Thermochimica Acta, 161 (1990) 363–367
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

ON THE CRYSTALLIZATION KINETICS OF SOME MIXED OXIDES FROM A BINUCLEAR COORDINATION COMPOUND AS PRECURSOR

VIORICA BUJOREANU and C. GHEORGHIES

Department of Metals and Materials Technology, Faculty of Mechanics, University of Galatz, Str. Republicii 111, Galatz (Romania)

MARIA BREZEANU

Department of Inorganic Chemistry and Technology, Faculty of Chemical Technology, Polytechnic Institute of Bucharest, Str. Dumbrava Roșie Nr. 23, Bucharest (Romania)

E. SEGAL

Department of Physical Chemistry and Electrochemical Technology, Faculty of Chemical Technology, Polytechnic Institute of Bucharest, Bulevardul Republicii 13,
Bucharest (Romania)

(Received 29 September 1989)

ABSTRACT

The authors present the results of a kinetic study concerning the crystallization of $MnFe_2O_4$, Fe_3O_4 and γ-Fe_2O_3 which are the final solid products of the thermal decomposition of the binuclear coordination compound $[Fe_4Mn(CH_3COO)_6(OH)_8]\cdot 12H_2O$. The experimental data, determined using methods concerning the kinetics of solid–solid reactions in mixtures of powders, are described by equations having anti-Jander and anti-Gintsling forms.

INTRODUCTION

One of the methods widely used to obtain mixed oxides, particularly those with magnetic properties, consists of the thermal decomposition of polynuclear coordination compounds [1]. In a previous paper [2] we presented the results of such an investigation concerning the thermal decomposition of $[Fe_4Mn(CH_3COO)_6(OH)_8]\cdot 12H_2O$. This paper deals with the isothermal crystallization kinetics of $MnFe_2O_4$, Fe_3O_4 and γ-Fe_2O_3. Due to the fact that all these solid compounds exhibit practically the same crystalline structure with the same lattice parameters, it was the crystallization of the spinelic structure of the mixture that was monitored. In order to follow the isothermal crystallization kinetics, the increase in the intensity of the strongest X-ray diffraction line, located at 2.56 Å, was measured with time.

EXPERIMENTAL

The compound $[Fe_4Mn(CH_3COO)_6(OH)_8] \cdot 12H_2O$ was used as the precursor for the above-mentioned mixture of oxides. According to the results obtained in our previous paper [2], the mean crystallite size of the powder is 58 Å.

The experimental measurements were performed on a DRON.3-URSS X-ray diffractometer using Mo $K\alpha$ radiation at $2\theta = 15.9°$ (corresponding to $d = 2.56$ Å), which was kept constant in isothermal conditions. The temperature in the diffraction chamber was kept constant to within ±1° C. The curves of intensity versus time, $I(t)$, were recorded at various temperatures in the range 270–375° C, corresponding to the temperature of the total decomposition of the precursor and to the limit of the thermal stability of $MnFe_2O_4$, respectively. The samples introduced into the evacuated diffraction chamber were heated at the working temperature for 60 s before recording the $I(t)$ curves.

The experimental data were determined according to the kinetic equations characterising reactions between solid powders limited by diffusion: the parabolic law, Jander's equation and the Gintsling–Brounshtein equation, the Kröger–Ziegler equation and the anti-Jander and anti-Gintsling–Brounshtein equations [3].

RESULTS AND DISCUSSION

As shown by the $I(t)$ curves recorded at various temperatures (Fig. 1), the temperatures suitable for the accurate measurement of the degree of conversion, α, from the intensity data ($\alpha = I/I_{max}$), are higher than 340° C. The data have been determined for $\alpha > 0.3$, and are described kinetically by the anti-Jander equation (Fig. 2)

$$\left[(1+\alpha)^{1/3} - 1\right]^2 = k_1 t \qquad (1)$$

and the anti-Gintsling–Brounshtein equation (Fig. 3)

$$1 + \tfrac{2}{3}\alpha - (1+\alpha)^{2/3} = k_2 t \qquad (2)$$

In Figs. 2 and 3, $F(\alpha)$ is represented by the left sides of eqns. (1) and (2) respectively.

From the slopes of the straight lines ($F(\alpha)$, t), the following values of the rate constants k_1 and k_2 have been obtained:

