

Synthesis of Group IVB Metals Oxycarbides by Carboreduction Reactions

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The metals of the group IV B (Ti, Zr, Hf) present a series of carbides and oxycarbides with scientific and technological interest. Many of these compounds belong to the subsystem “MO - MC” of the pseudoternary “MO - MN - MC” system (where M = Ti, Zr or Hf).

In this work carboreduction reactions of TiO₂ and ZrO₂ were performed in argon atmosphere, using temperatures from 1250° to 1650° and reaction times of 120 min. The oxycarbides obtained were in the range TiC_{0.16}O_{0.84} to TiC_{0.73}O_{0.27} and ZrC_{0.46}O_{0.54} to ZrC_{0.90}O_{0.10}, respectively.

The reaction products were characterized by X-ray diffraction (XRD), with the calculation of their cell constants by means of the Rietveld method. Scanning Electron Microscopy (SEM) was used in the characterization of powdered materials. Additionally, the carboreduction reaction was followed by weight loss.

Keywords: carboreduction, anatase, badeleyite, oxycarbides, carbides

1. Introduction

The group IV B metals, as titanium (Ti) and zirconium (Zr), present pseudoternary systems of the type “MO - MN - MC” (where M = metal). Both systems show substitutional solid solutions which correspond to extensive monophasic zones. The solutions, named M(C,N,O), have the same cubic crystalline structure (S.G.:Fm3m) that MN, MC and MO phases in the corners of diagrams. The unit-cell parameter (a_0) of M(C,N,O) phase depends on the MC, MO and MN content.

Figure 1 shows the pseudoternary phase diagram “TiO–TiN–TiC” proposed by Neumann *et al.*¹. The monophasic zone covers the whole diagram at temperatures higher than 1100 °C. This zone corresponds to the Ti(C,N,O) phase. The cell parameter a_0 varies between 4.12 Å and 4.32 Å¹.

The pseudoternary system “ZrO – ZrN – ZrC” was studied by Constant *et al.*². These authors observed a considerable solubility of “ZrO” (added as an equimolar mix of ZrO₂ + Zr) in ZrC, ZrN and Zr(C,N). Figure 2 shows the limit of

monophasic zone at 1600 °C. The a_0 parameter of the phase Zr(C,O,N) changes between 4.570 Å and 4.692 Å.

The monophasic zones cover in part the MO-MC axes in both systems. Thus, the subsystems “MO-MC” present oxycarbides M(C,O). These oxycarbides, Ti(C,O) and Zr(C,O), have the same cubic structure of M(C,N,O) with a_0 depending on MC and MO content. The values of a_0 increase with the MC content, the highest value corresponds to MC pure phase.

The synthesis of these compounds is usually obtained by TiO, TiC or ZrO₂, Zr, ZrC reactions in argon atmosphere or vacuum^{3,4}. Carboreduction reactions of the MO₂ (TiO₂-anatasa, ZrO₂- badeleyite) oxides constitute an alternative method to obtain these phases. This method is within the present tendency to use abundant and cheap raw materials to obtain ceramic powders (oxides as well as carbides). Ceramics are manufactured starting from well characterized raw materials and then purified in order to control the degree of impurities.

The Rietveld method allows to properly characterize

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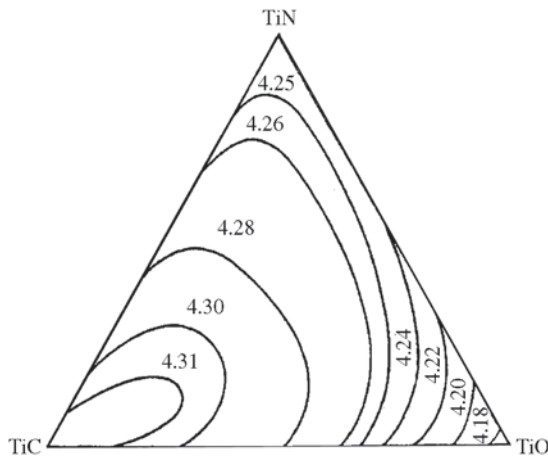


Figure 1. Pseudoternary diagram of the TiN-TiC-TiO system at 1100 °C (from Neumann *et al.*)¹. The cell parameters a_0 of Ti(C,N,O) are indicated. The lines separate zones of similar a_0 .

