EFFECT OF IRON OXIDE ON STRUCTURE OF Y-STABILIZED ZIRCONIA CERAMIC

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Abstract: The aim of present work is the investigation of structural peculiarities of zirconium oxide stabilized by combined dopant depending on chemical composition, synthesis conditions and heat treatment. It has been shown that solubility of iron in zirconium oxide increases with yttrium content. Increasing Y/Fe ratio in zirconia ceramics doped with the same total amount of doping oxides stabilizes the structure and inhibits low-temperature degradation. Nonequivalent sites of iron (III) in precipitated samples have been identified. Decrease in coordination number of iron ions in comparison with that of host cations stabilizes the structure and inhibits its degradation due to the increase in Me-O binding energy. It has been found that precipitated powders are composed of nanoparticles with the size of 10-20 nm.

Keywords: Stabilized Zirconia/Solid State Fuel Cell/Thermal Stability/Combined Dopant/ Mössbauer Spectra/Easy-Breaking Aggregates

1. INTRODUCTION

Fully stabilized zirconium dioxide is widely used as oxygen conductor for solid state fuel cell. One of the basic requirements to this material is the thermal stability of the structure. The most effective stabilizer for zirconium oxide is yttrium oxide. However, the structure of yttrium-stabilized ZrO_2 is susceptible to low-temperature degradation, which is caused by tetragonal-monoclinic transformation [1]. Therefore, the search for new stabilizers and modification of them are a topical problem. The choice of iron oxide as the third component of the system ZrO_2-Y_2O_3-Fe_2O_3 is dictated both by steric factors and by the possibility to lower the crystallization and sintering temperatures of ZrO_2-based solid solutions.

N. Sammes et al. (eds.), Full Cell Technologies: State and Perspectives, 279-285.

The aim of the work is to investigate the structure features of zirconium dioxide stabilized by a complex dopant (Y_2O_3 and Fe_2O_3) as a function of the chemical composition, precipitation, heat treatment, and ageing conditions.

2. EXPERIMENTAL PROCEDURE

Samples for investigation were prepared by calcining $ZrO(OH)_2$-$Y(OH)_3$-FeOOH hydroxides precipitated from concentrated solutions of $ZrOCl_2$, $Y(NO_3)_3$, and $Fe(NO_3)_3$ with an ammonia solution by two methods: coprecipitation (CPH) and sequential precipitation (SPH). Using the SPH method, $Y(OH)_3$ was precipitated on coprecipitated $ZrO(OH)_2$ and FeOOH. Heat treatments were performed in a chamber furnace at 970-1470 K. Compositions corresponding to the formula $[1-(x+y)]ZrO_2 \cdot xY_2O_3 \cdot yFe_2O_3$, where x = 0, 0.01, 0.015, 0.02, 0.03 and x+y = 0.03 (***series I***); x = y = 0.02, 0.025, 0.03, 0.04 and x+y>0.03 (***series II***). The samples were investigated just after heat treatment and after storing them under atmospheric conditions for three years. The X-ray investigations were carried out on a DRON 4-07 diffractometer (Co K_α radiation). Mössbauer spectra of samples were recorded at room temperature on an electrodynamic spectrometer operating in the constant-acceleration mode with a ^{57}Co γ-quantum source in Rh matrix. The calibrations of the velocity scale in the magnetic and paramagnetic measurement ranges were performed by means of α-Fe and sodium nitroprusside respectively. The spectra were processed using the least-squares method. The micrographs were taken on a JEOL JEM 100 CX II electron microscope.

3. RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of the content of ***monoclinic*** (*m*) modification of the samples from series I for different hydroxide precipitation methods, and different *x*:*y* ratios in as-heat-treated samples and after storage for 3 years. The optimal stabilization of zirconium dioxide for the compositions under study is observed at the ratio Y_2O_3:Fe_2O_3=0.02:0.01. The degree of stabilization at this ratio is higher than for the samples in which only Y_2O_3 was used as stabilizer (curves 3, 4). In the temperature range 1170-1570 K there is practically no stabilization of the high-temperature both ***cubic*** (*c*) and ***tetragonal*** (*t*) modifications of ZrO_2 in the case of complete substitution of Fe_2O_3 for Y_2O_3 (curve 1). The stabilizing effect of Fe_2O_3 on the structure of ZrO_2 at the above temperatures manifests itself only when Fe_2O_3 is present together with Y_2O_3 (curves 2-4). Fe_2O_3 also has a wholesome effect on the phase stability of ZrO_2 in time. During storage, zirconium dioxide powders undergo the transformations $t\text{-ZrO}_2 \rightarrow m\text{-ZrO}_2$ [2]. The results given in Fig. 1 indicate that the process of low-temperature degradation of zirconium dioxide in the ternary system $0.97\text{ZrO}_2 \cdot x\text{Y}_2\text{O}_3 \cdot y\text{Fe}_2\text{O}_3$ (curves 3-3′) is slower than in the binary system $0.97\text{ZrO}_2\text{-}0.03\text{Y}_2\text{O}_3$ (curves 4-4′).

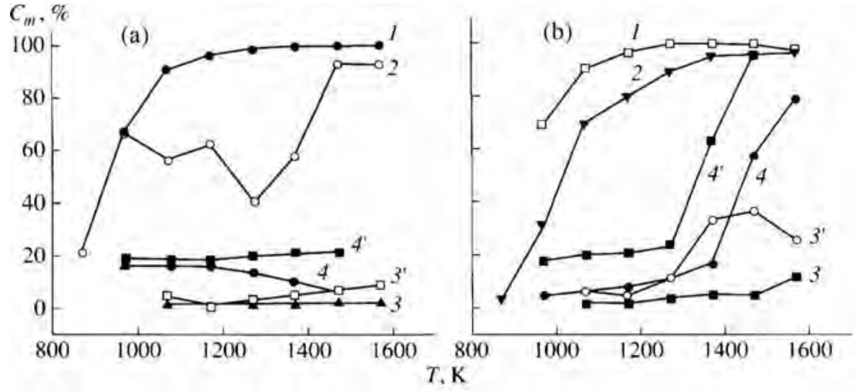


Figure 1. Content of monoclinic ZrO_2 modification (C_m) of $0.97ZrO_2 \cdot xY_2O_3 \cdot yFe_2O_3$ samples ($x+y = 0.03$) vs heat treatment temperature: (a) CPH, (b) SPH; $x = 0$ (1); 0.01 (2); 0.02 (3); 0.03 (4) - as-heat-treated samples; $x = 0.02$ (3′); 0.03 (4′) - after storage for 3 years.

Method of hydroxide precipitation affects greatly the degree of ZrO_2 stabilization, especially for samples after thermal treatment at $T > 1270$ K. SPH technique results in the much lower degree of ZrO_2 stabilization (Fig. 1b) as compared with CPH (Fig. 1a) for all $x : y$ ratios (curve 2-4) excepting ratio $x : y = 0.02 : 0.01$ (curve 3). Soft, readily destructible aggregates are formed after heat treatment of sequentially precipitated hydroxides (in contrast to coprecipitated hydroxides) [2]. This make it possible to produce fine ZrO_2 powders with a particle size of 10-20 nm (Fig. 2) without disaggregation and/or milling. Therefore, in the case of SPH it is very important to determine the composition of the powders, in which both the high stabilization degree and the friability are retained after heat treatment. The transformation $t\text{-ZrO}_2 \rightarrow m\text{-ZrO}_2$ during the ageing of the samples obtained by coprecipitation (Fig. 1a, curves *3*, *3*′ and *4, 4*′) is far slower than in the sequentially precipitated samples (Fig. 1b, curves *3*, *3*′ and *4, 4*′).

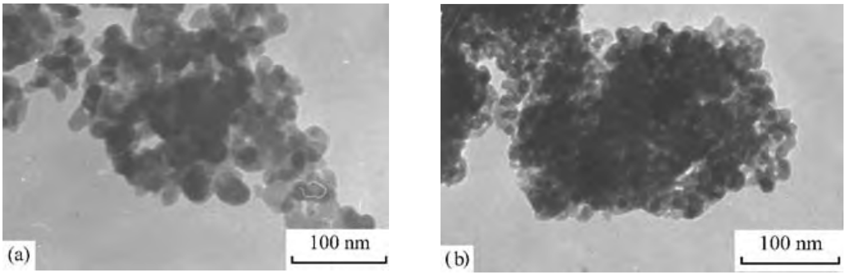


Figure 2. Micrographs of $Zr_{0.886}Y_{0.057}Fe_{0.057}O_{2-\delta}$ samples heat-treated at 870 K: (a) CPH, (b) SPH.