Anti-Jander

$k_1^{340° C} = 1.57 \times 10^{-4}$ s^{-1}, $r = 0.9978$

$k_1^{360° C} = 1.94 \times 10^{-4}$ s^{-1}, $r = 0.9989$

$k_1^{375° C} = 2.70 \times 10^{-4}$ s^{-1}, $r = 0.9984$

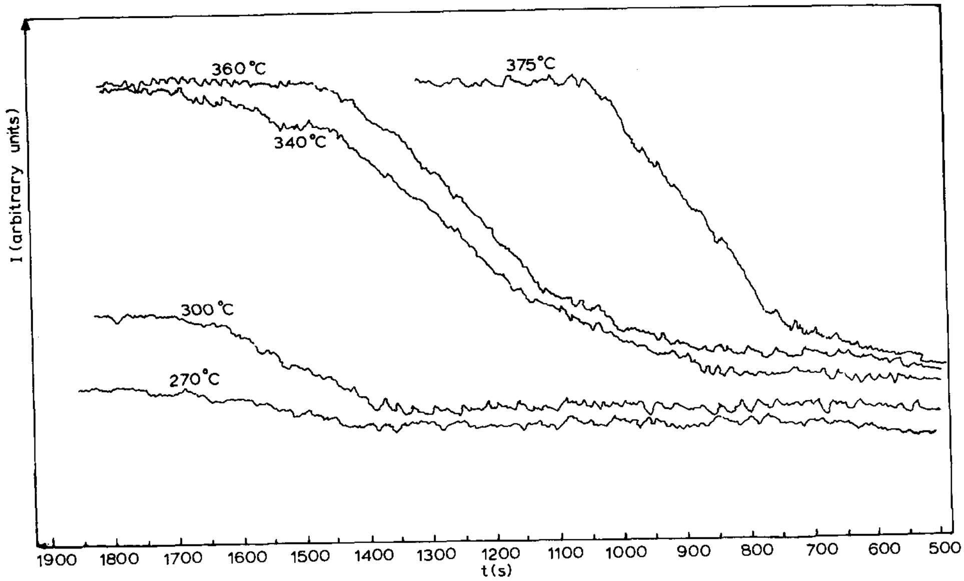

Fig. 1. Experimental $I(t)$ curves for various temperatures.

Anti-Gintsling–Brounshtein

$k_2^{340°\,C} = 1.95 \times 10^{-4}\ s^{-1}$, $r = 0.9956$

$k_2^{360°\,C} = 2.48 \times 10^{-4}\ s^{-1}$, $r = 0.9983$

$k_2^{375°\,C} = 3.075 \times 10^{-4}\ s^{-1}$, $r = 0.9957$

where r is the correlation coefficient of the linear regression.

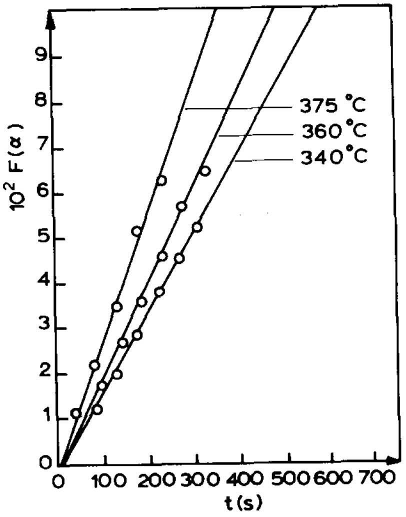

Fig. 2. Linear plot of $F(\alpha) \times 10^2$ (Jander) versus t.

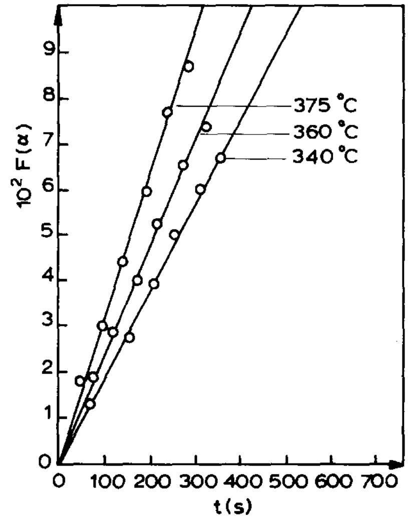

Fig. 3. Linear plot of $F(\alpha) \times 10^2$ (Gintsling–Brounshtein) versus t.

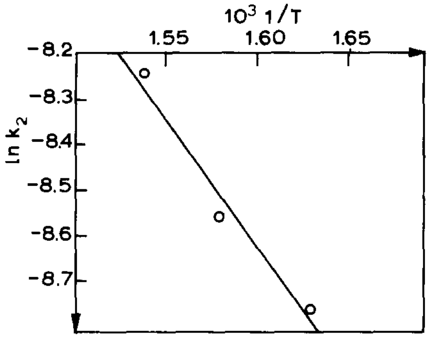

Fig. 4. Arrhenius plot for k_1.

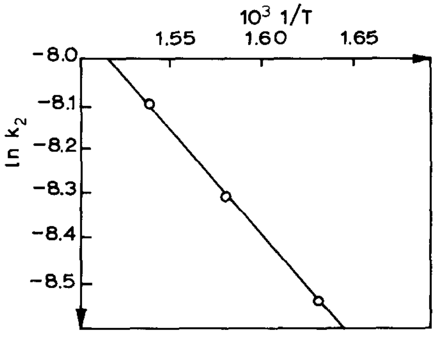

Fig. 5. Arrhenius plot for k_2.

As shown in Figs. 4 and 5, the temperature dependence of the constants k_1 and k_2 is described by the Arrhenius equation. The values obtained for the activation energies and pre-exponential factors are: $E_1 = 11.69$ kcal mol^{-1}, $A_1 = 2.24$ and $r_1 = 0.9750$; $E_2 = 9.91$ kcal mol^{-1}, $A_2 = 1.51$ and $r_2 = 0.9981$.

According to these results, the generation of the crystalline mixture of $MnFe_2O_4$, Fe_3O_4 and γ-Fe_2O_3 occurs by diffusion from the interior of a sphere which can be identified with one of the solid reactants (for instance, B) to the interface, AB/A. At this interface the growth of the product layer AB occurs. Taking into account the presence of oxygen in the reactants as well as in the solid reaction product (for instance, $MnFe_2O_4$), the diffusion is actually a cationic diffusion through the product layer.

CONCLUSIONS

The generation of the spinelic crystalline structure in the mixture $MnFe_2O_4$, Fe_3O_4 and γ-Fe_2O_3 occurs with measurable rates in the temperature range 340–375 ° C. The experimental relationship between the intensity of the strongest diffraction line and time obtained in this temperature range can be used to evaluate the kinetic parameters for the solid–solid reaction through which the spinelic structure is generated.

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