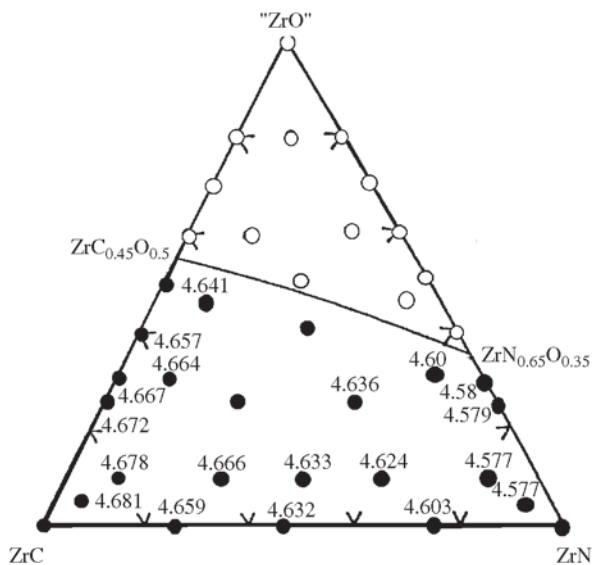


Figure 2. Pseudoternary diagram of the ZrN – ZrO – ZrC system at 1600 °C (from Constant *et al.*)². The unit-cell parameters a_0 of Zr(C,N,O) are indicated ● monophase zone and ○ polyphase zone.

crystalline phases by x-ray diffraction (XRD). This method was developed by Hugo Rietveld in 1969⁵, in order to refine crystalline structures using neutron diffraction data. At the present time, it is also used to perform analysis of structure and crystalline defects, reticular parameter measurement and quantitative analysis in X-ray diffraction.

In this work, the carborreduction reactions of anatase

and badeleyite were studied by XRD. Reaction products were characterized by XRD (Rietveld) and scanning electron microscopy (SEM). The weight loss was also measured.

2. Materials And Methods

Raw materials used were badeleyite Riedel-de Haën from Germany with more than 99% ($ZrO_2 + HfO_2$) content, anatase Fluka from Switzerland with more than 99% TiO_2 content and carbon black (carbon 97%, ash 1%, volatiles 2% and a specific surface area BET = 45 m²/g). All powders have an average particle size lower than 5 μ m. The argon used contains less than 5 ppm of O_2 and H_2O .

Samples were prepared by wet mixing of the calculated amounts of reagents, and then they were dried and pressed at 39 MPa into cylinders of 2 mm in height and 10 mm in diameter. Samples were called by a letter and the C/MO₂ relation. Letter A was used for samples prepared from anatase and letter B for samples from badeleyite. Thus, we obtain the samples A200 (C/TiO₂ = 0.200), A280, A360, A430 and A500 and the samples B180 (C/ZrO₂ = 0.180), B210, B240, B300 and B450.

Reactions were performed in a horizontal alumina reactor with argon flowing through it. The pressure used was 0.05 Mpa above the atmospheric pressure, and the flow was 1 l/min. Experiments were carried out within the range of 1250 to 1650 °C with reaction times of 120 min and the temperature slopes were 10 °C/min upward as well as downward. The Ar flow was kept during cooling up to 200 °C.

Crystalline phases were characterized by X-ray diffraction with a Philips 3020 Goniometer with a PW 3710 controller, Cu-K α , Ni filter, 40 kV-20 mA. The scanning was made between 10° and 75° with step size of 0.02° and a step counting time of 2 sec. Some samples were scanned with 40 kV-30 mA and a step counting time of 4 sec. The set of divergence, receiving and scattering slits were 1°, 0.2°, 1° and no monochromator was used. The unit cell parameters were refined using the Rietveld refinement FULLPROF⁶ program. The starting crystallographic data for each phase were taken from literature⁷⁻¹¹. The refining sequence began with the adjustment of the shift in 2 θ due to vertical sample displacement and the background. To do this, elemental Si was added to the samples as internal standard. Then, for each phase, the scale factors, the cell constants, the parameters for calculation of the full-width-at-half-maximum (FWHM), the profile (pseudo Voigt) function coefficients, the preferred orientation parameter for the March function, were sequentially refined. Quantitative phase analysis was also performed by FULLPROF program based on the scale factors of each phase.

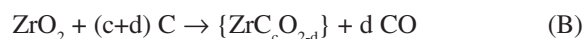
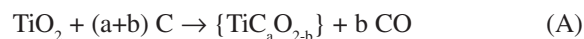
The Zr(C,O) and Ti(C,O) crystallite sizes were determined by the full-width-at-half-maximum of peak (200) for

obtained after refinement, 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.

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

3. Results And Discussion

The following theoretical equations describe the reactions carried out in these systems:



where a, b, c and d are stoichiometric coefficients ($0 \leq a \leq 1$,

$1 \leq b \leq 2$, $0.40 \leq c \leq 1$ and $1.4 \leq d \leq 2$). The phases $\{\text{TiC}_a\text{O}_{2-b}\}$ and $\{\text{ZrC}_c\text{O}_{2-d}\}$ are metal oxycarbides belonging to the MC-MO edge of the MC-MO-MN system. These phases are called Ti(C,O) and Zr(C,O) respectively.

