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Synthesis of Zr-Si-O-N Phases by Carbonitriding Reaction. Characterization of Crystalline Phases Using the Rietveld Method

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Zirconium compounds are of great interest for ceramic application due to their excellent thermal and mechanical properties. Zirconium phases of the system Zr-O-C-N were obtained using carbonitriding reactions of zircon mineral ($ZrO_2.SiO_2$), under different reaction conditions. The reaction products were studied by X-ray diffraction (XRD) using the Rietveld method. Silicon was employed as internal standard. Zirconium compounds formed were m-ZrO_2 (monoclinic), β"-zirconium oxynitride and a cubic Zr(C,N,O) phase whose lattice parameter a_o depends on the composition. The crystallite sizes of the three zirconium phases were determined also by XRD. The minority phases present are the ones of the Si-O-N-C system. The reaction conditions employed allows to obtain reaction products with low or without silicon content.

Keywords: *ZrC, ZrN, β"-phases, Rietveld*

1. Introduction

Structural ceramics based on nitrides, oxynitrides and carbides are of great scientific as well as technological interest due to their good physical and chemical properties. Among these ceramics, composites of the type ZrN-Si_2N_2O, ZrO_2-Si_2N_2O, etc. are found[1]. There exist several ways to obtain these composites employing different routes and reacting systems such as Si_3N_4-$ZrSiO_4$-N_2, Si-$ZrSiO_4$-N_2, etc.[1]. Carbonitriding reactions of minerals (reduction with carbon and simultaneous nitriding) constitute an interesting way to obtain oxynitride and oxycarbide compounds. Furthermore, these reactions have a great flexibility since it is possible to obtain a wide variety of products depending on the raw materials used as well as on the reaction conditions employed[2,3]. Using $ZrSiO_4$ as starting raw compound, phases like ZrN, ZrC, ZrO_2, Zr(C,N,O) can be obtained.

The Rietveld method allows to characterize properly these phases by XRD. This method was developed by Hugo Rietveld in 1969[4], in order to refine crystalline structures using data of neutron diffraction. At the present time, it is used to perform analysis of structure and crystalline defects, reticular parameter measurement and quantitative analysis with X- ray diffraction data.

The method consists in adjusting point by point the experimental intensities corresponding to the complete spectrum with the calculated intensities according to a determined model of crystal structure, diffraction optical effects, instrumental factors and other characteristics of the sample. Parameters included in the model are refined until the best least squares fitting is obtained between the entire observed powder diffraction pattern and the entire calculated pattern.

In this work, zirconium rich phases obtained from the $ZrSiO_4$ carbonitriding were studied and characterized by the use of the Rietveld method.

2. Materials and Methods

Raw materials used were: $ZrSiO_4$ from Germany (Table 1) and carbon black (carbon 97%, ash 1%, volatiles 2% and a specific surface area BET= 45 m^2/g). Both powders have d_{50} 10 μm. The N_2 used contained less than 5 ppm of O_2 and H_2O.

Samples were prepared by wet mixing of the calculated amounts of reactives, then, they were dried and pressed at 39 MPa into cylinders of 2 mm in height and 10 mm in diameter. The samples used were called Z1 (11.6% of C), Z2 (20.8% of C), Z3 (24.8% of C) and Z4 (33.3% of C).

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Table 1. Chemical composition of $ZrSiO_4$.

	SiO_2	ZrO_2	HfO_2	Al_2O_3	TiO_2	Fe_2O_3	P_2O_5
Wt (%)	32.60	64.70	1.30	0.90	0.11	0.05	0.10

Reactions were performed in a horizontal alumina reactor with N_2 gas flowing through it. The pressure used was 0.05 Mpa above the atmospheric pressure and the flow was 0.5 l/min (linear flow rate: 3 $cm.s^{-1}$). Experiments were carried out within the range 1350 to 1650 °C with reaction times of 120 min and the temperature slopes were 10 °C/min, upward as well as downward. The N_2 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-Kα radiation and Ni filter at 40 kv - 20 mA. The scanning were made at room temperature between 10° and 75° in 2θ with 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 The set of divergence, receiving and scattering slits were 1°, 0.2°, 1° and no monochromator was used.

