Ceramic Materials and Heat Effects of Their Formation

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Received May 21, 2010; in final form, December 5, 2010

Abstract—We have determined the main characteristics of ceramic materials prepared by modifying 2MgO·2Al₂O₃·5SiO₂ with MnO and FeO. The formation of the ceramics was analyzed by detailed thermal analysis, X-ray diffraction, IR spectroscopy, and differential scanning calorimetry. We have determined the heat effects of formation of Mg₁₋ₓMₓAlₓSi₅O₁₈ (0.25 < x < 0.75) and Mg₂₋ₓMₓAlₓSi₅O₁₈ (0.5 < y < 1.5) solid solutions with M = Mn(II) and Fe(II) and calculated the standard heats of formation of the Mg₁₋ₓMₓAlₓO₄ and Mg₂₋ₓMₓAlₓSi₂O₁₈ solid solutions.

DOI: 10.1134/S0020168511080188

INTRODUCTION

Cordierite, a magnesium aluminosilicate of composition Mg₂Al₄Si₅O₁₈, offers high thermal stability and good electrical insulating properties, which make it an attractive material for lining induction furnaces and fabricating heat-resistant parts of resistance furnaces for the engineering industry. Cordierite is commonly synthesized at temperatures from 1350 to 1450°C. The drawbacks that limit the use of this material include its insufficient mechanical strength and density and, accordingly, increased porosity. To extend the application area of aluminosilicate ceramics, we examined the effect of MnO and FeO modifiers on the properties of 2MgO·2Al₂O₃·5SiO₂ ceramics (cordierite stoichiometry). We also systematically studied phase formation processes in the ceramics and determined their heat effects (∆H°(T)).

The constituent binaries and ternaries of the multicomponent system MgO(MnO, FeO)–Al₂O₃–SiO₂ have been studied in detail [1]. The MgO–Al₂O₃–SiO₂ and MO–Al₂O₃–SiO₂ (M = Mn(II), Fe(II)) ternary systems are known to contain various aluminosilicates [1]. Characteristically, natural magnesium, manganese(II), and iron(II) aluminosilicates with the cordierite structure form solid solutions [2]. The binary systems MgO–Al₂O₃, MO–Al₂O₃, and MgO–SiO₂, MO–SiO₂ contain aluminates or silicates. The MgAl₂O₄, MnAl₂O₄, and FeAl₂O₄ aluminates have the normal spinel structure and a pronounced tendency to form continuous series of solid solutions [2]. The limits of solid-solution regions in the MgO–MnO–Al₂O₃ and MgO(MnO, FeO)–Al₂O₃–SiO₂ systems are, however, unknown. Available data for the MgO–FeO–Al₂O₃ system are rather contradictory and are influenced by the possible Fe₂O₃ formation.

EXPERIMENTAL

(2–x)MgO·x(MnO, FeO)·2Al₂O₃·5SiO₂ (x = 0–2; M = Mn(II), Fe(II)) samples were prepared through partial or complete (equimolecular) substitution of MnO or FeO for MgO in a magnesium aluminosilicate system corresponding to the stoichiometric ratio of MgO, Al₂O₃, and SiO₂ in the magnesium aluminosilicate Mg₂Al₄Si₅O₁₈ (cordierite) (series I). The starting chemicals used were natural mineral raw materials (clay from the Veselovskoe deposit, talc from Onotskoe, and commercial alumina) and reagent-grade compounds (manganese(II) carbonate and iron(II) oxide). Indices of modified compositions (M and F) correspond to the first letters of Mn and Fe, and numbers from 1 to 4 correspond to an increase in modifier content from 5.9 to 22.2 wt %.

The choice of oxide modifiers was prompted by the phase diagram of the magnesium aluminosilicate system and the nature of oxide modifiers. The Mg²⁺, Mn³⁺, and Fe³⁺ ions are close in size, which suggests the possibility of isomorphic substitution of Mg²⁺ and Fe³⁺ for Mg²⁺ in the crystal structure of Mg₂Al₄Si₅O₁₈.

Thermal analysis (DTA + TG + DTG) was carried out with a Paulik–Paulik–Erdey thermoanalytical system during heating from 20 to 1200°C (heating rate of 10°C/min, 1-g samples). X-ray diffraction (XRD) patterns were collected on a D8 Advance diffractometer (Bruker, Germany) and DRON-3 diffractometer (CuKα radiation, λ = 0.15417 nm, 2θ = 10°–70°, scan...
rate of 1–2°/min). Crystalline phases were identified using JCPDS PDF data.

IR absorption spectra were measured at room temperature in the range 400–1300 cm⁻¹ on a Nexus Fourier transform IR spectrometer (Thermo, USA) using samples pressed with KBr. The spectra were assigned using those of known substances [3–5]. The enthalpy of phase formation processes was determined by differential scanning calorimetry (DSC) using a TGA/DSC 1 HT/319 Star system (Mettler Toledo, Germany) and Star SW 9.20 software. Volume resistivity ρ_V was measured in the range 20–600°C (RF State Standard GOST 24409-83). The linear thermal expansion coefficient (L TEC) was measured at temperatures from 20 to 400°C (RF State Standard GOST 24409-83) with a DKV-2 horizontal quartz dilatometer (designed at the Institute of Glass and Ceramics). Bulk density ρ_b was determined by immersion and hydrostatic weighing (RF State Standard GOST 473.3-81). The mechanical strength of the materials was determined using static three-point bend tests (σ_b) on an AIsK-2 automatic testing system built around an IR 5046-5 tensile tester (RF State Standard GOST 24409-83).

RESULTS AND DISCUSSION

The main properties of the ceramic materials studied are summarized in Table 1. These data demonstrate that increasing the modifier content in a given system typically improves the properties of the ceramic materials in comparison with those of material I. One possible reason for this is that the oxide modifiers activate the sintering process. The best properties were achieved at firing temperatures from 1150 to 1250°C in the iron-containing systems and at lower temperatures, 1050–1150°C, in the manganese-containing systems [6]. The L TEC and ρ_V of materials F are comparable to those of the initial composition I, but their synthesis temperature is 200°C lower.

The activating effect of the modifiers is also evidenced by thermal analysis, XRD, and IR spectroscopy data.

It follows from the thermal analysis data in Fig. 1 that manganese- and iron-containing compounds form in the temperature range 825–960°C. The maximum peak temperatures of the exotherms due to the formation of iron- and manganese-containing phases are 920–960 and 825–830°C for compositions F and M, respectively. The thermal events below 820°C are the decomposition and dehydration of the starting materials. The DTA curve of composition I (Fig. 1a) lacks evidence for formation of any crystalline phases in the temperature range 820–960°C. The peaks between 230 and 495°C in the DTA curves of the manganese-containing samples are due to the thermal decomposition of manganese(II) carbonate.

XRD results for the modified magnesium aluminosilicate systems indicate that the major crystalline phases in the mixed-phase materials are Mg₂₉₋₉M₆Al₂Si₅O₁₈ (0.5 < y < 1.5), M = Mn(II) or Fe(II)) aluminosilicate solid solutions (Figs. 2c, 2d), which are similar in XRD pattern to the low- and high-temperature forms of Mg₂Al₂Si₅O₁₈ (Fig. 2b). The XRD patterns of samples M-1 (Fig. 2c) and F-1 (Fig. 2d) obtained at firing temper-