Table 1 shows the results obtained in the TiO_2 carborreduction. Estimated standard deviations of weight percents were derived from the estimated standard deviations on individual scale factors for the respective phases, and other error contributions were not included.

The Ti (C,O) content increase with the temperature and carbon content being the unique product obtained at high temperatures and high C content.

Table 2 shows the values of a_0 obtained by the Rietveld method for the Ti(C,O) phases. Ranges of values appear in some cases due to the necessity of using two or more Ti(C,O)

Table 1. Phases content (wt.%) of TiO_2 samples at different temperatures.

| Sample/ Temperature | 1250 °C | 1350 °C | 1450 °C | 1550 °C | 1650 °C |
|------------------------|---|---|---|---|--|
| A500 | Ti(C,O) 95.4(7)* Ti ₃ O ₅ 4.6(8) | Ti(C,O) 100 | Ti(C,O) 100 | Ti(C,O) 100 | Ti(C,O) 100 |
| A430 | Ti(C,O) 90.3(6) Ti ₃ O ₅ 9.7(8) | Ti(C,O) 95.5(7) γTi ₃ O ₅ 4.5(6) | Ti(C,O) 100 | Ti(C,O) 100 | Ti(C,O) 100 |
| A360 | Ti(C,O) 77.7(6) Ti ₃ O ₅ 22.3(4) | Ti(C,O) 89.9(6) γTi ₃ O ₅ 6.9(5) Ti ₅ O ₉ 3.9(7) | Ti(C,O) 100 | Ti(C,O) 100 | Ti(C,O) 100 |
| A280 | Ti(C,O) 71.1(6) Ti ₃ O ₅ 28.9(5) | Ti(C,O) 69.9(3) γTi ₃ O ₅ 2.4(5) Ti ₂ O ₃ 22.9(4) Ti ₅ O ₉ 4.8(6) | Ti(C,O) 70.0(6) γTi ₃ O ₅ 6.2 (5) Ti ₂ O ₃ 16.2(4) Ti ₅ O ₉ 7.5(4) | Ti(C,O) 88.8(4) Ti ₂ O ₃ 11.2(8) | Ti(C,O) 95.6(7) γTi ₃ O ₅ 1.5(9) Ti ₂ O ₃ 1.5(9) Ti ₅ O ₉ 1.5(8) |
| A200 | Ti(C,O) 52.6(5) Ti ₃ O ₅ 47.4(4) | Ti(C,O) 41.9(4) γTi ₃ O ₅ 22.1(6) Ti ₂ O ₃ 29.1(5) Ti ₅ O ₉ 6.9(8) | Ti(C,O) 41.0(7) γTi ₃ O ₅ 5.2(5) Ti ₂ O ₃ 50.1(5) Ti ₅ O ₉ 3.7(8) | Ti(C,O) 45.7(6) Ti ₂ O ₃ 54.3(7) | Ti(C,O) 74.4(8) γTi ₃ O ₅ 5.1(3) Ti ₂ O ₃ 14.7(6) Ti ₅ O ₉ 5.8(7) |

* Values in parenthesis represent estimated standard deviations in the last quoted place.

Table 2. Refined unit cell parameter a_0 (Å) for Ti(C,O) phase in TiO_2 samples at different temperatures.

| Sample/ Temperature | 1250 °C | 1350 °C | 1450 °C | 1550 °C | 1650 °C |
|------------------------|----------------|----------------|----------------|----------------|----------------|
| A500 | [4.261-4.281] | [4.292] | [4.294- 4.308] | [4.301- 4.308] | [4.304] |
| A430 | [4.275- 4.287] | [4.283- 4.296] | [4.289- 4.304] | [4.301- 4.308] | [4.290- 4.304] |
| A360 | [4.262- 4.287] | [4.275- 4.293] | [4.263- 4.293] | [4.285- 4.302] | [4.277- 4.297] |
| A280 | [4.266- 4.288] | [4.276- 4.293] | [4.265- 4.290] | [4.267- 4.296] | [4.277- 4.297] |
| A200 | [4.271- 4.286] | [4.274- 4.293] | [4.266- 4.288] | [4.259- 4.276] | [4.235- 4.255] |

