Synthesis of Peroxides Using Mechanical Activation and Sol–Gel Procedure

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Abstract

It was established by comparing the results of synthesis of peroxides using mechanical activation of the initial reagent mixture in a disintegrator and controllable precipitation both these procedures of preparation of the initial components lead to the same result: a decrease in synthesis temperature by 100 °C. It was demonstrated that in the case of mechanical activation the factor facilitating the course of the solid-phase reaction is excess enthalpy brought into the mixture by the shock action. In the case of chemical activation by the sol–gel procedure, the reaction course is facilitated due to efficient mixing. Simplicity and the possibility of rapid preparation of the initial mixture for the reaction in the solid phase make mechanical activation preferable.

INTRODUCTION

Numerous investigations of the problems connected with grinding and mechanical activation (MA) are caused by the necessity to use fine activated materials in many technological processes. Preparation for reactions in the solid phase by means of mechanical treatment of the substance is of special interest because the energy of mechanical action is accumulated by the lattice causing changes in the structure and energy content of the substance. The latter circumstance leads to changes in the reactivity of solids and favours the solid-phase reactions through acceleration of diffusion processes at high temperatures. Numerous aspects of this problem related to the efficiency of MA in various grinding devices were considered in detail in [1, 2]. At the same time, in spite of a large number of works in this area, the aspects of MA of peroxides are not described in literature.

Metal peroxides attract attention of researchers as a source of chemically bound oxygen which is at the same time active. Investigations [3–5] of barium peroxide mechanically activated in a disintegrator revealed substantial changes in its structural and energy parameters. The possibilities to use disintegrator as an efficient highly productive grinding device allowing one to carry out MA of a number of substances are well known [6, 7]. The mechanism of energy transfer during the shock action in a disintegrator, proposed in [9], allows expecting successful application of this device to mechanical treatment of oxide mixtures.

EXPERIMENTAL

The initial mixture for the synthesis of $Y_1Ba_2Cu_3O_y$ was a mixture of barium peroxide, copper and yttrium oxides; the mixture was treated mechanically in a disintegrator. In order to estimate the efficiency of MA procedure, the compound $Y_1Ba_2Cu_3O_y$ was also obtained by means of chemical activation (sol–gel procedure).

The samples with different degree of mechanical treatment were obtained by repeated admission of the mixture through the reaction chamber of the disintegrator. Sedimentation analysis showed that grinding occurs mainly during the first treatment. As a

result, the curve of particle size distribution shifts from the range 0.1–1.5 mm to the range 1–10 μm. Further treatment causes only insignificant changes in particle size distribution. At the same time, X-ray and thermal data point to changes in the structural and thermodynamic parameters after the grinding process is over.

RESULTS AND DISCUSSION

Analysis of the X-ray data showed that the lines broaden and their intensities change during mechanical treatment, but the X-ray lines of strong and medium intensities for all the three components (BaO_2, CuO, Y_2O_3) are observed in the diffraction patterns (Fig. 1, *a*). In order to determine an optimal temperature of the synthesis of $Y_1Ba_2Cu_3O_y$, mechanically activated mixtures were annealed at different temperatures. It was established that for all the mechanically activated samples annealing at 250 °C causes disappearance of reflections from the X-ray diffraction patterns (see Fig. 1, *b*). Further temperature rise caused the appearance of reflections related to $Y_1Ba_2Cu_3O_y$ phase at 700 °C. It was determined that this phase is formed rather rapidly at a temperature of 850 °C. Such a behaviour is characteristic of all the samples treated mechanochemically. Hence, it is sufficient to treat a mixture by passing it through the disintegrator chamber once. In addition, the data obtained allow us to conclude that the synthesis temperature is independent of the duration of mechanical treatment. It should be noted that the temperature of $Y_1Ba_2Cu_3O_y$ synthesis carried out using a conventional method (hand grinding) is 950 °C. Along with a decrease in the synthesis temperature, MA of the initial components BaO_2, CuO, Y_2O_3 also results in the formation of more uniform samples in which foreign phases, including a green Y_2BaCuO_5 phase, are absent.

The analysis of thermal data (Fig. 2) showed that mechanical treatment leads to the appearance of substantial exothermal effects on DTA curves within the temperature range 200–450 °C, which points to activation of the mixture of initial components. A noticeable exothermal effect appears immediately after the first treatment in the disintegrator. As the

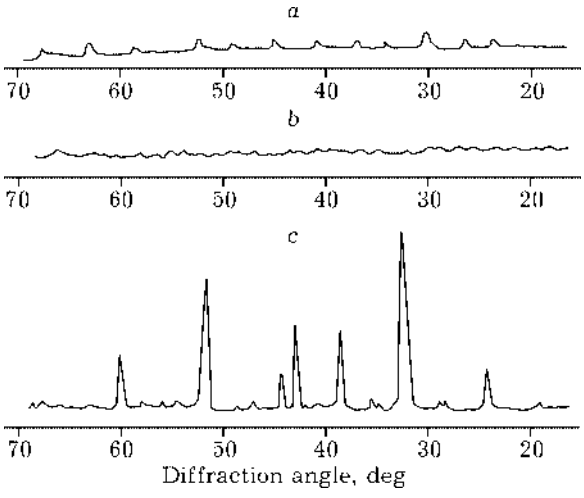

Fig. 1. X-ray diffraction patterns recorded with CuK_α radiation for the samples: *a* – a mixture of mechanically treated BaO_2, CuO, Y_2O_3; *b* – the same, annealed at 300 °C; *c* – the same, annealed at 800 °C.

