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Nanometric Y_2O_3–TiO_2–ZrO_2 solid solution powders and their utilization in the synthesis of composite powders with TiB_2 and TiC inclusions

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Carbothermal reduction of TiO_2 dissolved in ZrO_2 and B_2O_3 is a method of fabrication of fine composite powders in the ZrO_2–TiB_2–TiC system. The method requires nanopowders of the zirconia –titania solid solution with a high TiO_2 concentration. A technique of fabrication of zirconia nanopowders doped with 18 mol % titania and 2–3 mol % yttria is described in the paper. The nanopowders were obtained in a co-precipitation process followed by hydrothermal crystallization at 240 °C. The phase composition (XRD) and EDS measurements proved formation of a solid solution as the only phase. DTA and TG analyses showed that there are no amorphous phases. A nanometric morphology was proved by the TEM observations and the specific surface area measurements (BET). Dynamic light scattering was used to measure the agglomerate size distribution. A usefulness of the zirconia–titania–yttria nanopowders to the *in-situ* syntheses of composite powders in the ZrO_2–TiB_2–TiC system was described. The composite powders were fabricated in the reaction of titanium oxide dissolved in the TiO_2–Y_2O_3–ZrO_2 solid solution with boron oxide and carbon. A mixture of zirconia solid solution nanopowder containing 2–3 mol % of Y_2O_3, 18 mol % of TiO_2 and 79–80 mol % of ZrO_2, boric acid and 20 wt. % alcohol solution of phenol-formaldehyde resin was used for the synthesis. The phase compositions of the composite powders were characterized by X-ray diffractometry.

1. Introduction

Titanium oxide incorporated in the zirconium oxide solid solution can be used in an *in-situ* process leading to obtain fine inclusions of hard phases such as titanium carbide [1–4] and titanium boride [5] in zirconia based powders. The method is based on the carbothermal reduction of TiO_2 and B_2O_3. The so far presented technologies

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[1–5] involved Y_2O_3–TiO_2–ZrO_2 nanopowders crystallized in the solid state at temperatures around 650 °C. Y_2O_3 is introduced to the system to stabilize tetragonal ZrO_2 in sintered polycrystals. Such crystallization conditions do not enable one to maximize the surface area of the powder and an accessibility of TiO_2 for carbides and borides fabrication is not optimum. From that point of view, a hydrothermal process seems to be more suitable. It involves co-precipitation and hydrothermal crystallization of gels containing zirconium, titanium and yttrium cations. Because of low crystallization temperature (ca. 250 °C), such a method enables production of nanopowders with a large surface area. Additionally, water environment favours a decreased agglomerate strength. This is very useful for homogeneous distribution of the boron and carbide precursors within the Y_2O_3–TiO_2–ZrO_2 solid solution nanopowders and thus simplifies preparation of mixtures for the synthesis of carbides and borides.

The amount of TiO_2 dissolved in a zirconia solid solution limits the content of *in-situ* synthesized hard phases in an obvious way. Therefore, it is required to elucidate if the hydrothermal synthesis is an effective method of fabrication of Y_2O_3–TiO_2–ZrO_2 solid solution nanopowders with a high titanium oxide concentration.

2. Experimental

A co-precipitation method followed by hydrothermal crystallization was used to prepare the Y_2O_3–TiO_2–ZrO_2 solid solution nanopowders, containing from 2 to 3 mol % yttria, 18 mol % titania and from 79 to 80 mol % zirconia. Homogeneous yttria –titania–zirconia hydrogels were co-precipitated from aqueous solutions of appropriate chlorides with $NH_3{\cdot}aq$ at pH ≥ 9. The following chemical reagents were used: $ZrOCl_2{\cdot}8H_2O$ – zirconia content > 99.7% (Si – 0.03%, Fe – 0.02%, Al – 0.015%), Beijing Chemicals Import and Export Corporation, China; $TiCl_4$ – purity > 98 %, Fluka, Switzerland; Y_2O_3 – purity 99.99 %, $NH_3{\cdot}aq$ – analytically pure, Polish Chemical Works, Poland. The hydrogels were hydrothermally treated for 4 h at 240 °C under the pressure of saturated water vapour (ca. 3.8 MPa) at pH between 7.5 and 7.6. After the crystallization, the powders were dried at 65 °C.

