Solid-phase interaction in ZrO$_2$–Fe$_2$O$_3$ nanocrystalline system

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Based on the results of X-ray phase analysis and Mössbauer spectroscopy, it was demonstrated that in the ZrO$_2$–Fe$_2$O$_3$ system, represented by the mechanical mixture of $m$–ZrO$_2$ (14 ± 2 nm) and $\alpha$-Fe$_2$O$_3$ (43 ± 2 nm) nanoparticles, being heated above the temperature corresponding to the melting temperature of the two-dimensional nonautonomous phase, transformation of $\alpha$-Fe$_2$O$_3$ occurs resulting in appearing of the X-ray amorphous magnetically disordered state localized on the surface of ZrO$_2$ nanoparticles in the form of a thin layer. Transformation pattern in ZrO$_2$–Fe$_2$O$_3$ nanocrystalline system has been introduced.

Keywords: nanostructures, iron-zirconia, surface, X-ray diffraction, Mössbauer spectroscopy.

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1. Introduction

Interest in systems containing zirconium dioxide is caused by high refractory properties, strength, crack resistance, chemical inertness, superionic oxygen conductivity, biocompatibility, catalytic activity and other important characteristics of the materials, based on this substance [1, 2]. Ceramic and composite materials, based on ZrO$_2$–Fe$_2$O$_3$ system, are widely used as catalysts or catalyst carriers for hydrocarbons isomerization, carbon monoxide hydrogenization, selective hydrogenation (Fischer–Tropsch reaction) and ammonia synthesis [3, 4], as well as the magnetic materials [5, 6].

Different contradictory data, published in the scientific literature, are pertinent to possibilities and ranges of solid solutions formation in ZrO$_2$–Fe$_2$O$_3$ system. The study of phase formation processes in the considered system is connected with definite methodological difficulties, related to the behavior of the studied system components [7–16].

While extremely localized areas of the iron oxide-based solid solutions in zirconium dioxide may exist for the macroscopic particles, as it follows from data [17–26] (which is most pronounced for the low-temperature range), more wide solubility range of iron oxide in ZrO$_2$-based nanocrystals was detected, which is shown by data [27–36], in case of nano-scale particles. In this case, the possibility and the ranges of solid solutions existence in this system to a great degree are determined by the synthesis method of considered compositions.

Composition synthesis and subsequent study of their behavior during heating for ZrO$_2$–Fe$_2$O$_3$ system are generally realized with application of sol-gel synthesis followed by the annealing-quenching heat treatment of received precursors [16, 22–24, 31–33]; hydrothermal synthesis [5]; thermal decomposition of iron (III) and zirconium salts [27]; ZrO$_2$ impregnating with aqueous solution of ferric (III) nitrate and subsequent drying and incineration [3, 4]; solid-phase synthesis method [25, 37]; reaction media burning method (solid-phase flame method, solution burning) [26, 38, 39], etc. [6, 34–36].

Inconsistencies pertinent to ranges of solid solutions areas, a state of ZrO$_2$ surface and iron ions location in different positions still exist and may be found almost in any new paper devoted to this system. Therefore, it is of interest to study the behavior of ZrO$_2$ and Fe$_2$O$_3$ nano-scale particles during their thermal treatment.

2. Experimental procedures

In order to study the solid-phase interaction of the components, ZrO$_2$ and Fe$_2$O$_3$ nano-scale powders, which have been obtained by hydrothermal treatment method (refer to [40]), were mixed in ethyl alcohol. Specimens were formed by pressing under pressure of 5 MPa, after which these specimens were heat treated in the air following the annealing-quenching mode with exposure during 30 minutes at temperatures of 800, 900, 1000 and 1100 °C.

The phase composition of the specimens was studied by X-ray phase analysis using XRD-7000 Shimadzu diffractometer (CuK$_\alpha$-radiation). The X-ray diffraction pattern peak identification was performed using the PDWin 4.0 software solution and Crystallographica Search-Match package. Based on the data analysis pertinent to X-ray
diffraction pattern peak tailing, the average crystalline particle size has been calculated. Calculation was performed using the Sherrer equation [41].

