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Mechanochemical Reduction of GeO₂ with Magnesium

T. A. UDALOVA^{1,2}, T. F. GRIGOR'EVA¹, E. T. DEVYATKINA¹, S. V. VOSMERIKOV¹, and N. Z. LYAKHOV¹¹*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia*

E-mail: udalova@solid.nsc.ru

²*Novosibirsk State Technical University, Novosibirsk, Russia*

Abstract

The effect of conditions of mechanochemical activation and stoichiometric composition on generating products of mechanochemical reduction of β -germanium dioxide with magnesium was investigated by X-ray phase analysis. It was demonstrated that differently composed mechanochemical composites might be formed at certain steps during mechanical activation of germanium dioxide. They were comprised of germanium, magnesium oxide, germanium oxide, magnesium, and the GeMg₂ intermetallic compound. The process of mechanochemical reduction of germanium dioxide with magnesium comes to an end by 4 min of activation to form Ge/MgO composite. Conditions of separation of germanium powder from magnesium oxide in mechanochemical Ge/MgO composites were determined. As demonstrated by electron microscopic analysis, highly dispersed germanium powders consist of 50–100 nm primary particles similarly-shaped to spherical ones. The species are aggregated into secondary particles in 1 to 10 μ m size range. The magnesium content in highly dispersed germanium powders is less than 2 %.

Key words: mechanochemical reduction, highly dispersed germanium

INTRODUCTION

Highly dispersed germanium powders are used when obtaining a wide range of modern materials. This involves depositing coatings on optical components, using as alloy additives, making new composite materials, certain germanium alloys (Au-Ge, Cu-Ge, etc.), utilising in nanotechnologies, microelectronics, microwave devices, short-range radar detectors, fibre and infrared optics, nuclear physics (gamma radiation detectors), and also producing germanium single crystals [1–4].

Germanium is a trace element, its manufacture being related to the processing of base metal ores, ash from combustion of coal, coke chemistry products with the release of germanium concentrate in chemical and metallurgical enrichment [2, 5]. In order to separate it from concentrates,

germanium is sequentially transferred to GeCl₄ or GeO₂ followed by hydrogen reduction to germanium [2, 5, 6].

Among a wide range of methods to produce highly dispersed powder materials [7], mechanochemical synthesis (MCS) is notable for short preparation times for useful inorganic materials including those with a monophasic composition with a given stoichiometry and elimination of a whole series of environmental pollution problems. Mechanochemical reactions of reduction of metal and non-metal oxides with $E_{298}^0(E_{act}^{n+}/E_{act}) \geq 0$ (V), active metals with $E_{298}^0(Me_{act}^{n+}/Me_{act}) < -0.7$ (V) flowing with a large exothermic effect may be performed only during mechanical activation [8–10].

Mechanical activation (MA) of solid state of element oxides with an active metal results in an increase in contact surface area, acceleration of

mass transfer at the same time and therefore activation of their mechanochemical interaction to form composites ($E/(Me_{act})_x O_y$), *i.e.*, powder compositions of fine particles of the reduced elements and active metal oxides. The most advisable extraction the reduced element from such composites without the violation of its highly dispersed state is related to selecting active metal oxide yet inert in relation to the reduced element. Among active metals, magnesium is most reasonable to use, as the MgO phase that inhibits the significant sintering of mechanical activation products is generated during the mechanochemical redox reaction. Furthermore, when magnesium oxide reacts with aqueous HCl or H₂SO₄ solutions, highly soluble compounds are generated [11]. Germanium does not react with a solution of diluted hydrochloric acid [2, 5], hence it is possible to separate Ge from side products of mechanochemical reduction upon the acid processing of Ge/MgO composite. Reduction of metal oxides with magnesium by mechanical activation was explored in a number of research papers [12, 13].

The objective of the present research was to investigate mechanochemical interaction in the GeO₂–Mg system to produce Ge/MgO composites and to extract highly dispersed germanium therefrom.

EXPERIMENTAL

The research work used hexagonal β-phase germanium dioxide, magnesium powder (GOST 6001–79, MPF-2), hydrochloric acid (GOST 14261–77), sulphuric acid (GOST 14262–78), and ethylenediaminetetraacetic acid disodium salt (EDTA) (GOST 10652–73).

