Study of the structure of mixed Zr-Y-O and Zr-Y-Mg-O oxides by XRD and XAFS methods

E M Moroz¹*, D A Zyuzin¹, V V Kriventsov¹, A L Udovsky² and I S Saenko²

¹Boreskov Institute of Catalysis SB RAS, Lavrentiev Ave. 5, Novosibirsk, Russia
²Baikov Institute of Metallurgy and Materials Science RAS, Leninsky prospect, 49, 119991 Moscow, Russia

*emoroz@catalysis.ru

Abstract. A comparative study was carried out of the structure of samples of zirconium oxides modified by yttrium and magnesium, synthesized by coprecipitation and calcined during 10 days at a temperature of 1250 °C. Refinement of the structure of the samples according to diffraction data within the framework of the fluorite type, gives high uncertainty factors, regardless of composition, and variation of structural parameters does not reduce their value. EXAFS analysis of the local structure of the samples revealed separate clusters consisting only of yttrium and oxygen ions in the structure of both samples. It has been suggested that the presence of these clusters prevents refinement of structures using the model of statistical solid solution with a fluorite structure.

1. Introduction

It was proposed to strengthen ferritic steels with coherent dispersed oxide particles of a fluorite structure [1]. Zirconia with a fluorite-type structure satisfy this condition. However, according to the phase diagram, this structure is only stable in the temperature range 2370-2680 °C, which is unacceptable for ferritic steels. To stabilize ZrO₂ in the cubic form in a lower temperature range, it is necessary to create structural vacancies in the oxygen sublattice, for example, by replacing Zr⁴⁺ ions with ions of lower valency (Mg²⁺, Ca²⁺, Y³⁺, etc.). The crystalline and real structures of mixed oxide powders of the composition 0.82ZrO₂ • 0.18Y₂O₃ (Z18Y) were studied by X-ray diffraction and Raman spectroscopy [2]. The fluorite phase was shown to be stable from the solidus temperature to ~600 °C. However, the stabilization of the fluorite phase of ZrO₂ oxide by lower valence ions has not been sufficiently studied. In this work a comparative study of the structural features of oxides was carried out, for which samples were synthesized by coprecipitation with the following compositions: 82% ZrO₂ + 18% Y₂O₃ (Z18Y) and 86.5% ZrO₂ + 9% Y₂O₃ + 4.5% MgO (ZYM).

2. Research methods

X-ray diffraction studies of the samples were carried out on an ARL X’TRA powder diffractometer using CuKα doublet radiation by the scanning points method, in the range of angles 5–105 ° (2θ) with a step of 0.05 °, and accumulation at a point of 5 s. The parameters of the unit cells were determined
using the X’Pert HighScore Plus computer program, and the crystal structure parameters were refined using the Topaz program. The structure of the samples was refined by the Rietveld method after preliminary subtraction of diffuse scattering in the diffraction pattern of each sample. Several refinement steps have been taken. At the first stage, the occupations and temperature factors of atoms were specified, while cations and anions were in “fluorite” positions; at the second stage, an additional oxygen position was introduced with initial coordinates (0.3, 0.3, 0.3); and at the third stage, zirconium and magnesium cations were transferred to general positions and their coordinates were specified. At the fourth stage, the coordinates of oxygen atoms in general positions were refined.

The EXAFS spectra of the Y-K, Zr-K edges for all the studied samples were obtained at the EXAFS Station of Siberian Synchrotron and Terahertz Radiation Centre (SSTRC). The storage ring VEPP-3 with the electron beam energy of 2 GeV and the average stored current of 90 mA has been used as a source of radiation. The X-ray energy was monitored with a channel cut Si(111) monochromator. All EXAFS spectra were recorded under transmission mode with the steps ~1.5 eV. The EXAFS spectra were treated using the standard procedures [3-5]. The background was removed by extrapolating the preedge region on to the EXAFS region in the forms of polynomials. Three cubic splines were used to construct the smooth part of the absorption coefficient. The inflection point of the edge of the X-ray absorption spectrum was used as initial point (k = 0) of the EXAFS spectrum. The radial distribution of the atoms (RDFs) functions were calculated from the EXAFS spectra in k^3 by using Fourier transform modulus in the wave number interval of 3.0-12.0 Å⁻¹.

3. Results and discussion
The chemical composition of the synthesized samples was determined by mass spectrometry. Table 1 presents the estimated and measured data on the chemical composition of the samples.

| Sample | Chemical composition | Estimated by synthesis | According to mass spectroscopy (Germany) | Unit cell parameter, Å |
|--------|----------------------|------------------------|------------------------------------------|------------------------|
| Z18Y   | Zr0.695Y0.305O1.848□0.152 | Zr0.712Y0.287O1.856□0.1439 | 5.159                                    |
| ZYM    | Zr0.793Y0.1651Mg0.0413O1.876□0.1238 | Zr0.8075Y0.1526Mg0.0396O1.883□0.1162 | 5.134                                    |

Figure 1 shows the diffraction patterns of the studied samples at different scales. It is seen that the diffraction patterns contain only peaks belonging to the phases of solid solutions based on zirconium dioxide with a fluorite-type structure with space group Fm3m. At the same time, one can note the broadening of the bases of the 111 peaks and diffuse scattering in the region of 40-70° (2θ) (top insert).