The specimens’ elemental composition was determined by electron probe microanalysis using Hitachi S-570 scanning electron microscope, equipped with Bruker Quantax 200 microprobe system.

Exposure of Mössbauer spectra was realized using WISSEL spectrometer operating in the constant acceleration mode, at the room temperature and at the liquid nitrogen boiling point. $^{57}$Co in Rh-matrix, characterized by the radioactivity of 30 mC, was used as the source. Mathematical treatment of the experimental spectra was performed using the MOSSFIT software package [42]. The spectrometer velocity scale was calibrated using $\alpha$-Fe foil at the room temperature. The chemical shift values were presented relative $\alpha$-Fe.

3. Results and their discussion

Results of X-ray phase analysis of specimens, containing $6.4 \pm 0.3$ and $9.0 \pm 0.6$ mol.% FeO$_{1.5}$, which have been annealed at a temperature of 800, 900, 1000 and 1100 °C over 30 minutes, are presented in Figs. 1(a) and 2(a). The specimens were represented by the mechanical mixture of preliminary received nano-scale powders of ZrO$_2$ (monoclinic and tetragonal modification groups) and Fe$_2$O$_3$ [hematite, (104) peak, $I = 100 \%$]. After heating at a temperature of 800 – 900 °C, a decrease in the intensity of the $t$-ZrO$_2$ peaks was observed, and after heating at a temperature above 900 °C, diffractograms contained only those reflections, which corresponded to monoclinic modification group of ZrO$_2$. For the specimen containing $6.4 \pm 0.3$ mol.% FeO$_{1.5}$, which was annealed at 800 and 900 °C, a peak on diffractograms, corresponding to $\alpha$-Fe$_2$O$_3$, disappeared. During further increase of the thermal treatment temperature, (104) peak on diffractograms appeared again, however, its intensity was substantially less as compared with the initial composition. For the specimen, containing $9.0 \pm 0.6$ mol.% FeO$_{1.5}$, which has been annealed at a temperature of 800 – 900 °C, the relative intensity of (104) peak on diffractograms decreased as compared with the initial composition, while at a temperature of 1000 – 1100 °C the integral intensity of this peak has increased, becoming comparable with the initial composition.

It should be noted that sizes of $m$-ZrO$_2$ crystallites during heating up to a temperature of 900 °C have changed only slightly for the specimen, containing $6.4 \pm 0.3$ mol.% FeO$_{1.5}$ (Fig. 3), as well as for the specimen, containing $9.0 \pm 0.6$ mol.% FeO$_{1.5}$. Analysis of $m$-ZrO$_2$ unit cell parameters dependence on temperature has demonstrated their invariability within the measurement accuracy (Fig. 4). Absence of variation of ZrO$_2$ unit cell parameters may be indicative of the fact that heat treatment during 30 minutes at a temperature of up to 1000 and 1100 °C did not result in $m$-ZrO$_2$-based solid solution formation.

Mössbauer spectra for initial compositions of specimens, containing $6.4 \pm 0.3$ and $9.0 \pm 0.6$ mol.% FeO$_{1.5}$, as well as for specimens, annealed at 800, 900, 1000 and 1100 °C, are presented in Figs. 1(b) and 2(b), respectively. The results of experimental spectra analysis with detection of sextet and doublet components, corresponding to iron atoms in magnetically ordered and magnetically disordered phases, are also presented in Figs. 1(b) and 2(b). Mössbauer parameters for sextet and doublet components of the iron-containing phases are presented in Table 1. The quantitative estimation of the iron relative content in different phases was performed with precision determined by difference in values of $f_M$, Mössbauer factor (probability of resonance absorption in each phase).

