

Soft Mechanochemical Synthesis of Dispersed Zirconium Titanate

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Abstract

An amorphous compound, obtained by mechanical activation of a mixture of hydrated zirconium and titanium dioxides, under annealing at 600 °C forms crystalline zirconium titanate. Similarity between the soft mechanochemical synthesis and sol-gel procedure for obtaining dispersed zirconium titanate is demonstrated.

INTRODUCTION

The diagram of state of the ZrO_2 - TiO_2 system reported in monograph [1] was later verified by the authors of [2] for the low-temperature region. The high-temperature α - $ZrTiO_4$ is composed of zirconium and titanium atoms surrounded octahedrally by oxygen [3]. Below 1125 °C, a low-temperature β -form exists, in which zirconium atoms are surrounded by seven or eight oxygen atoms [4]. Ordering of the high-temperature α - $ZrTiO_4$ is observed in zirconium-deficient zirconium titanate $Zr_5Ti_7O_{24}$ at high temperature, while at temperature below 1200 °C all $ZrTiO_4$ - $Zr_5Ti_7O_{24}$ compositions undergo continuous phase transitions with an increase in ordering of the distribution of titanium and zirconium atoms [5, 6].

As a rule, investigating the indicated systems one starts from the samples obtained by calcination of a mixture of crystalline zirconium and titanium dioxides. The authors of [7, 8] obtained zirconium titanate using organometallic compounds or by means of electrolysis of chlorides. In this case, the formation of X-ray amorphous hydrated zirconium titanate $ZrTiO_4 \cdot xH_2O$ occurred during the formation

of sol, while crystallization of the anhydrous $ZrTiO_4$ was observed at the temperature of 450–600 °C [9]. Similarity in the interaction of ultrafine hydrated particles when using the sol-gel method and soft mechanochemical synthesis was revealed by us in obtaining aluminium titanate [10]. The synthesis of zirconium titanate was performed using prolonged (up to 50 h) mechanical activation of an equimolar mixture of crystalline titanium and zirconium dioxides followed by high-temperature treatment (a severe method) [11]. Soft mechanochemical synthesis of obtaining complex oxides is more promising for precursors in ceramic industry [12].

The goal of the present work is investigation of the formation of zirconium titanate by means of soft mechanochemical synthesis and its comparison with the sol-gel procedure.

EXPERIMENTAL

Zirconium-titanium samples with $Zr/Ti = 1$ composition were prepared by mechanical activation at room temperature in AGO-2 planetary mill with rotation frequency providing the

acceleration of balls 20–60 g, and grinding time 1–15 min. Hydrated zirconium dioxide $ZrO_2 \cdot nH_2O$ (with $n = 1.71\text{--}2.46$) and hydrated titanium dioxide $TiO_2 \cdot H_2O$ (“pure”) were used as the components of the reaction mixture. Hydrated zirconium dioxide was obtained by hydrolysis of $ZrOCl_2$ in aqueous solution of ammonia. The zirconium-titanium samples were dried at the temperature of 30–80 °C and then annealed up to 1200 °C for 4 h at each temperature point under investigation.

Thermal analysis was performed with C-1000 (MOM) instrument at the 10 °C/min heating rate (with the weighed portion of 200 mg). The X-ray diffraction patterns were recorded with DRON-4 instrument with $CuK\alpha$ radiation. Crystallite size (coherent length, d , nm) was estimated from broadening of diffraction lines 111 ($ZrTiO_4$) and 131 ($Zr_5Ti_7O_{24}$). The Raman spectra were recorded with the RFS-100 Raman-Fourier spectrometer, electron microscopic images with JEM-2000FX instrument. Specific surface of the samples was determined using BET procedure on the basis of thermal desorption of nitrogen. The density of samples was determined in pentane using pycnometer. The size of globules (D , nm) was estimated using the equation $D = 6 \cdot 10^3 / (\rho S)$, where S is the specific surface, m^2/g ; ρ is the sample density, g/cm^3 .

