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Study of carbonitriding reactions of zirconia. Synthesis of Zr(C,N,O) phases and β-type zirconium oxynitrides

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Abstract

Carbonitriding reactions of ZrO_2 permit obtaining Zr(C,O,N) phases that belong to the pseudoternary "ZrO–ZrN–ZrC" system and/or β-type zirconium oxynitrides belonging to the ZrO_2–Zr_3N_4 system. The Zr(C,O,N) phase has a cubic crystalline structure with a_o parameter depending on the C, O and N content. The β- type oxynitride obtained was the β″-phase corresponding to the $Zr_7O_{9,5}N_{3,0}$ formula with trigonal crystalline structure. The Zr(C,O,N) composition (a_o between 4.600 and 4.654 Å) and relative proportions of both phases depend on the reaction temperature (between 1400 and 1650 °C) and on the carbon content of the samples (between 0 and 33%). The reaction products were studied by X-ray diffraction (XRD). Some samples were analyzed using the Rietveld method with silicon as internal standard. The crystallite sizes of the zirconium phases were also determined by XRD. Additionally, microstructure analysis of raw materials and reaction products were performed by scanning electronic microscopy (SEM).

Keywords: D. ZrO_2; D. Carbides; D. Nitrides

1. Introduction

Carbonitriding reactions (reduction with carbon and simultaneous nitriding) of oxygenated compounds allow the synthesis of a large variety of products: nitrides, carbides, oxynitrides, etc. with important technological applications [1,2].

Using ZrO_2 (badeleyite) as raw material it is possible to obtain a wide variety of nitrides and/or carbides of great scientific and technological interest: ZrC [3], nitrides as Zr_3 N_4 and ZrN, oxynitrides called β-type phases [4], Zr(C,N,O) quaternary phases [5], etc.

β-Type oxynitrides are phases of ZrO_2–Zr_3N_4 system (Fig. 1a) [4]. These phases correspond to the general formula $ZrO_{2-2x}N_{4x/3}$.The β, β′ and β″ phases have $Zr_7O_8N_4$; $Zr_7O_8N_4$ and $\sim Zr_7O_{9.5}N_{3.0}$ compositions respectively and are ionic conductors [6]. The crystal structure of all β-type phases can be described by an arrangement of Bevan clusters ($Zr_7O_8N_4$) with anion vacancies and Zr_7O_{14} units. The individual β type phases differ in the stacking sequence of these atomic units along *c*-axis. In β″ phase, the observed average sequence is approximately four Bevan clusters and one Zr_7O_{14} unit [7]. This phase has a trigonal crystalline structure with unit cell parameters $a = 9.554$ Å and $c = 44.11$ Å [8].

Zirconium presents pseudoternary systems of the type "ZrO–ZrN–ZrC" (Fig. 1b). These systems show substitutional solid solutions that correspond to extensive monophasic zones. These solutions, named Zr(C,N,O), have the same cubic crystalline structure (S.G.: Fm3m) that ZrN, ZrC and ZrO phases in the corners of diagrams. The unit-cell parameter (a_o) of Zr(C,N,O) phase depends on the ZrC, ZrO and ZrN content.

The pseudoternary system "ZrO–ZrN–ZrC" was studied by Constant et al. [5]. These authors observed a considerable solubility of "ZrO" (added as an equimolar mix of ZrO_2 + Zr) in ZrC, ZrN and Zr(C,N). Fig. 1b shows the limit of monophasic zone at 1600 °C. The a_o parameter of the phase Zr(C,O,N) varies between 4.570 Å and 4.692 Å [5]. Zr(C,N,O) phases are electronic conductors [6].

The Rietveld method allows proper characterization of crystalline phases by X-ray diffraction (XRD). This