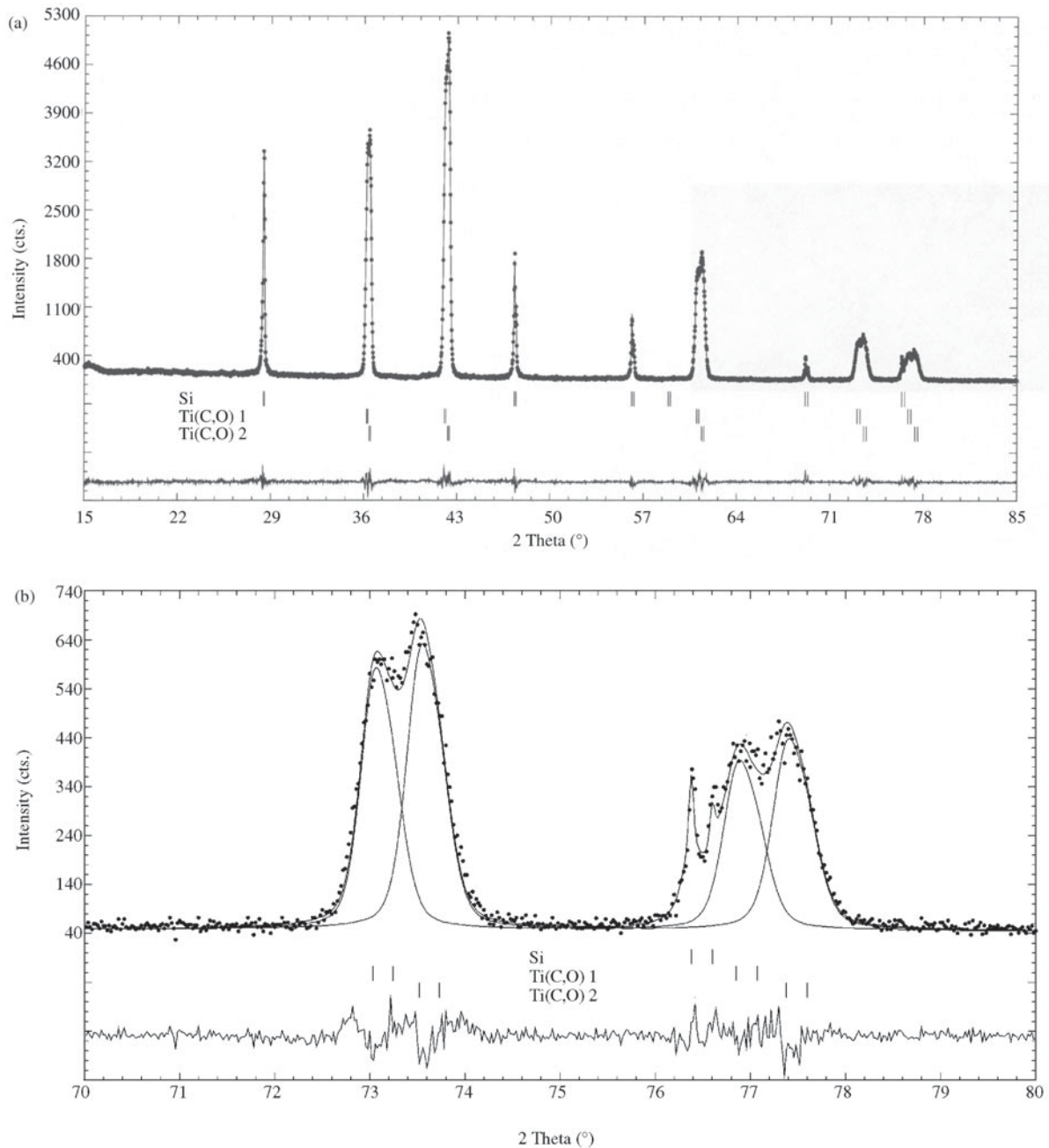


Figure 3. a) Final Rietveld plot for sample A360 treated at 1450 °C. b) Amplified plot of 70°-80° zone.

phases in order to obtain a good fitting of peak widths. Figure 3a shows the final Rietveld plot for sample A360 treated at 1450 and Fig. 3b is part of the same graphic amplified to show the overlap of Ti(C,O) peaks belonging to different phases. In Fig. 3b, individual calculated profiles for both Ti(C,O) phases are also shown.

