values remaining below 10^4 Pa. The carbon monoxide is provided by the carbon oxidation (Eq. (3)) which is the rate limiting step of the overall reaction (Eq. (2)). The carburising of zirconia by so-formed CO itself gives off the carbon dioxide necessary for oxidizing carbon (Eq. (3)). The nature of the oxidizing gas between CO_2 and O_2 has been elucidated from thermodynamical considerations.[31]

According to Maître et al.,[30] the second step of the reactional process is characterized by a significant increase in lattice parameter consecutive to a crossed substitution between oxygen and carbon, the atomic radius of the carbon ($r_C = 0.74$ Å) being superior to that of the oxygen ($r_O = 0.67$ Å).

Finally, Berger et al.[33] invoked that the very beginning of the transformation may be initiated between carbon and zirconia following:

$$ZrO_{2(s)} + xC_{(s)} = ZrO_{2-x(s)} + xCO_{(g)} \qquad (5)$$
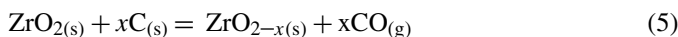
It may correspond to a very early transformation *via* a solid state reaction between zirconia and carbon. This reaction may then gives rise to the first formation of $CO_{(g)}$ as a major phase and is accompanied by the formation of sub-stoichiometric zirconia phase (ZrO_{2-x}). However, the presence of sub-stoichiometric zirconia has never been proved.

From the literature, it then appears that the reaction mechanisms invoked through kinematic studies for the carboreduction of zirconia are very likely to those either proposed by Weimer[35] for the carbothermal reduction of SiO_2 in SiC or Berger et al.[33] for the carbothermal reduction of TiO_2 in TiC.