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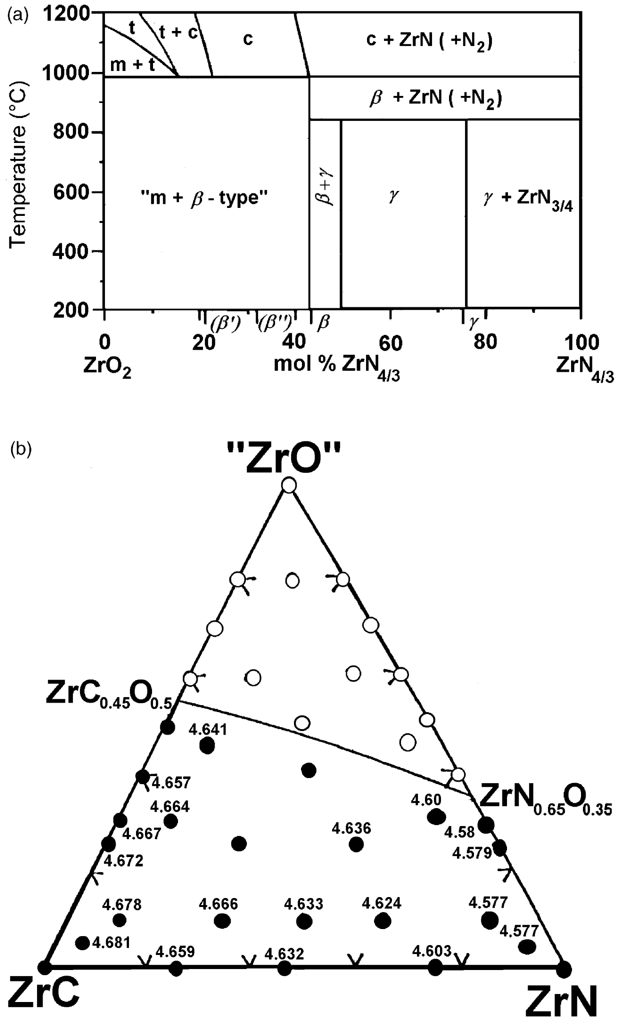

Fig. 1. (a) Observed phases in ZrO_2–Zr_3N_4 system (c, cubic fluorite structure; t, tetragonal distorted fluorite structure; m, monoclinic badeleyite structure; β/β′/β″, β-type phases) (from Ref. [4]). (**b**) Pseudoternary diagram of the ZrN–ZrO–ZrC system at 1600 °C (from Ref. [5]). The unit-cell parameters a_o of Zr(C,N,O) are indicated. ● monophase zone and ○ polyphase zone.

method was developed by Hugo Rietveld in 1969 [9], in order to refine crystalline structures using neutron diffraction data. At the present time, it is also used to perform several structural analyses by X-ray diffraction.

In this work, carbonitriding reactions of ZrO_2 were studied and the zirconium phases obtained were characterized by the Rietveld method.

2. Materials and methods

Raw materials used were badeleyite Riedel-de Haën from Germany with more than 99% (ZrO_2 + HfO_2) content and carbon black (carbon 97%, ash 1%, volatiles 2% and a specific surface area BET = 45 m^2/g). All powders have an average particle size lower than 5 μm. The nitrogen and the argon used contain less than 10 ppm of O_2 and H_2O.

Samples were prepared by wet mixing of the calculated amounts of reactives, and then they were dried and pressed at 39 MPa into cylinders of 2 mm in height and 10 mm in diameter. Samples were named by a letter B and the C/MO_2 relation. Thus, we obtained the samples B085($C/ZrO_2 = 0.085$), B110 ($C/ZrO_2 = 0.110$), B180, B210, B240, B300 and B450.

Reactions were performed in a horizontal alumina reactor with N_2 (or argon) flowing through it. The pressure used was 0.05 MPa above the atmospheric pressure, the gas flow was near 0.5 l/min. Experiments were carried out within the range 1400–1650 °C with reaction times of 120 min and the temperature slopes were 10 °C/min upward as well as downward. The N_2 (or argon) flow was kept during cooling up to 200 °C.

Crystalline phases were characterized by X-ray diffraction with a Philips 3020 Goniometer with PW 3710 controller, Cu-K_α radiation and Ni filter at 40 kV–20 mA. The scanning was made between 10 and 85° in 2θ with a step size of 0.02° and a step counting time of 2 s. Some samples were scanned with 40 kV–30 mA and a step counting time of 4 s for Rietveld analysis. The set of divergence, receiving and scattering slits was 1, 0.2 and 1°. No monochromator was used.

Fullprof program [10], which is a multipurpose profile-fitting program (including Rietveld refinement) was used to refine the lattice parameters. The starting crystallographic data were taken from literature. The refining sequence began with the adjustment of the shift in 2θ due to vertical specimen displacement and the background. To do this, elemental Si was added to the samples as an internal standard. Then, the scale factors, the cell constants, the parameters U, V and W for the calculation of full-width-at-half-maximum (FWHM), the mixing coefficient ν of the pseudo Voight profile function and the parameters of the March function for preferred orientation correction for each phase were sequentially refined.

In the case of β″ zirconium oxynitride, the atomic positions have not been determined and consequently the structure factors of the diffraction lines cannot be calculated. For cases in which the structure factors cannot be generated from the atomic positions, Fullprof uses the space group and the cell constants to generate all the permitted diffraction lines, fitting their intensities according to the observed intensities of the present Bragg lines. This mode of fitting the calculated intensities is called Profile Matching and permits to refine the cell constants and the peak positions of any crystalline phase.