Within the temperature range used in these experiments,

the Ti (C, O) cubic phase is throughout the TiO-TiC axis (Fig. 4) as well as the Ti (C, N, O) cubic phases cover the triangular diagram completely (Fig. 1). The carbon content of samples A would allow to obtain the complete composition range (100% TiO to 100%TiC). In Table 2, a_0 values of Ti(C,O) are between 4.234 Å and 4.308 Å. These values correspond to a composition range between $\text{TiC}_{0.16}\text{O}_{0.84}$ and

Table 3. Mean unit-cell parameters of titanium oxides obtained in the refinement

| Phase | a | b | c | α | β | γ | Space Group |
|--|-----------|-----------|-----------|----------|-----------|-----------|-------------|
| Ti ₂ O ₃ | 5.133(9) | 5.133(9) | 13.710(8) | | | | R-3C |
| Ti ₃ O ₅ | 9.815(10) | 3.788(10) | 9.892(11) | | 91.50(3) | | C2/m |
| γ -Ti ₃ O ₅ | 9.967(8) | 5.075(9) | 7.176(9) | | 109.10(9) | | I2/a |
| Ti ₅ O ₉ | 5.589(7) | 7.135(8) | 8.862(6) | 97.28(9) | 112.73(8) | 108.76(9) | P1 |

Table 4. Weight loss % in TiO₂ samples at different temperatures.

| Sample/ Temperature | 1250 °C | 1350 °C | 1450 °C | 1550 °C | 1650 °C |
|------------------------|---------|---------|---------|---------|---------|
| A500 | 42 | 45 | 45 | ~ 49 | 48 |
| A430 | 41 | 45 | 46 | 46 | 46 |
| A360 | 37 | 38 | 38 | 42 | 42 |
| A280 | 31 | 32 | 35 | 36 | 37 |
| A200 | 25 | 28 | 27 | 36 | 29 |

Table 5. Unit-cell parameter a₀ and weight % of Zr(C,O) for ZrO₂ samples.

| Sample/ Temperature | 1400 °C | 1460 °C | 1500 °C | 1600 °C | 1650 °C |
|------------------------|----------------------------|---------------------------|--------------------|----------------------------|--------------------|
| B450 | [4.643- 4.650] 12.9(7)* | [4.658- 4.660] 16.5(6) | [4.681] 34.6(6) | [4.657- 4.672] 87.2(6) | [4.682] 100 |
| B300 | [4.646- 4.658] 8.7(6) | [4.666] 13.8(7) | [4.679] 30.2(6) | [4.654-, 4.667] 66.7(8) | [4.678] 81.8(6) |
| B240 | [4.643- 4.661] 9.8(7) | [4.658- 4.667] 17.6(5) | [4.682] 31.5(5) | [4.655- 4.668] 64.2(5) | [4.678] 66.0(5) |
| B210 | [4.640-, 4.663] 6.5(6) | [4.650- 4.663] 16.3(5) | [4.681] 30.5(8) | [4.651- 4.669] 55.2(3) | [4.677] 63.2(7) |
| B180 | [4.650-4.669] 7.3(8) | [4.659- 4.670] 19.9(7) | [4.683] 33.0(4) | [4.648- 4.659] 56.8(6) | [4.672] 56.6(4) |

Note: Values between brackets are unit-cell parameters in Å.

* Values in parenthesis represent estimated standard deviations in the last quoted place for wt.% data.

Table 6. Weight loss % in ZrO₂ samples at different temperatures.

| Sample/ Temperature | 1400 °C | 1460 °C | 1500 °C | 1600 °C | 1650 °C |
|------------------------|---------|---------|---------|---------|---------|
| B450 | ~13 | 13 | 17 | 30 | 37 |
| B300 | 9 | 12 | 15 | 30 | 31 |
| B240 | 8 | 12 | 16 | 18 | 27 |
| B210 | 9 | 12 | 16 | 20 | 24 |
| B180 | 10 | 17 | 17 | 24 | 26 |

TiC_{0.73}O_{0.27} (between 16 and 73 mol% of TiC). The composition range was determined using the calibration curve a₀ vs. composition of Ti(C,O) (Fig. 4). This curve, from Neuman *et al.*¹, was determined from samples prepared by reaction of pure TiO and TiC.

The values of a₀ tend to be higher with the increase of

reaction temperature. It is not possible to determine a defined tendency of a₀ values changes with carbon content. This little a₀ variation is due to the low slope in Fig. 4 where big changes in composition produce little shift of the unit cell parameter.

