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Kinetics of high temperature recrystallization of $MnFe_2O_4$ from wet reaction prepared powders

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Abstract

The authors present some results regarding the thermal behaviour of $MnFe_2O_4$ prepared through a wet reaction, as well as isothermal kinetic data concerning the high temperature recrystallization of this compound.

INTRODUCTION

Following our research on mixed oxides with magnetic properties obtained through wet reaction [1], this paper contains the results of an investigation regarding $MnFe_2O_4$ obtained by a procedure which constitutes an application for a patent.

According to published data [2] on the investigated system, below 400 ° C the compound $MnFe_2O_4$ with spinel structure is stable. In the temperature range 450–750 ° C the phases Fe_2O_3, Mn_2O_3 and $MnFe_2O_4$ coexist and in the temperature range 800–1020 ° C the spinel is totally decomposed into other phases. At temperatures higher than 1020 ° C one may note the recrystallization of $MnFe_2O_4$ with the regeneration of its spinelic phase. In these conditions this phase is stable at atmospheric pressure and exhibits a maximum content of 0.5% of Mn_2O_3.

In order to investigate the thermal behaviour of $MnFe_2O_4$ synthesized by the wet reaction procedure, derivatographic analyses in the temperature range 20–1500 ° C, as well as dilatometric and X-ray diffractometric investigations in the temperature range 20–125 ° C, have been carried out.

EXPERIMENTAL

The granulometric composition of $MnFe_2O_4$, given in Fig. 1, was determined using a Cilas 71-S (France) granulometer after agitation for two minutes by supersonic waves.

The TG, DTG and DAT curves (Fig. 2) were recorded by means of a derivatograph (MOM-Budapest) of Paulik–Paulik–Erdey type in a static air atmosphere at a heating rate of 10 K min^{-1}.

The dilatometric curves (Figs. 3 and 4) were recorded in air at 5 K min^{-1} with a Harrop–TDA (USA) dilatometer on circular dropped samples ($9 \times 6 \times 6$ mm^3) pressed at 700 daN.

The X-ray diffractograms were recorded in air by means of a DRON-3 (USSR) diffractometer, using the Kα radiation of molybdenum, in a high temperature chamber. Under nonisothermal conditions, the diffractograms were recorded at 25 K min^{-1} (Fig. 5).

The isothermal curves recorded at three temperatures in the range 1020–1060 °C, showing the change with time of the intensity I for the (400) line of $MnFe_2O_4$ ($d = 2.108$ Å), are given in Fig. 6.

Before recording the isothermal curves $I(t)$, the samples were heated at 25 K min^{-1} to 920 °C, kept at this temperature for 10 minutes and then quickly brought to the working temperature. We established that 10 minutes was the time necessary for total decomposition of the spinelic phase