For the initial specimens, which were represented by the mechanical mixture of the preliminary produced $t$-, $m$-ZrO$_2$ and $\alpha$-Fe$_2$O$_3$ nano-scale powders, the Mössbauer spectrum was characterized by sextet, parameters of which have corresponded to the sextet parameters for $\alpha$-Fe$_2$O$_3$ [43].

For the specimens being thermally treated at 800 °C, the Mössbauer spectrum was characterized by doublet ($6.4 \pm 0.3$ mol.% FeO$_{1.5}$) or doublet and sextet superposition ($9.0 \pm 0.6$ mol.% FeO$_{1.5}$). It should be noted that for the specimen containing $6.4$ mol.% FeO$_{1.5}$ only doublet components have been commonly observed, while these doublet components are incidental to the atoms of iron in $3^+$ oxidation rate located in the form of thin layer on the surface of another oxide [44,45]. With a temperature increase, the sextet appeared again and the doublet share in experimental spectrum has decreased; at a temperature of 1100 °C a share of the magnetically disordered phase was about 23 %. Such an effect was observed in case of increasing of particles sizes [43]. For the specimen, containing 9.0 mol.% FeO$_{1.5}$, the sextet component is common for the whole heat treatment temperature range.

While comparing the data of X-ray phase analysis and Mössbauer spectroscopy, it may be concluded, that at a temperature of 800 °C, transformation of $\alpha$-Fe$_2$O$_3$ begins, which results in its transfer into X-ray amorphous magnetically disordered phase, localized on the surface of zirconium dioxide particles, as shown by the absence of (104) $\alpha$-Fe$_2$O$_3$ peak on the diffractogram, by sextet disappearance and doublet appearance in Mössbauer spectrum of the specimen, containing $6.4 \pm 0.3$ mol.% FeO$_{1.5}$. With increased thermal treatment temperatures, the sizes of $m$-ZrO$_2$ particles are increased (Fig. 3) that causes decrease of their surface area and, therefore, aggregation of the iron oxide surface layer, accompanied with $\alpha$-Fe$_2$O$_3$ bulk phase particles formation. Formation of $\alpha$-Fe$_2$O$_3$ particles is confirmed by the data of X-ray phase analysis and Mössbauer spectroscopy, i.e. (104) $\alpha$-Fe$_2$O$_3$ peak...
on the diffractogram appears again, in Mössbauer spectrum for the specimen, containing $6.4 \pm 0.3$ mol.% FeO$_{1.5}$, sextet corresponding to $\alpha$-Fe$_2$O$_3$, may be revealed against the doublet background.

Apparently, during thermal treatment at a temperature of 800 and 900 °C with exposure for 30 minutes, $\alpha$-Fe$_2$O$_3$ is transformed with the formation of the iron oxide layer on a surface of ZrO$_2$ nanoparticles. At temperatures of 800 – 900 °C, for $\alpha$-Fe$_2$O$_3$ are corresponding to the melting temperature of the surface (two-dimensional nonautonomous) phase [46]. It appears that transfer of the two-dimensional nonautonomous phase into a liquid (liquid-like) state initiates active mass transfer of the iron-containing component to a surface of ZrO$_2$ nanoparticles. It should be noted that similar processes were observed earlier in BeO–Fe$_2$O$_3$, MgO–Fe$_2$O$_3$, Al$_2$O$_3$–Fe$_2$O$_3$, SiO$_2$–Fe$_2$O$_3$ systems [44, 45]. The transformation pattern, corresponding to the described processes in ZrO$_2$–Fe$_2$O$_3$ system, in which zirconium dioxide is initially represented by $m$-ZrO$_2$ and by $\alpha$-Fe$_2$O$_3$ nanoparticles, characterized by the crystallites sizes of $14 \pm 2$ nm and $43 \pm 2$ nm, respectively, is presented in Fig. 5.

