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A LOW-TEMPERATURE ZONE OF THE SHS WAVE OF SOME METAL OXIDE SYSTEMS

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Regularities in the change in the phase composition and the state of the components of Al-Cr_2O_3 and A-chromium spinel powder mixtures in the heating zone prior to the onset of SHS are established. A characteristic of the "prestarting" state of a metal-oxide (complex and simple) system is given in terms of the indices of physical properties.

Taking the Cr_2O_3-Al and chromium spinel-Al systems as a case in point, the processes occurring in the mixture in the heating zone prior to the onset of SHS were studied. The state of the mixture material in the heating zone (the low-temperature zone of an SHS wave) determines the readiness of the system for the onset of the synthesis and the completeness of its subsequent development.

The samples with chromium spinel contained 15 and 20 wt. % Al, and those with chromium (III) oxide, 15, 20, and 26.5 wt. % of Al. They were shaped as cylinders with $h = d = 20$ mm and subjected to isothermal annealing with holding for 1.5 and 60 min in an air atmosphere at one of the following temperatures: 660, 700, 750, 800, 850, 900, and 950°C. The heating rate was 15 and 250 deg/min. The method of isothermal annealing was used for modeling the heating zone in the range from the temperature of aluminum melting to that of mixture self-ignition. After the heat treatment the samples were studied using a variety of physical methods.

X-ray phase analysis of the Cr_2O_3-Al samples showed that the chromium (III) oxide does not undergo any changes as a result of the annealing. Aluminum content changes considerably as compared to the initial one. The new phase α-Al_2O_3 is detected in the sample only after annealing at 800°C and higher. Chemical analysis demonstrated that the Al content in a sample after annealing at all temperatures corresponds to the initial amount. Changes in the amount of aluminum in the annealed samples, observable in Fig. 1, result from its oxidation with successive formation of an amorphous phase, highly dispersed crystalline γ-Al_2O_3, and α-Al_2O_3. By virtue of their structural features, the first two modifications are not revealed roentgenographically. The rate and the degree of development of each of the oxidation steps are determined by the specific experimental conditions.

Slow heating (15 deg/min) and brief holding (1.5 min) at annealing temperatures of up to 800°C decrease the Al content in the sample by 3-4% relative to that introduced into the mixture. At 850-900°C, the oxidation rate rises noticeably because of cracking of the oxide shell on the metal particles. As a result of such heating conditions, the amount of Al is reduced to half.

Lengthy holding in annealing appreciably decreases the content of Al in the sample and allows a graphic representation of its oxidation stages (Fig. 1b). According to results of x-ray phase analysis (XPA) and widely known literature data, reduction of Al with one-hour annealing at a temperature of up to 700°C is connected with an increase in the amount of the amorphous oxide. The formation, at temperatures above 700°C, of highly dispersed γ-Al_2O_3 of density higher than that of the amorphous film slows down the oxidation process, thus facilitating preservation of Al in the sample. The subsequent phase transition of γ-Al_2O_3 to a denser α-Al_2O_3 also decelerates the oxidation of Al at temperatures above 800°C.

Annealing at 800°C leads to a minimum Al content in the mixture. The extremum on the curve of the Al content vs the annealing temperature at 800°C is also retained with an increase in the heating rate to 250 deg/min. Hence, in sample heating prior to the onset of SHS the temperature of 800°C is hazardous, i.e., here the amount of aluminum is sharply reduced as a result of its oxidation to γ-Al_2O_3.

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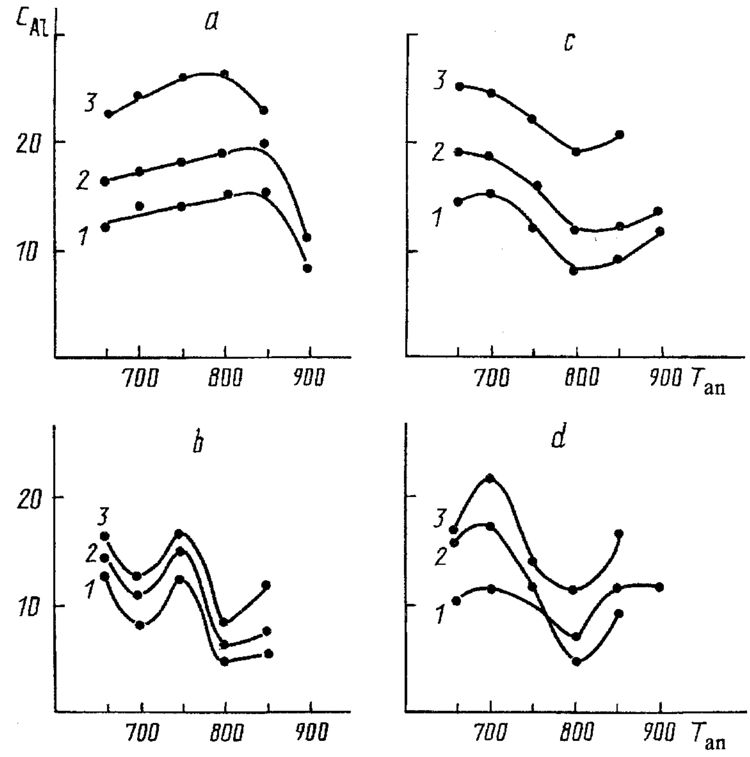