Fullprof program[5], which is a multipurpose profile-fitting program (including Rietveld refinement) was used to calculate the lattice parameters. The starting crystallographic data were taken from literature[6, 7, 8]. 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 internal standard. The background was adjust with a fourth order polynomial. 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 η of the pseudo Voight profile function and the parameters of the March function for preferred orientation correction for each phase were refined sequentially.

In the case of β" phase (Zr oxynitride), the atomic positions have not been defined exactly, 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, the Fullprof program 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.

Quantitative analysis of the crystalline phases were carried out employing the external standard method. The standard samples for m-ZrO_2, SiC and silicon oxinitrides were pure commercial compounds. The Zr(C,O,N) standard was synthesized by the authors, through ZrO_2 and carbon reaction in nitrogen atmosphere. The β" standard was a binary mixture of m-ZrO_2 (45.0 wt. %) and β" oxynitride (55.0 wt. %) synthesized by the authors.

The crystallite sizes of cubic Zr(C,N,O) and monoclinic ZrO_2 compounds were determined on the (200) and (111) peaks respectively, using the Scherrer equation and the PC-APD (PW 1877) Analytical Powder Diffraction Software, Version 3.6. Weight losses were measured by weighing the samples before and after the reaction process.

3. Results and Discussion

The following reactions are a description of the observed phenomena, taking into account the thermal behavior of $ZrSiO_4$ (it decomposes at T > 1600°C).

$$2ZrSiO_4 + 3C + N_2 \rightarrow Si_2N_2O + 2ZrO_2 + 3CO \quad (A)$$

$$2ZrSiO_4 + aC + bN_2 \rightarrow Si_2N_2O + 2\text{"Zr(C,N,O)"} + cCO \quad (B)$$

$$3ZrSiO_4 + dC + eN_2 \rightarrow 3\text{"Zr(C,N,O)"} + Si_3N_4 + fCO \quad (C)$$

$$ZrSiO_4 + gC \rightarrow \text{"Zr(C,N,O)"} + SiC + hCO \quad (D)$$

Where: a, b, c, d, e, f, g, h are stoichiometric coefficients produced by the variable Zr(C,N,O) composition.

Figure 1 shows the pseudoternary phase diagram "ZrO-ZrN-ZrC" proposed by K. Constant *et al.*[9] The monophasic zone below the line $ZrC_{0.45}O_{0.5}$ - $ZrN_{0.65}O_{0.35}$ corresponds to the Zr(C,N,O) phase, which has variable amounts of the four elements (Zr, C, O, N).

The Zr(C,N,O) phase has a cubic crystalline structure (S.G.: Fm3m (225)) similar to that of the phases: ZrN (JCPDS card N° 35-753); ZrC (JCPDS card n° 19-1487)

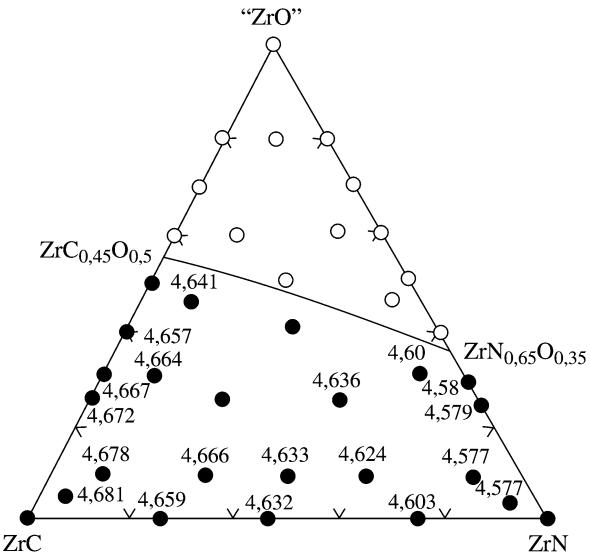

Figure 1. Pseudoternary phase diagram of the "ZrO-ZrN-ZrC" system. The cell parameters of Zr(C,N,O) phases are indicated as: (•) monophase zone and (o) polyphase zone.

and the calculated for the "ZrO" (JCPDS card n° 20-684). The cell constant a_o of Zr(C,N,O) changes between 4.570 and 4.692 Å. In Fig. 1, the numerical values correspond to the a_o values determined by K.

