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Note

KINETIC STUDY OF PHASE CHANGES IN SOME MIXTURES OF OXIDES

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The results of a DTA kinetic investigation concerning the crystallization of some oxide mixtures generating spinelic ferrites are presented.

INTRODUCTION

The thermal decomposition of polynuclear coordination compounds (PCC) is sometimes followed by phase changes of the reaction intermediates initially obtained in the amorphous state.

For an understanding of the formation of double oxides through the thermal decomposition of polynuclear coordination compounds, kinetic studies of the above mentioned phase changes were performed. This paper presents the results of such an attempt for the crystallization of the amorphous mixtures of oxides MgO–Fe_2O_3 and FeO–Fe_2O_3, obtained through the thermal decomposition of $(NH_4)_8[Fe_2Mg(C_2O_4)_8] \cdot 4 (NH_4)_2C_2O_4$, $(NH_4)_2[Fe_2Mg(C_2O_4)_2(OH)_6]$, $Fe_3O_4 \cdot 2 H_2O$ and $Fe_3O_4 \cdot 0.5 H_2O$. A general picture of the decomposition of such compounds is given by the following sequence

$$[\mathrm{Me}^{2+}\mathrm{Fe}^{3+}]_{\mathrm{PCC}} \xrightarrow{\text{thermal decomposition}} \text{amorphous mixture of oxides} \xrightarrow{\text{crystallization}}$$

$$\text{crystalline mixture of oxides} \xrightarrow{\text{solid state reaction}} \text{double oxide (ferrite)}$$

The first two steps can be distinguished on the thermal curves (TG and DTA) only if the first step occurs at relatively low temperatures. The exothermic peak which follows, corresponding to the crystallization, gives evidence for the amorphous mixtures of oxides.

In order to determine the kinetic parameters of crystallization, as well as to obtain information on the mechanism associated with the nucleation and growth of nuclei, a DTA method given by Sesták was used [1].

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Starting with the JMAEK (Johanson–Mehl–Avrami–Erofeev–Kolmogorov) equation [2–5]

$$-\ln(1-\alpha)=kt^{n} \qquad (1)$$

a simple treatment for non-isothermal conditions leads to

$$\frac{\left[-\ln(1-\alpha)^{1-n}\right]}{1-n}=\frac{A'}{a}\,\mathrm{e}^{-E/mRT} \qquad (2)$$

where a is the heating rate

$$A'=mA^{1/m} \qquad (3)$$

and

$$n=m-1/m \qquad (4)$$

From eqn. (2) by linearisation and taking into account eqns. (3) and (4) we obtain

$$\log[-\ln(1-\alpha)]=\log A/a-E/2.303RT \qquad (5)$$

The plot of $\log[-\ln(1-\alpha)]$ values against $1/T$ is a straight line whose slope and intercept allow the evaluation of the activation energy, E, and pre-exponential factor, A.

The value of the exponent m can be obtained using Piloyan's equation [6]

$$\log \Delta T=\text{const}-E/mRT \qquad (6)$$

where ΔT is the temperature difference recorded on the DTA curve between the sample undergoing phase change and the reference material. With a previously determined E value, the slope of the $(\Delta T,\ 1/T)$ straight line allows an easy evaluation of m.

EXPERIMENTAL

The following synthesised [7] powders were used: $(NH_4)_8[Fe_2Mg(C_2O_4)_8]\cdot 4\,(NH_4)_2C_2O_4$; $(NH_4)_2[Fe_2Mg(C_2O_4)_2(OH)_6]$; $Fe_3O_4\cdot 2\,H_2O$; $Fe_3O_4\cdot 0.5\,H_2O$, whose composition was established using chemical quantitative analysis, electronic spectra and electrical conductivity measurements [8]. The thermal decompositions were followed in non-isothermal conditions using a Paulik–Paulik–Erdey type derivatograph (MOM, Budapest) with a heating rate of 10 K min^{-1}.

The solid powdered intermediates and products were analysed using a Philips X Ray PW 1140/90 diffractometer with Cu K_α radiation.

RESULTS AND DISCUSSION

The X-ray diffractograms of the mixtures of oxides recorded before and after crystallization showed that: (1) before the phase change all the mixtures

TABLE 1

Values of the parameters E, m, and n for MeO–Fe_2O_3 mixtures

No.	Initial compound	Temperature interval of crystallization (°C)	E (kcal mol^{-1})	m	n
1	$(NH_4)_8[Fe_2Mg(C_2O_4)_8] \cdot 4\,(NH_4)_2C_2O_4$	405–440	59	1.12	0.110
2	$(NH_4)_2[Fe_2Mg(C_2O_4)_2(OH)_6]$	307–354	108	1.67	0.401
3	$Fe_3O_4 \cdot 2\,H_2O$	603–645	17	2.20	0.520
4	$Fe_3O_4 \cdot 0.5\,H_2O$	510–560	12.42 (for $0 < \alpha < 0.2$)	12.60	0.920
			4.92 (for $0.2 < \alpha < 1$)	9.6	0.890

were amorphous; (2) after the phase change the decomposition product of the first polynuclear coordination compound was a crystalline mixture of MgO and Fe_2O_3, while the decomposition products of the other three compounds were a crystalline mixture of Me(II)O, $Me(III)_2O_3$ and Me(II)-$Me(III)O_4$. These results show that the above mentioned phase changes correspond to the crystallization of a mixture of oxides.

The values of the kinetic parameters after the crystallization of stoichiometric MeO–Fe_2O_3 mixtures are given in Table 1. The m and n values suggest, for the first crystallization, an instantaneous nucleation followed by a growth controlled by diffusion towards the crystallite surface. In this case the overall activation energy, E, is given by

$$E = 3/2 E_d \qquad (7)$$

where the subscript d represents diffusion [9].

The second crystallization is described (even better) by the same mechanism. The values of m and n for the third crystallization suggest a constant nucleation rate followed by diffusion towards the crystallite surface. In this case

$$E = E_n + 3/2 E_d$$

where the subscript n represents nucleation. For the last crystallization quite a high value for the exponent m was obtained. According to Sesták et al. [10] the maximum value of this parameter is 4. Nevertheless, taking into account the experimental errors inherent for such measurements, one can assume a mechanism characterised by a constant nucleation rate followed by a growth controlled by the incorporation of constitutive particles in the crystallite surface.

CONCLUSIONS

(1) A kinetic study concerning the crystallization of oxide mixtures which are intermediates in the synthesis of ferrites from polynuclear coordination compounds was performed.

(2) Taking into account the values of kinetic parameters some characteristics of the crystallization (nucleation, and the growth of nuclei) were discussed.

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