The composite powders containing TiC and TiB_2 were prepared by an *in-situ* route. It involved a reaction between titanium oxide dissolved in the TiO_2–Y_2O_3–ZrO_2 solid solution, boron oxide and carbon. The uniform mixtures of a hydrothermally crystallized zirconia solid solution nanopowder, boric acid (a. p.) and 20 wt. % alcohol solution of phenol–formaldehyde resin were used. Each mixture was first dried in an argon flow to decompose H_3BO_3 and then the resin. Finally it was heat treated for 1.5 h at 1500 °C in vacuum under the pressure not exceeding 2×10^{-3} mbar to synthesize the composite powder.

Phase compositions of the powders were determined by the X-ray diffraction analysis (radiation $CuK_{\alpha 1}$, 2θ range 20–90°, step 0.008°). The Rietveld refinements of the diffraction data were carried out by means of the X'Pert Plus v1.0 program (Philips) to determine phase fractions. Scherrer's equation [6] was applied to calculate the crystallite sizes of Y_2O_3–TiO_2–ZrO_2 solid solution powders. DTA and TG curves were obtained in air at temperatures ranging from 30 °C to 1000 °C at the heating rates of 10 °C/min. Specific surface areas were measured by the multipoint nitrogen adsorption at –196 °C. The BET adsorption model was involved in calculations. TEM, combined with EDS, was used to characterize a morphology and chemical compositions of the Y_2O_3–TiO_2–ZrO_2 solid solution powders. The agglomerate size distributions were determined by the dynamic light scattering technique in the range up to 6 μm. These measurements were carried out in water dispersions at pH ranging from 9 to 11.

3. Results and discussion

3.1. Powders of Y_2O_3–TiO_2–ZrO_2 solid solution

The XRD measurements showed that the powders in the Y_2O_3–TiO_2–ZrO_2 system, crystallized at the hydrothermal conditions described above, consisted of tetragonal and monoclinic zirconia polymorphs (Fig. 1). The X-ray diffraction patterns did not contain peaks from either titanium or yttrium rich phases. This is a strong argument for the formation of zirconia solid solutions of the designed TiO_2 and Y_2O_3 concentration. The monoclinic ZrO_2 polymorph content was moderate, up to 12.6 vol. % (Table 1). It is ca. 45% lower than that measured for the powders with similar chemical composition but crystallized by using the calcination process at 650 °C [2–4].

