

## Phase composition evolution of co-precipitated zirconium and yttrium hydroxides during heat treatment

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Formation of complex amorphous hydroxide at co-precipitation of zirconium and yttrium hydroxides has been investigated by X-ray phase analysis and thermal analysis. Its thermal decomposition occurs in a single stage in the temperature interval 20–400°C and results in formation of amorphous zirconia. Parameters of amorphous zirconia "halo" are determined and absence of their dependence on the precursor compound and mass content of yttrium oxide is established. Crystallization temperature of amorphous zirconia (500 to 600°C), average size of coherent-scattering region (28±3 nm) and crystal structure of the phase obtained have been determined. The phase composition evolution depending on heat treatment temperature has been traced in the sequence complex amorphous zirconium/yttrium hydroxide — amorphous zirconia — tetragonal zirconia. In this case yttrium, while not forming independent phases, is successively a component of complex amorphous hydroxide, amorphous oxide and tetragonal zirconia.

Исследовано формирование сложного аморфного гидроксида при совместном осаждении гидроксидов циркония и иттрия методами рентгеновского фазового и термического анализов. Его термическое разложение проходит в одну стадию в интервале температур 20–400°C и завершается формированием аморфного оксида циркония. Определены параметры "гало" аморфного оксида циркония и установлено отсутствие их зависимости от соединения-предшественника и массового содержания оксида иттрия. Определены температура кристаллизации аморфного оксида (500–600°C), средний размер областей когерентного рассеяния (28±3 нм) и структура полученной кристаллической фазы. В зависимости от температуры термообработки прослежена эволюция фазового состава в ряду: сложный аморфный гидроксид циркония/иттрия — аморфный оксид — тетрагональный оксид циркония. При этом итрий, не образуя самостоятельных фаз, последовательно входит в состав сложного аморфного гидроксида, аморфного оксида и тетрагонального оксида циркония.

The application of stabilized zirconia as constructional, thermobarrier, buffer, optical materials, fuel cells, catalysts and substrates for them, etc. [1–6] is provided by its high physical and mechanical properties. Specialists of countries developing actively the atomic engineering conduct intensive research on creation of matrices for isolation of radioactive wastes [7], targets for actinides transmutation [8] and matrix fuel [9]

due to the high radiation and corrosion resistance of that material.

These properties of zirconia are realized most completely when using nanosized powders for production of ceramic materials. The main property of nanosized powders is increased sinterability at relatively low temperatures. Among various of preparation methods of nanosized powders, the "wet" preparation methods of so-called "soft"

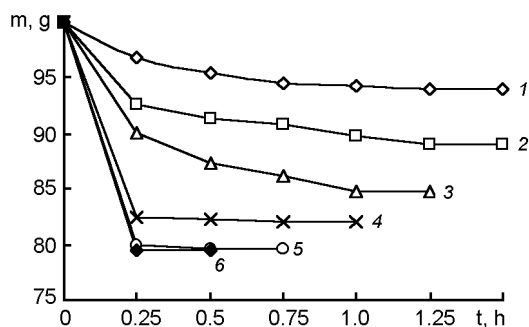


Fig. 1. Dependences of zirconium/yttrium hydroxide precipitate mass on heat treatment time at temperatures 100 °C (1), 150 °C (2), 200 °C (3), 300 °C (4), 400–500 °C (5,6).

powders (precipitation from solutions, hydrolysis, hydrothermal synthesis, sol-gel, etc.) [1, 4, 10–12]. To produce the weakly agglomerated nanosized powders, it is necessary to insight into features of intermediate amorphous phases formation and of tetragonal zirconia at the synthesis temperature, because these phase transformations influence strongly the morphology, compactibility, homogeneity, and monophasicity of oxide powders. The purpose of this work was to study the phase composition evolution at heat treatment of co-precipitated zirconium and yttrium hydroxides.

The precipitate of zirconium/yttrium hydroxide was obtained by co-precipitation from mixture of aqueous solutions of zirconium and yttrium nitrates. The precipitation was realized using 25 % ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) solution. Yttrium nitrate was obtained by processing of yttrium oxide ( $\text{Y}_2\text{O}_3$ ) with nitric acid, and zirconium nitrate, by processing zirconium hydroxide (obtained by hydrolysis of zirconium sulphate [ $\text{Zr}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ] with nitric acid. The precipitate was dried for 20–25 hours at 30–40°C. The zirconium and yttrium nitrates were taken in the ratio providing the preparation of zirconia with 5.4 wt % yttrium oxide after thermal decomposition of the precipitate. The heat treatment of co-precipitated zirconium and yttrium hydroxides was carried out at 100, 150, 200, 300, 400, 500 and 600°C for 0.25–1.25 h.