Table 2 presents the results of the first refinement stage of specifying the structure of the samples. Very high temperature factors for zirconium, magnesium and oxygen were registered, which is especially surprising for samples that have undergone prolonged calcination. This may be due to the fact that oxygen and zirconium should occupy common rather than own positions. In addition, there is also a low occupancy of the oxygen position (from the chemical composition, the occupancy of oxygen positions, according to the formula, should be 0.928 for Z18Y and 0.942 for ZYM) and high inconsistency factors.

The data on the second stage of refinement are shown in Table 3. As mentioned above, at the second stage, an additional oxygen position was introduced with the initial coordinates (0.3, 0.3, 0.3).
The table shows that the introduction of an additional oxygen position slightly affected the uncertainty factors (Rwp) and led to an excess of oxygen as compared to the calculated one.

At the third refinement stage (Table 4), zirconium and magnesium cations were transferred to common positions and their coordinates were specified. The transfer of zirconium cations to common positions led to a significant decrease in temperature factors, but the original chemical composition was at the same time disturbed.

![Figure 1. Diffraction patterns of samples.](image)

At the fourth stage (Table 5), oxygen atoms were transferred to common positions and their coordinates were specified. This led to a decrease in the oxygen temperature factors, however, the decrease of the Rwp factors was insignificant. In the resulting chemical composition, a significant excess of the amount of oxygen and magnesium is noticeable.

### Table 2. First stage of refinement.

| Atom grade | Multiplicity of position | Coordinates | Position occupied | Temperature factor |
|------------|--------------------------|-------------|-------------------|--------------------|
|            |                          | x           | y     | z    |                |                  |
| Z18Y       |                          |             |       |      |                |                  |
| Z          | 4                        | 0           | 0     | 0    | 0.7073         | 3.7              |
| Y          | 4                        | 0           | 0     | 0    | 0.2927         | 0.48             |
| O          | 8                        | 1/4         | 1/4   | 1/4  | 0.835          | 3.1              |
| Rwp = 9.512% |                             |             |       |      |                |                  |
| ZYM        |                          |             |       |      |                |                  |
| Z          | 4                        | 0           | 0     | 0    | 0.8053         | 2.75             |
| Y          | 4                        | 0           | 0     | 0    | 0.1527         | 1.91             |
| Mg         | 4                        | 0           | 0     | 0    | 0.0399         | 4.95             |
| O          | 8                        | 1/4         | 1/4   | 1/4  | 0.8141         | 3.26             |
| Rwp = 11.8% |                             |             |       |      |                |                  |
**Table 3. Second stage of refinement.**

| Atom | Grade | Multiplicity of position | Coordinates | Position occupied | Temperature factor |
|------|-------|--------------------------|-------------|------------------|-------------------|
| Zr   | 4     | 0                        | 0           | 0                | 0.7073            |
| Y    | 4     | 0                        | 0           | 0                | 0.2927            |
| O    | 8     | 1/4                      | 1/4         | 1/4              | 0.8671            |
| O1   | 96    | 0.2025                   | 0.0752      | 0.0752           | 0.0087            |

Rwp = 9.314%

**ZYM**

| Atom | Grade | Multiplicity of position | Coordinates | Position occupied | Temperature factor |
|------|-------|--------------------------|-------------|------------------|-------------------|
| Zr   | 4     | 0                        | 0           | 0                | 0.791             |
| Y    | 4     | 0                        | 0           | 0                | 0.159             |
| Mg   | 4     | 0                        | 0           | 0                | 0.04              |
| O    | 8     | 1/4                      | 1/4         | 1/4              | 0.852             |
| O1   | 192   | 0.003                    | 0.14        | 0.191            | 0.0089            |

Rwp = 9.34%

* there is a tendency to zero, if you do not put a limit

**Table 4. Third stage of refinement.**

| Atom | Grade | Multiplicity of position | Coordinates | Position occupied | Temperature factor |
|------|-------|--------------------------|-------------|------------------|-------------------|
| Zr   | 192   | 0.0495                   | -0.0003     | 0.0015           | 0.0148            |
| Y    | 4     | 0                        | 0           | 0                | 0.3               |
| O    | 8     | 1/4                      | 1/4         | 1/4              | 0.88              |
| O1   | 96    | 0.198                    | 0.081       | 0.081            | 0.0097            |