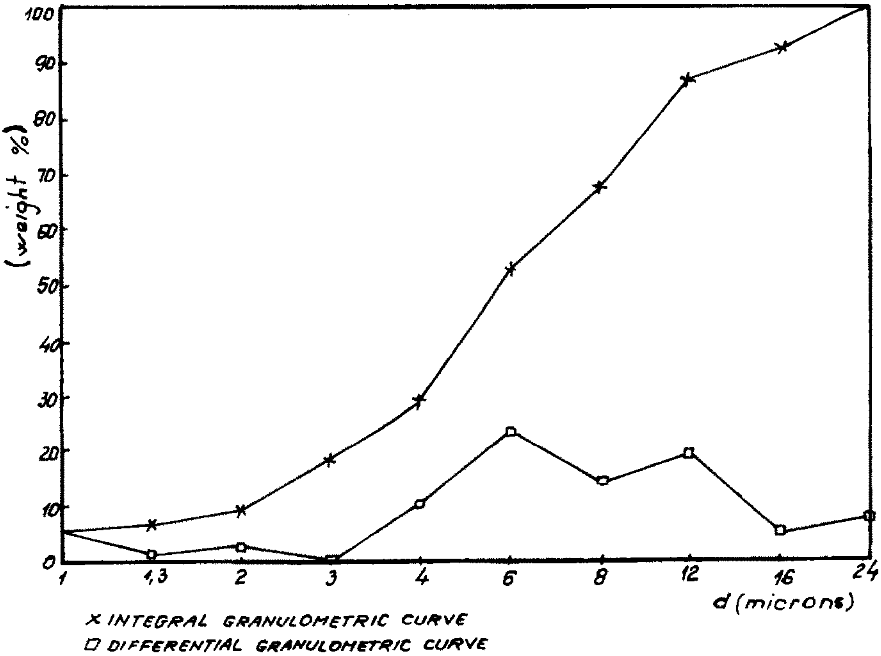

Fig. 1. Granulometric curves of $MnFe_2O_4$ powder prepared by wet reaction.