Some titanium sub-oxides were also detected. These

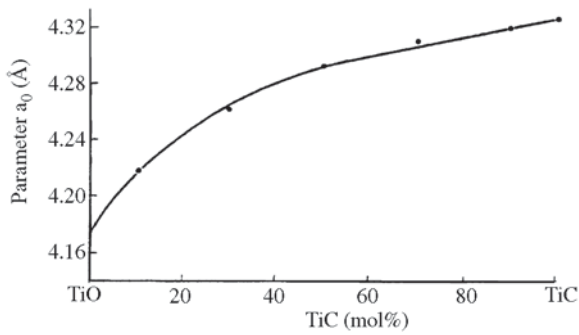


Figure 4. Unit-cell parameter a_0 vs. Ti(C,O) composition taken from Neumann *et al.*¹.

phases are Ti_3O_5 , $\gamma-Ti_3O_5$, Ti_2O_3 , and Magnéli phases (Ti_nO_{n+2}) similar to those observed by other authors¹². These oxides become more important at low temperature and in samples with low carbon content. In Table 3 the refined unit-cell parameters of these phases are in good agreement with published data⁸⁻¹¹.

The weight losses showed in Table 4 allow us to see that the reaction progresses with the increase of carbon content and temperature, being the obtained tendency consistent with the detected crystalline phases, within the margin of experimental error.

Badeleyite carborreduction results (reaction B) for the 5 studied samples are shown in Tables 5 and 6.

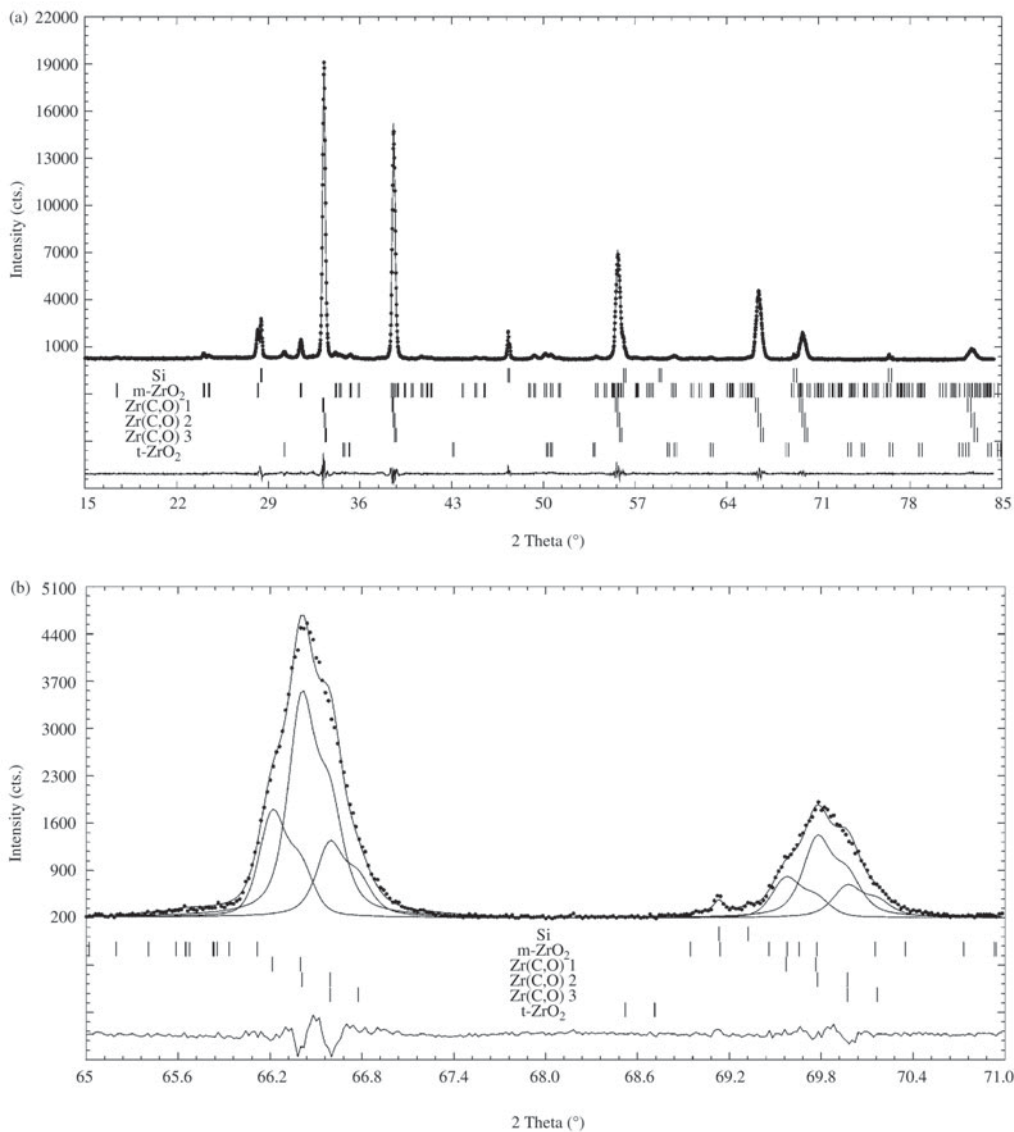


Figure 5. a) Final Rietveld plot for sample B450 treated at 1600 °C. b) Amplified plot of 61°-71° zone