Mixtures of magnesium and β-phase germanium dioxide of different stoichiometric compositions were processed in an AGO-2 high energy planetary ball mill (the volume of the drum is 250 cm³; the diameter of the balls is 5 mm; the balls loading is 200 g; the sample mass is 10 g, and the drum rotation speed around the common axis is 600 and 1000 rpm).

X-ray phase analysis (XPA) was carried out using the D8 Advance diffractometer (Bruker), CuK_α radiation. The research on the morphology of the resulting samples was performed using Oxford Instruments (England) and Hitachi TM 1000 (Japan) scanning electron microscopes (SEM). The accelerating voltage is 15 kV (constant) and the degree of increase is from 20 to 10,000; the maximum viewing area: 3.5 mm² (square), the sample size of 70 mm (diameter), and the sample thick-

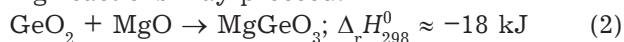
ness is less than 20 mm. The Hitachi TM 1000 microscope is equipped with a TM 1000 EDS detector designed to determine sample chemical composition.

RESULTS AND DISCUSSION

The value of the exothermic effect of the redox reaction of germanium dioxide and magnesium determines an opportunity for the progression of this process:



Upon mechanical activation of a mixture of germanium dioxide and magnesium, the following reactions may proceed:



Mechanochemical composites of various compositions, including germanium, magnesium oxide, germanium (IV) oxide, magnesium, magnesium meta and orthogermanates (MgGeO₃, Mg₂GeO₄), and also the GeMg₂ intermetallic compound may be generated. Thermal effects of reactions (2) and (3) are indicated considering the theoretically calculated standard enthalpy of formation of magnesium metagermanate and magnesium orthogermanate [14]. The value of the heat effect of the formation reaction of the Mg₂Ge intermetallic compound [15] is given according to literature data [16, 17] for temperatures of 700–900 K. The presence of Ge, MgO, and the by-products of mechanochemical reduction of germanium (IV) oxide with magnesium, such as MgGeO₃, Mg₂GeO₄, and Mg₂Ge, in the resulting composites was monitored by XPA (PDF-2 [47–304], [34–281], and [36–1479]).

As demonstrated by X-ray phase investigations of the effect of stoichiometric ratios of components in Ge₂O + Mg systems (1 : 2 and 1 : 2.5) and mechanical activation time (τ_a) on the degree of reduction of germanium dioxide with magnesium upon a drum rotation speed around the common axis of 600 rpm, the process of reduction of β-phase germanium dioxide within an activation time of less than or equal to 1 min does not proceed completely. The difference in X-ray analysis data for reduction of β-phase germanium dioxide with magnesium at the same activation times is mainly due to detection of reflexes related to the GeMg₂ intermetallic compound that is mainly generated upon the excess of magnesium. In order to eliminate the formation of the GeMg₂ intermetallic compound, research on the effect of activation time when changing the drum