Semiquantitative phases analysis was performed using peak area/time per step and expressed in arbitrary units. The peaks used were: m-ZrO_2 (111), β″-oxynitride (peak at ~2.95 Å) and Zr(C,N,O) (200).

The crystallite sizes of Zr(C,N,O) and β″-oxynitride were determined on the (200) and (Å) peak widths respectively, determined from the fitting results, using the Scherrer equation and the PC-APD (PW 1877) Analytical Powder Diffraction Software, Version 3.6.

The reaction products were also studied by scanning electron microscopy (SEM) using a Philips 505 equipment.

3. Results and discussion

The temperature range used, higher than 1400 °C, allows to discard the Zr_3N_4 as product because it decomposes at 900 °C in ZrN and N_2 [6]. Then, the only possible products are ZrN, ZrC and Zr(C,N,O) belonging to the "ZrO–ZrN–ZrC" system (Fig. 1b) [5] and β-type phases of the ZrO_2-Zr_3N_4 system (Fig. 1a) [4,11]. Therefore, the global equation in N_2 atmosphere can be proposed as follows:

$$ZrO_2 + aC + bN_2 \rightarrow d\{Zr(C_eN_fO_g)\} + h[ZrO_{2-2x}N_{4x/3}] \qquad (1)$$

where: a, b, c, d, e, f, g, h, and x are stoichiometric coefficients, $\{Zr\ (C_eN_fO_g)\}$ is a Zr (C,N,O) phase and $[ZrO_{2-2x}N_{4x/3}]$ is a β-type zirconium oxynitride.

Fig. 2 shows the evolution of the three crystalline phases as function of the temperature for different samples (different carbon content).

The monoclinic ZrO_2 (reactive) decreases continually with the increase of temperature in all samples. The decrease was more pronounced with the increase of the carbon content. In the B085, B110 and B180 samples, the zirconia was present at all temperatures in appreciable amounts, showing similar curves. In B240, B300 and B450 samples, the decrease was much more significant. The monoclinic ZrO_2 disappeared at 1650 °C. The last three samples present an identical behavior, especially above 1500 °C.

Zr(C,N,O) phase was present at 1400 °C as a minority product, continually increasing with the temperature. In samples with more carbon (B180–B450) it was the principal product at temperatures higher than 1550 °C.

The Rietveld analysis (Fig. 3) permitted to refine a_o values for this phase between 4.608 and 4.645 Å. These values tend to be higher with the increase of temperature and carbon content of the samples. The a_o variation is consistent with the increase of N and C content of the Zr(C,N,O) phase.

Under the same reaction conditions, products obtained from ZrO_2 seem to be nearer the ZrC phase composition (Fig. 1b) than those prepared from carbonitriding