RESULTS AND DISCUSSION

Thermograms of zirconium-titanium samples obtained by mechanochemical method exhibit one endothermic effect in the region 50–800 °C (Fig. 1). The indicated thermoeffect is accompanied by sample mass loss. At low temperature (an extremal point on DTA curve at 140 °C) water physically adsorbed on the sample surface is likely to be removed. Chemical composition of the sample annealed at 140 °C can be represented as $ZrO_2 \cdot TiO_2 \cdot 1.1H_2O$. A decrease in sample mass with further increase in annealing temperature is likely to be due to its gradual dehydration.

After mechanical activation of a mixture of hydrated oxides followed by thermal treatment at 400 °C, only a halo in the regions $\theta = 10\text{--}20^\circ$ and $20\text{--}30^\circ$ is observed in X-ray dif-

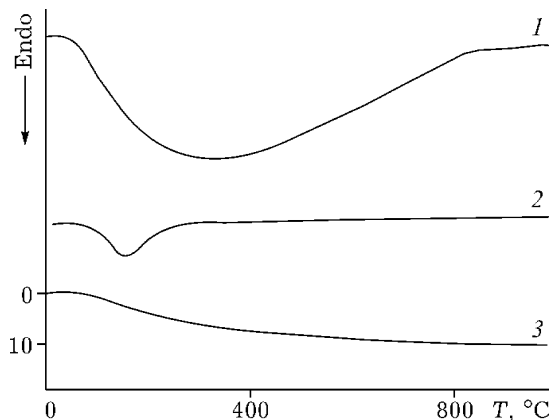


Fig. 1. The DTA (1), DTG (2) and TG (3) curves of zirconium-titanium samples obtained by soft mechanochemical synthesis.

fraction patterns. After thermal treatment at 600 °C, reflections characteristic of zirconium titanate appear. Maximal content of $ZrTiO_4$ is observed at temperatures within 600–1000 °C. With further temperature rise to 1200 °C, this compound disproportionates forming free zirconium dioxide in the monoclinic form and zirconium-deficient titanate $Zr_5Ti_7O_{24}$ (Fig. 2). Since X-ray diffraction patterns of the indicated titanates are rather similar to each other, question about completeness of the transformation of one compound into another remains open.

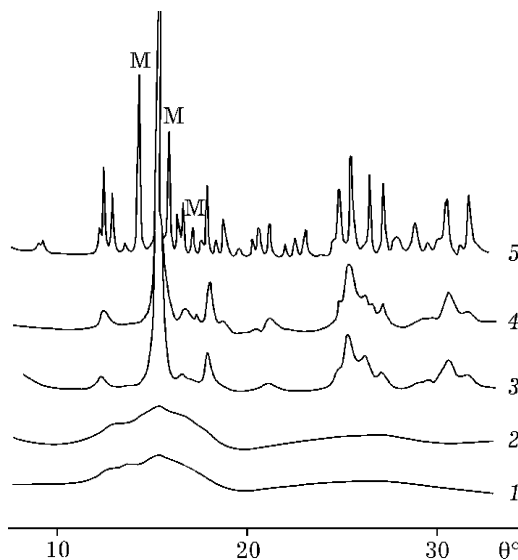


Fig. 2. The X-ray diffraction patterns of a mixture of hydrated zirconium and titanium dioxides ($Zr/Ti = 1$) after mechanical activation at 25 °C (1) and annealing at 400 (2), 600 (3), 800 (4), and 1200 °C (5). M indicates monoclinic form of ZrO_2 .

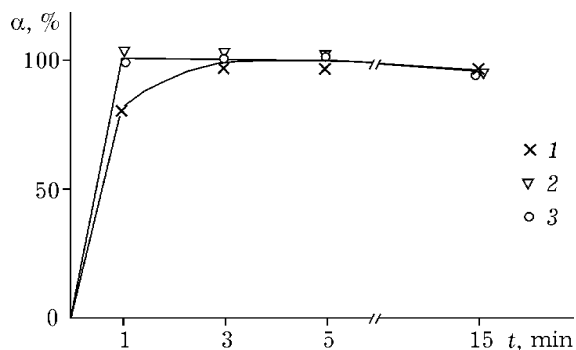


Fig. 3. Relative content of crystalline zirconium titanate in a mixture of hydrated oxides activated at 20 (1), 40 (2), and 60 g (3). Annealing temperature: 600 °C.