The Zr(C,N,O) phases (Fig. 2) appear in the three samples with higher carbon content and their amount tend to be higher with the increase of temperature and carbon content. The Zr(C,N,O) phases are the principal phases formed at temperatures higher than 1450 °C. The use of the Rietveld method permits to determine their lattice constants. In Fig. 3 the diffraction pattern of the Z4 at 1500 °C is shown. The principal phase formed is Zr(C,N,O), accompanied with silicon (internal standard), silicon nitride and zircon. Traces of Hf oxynitride (PDF Card n° 39-0520) were also formed.

In many samples, the phases Zr(C,N,O) show an excessive width of its XRD peaks and unfolding (Fig. 4).

To obtain a good fitting with the Rietveld method it is necessary to employ two phases of the Zr(C,N,O) system, one of them with an a_o between 4.577Å and 4.582Å and the other with an a_o higher than 4.600 Å. The use of these two phases allows to have R_{Bragg} values near 2.5 for those

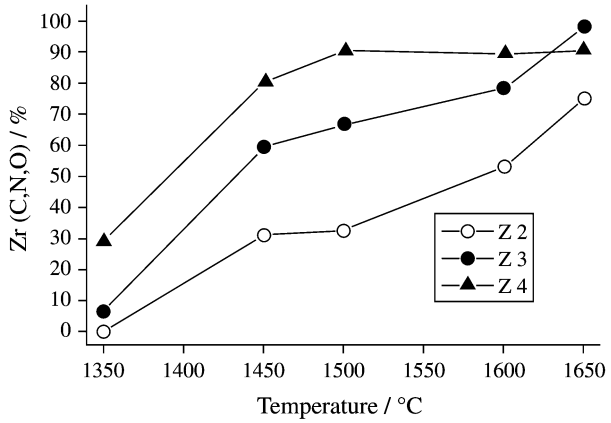

Figure 2. Evolution of the Zr(C,N,O) phase with temperature and carbon content. (Reaction time: 120 min).

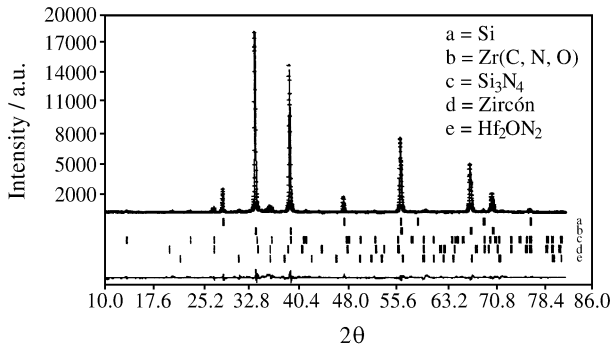

Figure 3. Rietveld analysis for sample Z4 treated at 1500 °C. (Reaction time: 120 min).

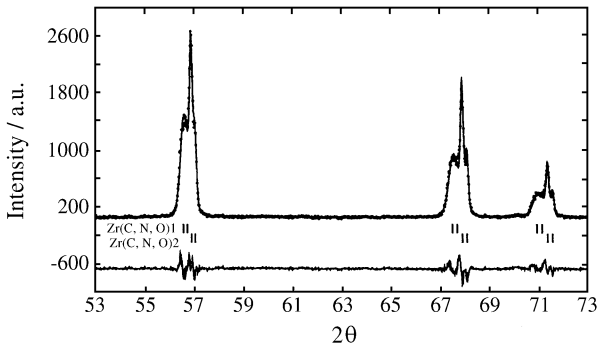

Figure 4. Diffractogram showing the unfolding of the Zr(C,N,O) phase.

phases. The R_{exp} are between 4.53 and 5.67 and the R_{wp} are between 10.9 and 16.0.

The values of the a_o parameter for both Zr(C,N,O) phases tend to be higher with the increase of temperature and carbon content, and they are unified in a unique phase with an a_o between 4.601 Å and 4.624 Å with values of residuals RBragg, Rexp, Rwp similar to those mentioned in the above paragraph. It is not possible to determine the exact composition of the Zr(C,N,O) phase only with the XRD measurements, since different compositions may have the same a_o (see Fig. 1). By the XRD technique, N, C and O cannot be differentiated in spite of using the Rietveld method because of their similar atomic weight. The chemical analysis is difficult to be performed because the C+O+N contents are below 16 wt.%, and for example, the expected oxygen content is lower than 4%. Thus, little composition errors produce a big shift in the phase diagram.