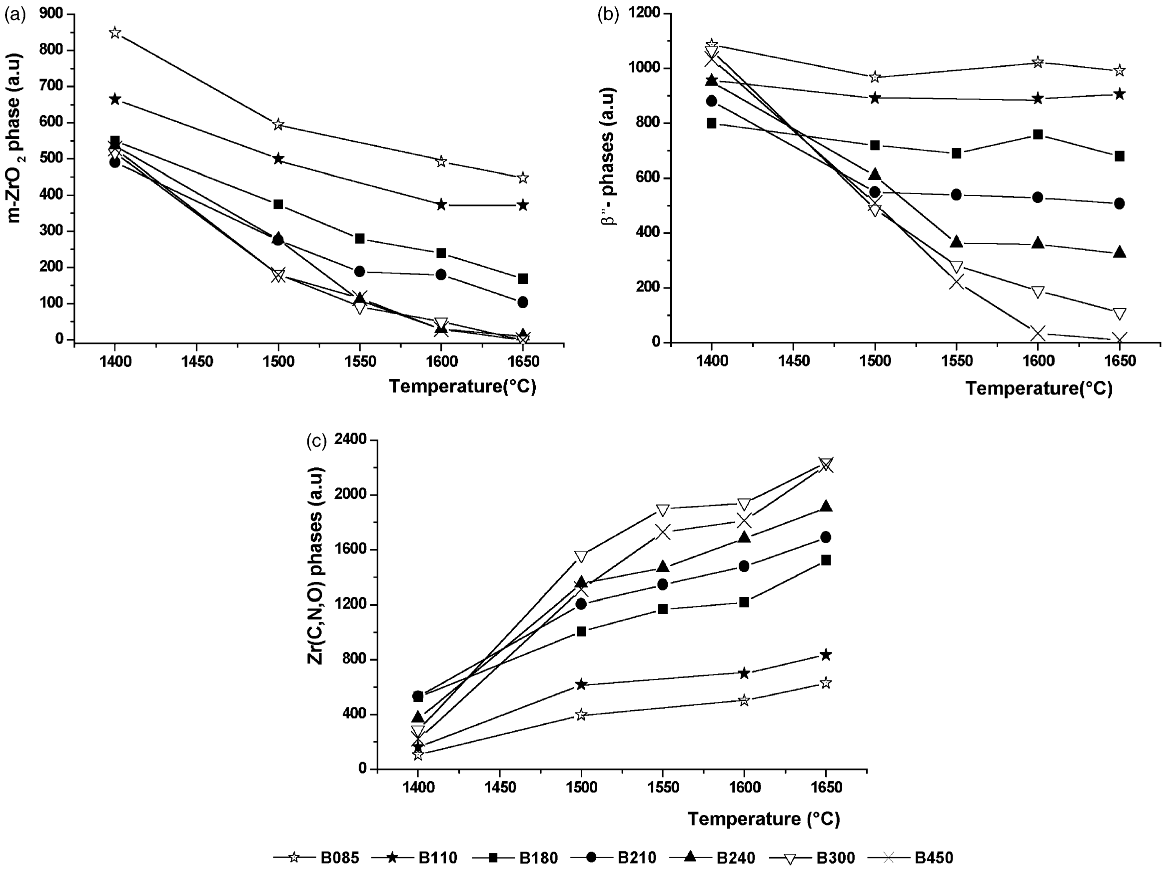

Fig. 2. Crystalline phase evolution with temperature for B samples: (a) ZrO_2, (b) β″-phase and (c) Zr(C,N,O).

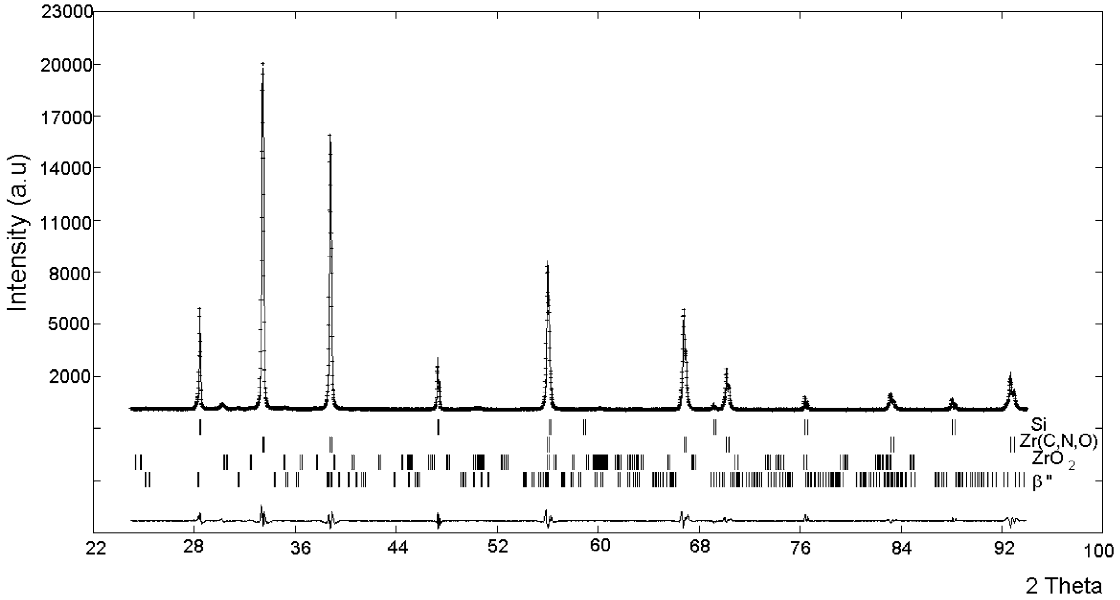

Fig. 3. Final Rietveld plot for sample B450 treated at 1600 °C.

reactions of $ZrSiO_4$ (a_o between 4.580 and 4.624 Å) [12,13], but pure ZrC ($a_o = 4.692$ Å) neither could be obtained.

In some samples, the peaks corresponding to the Zr(C,N,O) phase are too much wide. The Rietveld analysis permits obtaining a good fitting of them (R_{bragg} near 1.9) including in the refinement two or three Zr(C,N,O) phases with different but near a_o values (Fig. 4).