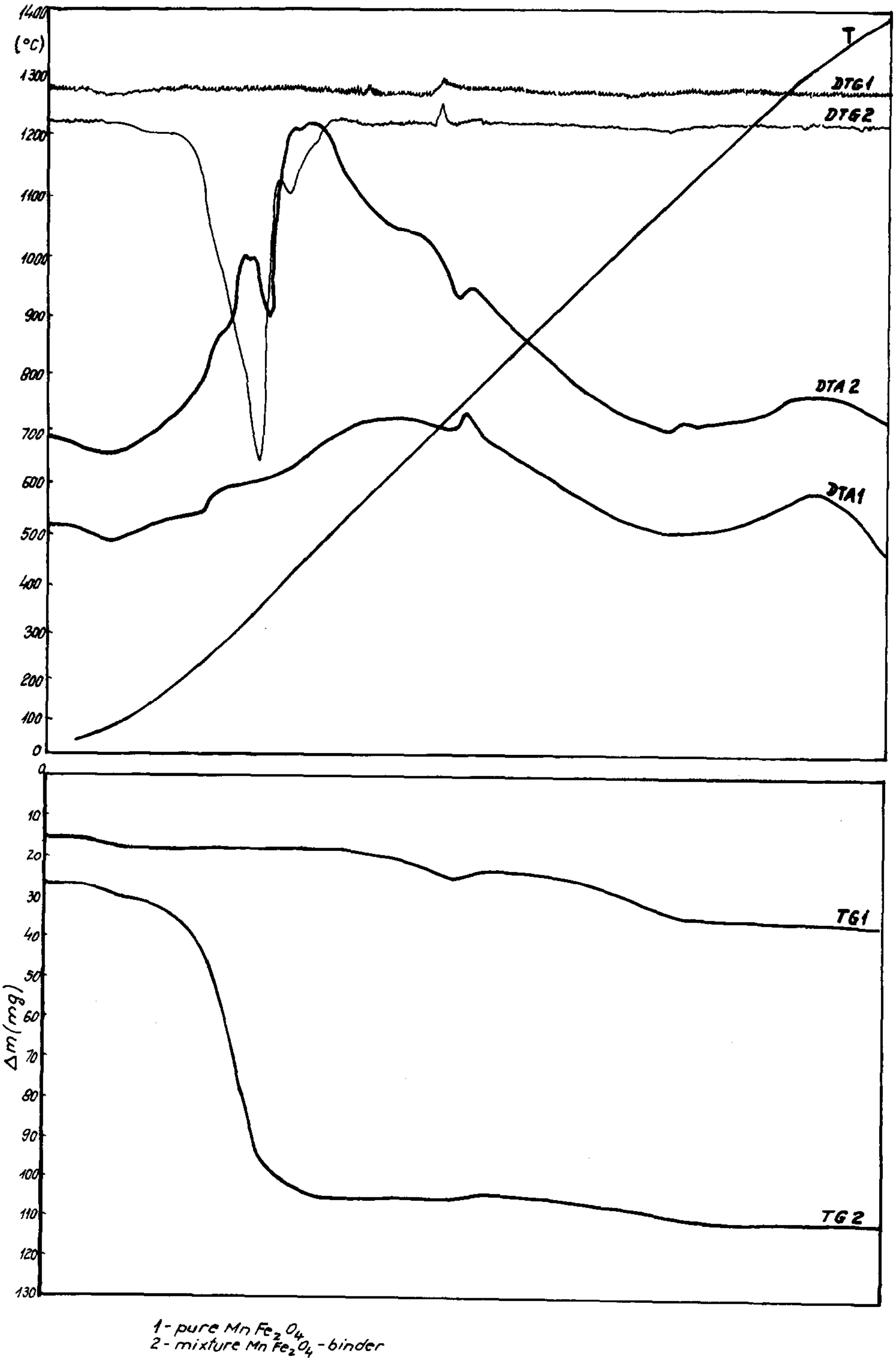

Fig. 2. Derivatograms of pure $MnFe_2O_4$ and $MnFe_2O_4$–binder mixture.

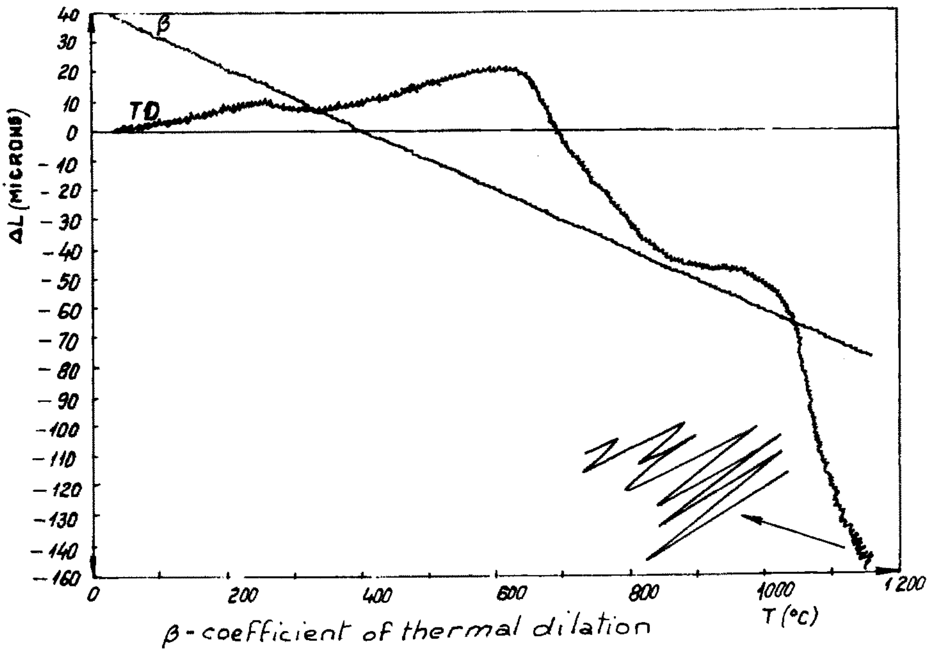

Fig. 3. Thermodilatometric curve (TD) of pressed $MnFe_2O_4$-binder sample.