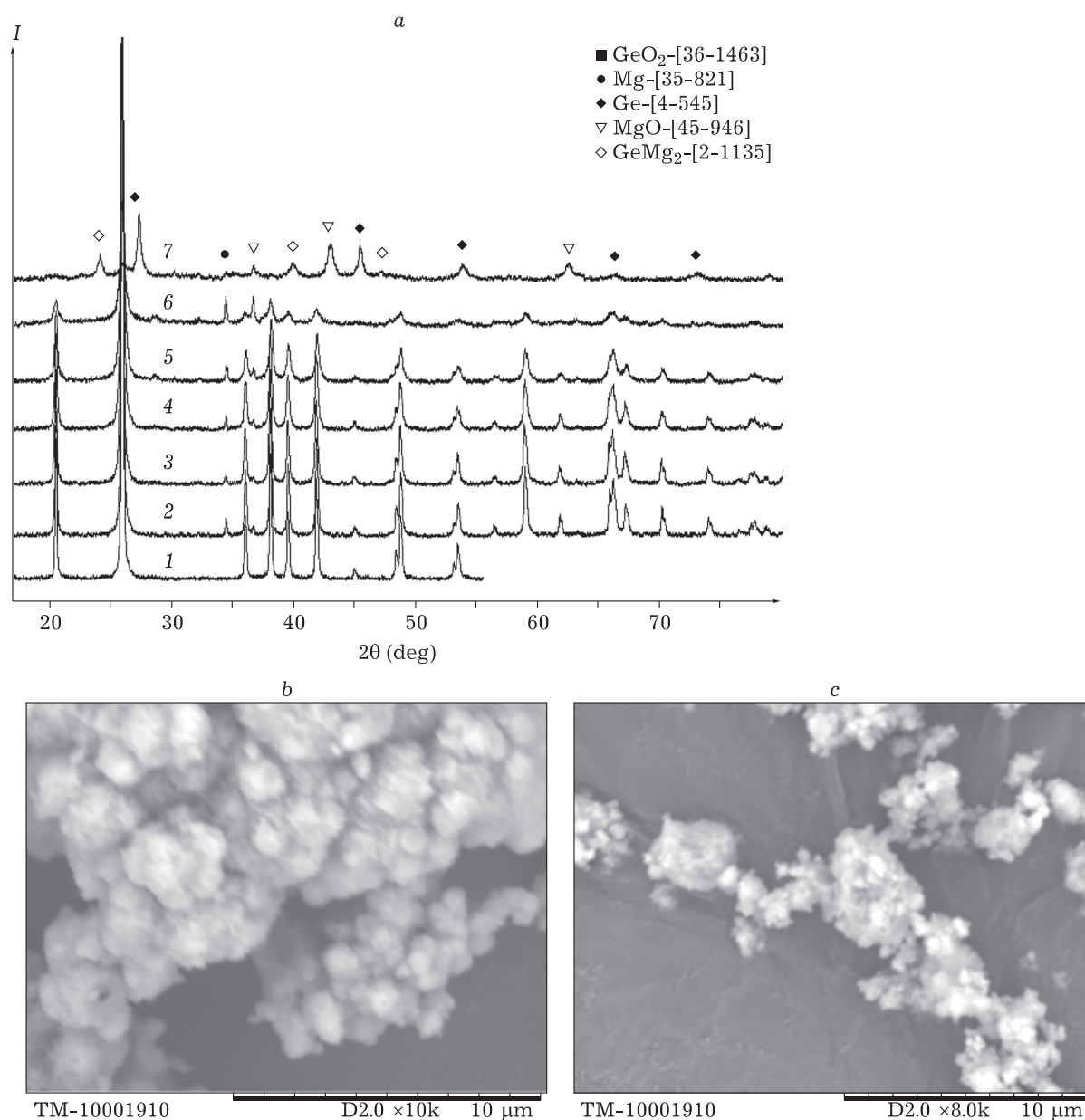


Fig. 1. *a* – X-ray diffraction patterns of samples of β -germanium oxide (1) and Ge/MgO mechanocomposites (2–7). Stoichiometric GeO_2/Mg ratio = 1 : 2.2, the drum rotation speed around the common axis is 600 rpm; τ_a , s: 10 (2), 30 (3), 60 (4), 120 (5), and 240 (6); *b*, *c* – electron micrographs of germanium oxide (*b*) and Ge/MgO mechanocomposite (*c*), τ_a is 8 min, 8000 \times Magnification.

rotation speed around the common axis from 600 to 1000 rpm were carried out for mixtures of stoichiometric compositions of 1 : 2.2.

As shown by X-ray phase analysis of the effect of mechanical activation time (from 10 to 480 s) of a mixture of GeO_2 and Mg on the degree of reduction of germanium dioxide, reflexes of the original compounds, *i.e.* germanium dioxide and magnesium, and also low-intensity reflections of magnesium oxide, are recorded in the XRD pattern upon a drum rotation speed around the common axis of 600 rpm (Fig. 1, *a*), the stoichiometric ratio

of components in the system GeO_2/Mg = 1 : 2.2 and an activation time of 10 s (see Fig. 1, *a*, curve 2).