This phenomenon is commonly found in phases having composition ranges with unit cell parameters depending on them, as the β-sialons [1,2] or the Zr(C,N,O) phases [12–14]. It could also be observed in the Zr(C,N,O) phases formed from $ZrSiO_4$ [12,13].

The crystallite sizes determined for Zr(C,N,O) phase vary between 590 and 1600 Å with well-defined tendency with temperature. The small crystal size observed in some samples could be associated to the presence of a second Zr(C,N,O) phase that causes an increase in the XRD peak widths.

The β-type oxynitrides were the principal reduced phase, at 1400 °C. Since their diffractograms are very similar, the identification between these phases, mainly between the β′ and the β″ ones, is complex.

The Rietveld analysis allowed us to determine that among the three phases of this type (β, β′ and β″), the β″ phase was the only one found. The identification is obtained from a series of rather weak peaks (about 0.01

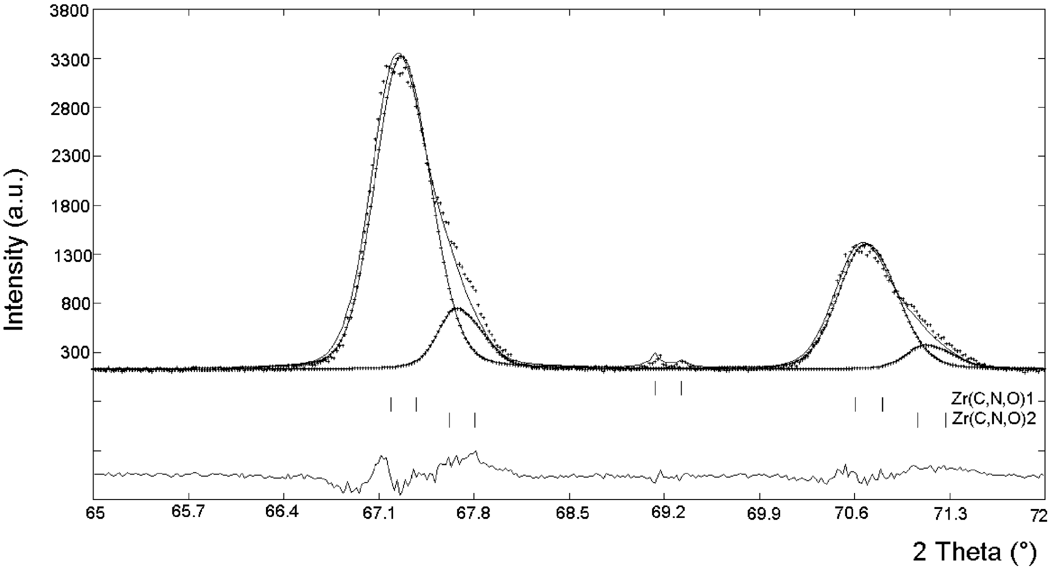

Fig. 4. Amplified Rietveld plot showing the use of two Zr(C,N,O) phases in the refinement.

of the main ones). Table 1 shows the distinctive peaks of the β′, β″ phases and two samples obtained in this work as an example. The β″ phase fits the $Zr_7O_{9.5}N_{3.0}$ formula [7] with trigonal crystalline structure. The lattice parameters refined by Fullprof were a_o between 9.540 and 9.553 and c_o between 44.352 and 44.443, while the reference values are $a_o = 9.554$ Å and $c_o = 44.411$ Å [7].

Table 1
Positions of diffraction lines for β-phases

β′	B240 (1400 °C)	ZrO_2 sample (1650°)	β″
2θ (d)	2θ (d)	2θ (d)	2θ (d)
11.80 (7.49)			
	12.25 (7.22)	12.26 (7.22)	12.24 (7.22)
18.53 (4.78)	18.57 (4.77)	18.58 (4.77)	18.55 (4.78)
22.94 (3.87)	22.93 (3.87)	22.95 (3.87)	22.91 (3.88)
	23.30 (3.81)	23.32 (3.81)	23.29 (3.81)
23.73 (3.75)	23.75 (3.74)	23.74 (3.75)	23.75 (3.74)

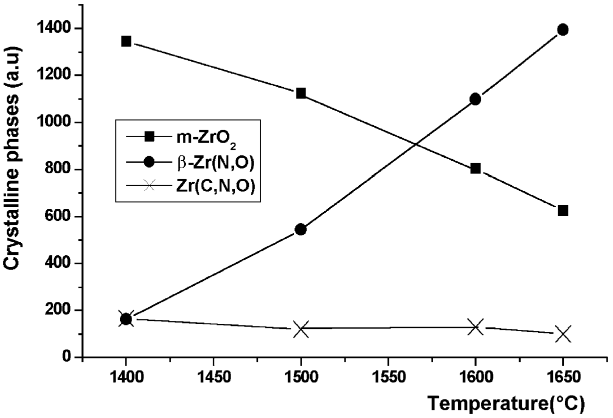

Fig. 5. Crystalline phases evolution with temperature for ZrO_2 sample (without carbon) in N_2 atmosphere.