Formation of crystalline zirconium titanate $ZrTiO_4$ (calcination temperature 600 °C) occurs almost completely after activation of a mixture of hydrated zirconium and titanium dioxides for 1 min with the acceleration of 40 g and above. A similar result is achieved with 20 g within 3 min (Fig. 3).

The samples annealed at the temperature up to 400 °C are X-ray amorphous. Question arises: what is the nature of chemical compound formed during mechanical activation of a mixture of hydrated oxides? The Raman spectra of amorphous and crystalline zirconium-titanium samples obtained by soft mechanochemical synthesis and by sol-gel procedure [4] are shown in Fig. 4. Activation products are not a mechanical mixture of components; bands at 145, 290, 410, 550, 645, 780 cm^{-1} appear in the spectra of these samples. As it was shown

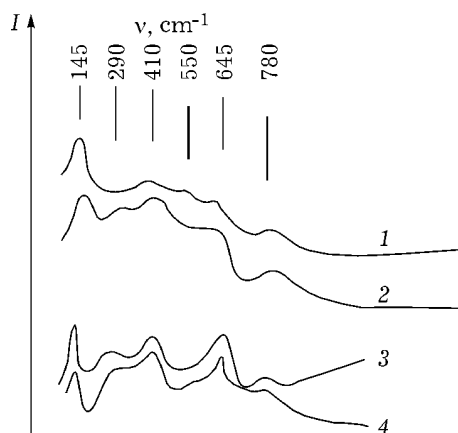


Fig. 4. The Raman spectra of mechanically activated mixture of hydrated zirconium and titanium dioxides (1, 3) and zirconium-titanium samples obtained by sol-gel procedure (2, 4) after thermal treatment at 400 (1, 2) and 800 °C (3, 4).

previously [8, 9], hydrated zirconium titanate ($Zr/Ti = 1$) obtained by sol-gel procedure under gradual loss of water exhibits a decrease in the intensity of band at 550 cm^{-1} and increase in the intensity of bands at 290 and 645 cm^{-1} in the Raman spectra. Comparing the spectra of X-ray amorphous samples obtained by mechanical activation and by sol-gel procedure and annealed at 400 °C, one may assume that the samples differ only by dehydration degree. However, after thermal treatment at 800 °C, when the structure of zirconium titanate gets ordered as suggested by the data of X-ray phase analysis, the Raman spectra become identical. It is likely that during mechanical activation of the mixture of hydrated zirconium and titanium dioxides, as well as during the joint electrolysis of chlorides (sol-gel technology), chemical interaction between the components occurs resulting in the formation of X-ray amorphous hydrated zirconium titanate $ZrTiO_4 \cdot n H_2O$.

A necessary condition for the mechanochemical formation of hydrated zirconium titanate is activation of closely contacting ultrafine particles of the hydrated zirconium and titanium dioxides. For comparison, we performed the entire cycle of thermal treatment with a simple mixture of initial non-activated components and with a mixture of hydrated hydroxides of zirconium and titanium activated separately. At room temperature, only traces of anatase were observed; in the second case, we also observed traces of tetragonal zirconium dioxide. At the temperature of 400–800 °C, final crystallization of titanium and zirconium dioxides occurs, with gradual transformation of anatase into rutile and transformation of the tetragonal ZrO_2 into the monoclinic form. The formation of crystalline zirconium titanate was not recorded in these experiments even at 1000 °C. For better homogenization, we also prepared water suspension of a mixture of preliminarily activated hydrated dioxides; however, in this case we did not detect the formation of a new compound, too.