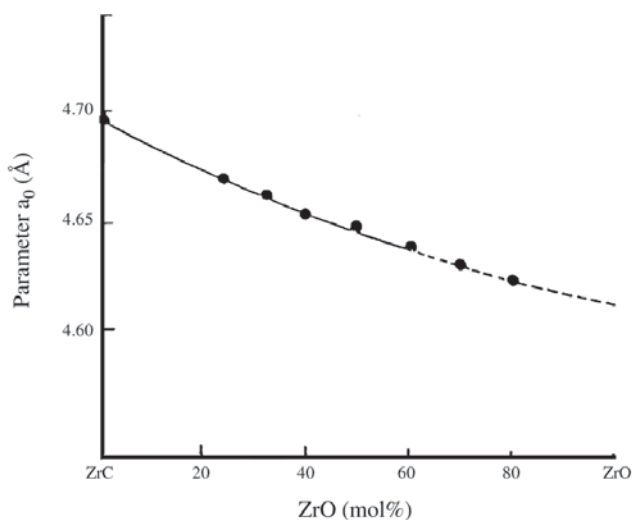


Figure 6. Unit-cell parameter a_0 vs. Zr(C,O) composition taken from Kosolapova *et al.*⁴.

All samples have enough carbon to obtain an oxycarbide as unique phase. Theoretically oxycarbide compositions would be between $\text{ZrC}_{0.45}\text{O}_{0.55}$ for B180 and ZrC for B300.

The zirconium phases obtained were: Zr(C,O) phase, monoclinic ZrO_2 (badeleyite) and tetragonal ZrO_2 in lower proportions. Figure 5a shows the final Rietveld plot for sample B450 treated at 1600 °C and Fig. 5b is part of the same graphic amplified to show the overlap of Zr(C,O) peaks belonging to different phases. In Fig. 5b, individual calculated profiles for all Zr(C,O) phases are also shown.

Badeleyite is the principal phase at temperatures lower than 1600°. The amount of this phase decreases with the increase of temperature and carbon content, being the minority phase at higher temperatures. Mean unit-cell parameters refined for badeleyite were: $a = 5.151(3)$ Å, $b = 5.210(5)$ Å, $c = 5.318(5)$ Å and $\beta = 99.27(4)^\circ$ Å.

Tetragonal zirconia content was between 1 and 3 wt.% in all samples containing ZrO_2 presenting similar behavior to the badeleyite.

Zr(C,O) increases with the increase of temperature and carbon content. It is the principal phase at a temperature of 1600° or higher.