The β″ phase (Fig. 2) decrease with the increase of temperature. This phenomena tends to be more pronounced at high carbon content. Thus, in B085–B180 samples the decrease was very low, being the amount of this phase at 1650 °C slightly lower than that at the beginning. In the other samples, the β″ phase at 1500 °C show rapid decreases, and disappears at 1600 °C in the B450 sample. This behavior is clearly due to the fact that the principal product was the Zr(C,N,O) phase, mainly when employing more carbon and higher temperatures.

The crystallite sizes determined for β″ phases vary between 500 and 900 Å without a definite tendency.

Lerch et al. [6–8] show that at temperatures higher than 1400 °C the m-ZrO_2 is directly nitrided by reactions of the following type:

$$ZrO_2 + 2x/3\ N_2 \rightarrow ZrO_{2-2x}N_{4x/3} + xO_2 \qquad (2)$$

The nitriding occurs with the presence of a captor of O_2, which allows a displacement of the reaction to the products. In our reactor, the use of graphite crucible produces a very low O_2 partial pressure, which makes the reaction possible.

In order to study the influence of the reaction [2] on the experiences shown in Fig. 2, the nitriding of ZrO_2 powder (without carbon) was made in graphite crucibles and under the same reaction conditions that those of the samples with carbon (samples B). The results obtained are shown in Fig. 5. This figure shows a very different behavior from that observed in Fig. 2. While the same

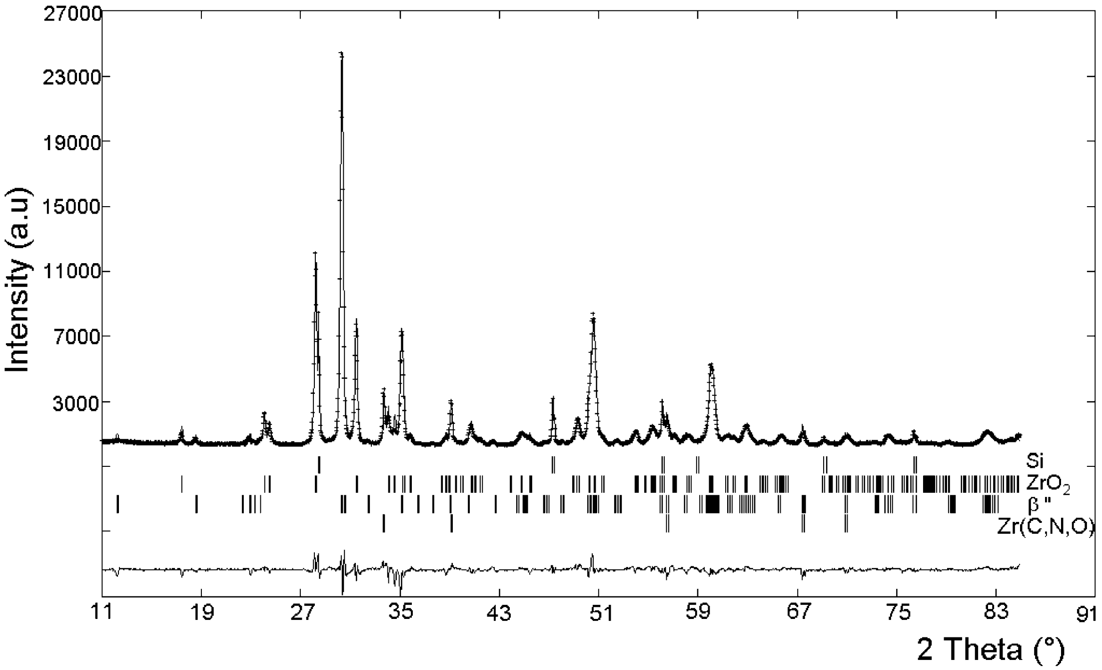

Fig. 6. Final Rietveld plot for ZrO_2 sample without carbon at 1650 °C in N_2 atmosphere.

three phases can be observed, the evolution of the two reduced phases is quite different.