The data on changes in density, specific surface, the size of globules and crystallites of zirconium-titanium samples obtained by soft mechanochemical synthesis and annealed at different temperatures are shown in Table 1. A

TABLE 1

Influence of thermal treatment on physicochemical characteristics of the products of mechanochemical synthesis in the $\text{ZrO}_2\text{-TiO}_2$ system

Characteristic	Temperature, °C					
	25	400	600	800	1000	1200
ρ , g/cm ³	3.4	3.4	3.3	3.4	3.5	4.0
S , m ² /g	26	21	20	6.2	3.3	0.46
D , nm	68	84	91	285	520	3260
d , nm	–	–	12	13	17	34

noticeable change in the density of samples is observed only at the temperature of 1200 °C. Specific surface of the samples decreases substantially at the temperature of 800 °C and above. With thermal treatment at the temperature below 600 °C, the size of globules (secondary particles) does not exceed 0.1 μm . Only at the temperature of 1200 °C the size of particles reaches several micrometers due to intensive agglomeration. As indicated above, crystalline zirconium titanate ZrTiO_4 is observed in the samples annealed at 600–1200 °C. The size of crystallites is 12–17 nm. At 1200 °C, with the formation of zirconium-deficient titanate $\text{Zr}_5\text{Ti}_7\text{O}_{24}$, noticeable increase in the size of both crystallites and globules occurs.

Electron microscopic images of the mixture of hydrated titanium and zirconium dioxides mechanically activated at 25 °C and annealed

at 600 °C are shown in Fig. 5. One can see globules of 50–200 nm in size, which are in rather close contact with each other. More attentive examination of thinner layers of non-annealed samples reveals primary particles (nuclei) of 2–4 nm in size. However, these particles are already absent from annealed samples, which is likely to be the result of their growth and ordering. A similar picture is observed for zirconium titanate obtained by sol-gel procedure [9].

So, there is a deep analogy between the soft mechanochemical synthesis of zirconium titanate (both in chemical composition and in the morphology of the formed primary particles) and sol-gel procedure of obtaining the same compound [8, 9]. In the samples synthesized by sol-gel procedure, further growth of the primary particles was revealed by means of small-

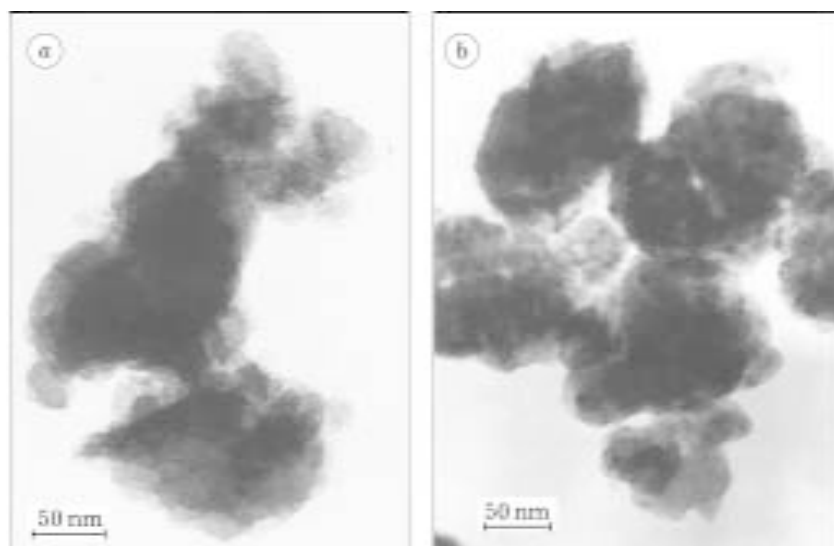


Fig. 5. Electron microscopic images of zirconium-titanium samples activated mechanically at 25 °C (a) and annealed at 600 °C (b).

angle X-ray scattering for temperature rise till the crystallization point [13]. It may be assumed that a similar growth of primary particles occurs during the mechanochemical synthesis; further formed crystallites of 12–17 nm in size are the consequence of this growth. The investigations performed indicate that in both cases crystalline zirconium titanate is formed from the corresponding hydrated compound under removal of water from it. A noticeable difference between the two methods can perhaps be smaller globules which can be obtained by sol-gel procedure than those obtained by mechanochemical synthesis.

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