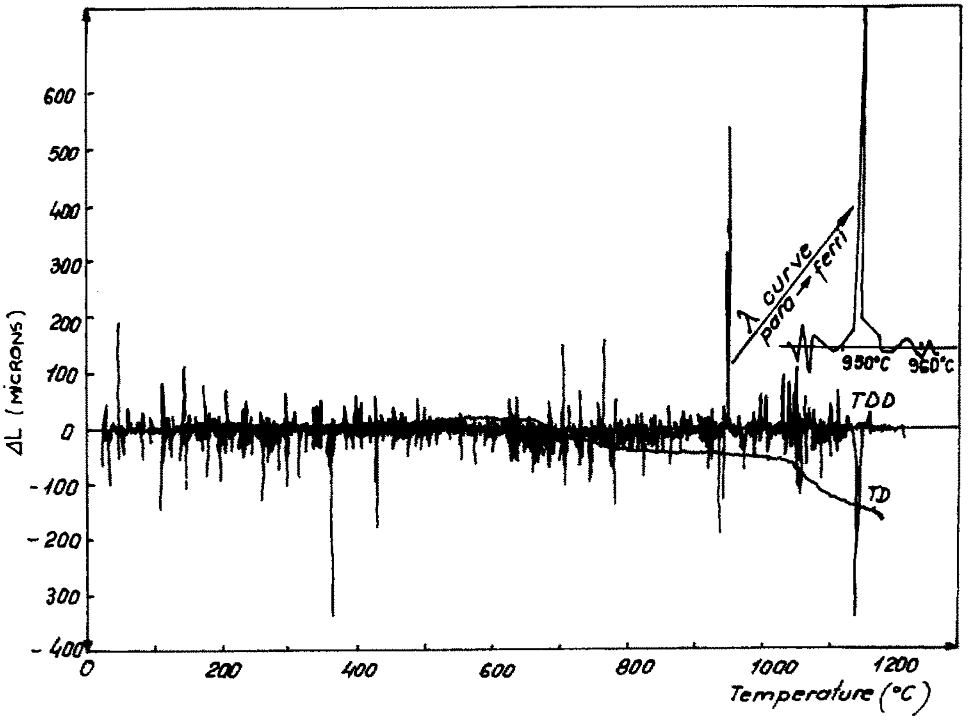

Fig. 4. Derivative thermodilatometric curve (TDD) of pressed $MnFe_2O_4$-binder sample.

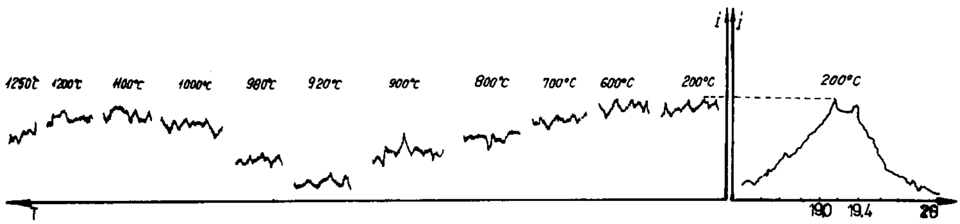

Fig. 5. Intensity change corresponding to the (400) diffraction peak (20 = 19.22 °) with temperature.

(see Fig. 5). The temperature of 920 ° C was chosen, as at this temperature the intensity corresponding to the (400) line under the mentioned conditions of heating (25 K min^{-1}) decreases, until the background value is reached (Fig. 5).

The experimental data were processed according to the kinetic equations describing the solid state reactions which occur in powders [3].

RESULTS AND DISCUSSION

According to the recorded derivatograms, dilatometric curves and X-ray diffractograms, the following changes occur during the progressive heating of the $MnFe_2O_4$ powders prepared by a wet reaction.

Around 100 ° C, a slight endothermic change in weight (≈ 1.5%) occurs corresponding to the loss of humidity.

In the temperature range 350–600 ° C, the $MnFe_2O_4$ powder exhibits an endothermic change of weight (≈ 1.8%) corresponding to the loss of water (probably from the OH groups generated during the wet reaction).