The phase composition of heat-treated precipitate was examined by X-ray phase analysis (XPA) using a DRON-1.5 diffractometer ( $\text{Cu K}\alpha$  radiation, Ni filter), and average size of coherent scattering region (CSR) was cal-

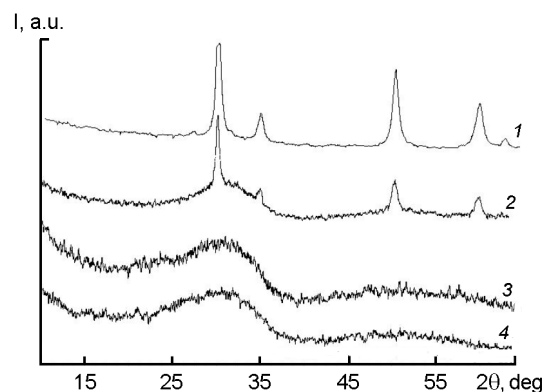


Fig. 2. Parts of diffraction patterns for zirconium/yttrium hydroxide precipitates heat-treated at 30–40 (1), 300 (2), 500 (3) and 600°C (4).

culated from width of the most intensive (101) X-ray line at its half-height ( $\beta$ ) [13].

The dependences of zirconium/yttrium hydroxide precipitate mass on the heat treatment duration at constant temperatures 100, 150, 200, 300, 400, and 500°C are presented in Fig. 1. The precipitate mass at all heat treatment temperatures decreases and eventually takes a constant value after a certain period. The constant mass is attained at 100°C in 1.25 h and amounts 94.3 wt. % of the initial one (hereinafter, wt. per cent are indicated); at 150°C, in 1.25 h and 89.0%; at 200°C, in 1 h and 85 %; at 300°C, in 0.75 h and 82.1 %; and at 400°C, in 0.5 h and 79.6 %, respectively. The mass of the sample heat-treated at 500°C for 0.25 h is the as of that treated at 400°C (79 % of the initial one).

Thus, it follows from the data presented in Fig. 1 that the constant mass value attained drops from 94.3 % to 79 % as the heat treatment temperature increases from 100 to 400°C and then remains unchanged up to 500°C. Thus, the final mass loss makes 21 %.

The X-ray phase analysis of dried zirconium/yttrium hydroxide precipitate has shown that the diffraction pattern does not contain lines typical of crystalline phases but only "halos" characteristic for amorphous state. The first and second "halos" are in the  $2\theta$  intervals from 20° to 38° and 40° to 62°, respectively (Fig. 2, curve 1). These "halos" show distinct maxima at  $2\theta$  31–32° and 48–50°, respectively. The width of first "halo" at its half-height is 9.5°, that of second one, 11°. Both "halos" are asymmetrical with respect to their maxima. The diffraction patterns of precipitated zirconium/yt-

trium hydroxide heat-treated at 100, 150, 200, 300, and 400°C also contain only the "halos" within the same angular intervals with maxima at the same angles as "halos" of dried precipitate (Fig. 2, curve 2).

Heat treatment at 500°C results in a considerable change in the diffraction pattern. Broadened X-ray lines (Fig. 2, curve 3) are observed against the "halo" background. Although the angular interval of the "halo" is somewhat decreased (22–37°) as compared to that for the samples heat treated at lower temperatures, the maximum position remained unchanged (31–32°). The X-ray lines indicate that the crystal phase is tetragonal zirconia (ASTM No.42-1164 [14]).

Heat treatment of the precipitate at 600°C results in a further change in the diffraction pattern. The "halo" is completely disappeared and broadened X-ray lines of tetragonal zirconium oxide (Fig. 2, curve 4) are observed. In Fig. 2, the intensities of X-ray lines for that sample are decreased by 4.5 times in comparison with intensities of "halos" for amorphous materials. The size of coherent scattering region is  $28 \pm 3$  nm.