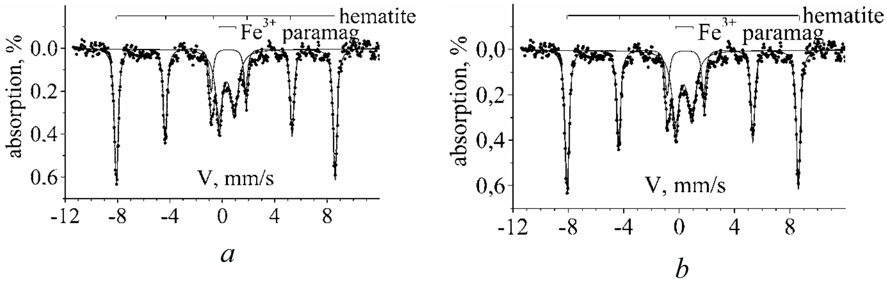
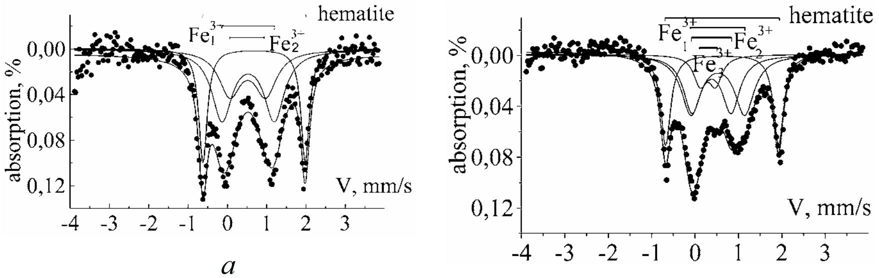


Figure 3. Mössbauer spectra of $Zr_{0.886}Y_{0.057}Fe_{0.057}O_{2-\delta}$ samples obtained in the magnetic measurement range: (a) CPH, (b) SPH.

Since for the composition $0.94ZrO_2 \cdot 0.03Y_2O_3 \cdot 0.03Fe_2O_3$ ($Zr_{0.886}Y_{0.057}Fe_{0.057}O_{2-\delta}$) complete stabilization of zirconium dioxide is observed at 1470 K for both methods of hydroxide precipitation (CPH and SPH), the above samples were chosen for the investigation of the local environment of Fe^{3+} ions by Mössbauer spectroscopy. X-ray investigations showed zirconium dioxide (CPH and SPH) to have a CaF_2-type structure with tetragonal distortion of lattice (space group P4/nmc (137)). The absence of other modifications (*c*-ZrO_2 and *m*-ZrO_2), evident from X-ray analysis, will make it possible to exclude the ambiguity of the interpretation of Mössbauer spectra.

The Mössbauer spectra of samples prepared by CPH and SPH, which were obtained in the magnetic range, are shown in Fig. 3. The spectra are represented by a superposition of a Zeeman splitting sextet and a quadrupole splitting doublet corresponding to high-spin Fe^{3+} ions in octahedral coordination [3]. The asymmetric character of absorption lines could be due to the presence of several nonequivalent sites of Fe^{3+} ions, whereas high values of absorption line full width at half-maxima (FWHM) could be ascribed to the inhomogeneity of the cation environment of Fe^{3+} ions.



a

b

Figure 4. Mössbauer spectra of $Zr_{0.886}Y_{0.057}Fe_{0.057}O_{2-\delta}$ *samples obtained in the paramagnetic measurement range: (a) CPH, (b) SPH.*

To reduce experimental errors and to explain the character of the asymmetry of the doublet lines, we examined spectra in the paramagnetic measurement range, in which the resolvability of spectra is over three times higher than that in the magnetic range. This allowed the precise determination of the components of the Fe^{3+} spectra (Fig. 4). The parameters of the resolved components are listed in the Table. The number of resolved doublets makes it possible to identify two and three nonequivalent sites of Fe^{3+} ions in the solid solutions $Zr_{0.886}Y_{0.057}Fe_{0.057}O_{2-\delta}$ obtained by CPH and SPH respectively. The Mössbauer spectra parameters of samples obtained by SPH do not practically change after storage for three years in air (Table, samples 2 and 2*). This denotes the absence or considerable suppression of the low-temperature degradation of the structure of stabilized zirconium dioxide in the ZrO_2-Y_2O_3-Fe_2O_3 system in comparison with the binary ZrO_2-Y_2O_3 system.