Increase of activation time from 30 to 60 s results in only changing the intensity of GeO_2 , Mg, and MgO reflexes and there are no germanium ones (see Fig. 1, *a*, curves 3–5). The low-intensity reflexes of germanium and the GeMg_2 intermetallic compound appear upon a simultaneous increase in the intensity of magnesium oxide reflexes only when increasing activation time to 4 min (see Fig. 1, *a*, curve 6). When activation time is further increased to 8 min, the reflexes of

germanium and magnesium oxide, and also the low-intensity reflections of the GeMg_2 intermetallic compound are clearly detected in X-ray diffraction patterns. It has been demonstrated by SEM that primary particles of mechanochemical composites generated within 480 s of mechanical activation had the shape close to the spherical one in a size range of ~ 50 – 100 nm. They are aggregated into larger particles (see Fig. 1, c).

An increase in the drum rotation speed around the common axis to 1000 rpm (Fig. 2, a) has demonstrated that the reflexes of initial β -ger-

manium dioxide and magnesium, and also low-intensity reflections of magnesium oxide are detected in X-ray diffraction patterns upon mechanical activation within 10 s (see Fig. 2, a, curve 2). Significant changes in X-ray diffraction patterns appear upon an activation time of 30 s (see Fig. 2, a, curve 3). In other words, there are clear reflexes of germanium, magnesium oxide, and the GeMg_2 intermetallic compound. At the same time, the intensity of germanium oxide reflexes is dramatically decreased. A further increase in activation time from 1 to 2 min (see Fig. 2, a, curves 4, 5)

