Investigation of Nanoparticle Phase Composition by Synchrotron Radiation [1]

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Abstract

The features of a phase composition for nanopowder (ZrO_2-5wt.%Y_2O_3), activated by ultrasonic (US) action of different power are studied. The data of precision XRD analyses carried out using collimated monochromated synchrotron beam with the resolution of 0.05° and 0.01° on 2θ, and also the results of transmission electron diffraction microscopy of nanopowder particles were analysed. It was found, that the US-activation of YSZ nanopowder results in formation and stabilisation of high-temperature modification of tetragonal phase ZrO_2 at room temperature; in the studied range of acting ultrasound power (W = 1, 2, 3 kW) the lattice parameters a, c do not depend on W; the ratio of tetragonal distortion c/a in the sonicated nanopowder decreases in comparison with initial one, that is evidence of approach of structure to a cubic phase; several intermediate phases (zirconia polymorphous modifications) with the closely spaced lattice parameters referred to the same syngony appear in nanocrystallites with the sizes of 25 - 45 nm of the sonicated YSZ nanopowder.

1. Introduction

The examination of a metastable nanoparticle state is an actual fundamental and applied problem. There are data about observation of not only structure microdistortions in nanomaterials relative to parameters of a solid state, but also coexistence of several metastable phases of different syngonies (e.g. cubic phase and its tetragonal splitting in nanopowder and in the ceramic grains of yttrium-stabilised zirconia - YSZ, different phases of Al_2O_3 on a radius of alumina nanoparticles) [1 - 4].

However, the observations of such coexistence in separated nanoparticles of polymorphous YSZ are not known. For this purpose the precision XRD analyses with a high space resolution and intensity of transmitted radiation, sufficient for correct statistical handling, together with TEM analyses and electron diffractometry examinations are required.

To study the phase constitution of YSZ particles by the indicated methods the powder (ZrO_2-5wt.%Y_2O_3) in natural state and activated by ultrasonic action of a different power was examined.

2. Experimental techniques and results

The studied YSZ powder consisted of agglomerates of particles with a mean size of 50 nm. The samples were activated by ultrasound with a power of 1, 2 and 3 kW in a cavity of US-mould such as in [5] for 20 minutes.

XRD analyses of each sample was carried out using a beam of monochromatic and collimated synchrotron radiation (SR). The wave length of SR was λ = 1.5405 E at $\Delta\lambda/\lambda$ = 4*10^{-4} and corresponded to CuKα radiation; the beam diaphragm diameter was 179 or 538 μm; an angular resolution of a XRD pattern on 2θ was 0.05°, and for several characteristic peaks - 0.01°. The survey of patterns was carried out in a range of angles 2θ from 20° to 100°. The intensity of background SR was 20-25 pulses/s, the intensity of maximal diffraction reflexes achieved 800 pulses/s. The indicated parameters of SR ensured the necessary statistics of experimental data and allowed to determine the lattice parameters to an accuracy of 0.02 E. Then XRD spectra of initial YSZ powder (sample "0") and US-activated samples were compared: sample "1" was sonicated at 1 kW; sample "2" – at 2 kW; sample "3" – at 3 kW, as well as for the nanopowder of pure ZrO_2 (sample "4"). XRD patterns of "1", "2", "3" samples were moved by 1.1° down the smaller angles in comparison to pattern of a sample "0". XRD pattern of the sample "4" showed the presence of