The experimental results argue that the precipitated zirconium/yttrium hydroxide is an amorphous substance. The products of the precipitate thermal decomposition at temperatures from 100 to 400°C are also amorphous. Crystallisation of the amorphous material with tetragonal zirconia formation starts at 500°C and is over at 600°C.

The data on weight loss of zirconium/yttrium hydroxide precipitates at heat treatment (Fig. 1) coincide within the measurement accuracy (0.5–0.7 %) with those concerning the zirconium hydroxide precipitate obtained before [2]. The precipitate of zirconium/yttrium hydroxide pre-dried at 30–40°C, loses 21 % of its mass (Fig. 1) at heat treatment temperatures up to 500°C. The calculated mass loss for zirconium hydroxide  $Zr(OH)_4$  at thermal decomposition is 22.6 %. Thus, the presence of yttrium hydroxide does not influence essentially the mass loss at thermal decomposition of zirconium hydroxide.

Comparison of thermogravimetric/differential thermal analysis (TG/DTA) results for precipitate of zirconium hydroxide [2] and precipitate of zirconium/yttrium hydroxide [3] shows that the presence of yttrium hydroxide co-precipitated with zirconium hydroxide causes a reduction of thermal decomposition final temperature. The dried zirconium/yttrium hydroxide precipi-

tate contains only 5.2 % of yttrium hydroxide, but its diffraction pattern (Fig. 2) differs from that of zirconium hydroxide [3]. While angular intervals of the "halos" differ only slightly (20°–38° and 17°–38°), positions of their maxima are different, 31° and 28.5°, respectively. The difference in the "halo" parameters indicates difference of structures belonging to different amorphous materials. The co-precipitation of zirconium hydroxide with yttrium hydroxide results in formation of a complex amorphous hydroxide. Its structure differs from that of amorphous zirconium hydroxide.

Comparison of the "halo" parameters of zirconium/yttrium hydroxide precipitate heat-treated at 300°C with those for amorphous zirconia [2] shows a good coincidence. Therefore, the zirconium/yttrium hydroxide precipitate after the heat treatment at 300°C is amorphous zirconia. The absence of X-ray lines for yttrium hydroxides and/or oxyhydroxides does not yet mean that those are absent in the material. In the case of small content of yttrium compounds as well as in the case of their presence as nanosized grains, X-ray lines with great broadening and low intensity cannot be recorded reliably. According to our estimates, if yttrium hydroxides and/or oxyhydroxides are present in the zirconium/yttrium hydroxide precipitate heat-treated at 300°C, those must have a CSR size no more than 2.5–5 nm.

The close values of "halo" parameters in diffraction patterns of complex zirconium/yttrium hydroxide (obtained by the precipitate drying) and of amorphous zirconia evidences a structural similarity of these amorphous materials, although the thermal decomposition of the complex zirconium/yttrium hydroxide into amorphous oxide is accompanied by mass loss of 18 % (Fig. 1).

The "halo" parameters of zirconium/yttrium hydroxide precipitates heat-treated at 400 and 500°C coincide with those for amorphous zirconia. Taking into account that the heat treatment results in the mass loss (21 %) close to the calculated one (22.6 %), i.e. thermal decomposition is essentially complete, it is probable that yttrium oxide is included into amorphous zirconia in the form of solid solution. Since the crystallisation of tetragonal zirconia as a single phase is fully finished at 600°C and, according to DTA data [2,3], zirconia does not transit in monoclinic state at the subsequent temperature increase up to 1000°C, this points unequivocally that yttrium is in crystal lattice of that phase. The fact that tetragonal zirconia starts to crystal-

lize itself from amorphous one at 500°C, confirms that yttrium oxide already was present in amorphous zirconia.

It is known that yttrium hydroxide  $Y(OH)_3$  is decomposed into oxyhydroxide  $YO(OH)$  at 280°C and to yttrium oxide  $Y_2O_3$  at 470°C [15]. Since the thermal decomposition of zirconium/yttrium hydroxide precipitate is already finished at 400°C (Fig. 1), that makes us think that yttrium hydroxide as a compound was not present in the precipitate but formed a part of the complex amorphous hydroxide.