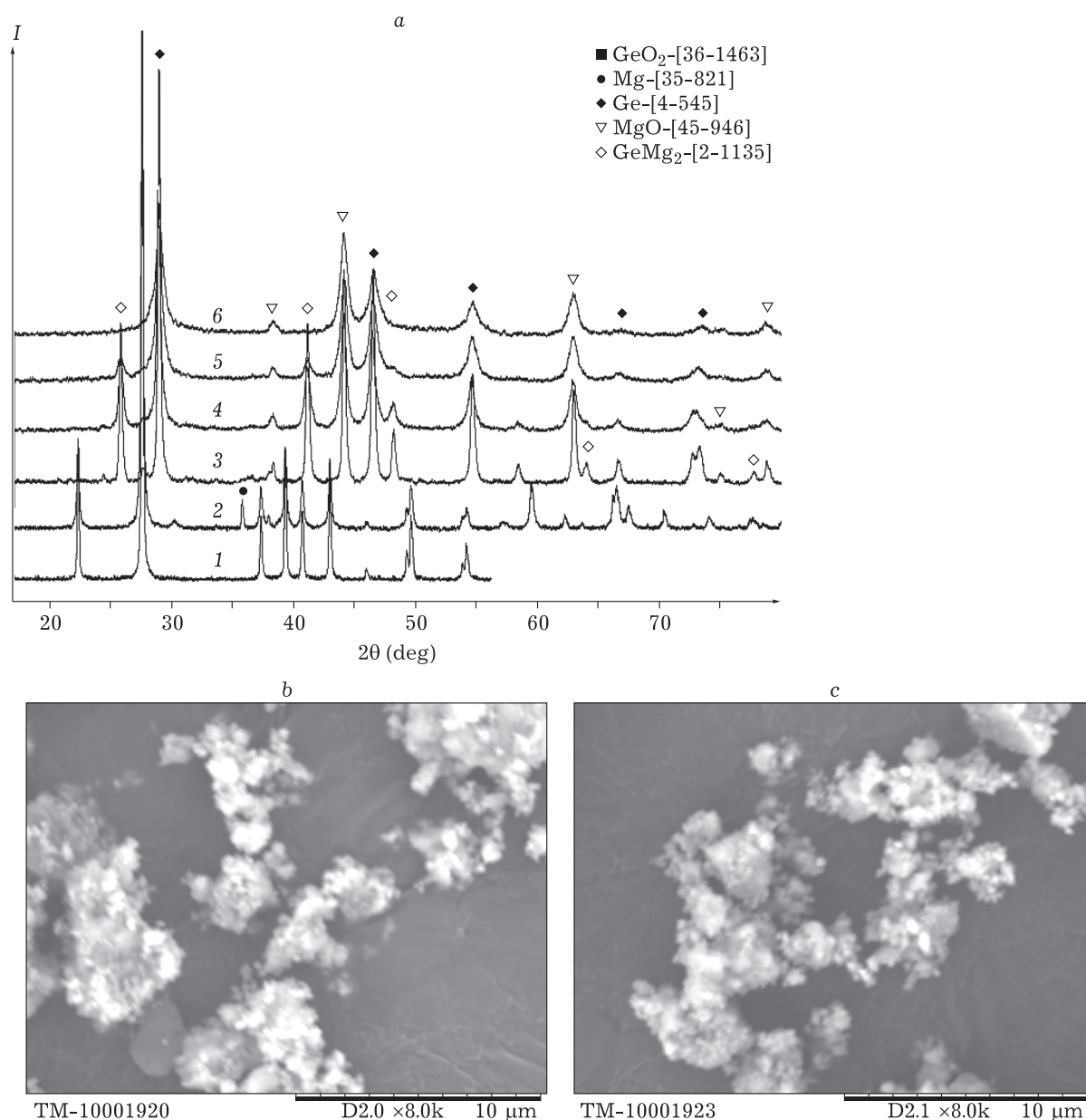


Fig. 2. a – X-ray diffraction patterns of samples of β -germanium oxide (1) and Ge/MgO mechanochemical composites (2–7). Stoichiometric GeO_2/Mg ratio = 1 : 2.2, the drum rotation speed around the common axis is 1000 rpm; τ_a , s: 10 (2), 30 (3), 60 (4), 120 (5), 240 (6), and 480 (7); b, c – electron micrographs of Ge/MgO mechanochemical composite; τ_a is 30 (b) and 240 s (c), 8000 \times Magnification.

leads to a reduction in the intensity of reflexes of the GeMg₂ intermetallic compound and the almost complete disappearance of germanium dioxide reflexes. At the same time, intensities of germanium and magnesium oxide get reduced, their reflexes being broadened. This is likely to be related to a decrease in the particle size of the mechanochemical composite. When activation time is increased to 4 min (see Fig. 2, *a*, curve 6), the Ge/MgO mechanochemical composite is generated and only the broadened reflexes of germanium and magnesium oxide are recorded in X-ray diffraction patterns. The shape and size of composite particles generated upon mechanical activation were examined by SEM (see Fig. 2, *b*, *c*). The research was carried out on Ge/MgO composites generated upon mechanical activation within 4 min, stoichiometric compositions of GeO₂/Mg = 1 : 2.2 and a drum rotation speed around the common axis of 1000 rpm regarding an opportunity to separate off germanium from by-products of the reduction (Fig. 3, *a*) and primarily from magnesium oxide. Magnesium oxide is dissolved most completely in solutions of HCl and H₂SO₄ [11]. In order to separate off germanium particles from MgO, the processing of Ge/MgO mechanochemical composites with diluted solutions of HCl was explored. The optimum conditions for separating off germanium from the main by-product (MgO) based on the composite were determined. They were as follows: the processing with 1 M HCl (340–350 K, 30 min) to generate a highly soluble compound (MgCl₂); herewith, germanium remains as a powder.

When mechanochemical composites that contain minor amounts of magnesium germanide (Mg₂Ge) are exposed to diluted solutions of HCl, in parallel to

magnesium oxide dissolution, the following process proceeds:



In this case, magnesium from the intermetallic compound goes into a solution as highly soluble magnesium chloride [18], whereas germanium hydride (GeH₄) released as gas should be forwarded for further processing, as hyperpure germanium used in electronics is generated. Nevertheless, the yield of GeH₄ is too low (<<20 %).