Fig. 1. Aluminum content vs annealing temperature of mixtures of Cr_2O_3 with 15 (1), 20 (2), and 26.5% Al (3). Annealing conditions: the heating rate is 15 (a, b) and 250 deg/min (c, d), the time of isothermal holding is 1.5 (a, c) and 60 min (b, d). C_{Al}, wt. %; T_{an}, °C.

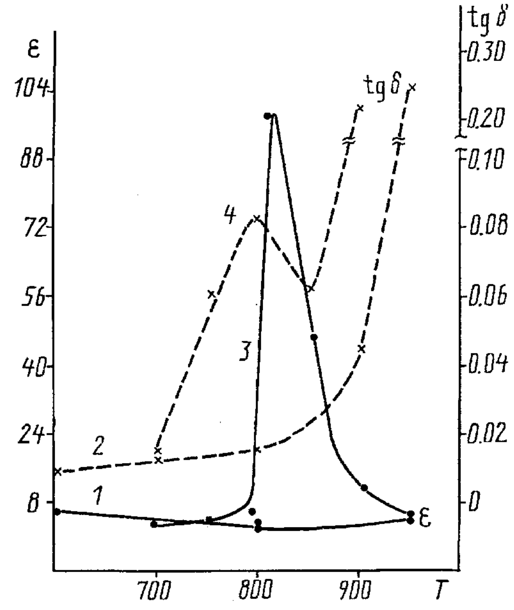

Fig. 2. Permittivity ε and dielectric loss tg δ of chromium oxide (curves 1 and 2) and a chromium oxide-15% Al mixture (curves 3 and 4) as functions of the temperature of isothermal annealing. T, °C.

This assumption is verified by the results of measuring the permittivity ε and the loss tangent tg δ of the samples after annealing. The value of ε for Cr_2O_3 alone virtually does not change after annealing (Fig. 2), and the value of tg δ rises, especially at temperatures above 950°C. Such a rise in tg δ practically by two orders of magnitude might be associated with the presence of a large quantity of hardening vacancies in the material.

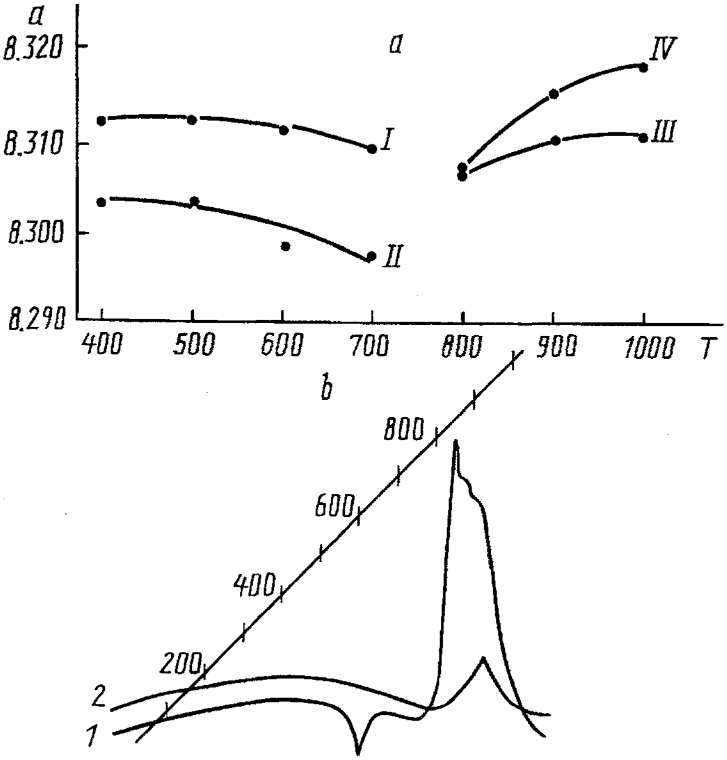

Fig. 3. Parameter of an elementary cell of spinels vs temperature of isothermal annealing ($\tau = 1$ h) of chromium spinel (curves I, II, and III) and a chromium spinel-15% Al mixture (curves I, II, and IV) (a) and thermograms of the chromium spinel-15% Al mixture after annealing at 900°C with a holding of 1.5 (1) and 60 min (2) (b). a, Å.