which have appeared in XRD patterns of US-activated samples, and they are not identified in a standard XRD pattern of a tetragonal phase ZrO_2. Such re-
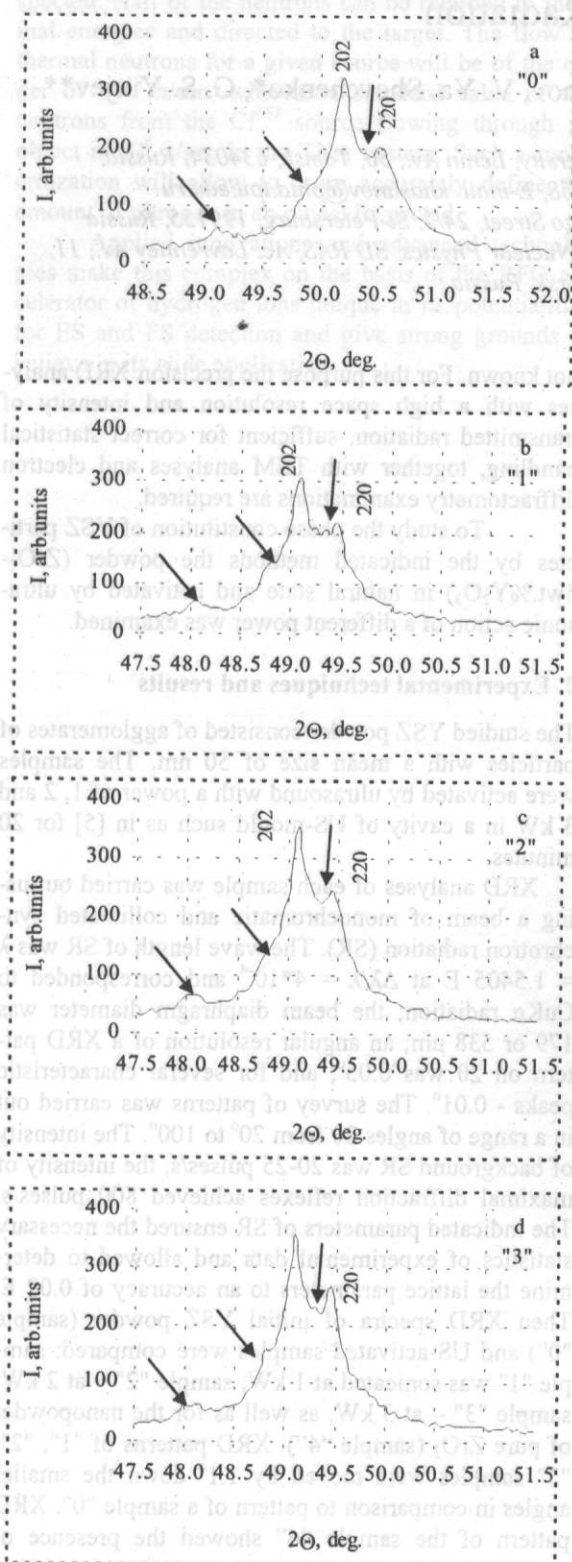

Fig.1. The evolution of peaks 202 and 220 depending on a power of US-action: a – sample "0"; b –sample"1"; c – sample "2"; d – sample "3".

flexes are evidence of metastable intermediate phases with closely spaced lattice parameters. The hkl line positions (space group $P4_2/nmc$) in XRD patterns of samples ""0", "1", "2, "3 and corresponding lattice spacing d calculated by Bragg law are shown in Table 1. The lattice parameters a, c of the studied samples obtained from the known equations for tetragonal syngony as well as the ratio of tetragonal distortion c/a are presented in Table 2.

Each sample was also examined by TEM and electron diffractometry techniques using the microscopes EM-125, JSM-820 JEOL. By the procedure [6] the powders were placed on a coal replica located on copper cross-line screen. For electron diffractometry analyses the separate polycrystalline plates – flakes with a mean size of not less 1 x 1 µm were chosen.

The YSZ powder, synthesized by plasma-chemical method, consists of many such polycrystalline plates. Depending on a size of plates, the sizes of crystallites, of which the plates consist, vary in the range from 6 to 150 nm; thus the size of crystallites in each plate varies insignificantly [6 - 8]. In TEM photomicrographs separated nanoparticles were selected, in which the mean size of crystallites, determined from sampling of 600-800 measurements, was $< d_p > 6$; 9; 14; 21; 25; 35; 38; 45 and 53 nm. For each of indicated $< d_p > 5$ - 8 particles were studied. In all the analyzed cases the histograms of crystallite distribution on sizes were single-modal with clearly defined maximum; the standard deviation practically did not exceed $0.5 < d_p >$.
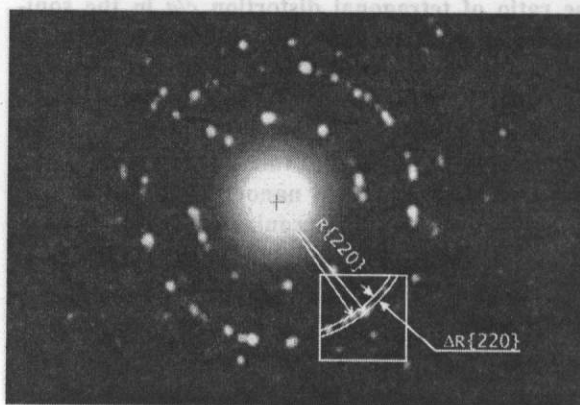

Fig.2. The electron diffraction micrographs of selected YSZ polycrystalline plates.