X-ray diffraction patterns of samples produced by the processing of Ge/MgO composite with 1 M HCl, in addition to germanium reflexes, have low-intensity reflections of β-germanium dioxide (see Fig. 3, *a*, curve 1). According to literature data, the latter is well soluble in diluted aqueous solutions of NaOH and NH₃, and also partly water-soluble [2, 5]. Therefore residual quantities of β-germanium dioxide from germanium powder separated off from magnesium oxide with 1 M HCl were removed using 0.1 M aqueous solutions of NaOH or NH₃ (see Fig. 3, *a*, curves 2 and 3). According to X-ray analysis data, separating off residual quantities of β-germanium dioxide proceeds more completely when processing with a 0.1 M aqueous solution of sodium hydroxide.

Particle size determination for germanium powder separated off from by-components based on Ge/MgO mechanochemical composite has been carried out by SEM. It has been demonstrated that sequential processing of Ge/MgO mechanochemical composite with 1 M HCl and 0.1 M NaOH solutions results in the formation of highly dispersed Ge powders. Germanium particles are secondary aggregates in 1 to 10 μm size range. They are comprised of primary particles between ~50 and 100 nm in size

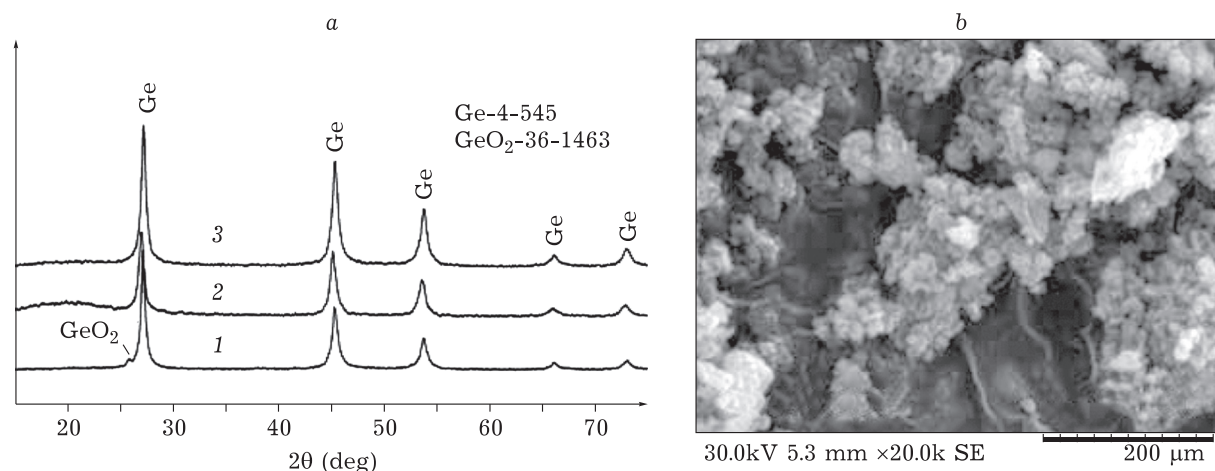


Fig. 3. Germanium powder: *a* – X-ray diffraction patterns of samples after acid separation of MgO from Ge/MgO mechanochemical composite (1), after processing with 0.1 M aqueous solutions of NH₃ (2) or NaOH (3); *b* – electron micrograph of purified highly dispersed germanium, 20 000× Magnification.

(see Fig. 3, b). It has been demonstrated by energy-dispersive X-ray spectroscopy (EDS analysis) that Mg content in highly dispersed germanium powders is less than 2 %.

CONCLUSION

1. Mechanochemical reduction of GeO₂ by magnesium with the stoichiometric GeO₂/Mg ratio = 1 : 2.5 and a drum rotation speed around the common axis of 1000 rpm comes to an end by 4 min of activation to form Ge/MgO composite.

2. The sequential mode of the processing of Ge/MgO mechanocomposite with dilute solutions of hydrochloric acid and distilled water makes it possible to separate germanium powder from magnesium oxide. Separating residual quantities of β-phase germanium dioxide proceeds more completely when processing with a 0.1 M aqueous solution of sodium hydroxide.

3. As demonstrated by scanning electron microscopy, germanium powder is highly dispersed, consisting of 50–100 nm primary particles aggregated into 1–10 μm secondary species.

4. It has been determined by energy-dispersive X-ray spectroscopy (EDS analysis) that Mg content in highly dispersed germanium powders is less than 2 %.

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