With respect to the crystallite size, these phases show values between 576 and 1800 Å with a well defined tendency to increase with temperature. Crystallite sizes may be larger because in phases like these ones, where there are wide ranges of solid solutions, peaks tend to widen[10,11].

Other zirconium phase found is the monoclinic ZrO_2. The Rietveld analysis of this phase shows the following average value of the crystal constants: a_o = 5.155 Å, b_o = 5.2012 Å, c_o = 5.3252 Å and β = 99.158°. These values are near the theoretical ones. (a_o = 5.1454 Å, b_o = 5.2075 Å, c_o = 5.3107 Å, β = 99.23°)

The evolution of the m-ZrO_2 phase as a function of the reaction conditions is shown in Fig. 5. This phase becomes less important when the carbon content increases. Thus, in Z2 to Z4 samples a continuous decrease of ZrO_2 with temperature is observed, related with the increase in the Zr(C,N,O) content. The Z1 sample presents a different behavior with respect to the other samples, with an initial growth of the ZrO_2 and then a decrease of this phase above 1600 °C.

Also, β type zirconium oxynitride phases $ZrO_{2-2x}N_{4x/3}$ were detected[12]. These phases are called β, β' and β" depending on their composition. The differences between

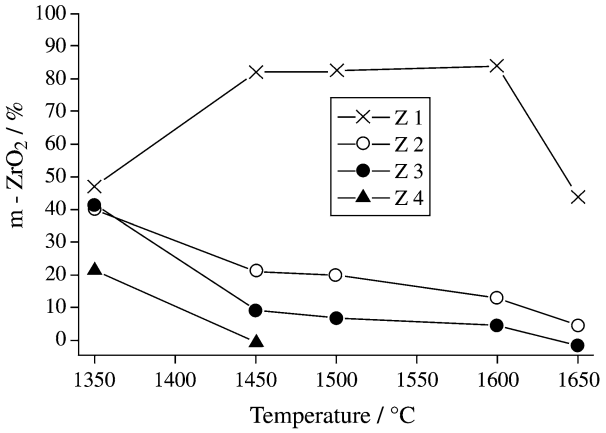

Figure 5. Evolution of the m-ZrO_2 with temperature and carbon content. (Reaction time: 120 min).

the β phases are little, mainly between β' and β". The Rietveld analysis made on the β type phases showed that the β" phase fitted very well the diffractogram obtained (Fig. 6). In Table 2, the experimental measurements are compared with the β' phase (PDF card 48-1637) and the β" phase peaks calculated with de Profile Matching mode of the Fullprof program. This table shows the position of the diffraction lines of these phases between 10 and 25°. The

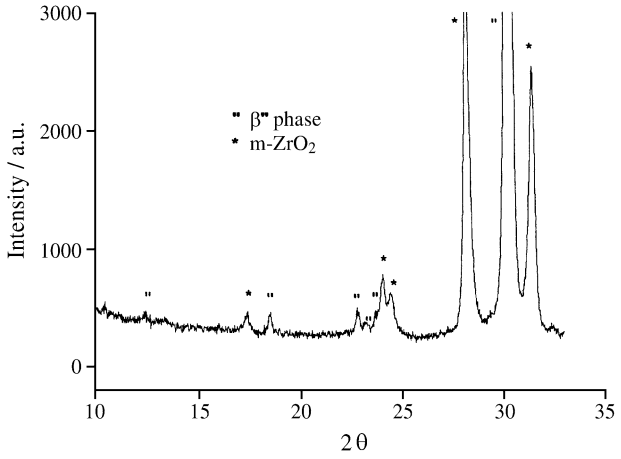

Figure 6. Diffractogram of the β" phase between 10° and 25°.

Table 2. Positions of diffraction lines for β phases.

β'	Typical sample	β''
2θ (d)	2θ (d)	2θ (d)
11.80 (7.49)		
	12.4 (7.13)	12.24 (7.22)
18.53 (4.78)	18.53 (4.78)	18.55 (4.78)
22.94 (3.88)	22.88 (3.89)	22.91 (3.88)
	23.20 (2.83)	23.29 (3.81)
23.73 (3.75)	23.75 (3.74)	23.75 (3.75)

relative intensities of the diffraction peaks were also in agreement with those reported by Lerch[12] for the β" phase. To prove this, samples with higher β" phase content were analyzed by XRD using long periods of measurement (scanned with 40 kv – 30 mA and a step counting time of 4 s).