In the electron diffraction micrographs of selected polycrystalline plates with the known $<d_p>$ we determined radial deviation of the diffraction spots (reflexes) ΔR from a value R, which was determined from tabulated data (ASTM) for a ring {220} of tetragonal phase ZrO_2 (Fig. 2). We took into account the known relation between ΔR (hkl) and broadening of a diffraction angle $\Delta\theta$: $\Delta\theta \sim \Delta R(hkl)/2L$, where L is a length of the diffraction chamber of the electron microscope. A value $\Delta R(hkl)$ was determined using the comparator "Iza-2". On electron diffraction mi-

crographs we measured the distance between centres of closely spaced reflexes belonging to a ring {220} along radius of this diffraction ring. This ring is rather far from centre of an electron diffraction pattern, that increased an absolute value ΔR, and its intensity is comparable to intensity of the brightest diffraction ring {111} of cubic and tetragonal phases of ZrO_2. The micrometer motion of the comparator ensured an measurement error of ±0.0005 cm. The dependencies
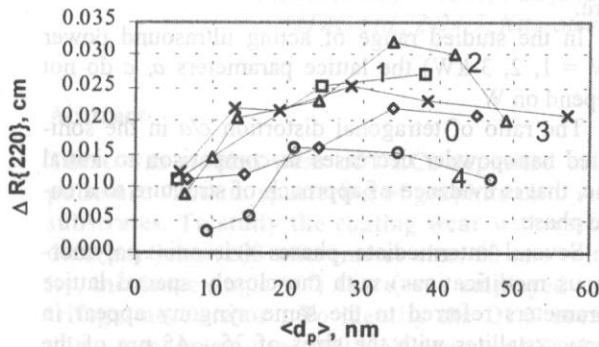

Fig.3. The dependences $\Delta R\{220\}$ versus $<d_p>$ for samples "0", "1", "2", "3", "4".

$\Delta R\{220\}$ versus $<d_p>$ are presented in Fig. 3.

3. Discussion

XRD data show, that US-action on YSZ powder results in increase of the parameters of a tetragonal lattice a from 5.05 to 5.15Å, c from 5.21 to 5.29Å in comparison with the initial powder, but the dependencies of these parameters on ultrasound power in the studied range of W do not appear. The ratio of tetragonal distortion of a lattice c/a after US-action decreases (Tables 1, 2). The obtained results point to the US-activation of YSZ nanopowder brings about the formation and stabilisation of high-temperature modification of a tetragonal phase ZrO_2 at room temperature. This modification is found at heating pure ZrO_2 above 1100°C [9] and its $a = 5.14 \div 5.22$Å; $c = 5.26 \div 5.33$Å in comparison to the parameters of low-temperature modification with $a = 5.08$ Å; $c = 5.22$ Å. The US-activation also results in decrease of tetragonal distortion ratio of the lattice, it means its approach to the cubic phase.

The XRD patterns parameters, lattice spacing d for samples "0", "1", "2", "3" (space group P4$_2$/nmc)   *Table 1.*

hkl	2θ, °				d, Е			
	"0"	"1"	"2"	"3"	"0"	"1"	"2"	"3"
101	30.15	29.05	29.05	29.05	2.96	3.07	3.07	3.07
002	34.10	33.55	33.55	33.55	2.63	2.67	2.67	2.67
110	35.15	34.05	34.05	34.05	2.55	2.63	2.63	2.63
112	50.20	49.10	49.10	49.10	1.82	1.85	1.85	1.85
200	50.50	49.45	49.45	49.45	1.81	1.84	1.84	1.84
103	59.35	58.25	58.25	58.25	1.56	1.58	1.58	1.58
211	60.00	58.90	58.90	58.90	1.54	1.57	1.57	1.57
202	62.75	61.65	61.65	61.65	1.48	1.50	1.50	1.50
004	73.15	72.05	72.00	72.05	1.29	1.31	1.31	1.31
220	74.30	73.20	73.20	73.20	1.28	1.29	1.29	1.29
213	81.65	80.60	80.55	80.55	1.18	1.19	1.19	1.19
301	82.25	81.15	81.10	81.15	1.17	1.18	1.18	1.18
114	83.80	82.70	82.65	82.70	1.15	1.17	1.17	1.17
222	84.65	83.55	83.65	83.55	1.14	1.16	1.16	1.16
310	84.80	83.85	83.85	83.85	1.14	1.15	1.15	1.15
204	94.25	93.15	93.15	93.20	1.05	1.06	1.06	1.06
312	95.15	94.00	94.05	94.05	1.04	1.05	1.05	1.05

The lattice parameters c, a, ratio of tetragonal distortion c/a *Table 2.*

Samples	"0"	"1"	"2"	"3"
Lattice Parameters c; a (for space group F), ч	5.21; 5.05	5.29; 5.15	5.29; 5.15	5.29; 5.15
Tetragonal distortion c/a (for space group F)	1.032	1.027	1.027	1.027

It is known, that the high-temperature phases of tetragonal syngony are stabilized in zirconia at room temperature, if the crystallite size does not exceed the critical value (less than 200 nm) [10 - 12]. Then our result can be explained by decrease of crystallite sizes in YSZ particles after US-action. This supposition is also confirmed by following facts.