4. Conclusion

As distinct from the cases, in which compositions are received via codeposition, hydrothermal synthesis, etc., and in which mixing of components is initially possible at the atomic level, in the case of the solid-phase interaction of the nano-scale particles in ZrO$_2$–Fe$_2$O$_3$ system in the range of low contents of the iron-containing component increasing of the treatment temperature up to 800 – 900 °C does not cause stabilization of zirconium dioxide tetragonal modification and the formation of tetragonal solid solution, as well as Fe$^{3+}$ ions are not included into $m$-ZrO$_2$ structure.

During the thermal treatment of ZrO$_2$ and Fe$_2$O$_3$ nanoparticles, at definite critical value of temperature in range of 800 – 900 °C, $\alpha$-Fe$_2$O$_3$ transformation occurs with thin layer formation on $m$-ZrO$_2$ nanoparticles surface, i.e. formation of the composite nanoparticles of “nucleus ($m$-ZrO$_2$ nanoparticles) – shell (amorphous Fe$_2$O$_3$)” type takes place.
Fig. 2. X-ray diffractograms (a) and Mössbauer spectra series, measured at 25 °C (b) of the specimen, containing 9.0 ± 0.6 mol.% FeO$_{1.5}$, which has been annealed at a temperature of 800, 900, 1000 and 1100 °C during 30 minutes.

Fig. 3. $t$-ZrO$_2$ (■) and $m$-ZrO$_2$ (○) crystallites sizes dependence on the heat treatment temperature for the specimen, containing 6.4 ± 0.3 mol.% FeO$_{1.5}$. 
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FIG. 4. $m$-ZrO$_2$ unit cell parameters dependence on the heat treatment temperature for the specimen, containing 6.4 ± 0.3 mol.% FeO$_{1.5}$

**TABLE 1. Mössbauer parameters of spectra, measured for the studied specimens at a temperature of 25 °C**

| FeO$_{1.5}$ content, mol.% | Annealing temperature, °C | Parameters of Mössbauer spectra | Paramagnetic component content, % |
|---------------------------|---------------------------|---------------------------------|----------------------------------|
|                           |                           | sextet                          | doublet                          |
|                           |                           | Isomer shift, mm/s              | Quadrupole splitting, mm/s       | Effective field, $T$              | Isomer shift, mm/s | Quadrupole splitting, mm/s |
| 6.4±0.3                   | –                         | 0.378±0.013                     | 0.218±0.026                     | 50.871±0.099                     | –                 | –                           | 0 |
|                           | 800                       | –                               | –                               | 0.326±0.000                      | 1.032±0.000         | 100                          |
|                           | 900                       | 0.375±0.018                     | 0.221±0.037                     | 51.734±0.122                     | 0.331±0.000         | 1.092±0.011                  | 84.85 |
|                           | 1000                      | 0.376±0.005                     | 0.188±0.010                     | 51.693±0.038                     | 0.340±0.014         | 1.152±0.029                  | 41.51 |
|                           | 1100                      | 0.376±0.004                     | 0.185±0.007                     | 51.594±0.028                     | 0.337±0.021         | 1.123±0.042                  | 22.62 |
| 9.0±0.6                   | –                         | 0.357±0.005                     | 0.228±0.010                     | 50.905±0.040                     | –                 | –                           | 0 |
|                           | 800                       | 0.383±0.016                     | 0.192±0.033                     | 51.458±0.136                     | 0.324±0.042         | 1.128±0.080                  | 52.54 |
|                           | 900                       | 0.374±0.008                     | 0.240±0.015                     | 51.984±0.060                     | 0.342±0.040         | 1.093±0.078                  | 35.01 |
|                           | 1000                      | 0.372±0.005                     | 0.193±0.009                     | 51.976±0.037                     | 0.203±0.077         | 1.292±0.169                  | 14.18 |
|                           | 1100                      | 0.373±0.006                     | 0.211±0.011                     | 51.938±0.044                     | 0.193±0.087         | 1.282±0.179                  | ∼ 5 |

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Fig. 5. Transformation pattern in ZrO2–Fe3O4 system
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