The formation of the β" phase could be expected in our working conditions[12]. The unit cell parameters measured were the following: "a_o" between 9.459 - 9.552 Å [9.554 Å[12]] and "c" between 44.33 - 44.35 Å [44.11 Å[12]]. Thus, this phase will be called henceforth β".

The XRD peaks that allow to differentiate between the β' and β" (Table 2) are quite small, near 1/1000 of the more intense peaks. These peaks are visible only in samples with a high content of β phases. The high intensity peaks of the β phases appear in all the samples. These peaks are very similar to that of the cubic-ZrO_2. Experiments carried out using argon instead of nitrogen showed that "cubic-ZrO_2 peaks" were not detected; this fact confirms that they are oxynitride compounds. The Rietveld analysis of "cubic-ZrO_2 peaks" of the β" phase is in accord with a cubic crystal structure with a_o between 5.100 and 5.112 Å depending on the sample studied. This is in agreement with the phase called "nitrogen stabilized cubic zirconia" ("N-ZrO_2") found by Claussen *et al.*[13]. Other researchers[14-17] established that "N-ZrO_2" phases are β-type zirconium oxynitrides with the following composition: $ZrO_{2-2X}\ N_{4X/3}$.

Figure 7 shows the evolution of the β" phase with temperature. The β" phase appears in important amounts in Z2 sample and in lower proportion in Z3 between 1350 °C and 1600 °C. In Z4 sample, the β" phase appears up to 1450 °C while in Z1 the β" phase increases slowly with the temperature increase, showing an important growth at 1650 °C where the β" phase reaches contents higher than 50%.

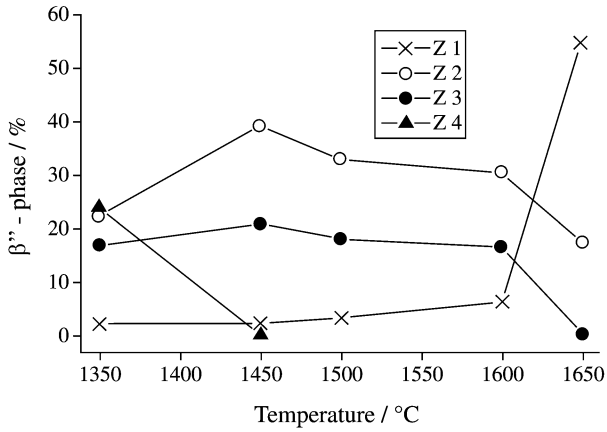

Figure 7. Evolution of the β" phase with temperature and carbon content. (Reaction time: 120 min).

Table 3. Mean unit-cell parameters for Silicon phases.

Phase	a_o	b_o	c_o
β-Si_3N_4	7.6165(2)		2.9109(3)
Si_2N_2O	5.5046(1)	8.8969(3)	4.8538(2)
β-SiC	4.3619(3)		

Silicon phases formed were: Si_2N_2O, Si_3N_4 and SiC. Using the Rietveld analysis, the lattice parameters of these phases were determined (Table 3). These values are in agreement with those of other authors 8,18.

Silicon phases were not formed in Z1. Si_2N_2O was found as principal phase in Z2 and Z3. In Z4 a mix of SiC and Si_3N_4 was found, but always in lower amounts than the expected ones using stoichiometric calculation. This phenomenon is produced by silicon loss as it is explained in the following reactions:

$$ZrSiO_4 + C \rightarrow ZrO_2 + SiO_{(g)} + CO_{(g)} \quad (E)$$

$$SiO_2 + C \rightarrow SiO_{(g)} + CO_{(g)} \quad (F)$$

This is confirmed by the high weight loss, higher than the loss expected for the reactions (A)-(D).

4. Conclusions

- The carbonitriding of zircon generates Zr-phases corresponding to the "ZrO-ZrN-ZrC" system together with silicon oxynitrides or oxycarbides as secondary phases.

- It is possible to obtain Zr(C,N,O) and/or Zr-oxynitrides of the β" type regulating the reaction conditions.

- The Rietveld method permitted to characterize the structure of Zr-phases obtained by the carbonitriding of zircon.

- The $SiO_{(g)}$ loss is an important phenomenon that decreases the silicon content in the reaction products.

- Using controlled reaction conditions allow to obtain products with very low or without silicon in their composition.

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