In the temperature range 200–550 ° C the $MnFe_2O_4$–binder mixture

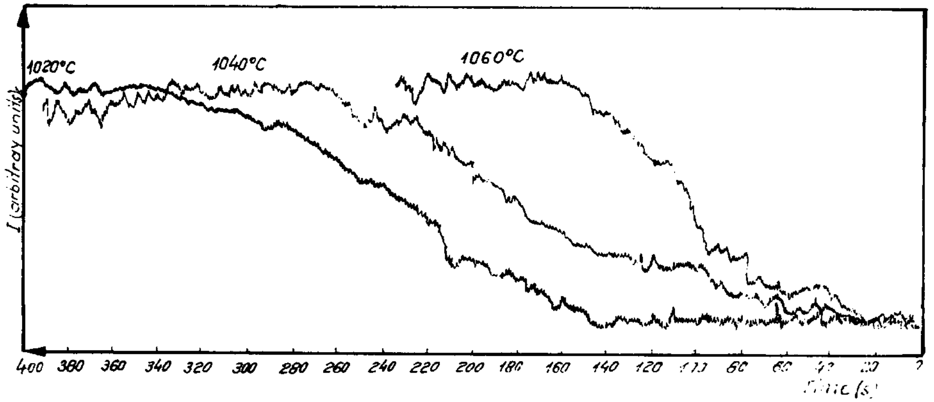

Fig. 6. Experimental $I-t$ curves for various temperatures.

exhibits complex endothermic and exothermic degradation with loss of weight accompanied by oxidative degradation of the binder.

In the temperature range 100–600 ° C, as shown by the thermodilatometric curve, a two step dilation (curve TD in Fig. 3) is evident, due to the two previously mentioned reactions with loss of weight; because of the compaction of the samples through their previous treatment, the rate of diffusion of the volatile products of decomposition is lower than the rate of their generation, and the accumulation of these products is responsible for the dilation of the material.

In the temperature range 700–800 ° C there is a slight exothermic increase in weight (the corresponding peak of the DTA curve, as shown in Fig. 2, is located at 750 ° C) corresponding to the oxidation of Mn^{2+} to Mn^{3+}, as predicted by the equilibrium diagram [2].

The same phenomenon which corresponds to the destruction of the spinelic structure is manifested by the beginning of a pronounced decrease in the intensity of the (400) X-ray diffraction line of $MnFe_2O_4$ (Fig. 5).

In the temperature range 800–1100 ° C a slight decrease in weight occurs, owing to the reaction

$$Mn_2O_3(s) \rightarrow 2\ MnO(s) + 0.5O_2\ (g)$$

and to its reaction product becoming nonstoichiometric.

In the temperature range 850–950 ° C, which corresponds to a dramatic structural change, the system exhibits practically no contraction.

At 950 ° C the derivative thermodilatometric curve (the "Lambda" curve TDD, in Fig. 4) exhibits a phase transition of second order [4]. The "Lambda" curve corresponding to the increase in the (400) X-ray diffraction line intensity (Fig. 5) could be assigned to a change from paramagnetic to ferromagnetic associated with the onset of $MnFe_2O_4$ recrystallization.

At temperatures higher than 1000 ° C, the contraction of the samples increases, mainly in the range 1020–1070 ° C. This temperature range was chosen for kinetic measurements because, as shown in Fig. 5, in this range recrystallization occurs, the (400) X-ray diffraction line intensity reaching its initial value as at 20 ° C.

At temperatures higher than 1100 ° C superficial melting of the material at the boundary of the crystalline grains occurs, as shown by the "funnel" in the dilatometric curve (Fig. 3) as well as by the decrease in the intensity corresponding to the (400) X-ray diffraction line.

Around 1350 ° C the exothermic peak on the DTA curve (Fig. 2) corresponds to formation of the perfect spinel structure as a consequence of an increase in the rate of diffusion of the lattice defects, which according to Tamman's rule becomes important at a temperature higher than two thirds of the temperature of melting. These defects probably consist of interstitial Mn^{2+} ions, their interaction with the magnetic cubic γ-Fe_2O_3 leading to the spinel structure of $MnFe_2O_4$.