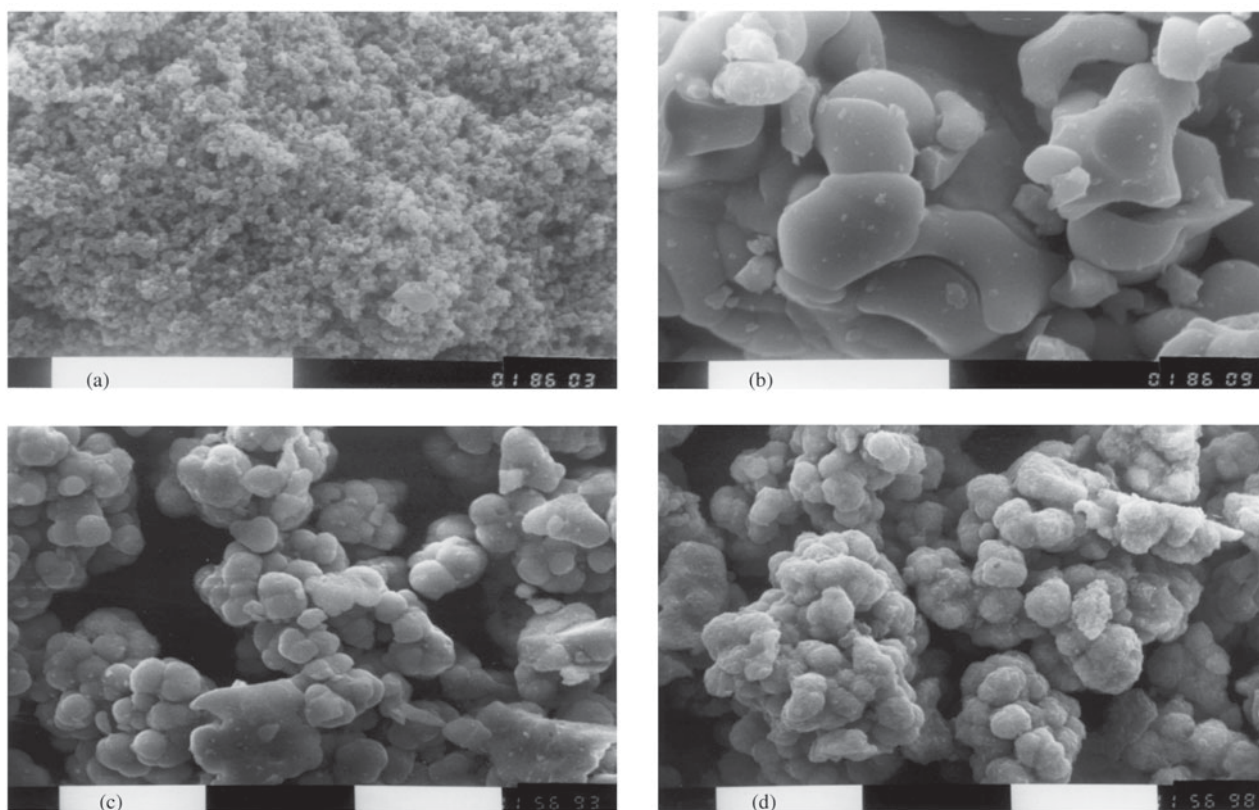


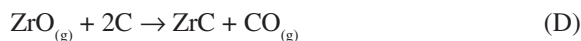
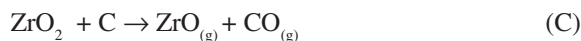
Figure 7. Micrographies (SEM) of reagents and products (scale: white bar = 10 μm). a) Anatase; b) A200 sample treated at 1650 °C; c) Badeleyite; d) B300 sample treated at 1650 °C.

The obtained values of a_0 (4.640 Å – 4.683 Å) show that the formed oxycarbides were within the range $ZrC_{0.46}O_{0.54}$ - $ZrC_{0.9}O_{0.1}$ (between 54 and 10 mol%. of ZrO). The composition range was determined using the calibration curve a_0 vs. Zr(C,O) composition (Fig. 6). This curve, from Kosolopova *et al.*⁴, was obtained from samples prepared by reaction of pure Zr, ZrO₂ and ZrC.

The Rietveld analysis shows that the wide peaks can be fitted using two or more phases M(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 M(C,O). The R_{exp} are between 4.63 and 5.97 and the R_{wp} are between 9.20 and 15.56. This phenomenon can be observed in other systems where there are phases having changeable compositions and unit-cell parameters associated¹³⁻¹⁵.

The crystal sizes of the Zr(C,O) and Ti(C,O) were calculated using the width of peaks (200) determined from the fitting results. Both phases presented similar behavior, with crystal size values between 560 Å and 3000 Å without a definite tendency.

Table 6 shows a weight loss increase with the increase of temperature in all samples. The carbon content has influence at 1600 °C or higher temperatures when the Zr(C,O) is the principal phase. High weight loss values obtained principally for sample B180 may be due to ZrO_(g) loss (reaction C).



But in samples with high carbon content, the ZrO_(g) loss may be limited by reaction D.

Finally, reagents and reaction products were characterized by scanning electron microscopy (SEM). Morphology variations caused by reactions were observed (Fig. 7).

When comparing the TiO₂ reagent with the reaction products an important increase of the particle size is observed, indicating their sintering. This phenomenon can also be observed in low temperature samples. Besides, the TiO₂ grain morphology and that of the products are different.

Nevertheless, B samples seem to preserve the morphology and size of the raw material that originates them (the badeleyite).

4. Conclusions

1. Carborreduction reactions of TiO₂ and ZrO₂ are a suitable method to prepare oxycarbides of TiO-TiC and ZrO-ZrC systems respectively.
2. All oxycarbides obtained belong to MO-MC axes of MO-MC-MN system.
3. The carbon content of oxycarbides increased with

reaction temperature.

4. Carborreduction of TiO₂ produced Ti(C,O) as unique product at temperatures higher than 1450 °C and carbon/mineral ratios higher than 0.360. In the other samples some titanium oxides and suboxides were obtained but non remainder TiO₂ was detected.
5. Carborreduction of ZrO₂ produced Zr(C,O) as unique reaction product.
6. The Rietveld method allowed to characterize titanium and zirconium oxycarbides obtained by carborreduction and also to refine unit cell parameters of minority phases.
7. The observation by SEM permitted to see the TiO₂ and ZrO₂ different behavior with regard to their morphology modification during these reactions.

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