THEORY, MANUFACTURING TECHNOLOGY, AND PROPERTIES OF POWDERS AND FIBERS

FORMATION OF MAGNESIUM TITANATES

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UDC 621.762

The paper examines the phase formation in the mechanochemical treatment and subsequent annealing of TiO$_2$ and MgO mixtures. It is established that the MgTiO$_3$ phase forms during annealing of the above powder mixtures at 900, 1000, and 1100 °C. Preliminary grinding of oxides in a high-energy planetary-ball mill after annealing produces the MgTiO$_3$ phase within its homogeneity range. The lattice parameters are determined at the boundary of the homogeneity region. Preliminary grinding of the oxide mixture produces the spinel-type Mg$_2$TiO$_4$ phase.

Keywords: oxides, grinding, annealing, magnesium titanates.

INTRODUCTION

Great attention has been recently paid to the development of materials with high, stable dielectric properties. Among them are titanates of many metals, including magnesium titanates. The Mg–Ti–O system has a number of compounds, of which MgTiO$_3$ and Mg$_2$TiO$_4$ are noteworthy as those having valuable electrophysical properties.

The properties of a material are determined by its phase composition, which in turn depends on the production method. It is established [1–6] that joint grinding of compounds in a ball mill can reduce the temperature of many solid-phase reactions and accelerate the phase formation in high-temperature annealing.

EXPERIMENTAL PROCEDURE

We produced magnesium titanates by the interaction of magnesium oxides (MgO) and titanium oxides (TiO$_2$) in the ratio 2 : 1. It was examined how the time of preliminary grinding of the starting components influenced the composition of the material following its annealing. The mixtures of oxide powders were ground in an RN100 high-energy planetary-ball mill with balls made of WC–Co hard alloy. The charge ratio was 20 : 1 and...
Fig. 1. Diffraction patterns of powder mixtures after grinding in a planetary-ball mill: starting mixture (1), grinding for 5 (2), 10 (3), 20 (4), 40 (5), 80 (6), and 120 min (7) 1

Fig. 2. Diffraction patterns of samples: 1, 3, 5) annealing of the starting mixture at 900, 1000, and 1100°C; 2, 4, 6) annealing at 900, 1000, and 1100°C after 120-min grinding

grinding time 5, 10, 20, 40, 80, and 120 min. After the grinding, the powders were pressed under 1 GPa into disks 10 mm in diameter. Then the disks were annealed in a furnace with silite heaters in corundum crucibles in air at 900, 1000, and 1100°C at a rate of 10°C/min.

The phase composition of the samples was determined using a DRON-3M diffractometer. X-ray photographs were taken in Cu-Kα radiation between 10 < 2θ < 80º at a scan angle of 0.1º and 5-sec exposure at each point; the data were processed. The phase composition of the powder mixtures of the above oxides after grinding in a ball mill before high-temperature annealing was determined in the same way.

RESULTS AND DISCUSSION

The main phases in the starting powder mixture are represented by titanium oxide TiO₂ with anatase structure and cubic magnesium oxide MgO (Fig. 1). A small amount (admixture) of the Mg(OH)₂ phase is present. The phase composition of the mixture hardly changed after grinding for 5 and 10 min. Along with the above phases, diffuse weak reflection lines of orthorhombic TiO₂ appear after 20-min grinding. With increasing grinding time, the x-ray reflection lines of orthorhombic titanium oxide become more intensive. It is noteworthy that, according to [7], the orthorhombic TiO₂ phase with α-PbO₂ structure forms under high pressure. This is evidence that particles are ground under quite high pressures and strains. This is testified by the broadening of the x-ray reflection lines of all phases even after 10-min grinding; the longer the grinding, the more intensive the broadening. Unfortunately, the effect of grinding on the size of coherent scattering regions and microdistortion of crystal lattices cannot be assessed since the reflection lines of different phases overlap. After 80- and 120-min grinding, weak and diffuse reflection lines of the MgTiO₃ phase show up. It is assumed that the high-pressure orthorhombic TiO₂ phase should necessarily form for the ternary rhombohedral phase of magnesium titanate MgTiO₃ to show up. At the same time, when magnesium titanate starts forming in grinding oxide powder mixtures, the reflection lines of TiO₂ anatase-type structure become weaker.

It may be assumed that the nucleation of the ternary MgTiO₃ phase during mechanochemical treatment should facilitate its formation during annealing. However, annealing at 900°C (Fig. 2) has not shown any effect of mechanochemical treatment on the formation of magnesium titanate. Annealing of MgO–TiO₂ powder mixtures at all temperatures, even without preliminary grinding, leads to the formation of MgTiO₃ (Fig. 2). The grinding of powders for 5–120 min and subsequent annealing at 900°C do not lead to the formation of new phases. Nevertheless, the interplanar spacing of magnesium titanate increases depending on the time during which the powder mixtures are preliminary ground: with its increasing, the interplanar spacing and, accordingly, lattice