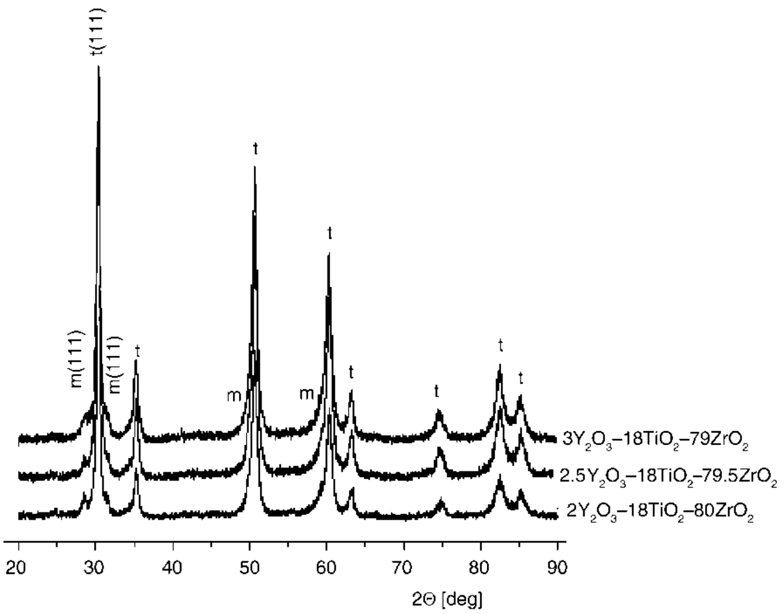

Fig. 1. XRD patterns of the powders; t – tetragonal ZrO_2, m – monoclinic ZrO_2

Table 1. Phase composition of the Y_2O_3–TiO_2–ZrO_2 powders

Powder	Tetragonal ZrO_2 [vol. %]	Monoclinic ZrO_2 [vol. %]
$2.0Y_2O_3$–$18TiO_2$–$80ZrO_2$	87.4 ± 0.4	12.6 ± 0.3
$2.5Y_2O_3$–$18TiO_2$–$79.5ZrO_2$	92.2 ± 0.4	8.0 ± 0.3
$3.0Y_2O_3$–$18TiO_2$–$79ZrO_2$	89.7 ± 0.4	10.3 ± 0.3

Table 2. Specific surface area of the Y_2O–TiO_2–ZrO_2 hydrothermal powders and mean crystallite sizes of tetragonal ZrO_2 in the direction perpendicular to the (011) lattice plane for various chemical compositions

Powder	S_{BET} [m^2/g]	$d_{t(111)}$ [nm]
$2.0Y_2O_3$–$18TiO_2$–$80ZrO_2$	83.0 ± 0,2	18.6
$2.5Y_2O_3$–$18TiO_2$–$79.5ZrO_2$	86.3 ± 0,3	17.8
$3.0Y_2O_3$–$18TiO_2$–$79ZrO_2$	90.3 ± 0,8	16.5

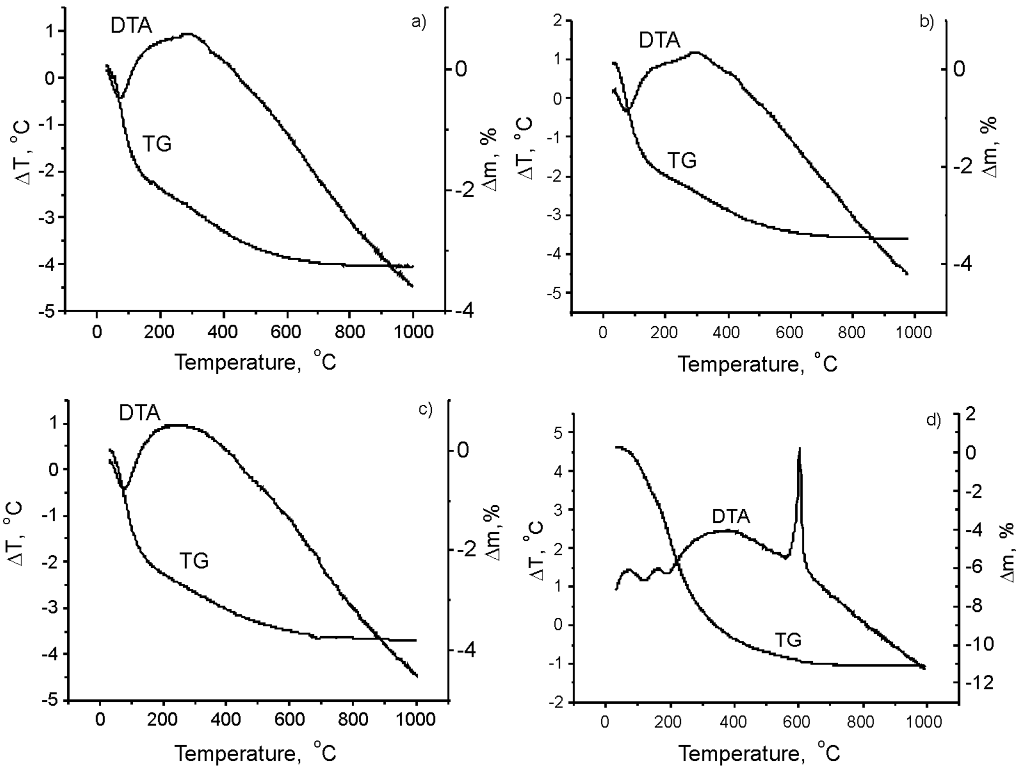

Fig. 2. DTA and TG curves: a) $2Y_2O_3$–$18TiO_2$–$80ZrO_2$ hydrothermal powder, b) $2.5Y_2O_3$–$18TiO_2$–$79.5ZrO_2$ hydrothermal powder, c) $3Y_2O_3$–$18TiO_2$–$79ZrO_2$ hydrothermal powder, d) hydrogel corresponding to $2.5Y_2O_3$–$18TiO_2$–$79.5ZrO_2$