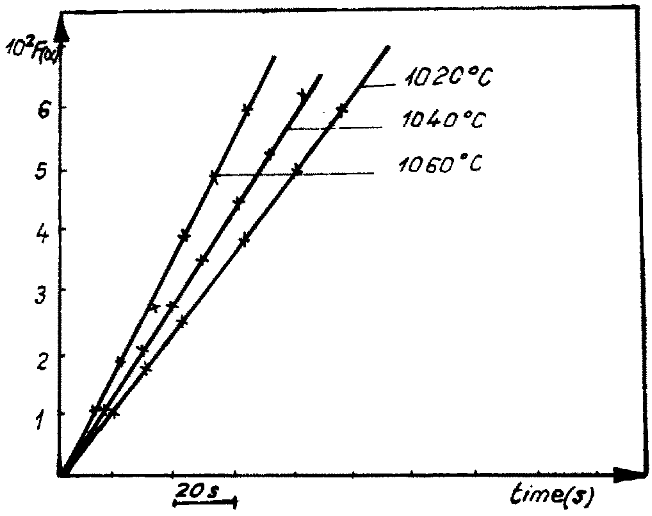

Fig. 7. Linear plot of $F(\alpha)\times 10^2$ (anti-Ghinstling–Brounshtein) versus t.

To calculate the activation energy corresponding to this high temperature manganese ferrite recrystallization, the $I(t)$ curves from Fig. 6 have been used. Using the values of the degree of conversion α given by

$$\alpha = \frac{I}{I_{\max}} \tag{1}$$

from the pair of points (α, t), the anti-Ghinstling–Brounshtein integral kinetic equation has been checked.

$$1 + \tfrac{2}{3}\alpha - (1+\alpha)^{2/3} = kt \tag{2}$$

From the plots of $[F(\alpha), t]$ presented in Fig. 7, where

$$F(\alpha) = 1 + \tfrac{2}{3}\alpha - (1+\alpha)^{2/3} \tag{3}$$

the following values of the rate constant, for values of α in the range 0.34–0.86, have been obtained (where r denotes the correlation coefficient of the linear regression)

$k_{1020\,^\circ\mathrm{C}} = 6.96\times 10^{-4}\ \mathrm{s}^{-1}$ $\quad r = 0.9998$

$k_{1040\,^\circ\mathrm{C}} = 8.33\times 10^{-4}\ \mathrm{s}^{-1}$ $\quad r = 0.9986$

$k_{1060\,^\circ\mathrm{C}} = 10.14\times 10^{-4}\ \mathrm{s}^{-1}$ $\quad r = 0.9994$

As shown in Fig. 8, these values are well described by the Arrhenius equation. From the slope and the intercept of the straight line the following values of the activation energy E and preexponential factor A have been obtained: $E = 34.8$ kcal mol^{-1}; $A = 4.83\times 10^2\ \mathrm{s}^{-1}$; $r = 0.9994$.

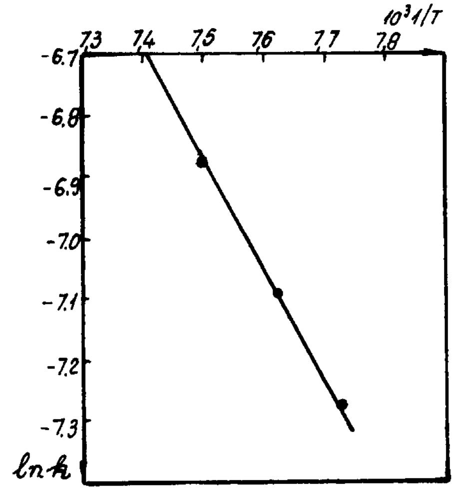

Fig. 8. Arrhenius plot.

CONCLUSIONS

The thermal behaviour of $MnFe_2O_4$ with spinel structure, prepared by wet reaction, has been investigated in the temperature range 20–1500 °C. The kinetic parameters of the high temperature recrystallization of the spinelic $MnFe_2O_4$ have been determined.

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