Rwp = 9.268%

**ZYM**

| Atom | Grade | Multiplicity of position | Coordinates | Position occupied | Temperature factor |
|------|-------|--------------------------|-------------|------------------|-------------------|
| Zr   | 96    | 0.0234                   | 0.126       | 0.0234           | 0.0329            |
| Y    | 4     | 0                        | 0           | 0                | 0.159             |
| Mg   | 96    | 0.0263                   | 0.0004      | 0.0263           | 0.0015            |
| O    | 8     | 1/4                      | 1/4         | 1/4              | 0.852             |
| O1   | 192   | 0.003                    | 0.14        | 0.191            | 0.0089            |

Rwp = 11.315%

* there is a tendency to zero, if you do not put a limit

The calculations show that the Rwp factor is apparently determined not by possibility of clarifying the structural characteristics within the framework of the fluorite structure, but by other properties of the materials, for example, their real structure: the presence of stresses at the grain boundaries and changes of the their structural characteristics.

Local structure information was obtained by EXAFS method. The RDFs curves, which are the functions of the radial distribution of atoms of the local Zr arrangement (obtained from EXAFS spectra), are shown for samples Z18Y, ZYM on Figure 2 (1, 2), and the RDFs curves (RDFs) of the local arrangement Y are shown on Figure 2 (3, 4). The radial atomic distributions for both samples have a number of characteristic features: 1) the first coordination spheres (CS) of the Me-O and Me-Me types are clearly defined, and long-range coordination spheres located further than ~ 0.45 nm are practically not observed, which can indicate long-range distortions in the structures; 2) the local
arrangement of yttrium is stable when the composition of the samples changes, which may indicate the formation of clusters that include only Y and O; 3) the local arrangement of zirconium depends on the composition of the samples, since differences are observed in the RDFs curves. Thus, the amplitudes of the peaks assigned to the Zr-O and Zr-Me coordination spheres are significantly (more than 25%) reduced for the ZYM sample in comparison with those for the Z18Y sample, which indicates large distortions of the initial fluorite structure of the ZYM sample. The observed changes in the Zr-O and Zr-Me distances (by more than 0.05 Å) are larger than the changes due to the differences in the cell parameters of the samples compared (see Table 1). The fitting method within the fluorite structure does not give satisfactory results.

| Table 5. Fourth stage of refinement. |
|-------------------------------------|
| Atom  | Multiplicity of position | Coordinates | Position occupied | Temperature factor |
|-------|--------------------------|-------------|-------------------|--------------------|
| Z18Y  |                          |             |                   |                    |
| Zr    | 192                      | 0.0495      | -0.0003           | 0.0015             | 0.0148             | 1.13                |
| Y     | 4                        | 0           | 0                 | 0                  | 0.2993             | 0.95                |
| O     | 192                      | 0.215       | 0.285             | 0.215              | 0.036              | 0.4→0*              |
| O1    | 96                       | 0.195       | 0.085             | 0.085              | 0.0258             | 0.4→0*              |
|       |                         | Zr0.71Y0.3O2.35 | Rwp = 9.138%       |                    |
| ZYM   |                          |             |                   |                    |
| Zr    | 96                       | 0.025       | 0.00015           | 0.025              | 0.0328             | 1.8                 |
| Y     | 4                        | 0           | 0                 | 0                  | 0.16               | 1.91                |
| Mg    | 96                       | 0.0051      | 0.184             | 0.0051             | 0.0018             | 0.4→0*              |
| O     | 96                       | 0.22        | 0.28              | 0.22               | 0.0724             | 1.94                |
| O1    | 192                      | 0.003       | 0.14              | 0.191              | 0.0175             | 0.4→0*              |
|       |                         | Rwp = 11.21% |                   |                    |

* there is a tendency to zero, if you do not put a limit.

Figure 2. RDFs curves - functions of the radial distribution of atoms of the local arrangement concerning to zirconium and yttrium of the samples studied: (Zr-K) 1. Z18Y, 2. ZYM; (Zr-K) 3. Z18Y, 4. ZYM.
4. Conclusion
A feature of X-ray diffraction from samples of mixed zirconium oxides modified with yttrium and magnesium ions was revealed as consisting in anomalous broadening of the peaks and diffuse scattering in the region of 40-70° (2Θ).

Using two well-known structural methods - the method of full-profile analysis and EXAFS spectroscopy within the model of the fluorite type of structure, an attempt was made to refine the structure of the samples. Clarification of the structure of samples using both methods yields high uncertainty factors. The reason for this, apparently, is the non-phase (few phases) state of the samples, which, in particular, is indicated by the diffraction anomalies and, according to EXAFS, the possible formation in the structure of clusters containing only Y and O.

For further study of the structure of the samples, it is necessary to use other physical methods, in particular, such as high resolution electron microscopy and the XPS method.

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