The DTA and TG analyses of hydrothermally treated powders revealed no thermal effects at 625 °C (Fig. 2) as distinct from the amorphous zirconia hydrogel (Fig. 2d).

The comparison proves that the originally amorphous yttria–titania–zirconia hydrogels crystallized totally under applied hydrothermal conditions.

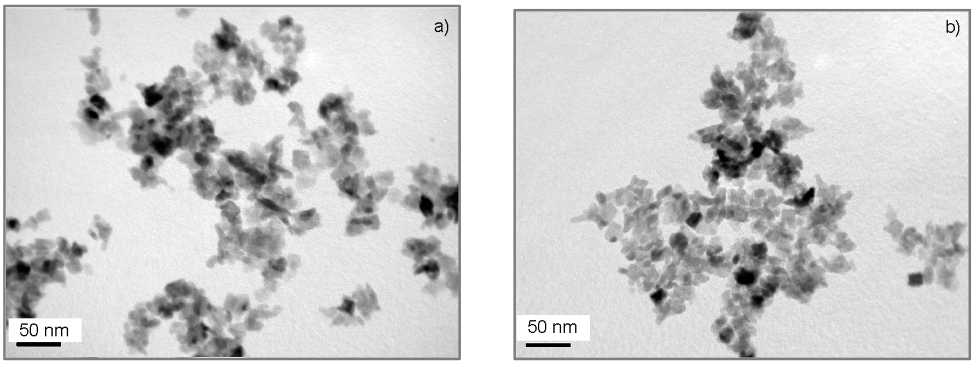

Fig. 3. TEM micrographs of the hydrothermal zirconia powders:
a) $2Y_2O_3$–$18TiO_2$–$80ZrO_2$, b) $2.5Y_2O_3$–$18TiO_2$–$79.5ZrO_2$

The TEM observations (Fig. 3) together with specific surface area and crystallite size measurements (Table 2) proved the nanometric size of the powder particles. The mean crystallite size was between 15 and 20 nm. The specific surface area was close to 90 m^2/g. The value is over 30 higher than that of the zirconia powders of similar chemical composition, crystallized by calcination at 700 °C [3, 4]. On the other hand, the presented Y_2O_3–TiO_2–ZrO_2 nanopowders consist of slightly bigger grains than those hydrothermally treated without titanium oxide dissolved in the solid state whose mean grain size was of ca. 10 nm [7]. This suggests that TiO_2 affects significantly crystallite growth during the hydrothermal crystallization process.

As shown in Fig. 3, the zirconia nanopowders contained crystallites not only isometric in shape but also a small content of needle-shaped ones. This observation, together with the data collected in Table 1, suggests that these crystallites belong to monoclinic zirconia.

Figure 4 shows the results of EDS chemical composition measurements for the $3Y_2O_3$–$18TiO_2$–$79ZrO_2$ nanopowder. The analysis, made along the line marked, proved that the crystallites consist of yttrium, titanium, zirconium and oxygen. Local signal maxima for particular elements align together very well. This observation is the second evidence, together with the XRD measurements, for the lack of titanium and/or yttrium segregation into separate phases, additionally proving that titanium and yttrium oxides are totally dissolved in the zirconia solid phase. Unfortunately, the EDS scan is insufficiently sensitive for evaluation of the titanium and yttrium segregation inside a single nanocrystallite.

Agglomerate size distributions of the zirconia nanopowder depend on the preparation history as is shown in Fig. 5. The powder which was not dried after hydrothermal treatment consisted of the agglomerates of practically monomodal size distribution

(Fig. 5a) with a modal size close to 50 nm. Such an agglomerate consists of a few crystallites.

