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KINETICS OF MANGANESE FERRITE GENERATION FROM AQUEOUS SOLUTION OF MnO_2 AND $FeSO_4 \cdot 7H_2O$ THROUGH COPRECIPITATION AND AGEING

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Abstract

The authors present a kinetic investigation of the generation of manganese ferrite by the ageing of some coprecipitates in contact with the residual solution.

Keywords: ageing, coprecipitation, kinetic parameters, manganese ferrite, mechanism

Introduction

In a previous paper [1] the results of a detailed investigation concerning the generation of manganese ferrite through ageing of oxidic coprecipitates containing manganese and iron ions at temperatures in the range 55–95°C have been presented. The present paper deals with the kinetics of ageing of the coprecipitates generating cubic manganese ferrite with tetragonal distortion.

Experimental

The kinetic investigation is based on data concerning the changes that can be recorded in the X-ray diffractograms during ageing, as shown qualitatively in our previous paper [1].

Samples taken from the coprecipitate at various ageing times were filtered, washed, dried in air at ambient temperature and sieved through a 0.16 mm^2 mesh net.

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The changes with time of the intensity and half-width of the (311) line of the spinel $MnFe_2O_4$ were used for the kinetic investigation. The experimental data were processed by fitting them to various kinetic equations known from the literature [2, 3].

The conversion degree of the coprecipitate to the ferritic phase, α, was calculated according to the relationship:

$$\alpha = \frac{\Delta I}{\Delta I_\infty} \tag{1}$$

with

$$\Delta I = I - I_o \tag{2}$$

$$\Delta I_\infty = I_\infty - I_o \tag{3}$$

where I is the intensity of the (311) diffraction line of $MnFe_2O_4$ spinel at time t, subscripts o and ∞ mean initial and final respectively. The considered final moments are 480 min for ageing at 55°C and 300 min for ageing at 75, 80 and 95°C.

The conversion degree for the growth of the manganese ferrite crystallites, β, was estimated by means of the relationship:

$$\beta = \frac{\Delta B}{\Delta B_\infty} \tag{4}$$

with

$$\Delta B = B - B_o \tag{5}$$

$$\Delta B_\infty = B_\infty - B_o \tag{6}$$

where B is the half-width of the (311) diffraction line belonging to the mentioned compound and the subscripts have the same meaning as in relationships (2) and (3).

Results and discussion

Figure 1 shows the change with time of the conversion degree, α, for various ageing temperatures. The sigmoid form of the curves (α, t), clearly evidenced at low temperatures, shows that the generation of the ferritic phase is a nucleation – growth process which consists in:

– the formation of stable nuclei with supercritical sizes;
– the subsequent growth of the formed nuclei.

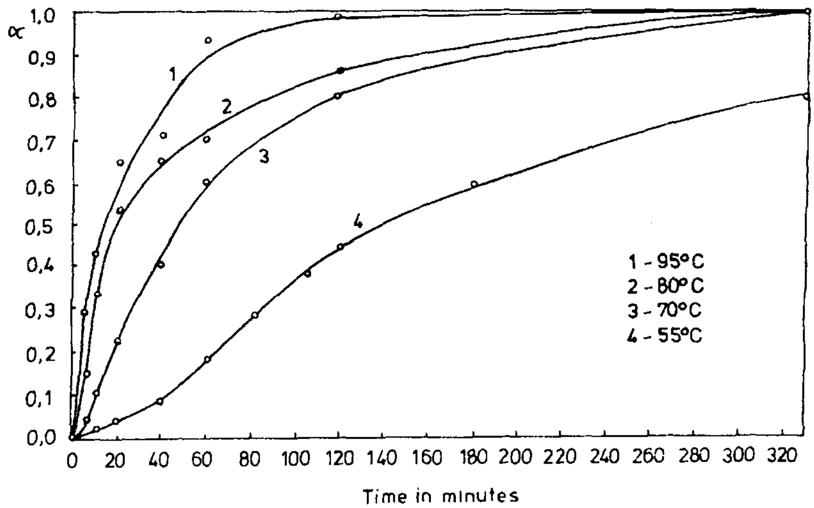

Fig. 1 The ageing (α, *t*) curves

The higher the sizes of the ferritic nuclei, the more shifted the inflexion point of the (α, *t*) curve towards the origin. Such curves are those obtained at 80 and 95°C that correspond to the growth of fast formed nuclei. From Fig. 1 one obtains the following values for the first period of nuclei formation: at 95 and at 80°C – practically 0 min, at 70°C – 5 min, and at 55°C – 40 min.

Similar results have been presented by Gribanov et al. [4]. They showed that the formation of magnetite by precipitation with hydroxide from aqueous solution of iron salts occurs in two stages: the induction period (I) and the growth of magnetite crystalline particles (II). The induction period characterised by the absence of magnetic properties, decreases with the increase of temperature and disappears above 70°C.