Table. Parameters of Mössbauer spectra of $Zr_{0.886}Y_{0.057}Fe_{0.057}O_{2-\delta}$ *samples obtained in the paramagnetic measurement range.*

Sample	Phase, ion	IS, mm/s	QS, mm/s	FWHM, mm/s	S, %	S_o, %
1 (CPH)	Hematite	0.76	2.60	0.27	30.5	72.5
	Fe_1^{3+}	0.64	1.33	0.54	42.0	16.6
	Fe_2^{3+}	0.63	0.84	0.53	27.5	10.9
2 (SPH)	Hematite	0.75	2.60	0.25	26.6	68.5
	Fe_1^{3+}	0.66	1.21	0.55	36.5	15.7
	Fe_2^{3+}	0.52	0.92	0.46	26.2	11.2
	Fe_3^{3+}	0.43	0.40	0.37	10.7	4.6
2^* (SPH, after three years)	Hematite	0.75	2.61	0.29	29.8	71.8
	Fe_1^{3+}	0.66	1.18	0.52	34.0	13.7
	Fe_2^{3+}	0.49	0.94	0.62	26.4	10.6
	Fe_3^{3+}	0.40	0.44	0.42	9.8	3.9

Note: H_{eff} = effective magnetic field; IS = isomer shift relative to α-Fe, QS = quadrupole splitting; FWHM = absorption line full width at half-maxima; S = relative area of component; S_o = areas of components reduced with respect to the six-line spectrum of hematite. IS's have been reduced with respect to sodium nitroprusside. Measurement error IS, QS and FWHM: ± 0.03 mm/s, S: ≤10 %.

When interpreting Mössbauer spectra, the value of quadrupole splitting (QS) can be used as a measure of the distortion of coordination polyhedra, and deviation of their symmetry from cubic symmetry. The value of isomer shift (IS) can be associated with the coordination of Fe^{3+} ions.

Taking into account the results of [4], where clusters were found using high-resolution electron microscopy, the presence of several doublets with different areas in the Mössbauer spectra of $Zr_{0.886}Y_{0.057}Fe_{0.057}O_{2-\delta}$ samples can be attributed to the cluster character of iron distribution in the solid solution ZrO_2-Y_2O_3-Fe_2O_3. The doublets due to Fe_1^{3+}, Fe_2^{3+}, Fe_3^{3+} can be attributed to the presence of Fe^{3+} sites with the coordination number of six (IS = 0.63–0.66; QS = 0.84–1.33), five (IS = 0.49 – 0.52; QS = 0.92–0.94) and four (IS = 0.40–0.43; QS = 0.40–0.43) respectively in $Zr_{0.886}Y_{0.057}Fe_{0.057}O_{2-\delta}$. It is evident that the change in the local environment of cations and Me–O bond energy corresponding to the decrease in the coordination number (CN) of Fe^{3+} ions as compared with that of Zr^{4+} in the basic structure (*c*, *t*-ZrO_2, CN 8; *m*-ZrO_2, CN 7) stabilizes high-temperature zirconium dioxide modifications and considerably suppresses (depending on the Zr/Y/Re ratio) low-temperature degradation of the structure.

4. CONCLUSION

The polymorphic composition of ZrO_2-based materials has been determined in the series of samples, which correspond to the formula $[1-(x+y)]ZrO_2 \cdot xY_2O_3 \cdot yFe_2O_3$, in the temperature range 620-1570 K. It has been found that at the same molar ratio ZrO_2 : doping oxides, the degree of ZrO_2 stabilization increases, and the low-temperature degradation process is suppressed by the partial substitution of Fe^{3+} for Y^{3+}. Nonequivalent sites of Fe^{3+} ions have been identified: two sites with octahedral coordination (CPH), and three sites with octa-, penta- and tetrahedral coordination (SPH). The possibility of cluster distribution of Fe^{3+} ions as well as the dependence of the number of vacancies on synthesis conditions have been shown.

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