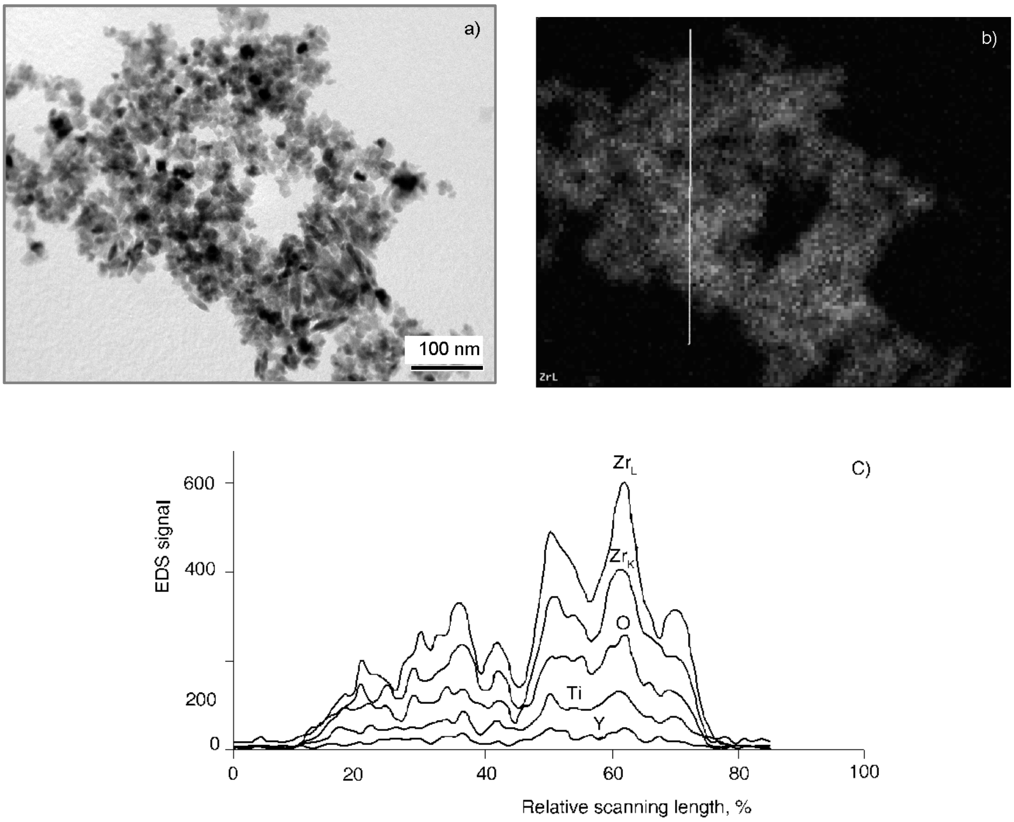

Fig. 4. Results of chemical analysis of $3Y_2O_3$–$18TiO_2$–$79ZrO_2$ nanopowder: a) TEM micrograph, b) map of zirconium distribution c) EDS analysis along the line marked in Fig. 4b

During final drying stages, because of capillary and dispersion attractive forces among crystallites, the nanopowder becomes more and more agglomerated. The resultant agglomerate size distribution turns into trimodal (Fig. 5b), and the majority of agglomerates becomes larger than 1 μm. However, the agglomerates are still relatively mechanically weak. Their sizes can be easily reduced by external forces, for example by ultrasonic treatment. After 5 min of ca. 100 W sonification, the modal size of agglomerates reverts to 50 nm (Fig. 5c). This confirms usability of the hydrothermal crystallisation for fabrication of zirconia nanopowders composed of soft agglomerates. This feature seems to be advantageous for a synthesis of ZrO_2/TiC/TiB_2 composite powders using the *in-situ* method [5].