Annealing of Cr_2O_5-Al mixtures at 700-800°C causes a sharp increase in ε and $\mathrm{tg}\,\delta$. At 900°C the second maximum $\mathrm{tg}\,\delta = f(T_{an})$ is observed. The increase in ε higher than 100 units means that electron-relaxation polarization becomes predominant. It is typical of the compounds with a noticeable portion of a metallic bond and may take place in the presence of an ultradispersed phase.

Such changes in ε and $\mathrm{tg}\,\delta$ can be caused by γ-Al_2O_3 produced in the oxidation of Al vapor over the range of 750-800°C with subsequent crystallization of ultradispersed particles. The decrease in the dielectric characteristics at temperatures above 800°C is related to coarsening of γ-Al_2O_3, formation of α-Al_2O_3, and increase in its amount. The second maximum of $\mathrm{tg}\,\delta$ after annealing, at 900°, of the Cr_2O_3-15% Al mixture, as with Cr_2O_3 alone, indicates a significant number of hardening vacancies and accounts for energetic preparedness of the Cr_2O_3 lattice for chemical interaction.

When the simple oxide Cr_2O_3 is replaced by chromium spinel (Fe, Mg)O, (Cr, Al, Fe)$_2$O$_3$ with lattice parameter a = 8.313 Å, the basic regularities of the change in the state of an oxide-metal thermite system in heating persist. With increasing annealing temperature, the amount of Al in the sample is reduced. The processes of the release of FeO, oxidizing to Fe_2O_3, and of Cr_2O_3 occur in chromium spinel. X-ray phase analysis of the samples after annealing in the temperature range of 400-700°C records two spinels with close lattice parameters (Fig. 3a) instead of the original spinel. Raising the annealing temperature to 800°C changes the phase composition considerably. One spinel is recorded in the sample. As in the Cr_2O_3-Al system, starting with 800° the amount of Al is reduced due to formation of finely dispersed γ-Al_2O_3 and conversion to α-Al_2O_3. A more significant increase in the lattice parameter of chromium spinel with heating in the presence of Al is caused by partial dissolution of the formed α-Al_2O_3 in chromite.

As a result of annealing both in the air and in an inert medium (Ar) at 900-950°C, the amount of Al in the mixture, recorded by XPA, is reduced by 80-90%, and the lattice parameter of spinel increases to a = 8.318 Å here. Thermographic analysis of the samples after one-hour annealing at 900°C does not give an endoeffect of melting of Al at 670°C, as is the case with samples annealed for 1.5 min (Fig. 3b). A virtually total disappearance of aluminum in chromium spinel resulting from annealing was also observed in electron-microscopic investigations of the samples. It is presumed that only a part of the Al oxidized to α-Al_2O_3 dissolves in the spinel, while the other part changes to the gas phase and fills volumes with a defective structure. The system is in a nonequilibrium "prestarting" state, and with disturbance of the dynamic equilibrium, for example, with additional heating to 1000-1050°C, SHS may develop.

Thus, in preparing the mixture material for commencement of synthesis in the heating zone the following processes take place: conversion of aluminum to the gas phase, its oxidation by the oxygen of air with the formation of ultradispersed γ-Al_2O_3 and crystalline α-Al_2O_3 phases, and intense increase in the lattice imperfection of the oxide component of the mixture. An extreme change in the state of aluminum is associated with temperatures of 750-800°C, and for chromium oxide and chromium spinel, with 900-950°C. The onset of SHS is determined by the energetic preparedness of the oxide with preservation of an amount of active metal sufficient for the synthesis to develop. The results obtained may be of interest in developing technological modes of heating in an air atmosphere with the use of SHS of materials made up of mixtures containing Al, Cr_2O_3, and chromite ore.

NOTATION

ε, permittivity; tg δ, loss tangent; a, lattice parameter.