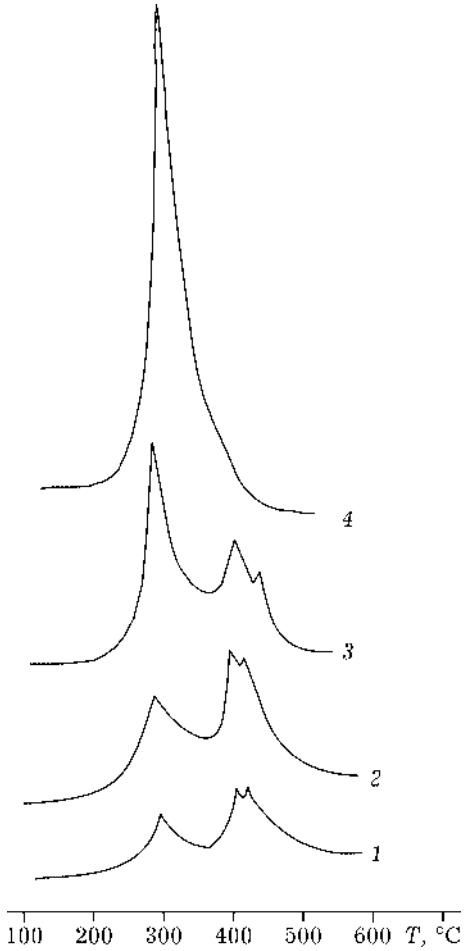

Fig. 2. DTA curves of a mixture of mechanically treated BaO_2, CuO, Y_2O_3 after the first (*1*), second (*2*), third (*3*) and fourth (*4*) treatment.

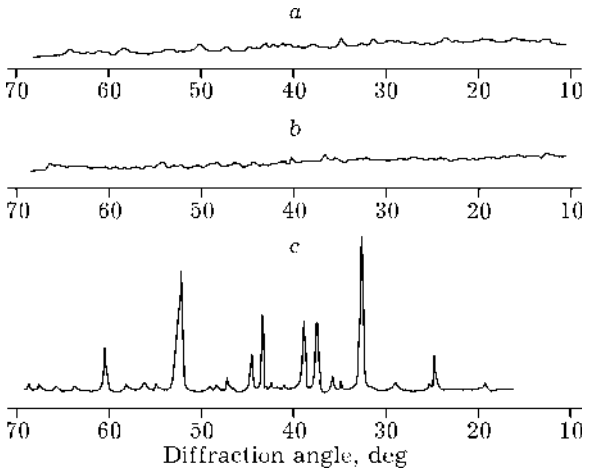

Fig. 3. X-ray diffraction patterns recorded with the CuK_α radiation for the samples obtained using sol–gel procedure: *a* – the initial mixture of Ba, Cu abd Y hydroxides; *b* – the same after annealing at 300 °C; *c* – the same after annealing at 850 °C.

duration of mechanical treatment increases, the intensity of the exothermal effect increases, and a broad peak gets transformed into a narrow, sharply exhibited exoeffect. Visually, exoeffects appear as bright flares; among them, the most bright one corresponds to sample 4 which exhibits a clear narrow peak of high intensity (see Fig. 2).

So, intensive mechanical treatment with the disintegrator improves synthesis conditions (decreasing the synthesis temperature) and sample quality substantially. It should be noted that similar results were obtained previously by the authors of [9] who carried out intensive mechanical treatment of the same components (BaO_2, CuO, Y_2O_3) in a vibratory mill. Those authors concluded that the formation of a single-phase product is promoted by the intermediate compound $BaCuO_2$; its appearance allows one to exclude the formation of the side green phase Y_2BaCuO_5. The compound $BaCuO_2$ may be formed also after the mechanical treatment of the components BaO_2, CuO, Y_2O_3 in the disintegrator, but this cannot be determined unambiguously since strong reflections of this compound overlap with the reflections of the initial components. A different character of derivatograms observed in Fig. 2 and in [9] should also be noted.

It is interesting to compare the effective method of mechanical treatment with the chemical activation procedure. Sol–gel method, a procedure involving controllable deposition, was chosen as such a procedure. Gels were obtained by adding an aqueous solution of tetraethylammonium hydroxide to a mixture of aqueous solutions of barium, copper and yttrium chlorides taken in the corresponding molar ratios. The aqueous solutions were brought to pH 6–7. With an excess tetraethylammonium hydroxide, the blue gel was transformed into a brown fine amorphous powder (Fig. 3, *a*). The curve of particle size distribution for the powder obtained using sol–gel procedure was within the range 0.1–7 μm. Similarly to the case of mechanical activation, the powder was annealed at different temperatures. It was discovered that the $Y_1Ba_2Cu_3O_y$ phase appears at the same temperature, 700 °C, and is formed rather rapidly at 850 °C.

CONCLUSIONS

So, the results of the investigation show that two different methods (chemical and mechanical activation) give similar results, in spite of the fact that the crystal and structural state of the mixture of mechanically activated BaO_2, CuO, Y_2O_3 differs from the amorphous state of the hydroxides of Ba, Cu and Y obtained using sol–gel procedure. The reasons promoting the synthesis of $Y_1Ba_2Cu_3O_y$ phase are different. In the case of mechanical activation, the formation of $Y_1Ba_2Cu_3O_y$ phase is promoted by the excess enthalpy which is introduced into the system by mechanical collisions. This assumption can be confirmed by the curves shown in Fig. 2: the area below the curves is proportional to the excess enthalpy, the presence of which, according to [2], facilitates solid-phase reactions. In the case of chemical activation (sol–gel) procedure, reactions in the solid phase are facilitates due to the efficient mixing of the components during controllable deposition allowing mixing till the formation of the amorphous state. As a result, diffusion during reaction in the solid state is facilitated. A comparison of the two methods shows that with the same results the method of mechanical activation can be preferable due to its simplicity and a more rapid preparation of the initial mixture to the reaction in the solid state.

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