The "halo" parameters of amorphous zirconium hydroxide obtained by us [2] agree well with data from foreign sources [4, 16–18] in spite of the fact that the precipitation was carried out from solutions of various salts (oxychloride, nitrate or alkoxide of zirconium) using various precipitants (ammonium or sodium hydroxides). The coincidence of results is observed also for the "halo" parameters of zirconium/yttrium hydroxide precipitates [5, 12, 19]. The obtained TG/DTA data [3] for the zirconium/yttrium hydroxide precipitate coincide with results from [10] both in the temperature of endothermic maximum and in crystallisation temperature, although in [10] the temperature interval of exothermic effect is somewhat less. In that work, zirconium hydroxide, yttrium hydroxide and coprecipitated zirconium/yttrium hydroxide have been studied by infrared spectroscopy. The authors have shown convincingly that the precipitate obtained by coprecipitation is not a mechanical mixture of zirconium and yttrium hydroxides but is a product of complex composition. Our TG/DTA and XPA results confirm the foregoing conclusion.

The "halo" parameters of amorphous zirconia obtained by us both with yttrium oxide and without it [2, 6, 20] by thermal decomposition both of basic carbonate [6, 20] and hydroxide [20], coincide essentially with data from foreign publications [1, 5, 11, 12, 17–19, 21–23]. The structure of amorphous zirconia does not depend on the precursor compound (hydroxide, basic carbonate, oxycarbonate, alkoxide or oxalate), that forms amorphous zirconia under thermal decomposition. It is important to note that the yttrium oxide content also does not influence the structure of amorphous zirconia. In all cases, amorphous zirconia is crystallised at 400–450°C with formation of tetragonal oxide having average CSR size of 15–40 nm. Tetragonal oxide does not transit in monoclinic at further temperature in-

crease only in the presence of not less than 3.5 % of yttrium oxide.

To conclude, it has been confirmed that the zirconium/yttrium hydroxide precipitate obtained from mixed solutions of corresponding nitrate salts by precipitation with ammonium hydroxide, according to data of X-ray phase and TG/DTA, is a complex amorphous hydroxide but not a mechanical mixture. It has been established that heat treatment in the temperature range of 20 to 400°C results in thermal decomposition of the hydroxide and formation of amorphous zirconia. The complex hydroxide diffraction data (angular interval, shape of "halos" and position of their maxima) coincide with those for amorphous zirconia obtained by other authors using thermal decomposition of hydroxide, carbonate, alkoxide, or oxalate and do not depend on yttrium oxide content. The crystallisation of amorphous zirconia occurs within temperature interval of 500–600°C with formation only of tetragonal phase having the coherent scattering region size of  $28 \pm 3$  nm. It has been shown that independent phases of yttrium are absent during phases evolution from complex amorphous hydroxide to tetragonal zirconia. Yttrium is a part of complex amorphous hydroxide, amorphous oxide, and tetragonal zirconia. The study has established that with increasing heat treatment temperature of complex amorphous zirconium/yttrium hydroxide, evolution of phase composition takes place according to the following scheme: amorphous  $Zr(Y)(OH)_{4-x} \rightarrow$  amorphous  $Zr(Y)O_2 \rightarrow t\text{-}Zr(Y)O_2$ .

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## **Еволюція фазового складу при термічній обробці співосаджених гідроксидів цирконію та ітрію**

**С.В.Габелков, Р.В.Тарасов, Н.С.Полтавцев, Ф.В.Белкин**

Формування складного аморфного гідроксиду при спільному осадженні гідроксидів цирконію та ітрію досліджено методами рентгенівського фазового та термічного аналізів. Його термічний розклад проходить в одну стадію в інтервалі температур 20–400°C і завершується формуванням аморфного оксиду цирконію. Визначено параметри "гало" аморфного оксиду цирконію та встановлено відсутність їх залежності від сполуки-попередника та масового вмісту оксиду ітрію. Визначено температуру кристалізації аморфного оксиду (500–600°C), середній розмір областей когерентного розсіювання ( $28 \pm 3$  нм) і структуру отриманої кристалічної фази. У залежності від температури термообробки простежено еволюцію фазового складу у низці: складний аморфний гідроксид цирконію та ітрію — аморфний оксид — тетрагональний оксид цирконію. При цьому ітрію, не утворюючи самостійних фаз, послідовно входить до складного аморфного гідроксиду, аморфного оксиду та тетрагонального оксиду цирконію.