The Zr(C,N,O) is the minority phase at all temperatures (interaction with crucible). The a_o ranges of this phase vary between 4.600 and 4.628 Å, whereas most of the samples have values lower than 4.612 Å.

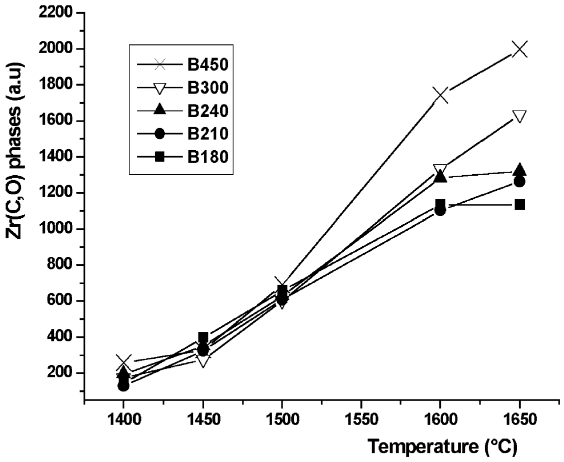

Fig. 7. Zr(C,O) evolution with temperature for B samples in Ar atmosphere.

Lerch et al. [6], using graphite crucibles for the ZrO_2–N_2 reaction at temperatures lower than 1800 °C, found traces of Zr(C,N,O) phases. These phases were of two types, some of them with a_o from 4.610 to 4.625 Å, and the others with values from 4.635 to 4.645 Å. The first ones (P) are caused by the reaction with the atmosphere inside the pores of the ZrO_2 pellet and the second ones (S) are formed on the graphite (crucible)–ZrO_2 pellet contact surface. Zr(C,N,O) phases represented in Fig. 5 have a_o ranges that coincide with (P) phases [6].

In samples with carbon (B samples of Fig. 2) the ZrO_2 is in contact with a very reactive carbon. This could explain the great quantity of Zr(C,N,O) formed. The a_o values for B samples at temperatures lower than 1600 °C are similar to (P) phases, while above 1600 °C are similar to (S) phases suggested by Lerch [6].

β'' phase (Fig. 5) shows a constant growth with temperature, being the principal product above 1600 °C (Fig. 6). The amount of β'' phase seems to be higher than those indicated by Lerch [6,7] at similar temperatures for crystalline ZrO_2.

The general equation for ZrO_2–C reaction in Ar atmosphere is

$$ZrO_2 + (c+d)C \rightarrow \{ZrC_cO_{2-d}\} + dCO \qquad (3)$$

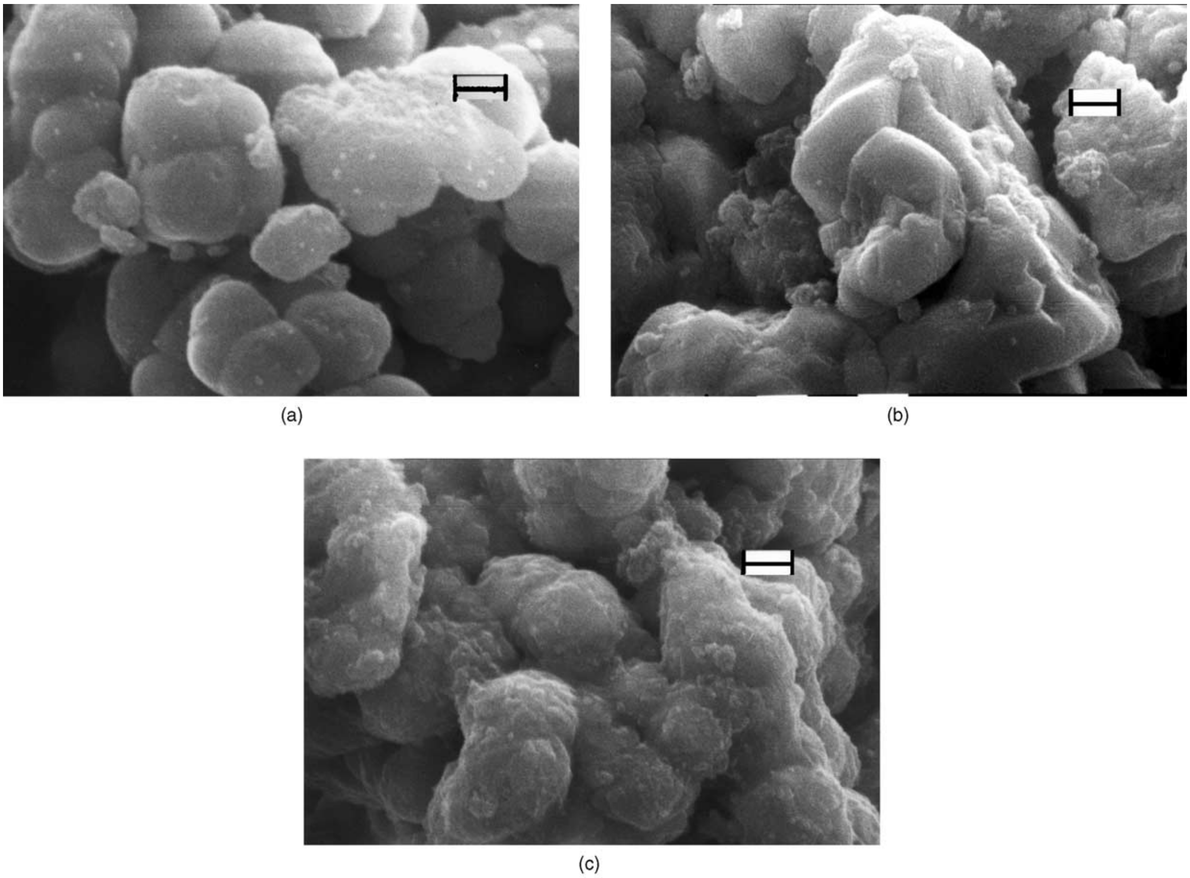
(a)
(b)
(c)