The evolution of a peak (200) in XRD patterns of the samples "0", "1", "2", "3" (Fig.1) reflects the sensitivity of intermediate metastable phases to the power

of US-action: at W = 2 kW the peak (200) broadens out, and the presence of metastable phases is less pronounced. At W = 1 and 3 kW, on the contrary, the peak (200) becomes more narrow, but the reflexes of metastable phases appear.

This result correlates with the data obtained from the electron diffraction patterns (Fig.3): at W = 2 kW the value of the broadening ΔR of a ring {220} for the crystallites with $<d_p>$ = 34 and 43 nm is maximum, and at others $<d_p>$ it is close to the values of ΔR {220} for the samples "1", "3".

Broadening of the diffraction rings ΔR can be connected with the following reasons: 1) dimension factor; 2) elastic stress fields acting along the interfaces of the crystallites; 3) inhomogeneity of crystallite chemical composition; 4) tetragonal distortions of a crystalline lattice of zirconia cubic phase; 5) presence of several phases in a crystallite, which are polymorphous modifications of a crystalline lattice referred to the same syngony.

On the data of Fig.3 the dimension factor (dependence $\Delta R\{220\}$ on $< d_p >$) is most pronounced for US-activated samples "1", "2", "3". However, the low values of $\Delta R\{220\}$ at low $< d_p >$ (5, 10 nm) for all the samples show, that the dimension factor is not predominate.

Nonmonotonic behaviour of the indicated dependencies and TEM data are evidence of the influence of intercrystallite elastic stresses at US-action. In the initial samples "0", "4" the cracks in the plates with a crystallite size $<d_p>$ = 80-100 nm were observed, whereas for US-activated powders the cracks were observed in the plates with $<d_p>$ = 40-50 nm. But in this range the dependencies $\Delta R(<d_p>)$ for the samples "2", "3" tend to lowering, i.e. the mechanism of intercrystallite elastic stresses relaxation by the cracking under ultrasound action is also not the main one.

According to tabulated ASTM data the inhomogeneity of chemical composition in YSZ nanocrystallites on yttrium can give the contribution in $\Delta R\{220\}$ at a level of 0.011 cm, and the influence of tetragonal distortions of a cubic lattice - at a level of 0.013 cm. In this connection the dependence $\Delta R(<d_p>)$ for polycrystals of the sample "4", which have corresponding electron diffraction pattern, can be satisfactorily explained by the influence of tetragonal distortions. Alloyage of ZrO_2 by yttrium (the curve "0") results in increasing value ΔR, it can be explained by the indicated inhomogeneity of chemical composition for YSZ nanocrystallites on yttrium.

From all the examined samples the maximum value of broadening the position of reflexes ΔR on a ring {220} is observed for the sonicated YSZ nanopowder with the crystallites $<d_p>$ = 25 - 45 nm. As the mechanisms discussed above do not explain such increasing ΔR, we suppose, that the reason of blurring the electron diffraction ring {220}, as well as appearances of additional reflexes in a vicinity of the peak (220) for US-activated samples in XRD patterns, can

be the presence of several phases in the crystallites with the sizes of 25 - 45 nm. Such metastable phases are polymorphous modifications with closely spaced parameters of a crystal lattice referred to one syngony.

4. Conclusions

1. US-activation of YSZ nanopowder results in formation and stabilisation of high-temperature modification of tetragonal phase of ZrO_2 at room temperature.
2. In the studied range of acting ultrasound power (W = 1, 2, 3 kW) the lattice parameters *a, c* do not depend on W.
3. The ratio of tetragonal distortion *c/a* in the sonicated nanopowder decreases in comparison to initial one, that is evidence of approach of structure to a cubic phase.
4. Several intermediate phases (zirconia polymorphous modifications) with the closely spaced lattice parameters referred to the same syngony appear in nanocrystallites with the sizes of 25 - 45 nm of the sonicated YSZ nanopowder.

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