The kinetic parameters of the growth of nuclei (second step) were obtained by processing the (α, *t*) curves for the following conditions:

– at 95°C for 0 min $\leq t \leq$ 40 min and $0.00 \leq \alpha \leq 0.72$;
– at 80°C for 0 min $\leq t \leq$ 60 min and $0.00 \leq \alpha \leq 0.69$;
– at 70°C for 10 min $\leq t \leq$ 120 min and $0.05 \leq \alpha \leq 0.78$;
– at 55°C for 60 min $\leq t \leq$ 330 min and $0.18 \leq \alpha \leq 0.72$;

For these time intervals and conversion degree ranges, the best fitting of the experimental data was obtained for equation

$$\alpha = 1 - e^{-kt^n} \tag{7}$$

Table 1 Values of the kinetic parameters k and n for various temperatures of ageing in the original solutions

$T_{Ageing}/^{o}C$	k/min^{-n}	n	r*
95	$9.44\ 10^{-2}$	0.89	0.9936
80	$5.50\ 10^{-2}$	0.87	0.9889
70	$1.50\ 10^{-2}$	0.91	0.9997
55	$0.36\ 10^{-2}$	1.03	0.9961

*correlation coefficient of the linear regression

The values of the 'rate constant' k, as well as of the exponent n are listed in Table 1.

From the change of k with temperature, the following values of the activation parameters were obtained:

$$E = 86\ \text{kJ mol}^{-1}, A = 1.83\ 10^{11}\ \text{min}^{-1}, r = 0.9823.$$

Taking into account the values of the exponent n being close to unity we expressed roughly the preexponential factor in min^{-1}.

Equation (7) is known in the kinetics of precipitation [3] as describing (for n=1) reactions with homogeneous nucleation and growth controlled by surface processes. Through precipitation with homogeneous nucleation each stable nucleus is resulted by simultaneous precipitation of a number of Fe^{3+}, Mn^{2+} and OH^- ions sufficient in order for the nuclei to attain a size equal to or larger than the critical value [3, 5]. The formation of ferrite crystallites through the growth of nuclei is controlled by an interface process being the result of intergrowth of many individually nucleated surface nuclei. To put it differently, the development of the ferritic phase occurs according to the mechanism of the polynuclear layer growth [3].

The pairs of points β,t are described also by Eq. (7). The values of the kinetic parameters of this equation which characterize the growth of nuclei (second step) are listed in Table 2.

Table 2 Values of the kinetic parameters k and n calculated from the (β,t) data

$T_{Ageing}/^{o}C$	k/min^{-n}	n	r*
95	$4.90\ 10^{-2}$	1.08	0.9969
80	$3.65\ 10^{-2}$	1.10	0.9858
70	$2.70\ 10^{-2}$	1.01	0.9902
55	$1.87\ 10^{-2}$	0.92	0.9903

*correlation coefficient of the linear regression

Using the Arrhenius equation, the following values of the activation parameter were obtained:

$$E = 24.75 \text{ kJ mol}^{-1}, A = 163 \text{ min}^{-1}, r = 0.9983.$$

The obtained value of the activation energy is close to that given in the literature [5], namely 25 kJ mol^{-1} for the ageing of coprecipitates obtained from solutions of Fe^{3+} and Mn^{2+} ions, coprecipitates which contain from the very beginning (t=0) only ferritic nuclei. This value of the activation energy can be assigned to the growth of the ferritic nuclei.

Thus, the kinetic parameters obtained by processing the α, t data characterize the whole history of manganese ferrite generation in the coprecipitate in contact with the residual solution. As far as the data β, t are concerned, they express mainly the growth of the $MnFe_2O_4$ nuclei after they have attained the critical size.

Conclusions

1. A kinetic investigation was carried out of the ageing of the oxidic mixture obtained by coprecipitation of an aqueous solution of MnO_2 and $FeSO_4{\cdot}7H_2O_4$ to yield the $MnFe_2O_4$ spinel.

2. The formation of $MnFe_2O_4$ through ageing occurs according to a homogeneous nucleation and growth mechanism controlled by surface processes.

3. An attempt was made to separate kinetically the growth of $MnFe_2O_4$ nuclei using the change with time of the half-width of the (311) diffraction line of the spinel.

References

1 V. Musat Bujoreanu, E. Segal, M. Brezeanu, R. Salmon, J. J. Videau and C. Georghies, Thermochim. Acta, submitted to publication.
2 I. G. Murgulescu, T. Oncescu and E. Segal, 'Introduction in Physical Chemistry' (in Romanian), Vol. II. 2, Publishing House of the Academy, Bucharest 1981, p. 689.
3 A. E. Nielsen, 'Kinetics of Precipitation', Pergamon Press, Oxford-London-Edinburgh-New York-Paris-Frankfurt 1964, p. 89.
4 N. M. Gribanov, E. E. Bibik, O. V. Buzunov and V. N. Naumov, J. Magn. Mat., 85 (1990) 7.
5 Z. X. Tang, C. M. Sørensen, K. J. Klabunde and G. C. Hadjipanayis, J. Colloid. Interface Sci., 146 (1991) 38.