Fig. 8. Micrographies (SEM) of reagents and products (scale bar = 1 μm): (a) Badeleyite, (b) B330 sample treated at 1650 °C in N_2, (c) B330 sample treated at 1650 °C in Ar.

where c and d are stoichiometric coefficients and Zr (C_cO_{2-d}) is a Zr(C,O) phase of the ZrO–ZrC axe in the ZrO–ZrN–ZrC system. In Fig. 1b, the monophasic zones cover in part the ZrO–ZrC axes. These oxycarbides, Zr(C,O), have the same cubic structure of Zr(C,N,O) with a_o depending on ZrC and ZrO content. The values of a_o increase with the ZrC content and the highest value corresponds to ZrC pure phase.

B samples have enough carbon to obtain an oxycarbide as a unique phase by reaction in argon atmosphere. Theoretically oxycarbide compositions would be between $ZrC_{0.45}O_{0.55}$ for B180 and ZrC for B300.

Zr(C,O) increases with the increase of temperature and carbon content (Fig. 7). It is the principal phase at a temperature of 1600° or higher. m-ZrO_2 has similar behavior than in Fig. 2.

The obtained values of a_o (4.640–4.683 Å) show that the formed oxycarbides were within the range $ZrC_{0.45}O_{0.54}$–$ZrC_{0.9}O_{0.1}$ (Fig. 1b, axes ZrO–ZrC).

Also in this case, the Rietveld analysis shows that the Zr(C,O) peaks can be fitted using two or more phases Zr(C,O) indicating that the wide peaks are actually due to overlap of several narrow peaks. In almost all the samples, the use of two phases allowed to have R_{Bragg} values near 2.85 for both Zr(C,O). The R_{exp} are between 4.63 and 5.97 and the R_{wp} are between 9.20 and 15.56. The crystallite size values were between 560 and 3000 Å without a definite tendency.

Finally, reagents and reaction products were characterized by scanning electron microscopy (SEM). Morphology variations caused by reactions were observed (Fig. 8). The final products of B samples seem to preserve the morphology of raw material and show an increase in particle size, indicating an incipient sintering process.

4. Conclusions

- The ZrO_2 carbonitriding allows to obtain Zr(C,N,O) phases and/or β″ zirconium oxynitrides.
- It is relatively easy to nitride the ZrO_2 at temperatures higher than 1400 °C if the partial pressure of the oxygen is low enough.
- The carbon content and the reaction temperature have strong influence on the β″/Zr(C, N,O) relation obtained, favoring the Zr(C,N,O) formation.
- The Zr(C,N,O) phase tend to the ZrC corner of the pseudoternary system with the increase of the temperature and the carbon content.
- ZrO_2–C reaction in Ar produces Zr(C,O) phase unique product.
- The carbon content of Zr(C,O) and the produced amount of this phase increase with C/ZrO_2 ratio and temperature.
- The Rietveld method is suitable for the characterization of the Zr(C,N,O) type phases, whose composition ranges and lattice parameters are variable and is an efficient tool to distinguish between similar phases as the β′ and β″ zirconium oxynitrides.

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