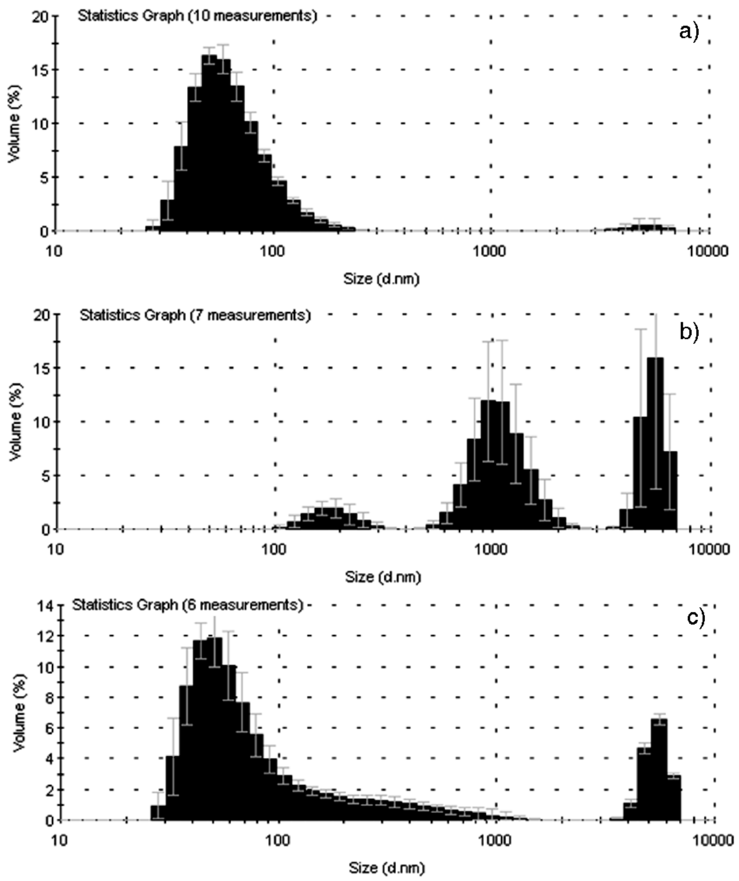

Fig. 5. Agglomerate size distributions of the $2.5Y_2O_3$–$18TiO_2$–$79.5ZrO_2$ nanopowders: a) without drying after hydrothermal crystallization, 5 min of ultrasonic treatment, b) dried, without ultrasonic treatment; c) dried, 5 min of ultrasonic treatment

3.2. Composite powders in the Y_2O_3–ZrO_2/TiC/TiB_2 system

Figure 6 and Table 3 show phase compositions of zirconia composite powders synthesized by using the *in-situ* reactions in a qualitative and quantitative way, respectively. The powders consisted of tetragonal and monoclinic zirconia polymorphs blended with TiC, TiB_2 and ZrB. This confirms that TiO_2 dissolved in zirconia was involved in production of the TiB_2 and TiC inclusions, most probably according to the following reactions:

$$TiO_{2(s)} + B_2O_3(l) + 5C_{(s)} = TiB_{2(s)} + 5CO_{(g)} \quad (1)$$

$$TiO_{2(s)} + 3C_{(s)} = TiC_{(s)} + 2CO_{(g)} \quad (2)$$

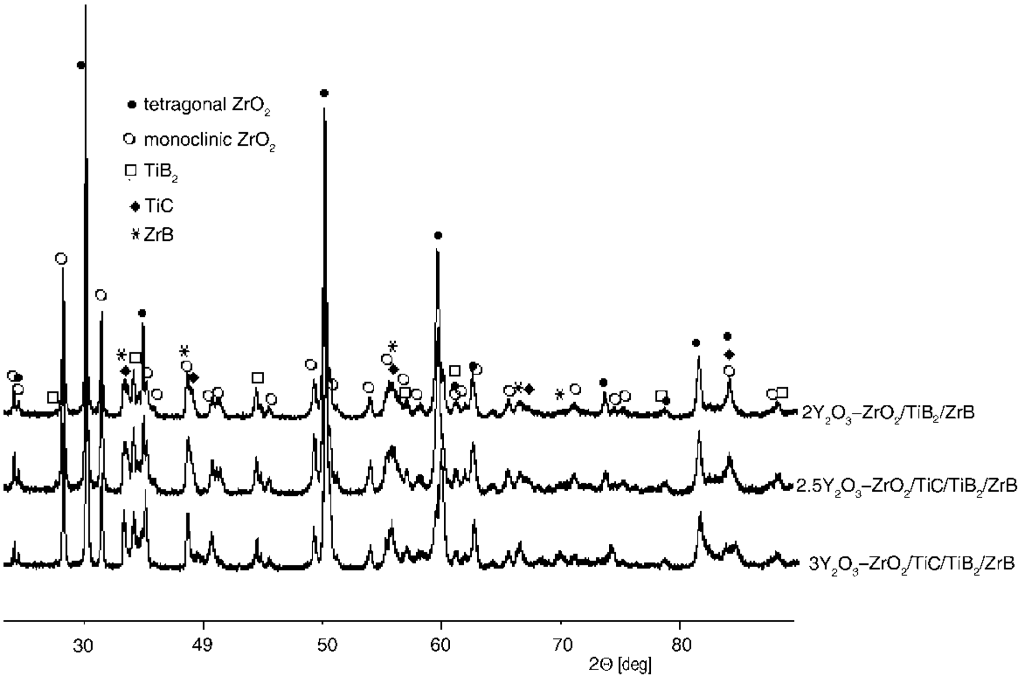

Fig 6. XRD patterns of the composite powders of the original zirconia nanopowders

Table 3. Phase compositions [wt. %] of the composite powders

Original powder	Tetragonal ZrO_2	Monoclinic ZrO_2	TiB_2	TiC	ZrB
$2Y_2O_3$–$18TiO_2$–ZrO_2	48.9 ± 0.3	34.8 ± 0.3	7.7 ± 0.3	–	8.6 ± 0.1
$2.5Y_2O_3$–$18TiO_2$–ZrO_2	37.1 ± 0.2	41.2 ± 0.2	5.1 ± 0.2	12.3 ± 0.3	4.4 ± 0.1
$3Y_2O_3$–$18TiO_2$–ZrO_2	43.2 ± 0.2	35.4 ± 0.2	5.4 ± 0.2	11.7 ± 0.1	4.5 ± 0.3

At 1500 °C under the CO partial pressure of 2×10^{-3} mbar, changes of the Gibbs free energy for reactions (1) and (2) were calculated to be –1107.5 kJ/mol and –458.2 kJ/mol, respectively. Thus the former reaction is more favourable than the latter one. The content of TiB_2 will be higher than that of TiC in the equilibrium state. However, the data collected in Table 3 show that the system was not in equilibrium. In the case of the $2.5Y_2O_3$–$18TiO_2$–ZrO_2 and $3Y_2O_3$–$18TiO_2$–ZrO_2 nanopowders, TiC dominates over TiB_2, while it is absent in the composite powder originated from the $2Y_2O_3$ –$18TiO_2$–ZrO_2 nanopowder. It clearly points that the reaction kinetics controls the final composition of the composite powder. The presence of zirconium boride indicates that ZrO_2 reacted with B_2O_3 and C according to Eq. (1). ZrB seems to be a secondary inclusion phase but not in the case of the powder based on the $2Y_2O_3$–$18TiO_2$–ZrO_2 nanopowder. This may suggests that Y_2O_3 affected the kinetics of TiB_2, TiC, ZrB formation. Nevertheless, ZrB seems to be stable only at low CO pressures. It disappeared during sintering of the analogical composite powder in argon of technical purity at 1500 °C [5].

4. Conclusions

Co-precipitation followed by hydrothermal crystallization is an effective way for production of zirconia solid solution nanopowders with 18 mol % titania and 2–3 mol % yttria. Mean crystallite sizes of the nanopowders are 15–20 nm, while specific surface area is close to 90 m^2/g. Titanium oxide dissolved in the nanosized crystallites can react with B_2O_3 and carbon resulting in the formation of TiC and TiB_2. The same process of carbothermal reduction gives ZrB as a secondary phase in the composite powders.

Acknowledgements

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