

ON THE KINETICS OF MANGANESE FERRITE FORMATION FROM AQUEOUS SOLUTION OF MnO_2 AND $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

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Abstract

The authors present the results of a kinetic investigation concerning the formation and growth of the primary particles of the ferrite phase in isothermal conditions, in static and well-stirred regimes. The kinetics of coprecipitation is described with the help of equations corresponding to the homogeneous nucleation.

Keywords: coprecipitation, homogeneous nucleation, kinetic parameters, manganese ferrite

Introduction

Following our research concerning the kinetics of manganese ferrite co-precipitation [1], this work deals with the kinetics of the main crystalline planes of the spinelle structure formation in static as well as in well-stirred regimes. For a proper description of the ferrite crystallites generation, the kinetic equations of the precipitation with homogeneous nucleation [2] have been used.

The increase of the amount of coprecipitated crystalline compound can be obtained either through the simultaneous increase of the particle number and size (A), or through the increase of sizes of a constant number of particle (B). Case (A) corresponds to a mechanism of precipitation through homogeneous nucleation. The corresponding kinetic equations are listed and explained in appendix. Case (B) corresponds to the increase of the amount of crystalline phase through the growth of the sizes of a constant number of particles. The kinetic equations describing it are also listed and explained in appendix.

There are two ways to identify the mechanism of the formation and growth of these particles in solution:

– the experimental determination of the mean linear sizes of the particles as a function of the initial value of the solution supersaturation, at the same value of the

maturation time and the comparison of the so obtained value with those from the Nielsen's diagram [2, 3];

– the experimental determination of the change in time of the particle sizes for an initial constant value of the solution supersaturation ratio and subsequent evaluation of the kinetic parameters corresponding to the conversion curve (α , t). The portion of the curve located under the inflection point, generally in the conversion range $0 < \alpha < 0.2$, is very important in order to discriminate, according to the equations (I)–(III) and (IX)–(XI) from the Appendix, among the mentioned growth mechanisms; this discrimination is based on the value of the slope of the straight line ($\log \alpha$, $\log t$). Working the data corresponding to the region located over the inflexion point of the curve (α , t), allows to evaluate, by help of equation (IV)–(VIII) and (XII)–(XIV) from the Appendix, the values of the apparent rate constant as well as of the m and p apparent parameters corresponding to the above identified mechanism [2].

In this work, the second procedure is going to be used in order to identify the formation and growth mechanism of the ferrite particles in solution.

Experimental

The isothermal kinetic investigations are performed using the change of the intensity and half-width of the main X-ray diffraction lines of the ferrite phase during maturation of coprecipitates [4]. Besides the usual way to investigate the kinetics of precipitation by following the change of the detectable particles number or their size distribution, in literature there are some papers concerning the kinetics of precipitation from X-ray diffraction data [5–8].

Samples taken from the coprecipitates at various maturation times in solution, under isothermal conditions at temperatures in the range 55–95°C, with or without stirred-flow, without air bubbling and without adding other oxidants, were filtered, washed and dried in air at the ambient temperature.

The X-ray powder diffractograms were recorded at ambient temperature with the help of a DRON-3 diffractometer using the K_{α} radiation of molybdenum.

At constant values of the experimental parameters and particle size under 400 Å, the intensity, I , of the diffraction line is proportioned with the volume of irradiated crystalline phase [9] and the angular width, B , correspondingly to the mean size of the crystallites. Thus, for the first period of maturation, we considered that the conversion degree, α , calculate with the help of the relation:

$$\alpha = \frac{\Delta I_t}{\Delta I_{\infty}} = \frac{I_t - I_0}{I_{\infty} - I_0} \quad (1)$$

where I_0 , I_t and I_{∞} stand for the initial, current and final intensities, express the increase of the amount of ferrite phase. The conversion degree, β , calculate with the help of the relation:

$$\beta = \frac{\Delta B_t - B_t - B_0}{\Delta B_\infty - B_\infty - B_0} \quad (2)$$

where B_0 , B_t and B_∞ stand for the initial, current and final halfwidth, express the increase of the linear crystallite size. As final moment, there were considered 480 min for the maturation at 55°C and 330 min for the maturation at temperatures in the range 70–90°C.

The experimental data concerning the conversion degrees α and β have been kinetically worked (out) by using equations (I)–(XIV) from Appendix.

Results and discussion

The conversion curves (α, t) and (β, t) corresponding to the formation of the planes (311) and (440) of the spinelle lattice of the manganese ferrite during the maturation of the coprecipitates at various temperatures with or without stirring, are given in Figs 1–6. The slope of the curves indicates several steps of the ferrite phase growth in solution. In this work we shall discuss only the formation and growth step of primary particles.

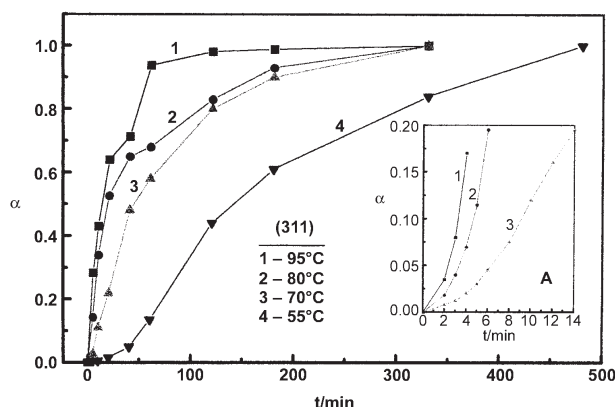


Fig. 1 The maturation (α, t) curves, corresponding to the formation of the (311) plane of the ferrite phase, at different temperatures in static conditions

The sigmoid shape of the curves, specific for the topochemical processes [10] shows that the formation of the ferrite phase in solution is a process with nucleation. The time corresponding to the nucleation period is temperature dependent. According to Griбанov *et al.* [11], the magnetite formation from Fe^{2+} and Fe^{3+} salts in solution through coprecipitation with NaOH, exhibits an induction period which is characterised by the absence of magnetic properties. This period decreases with temperature and practically vanishes at temperatures higher than 70°C.

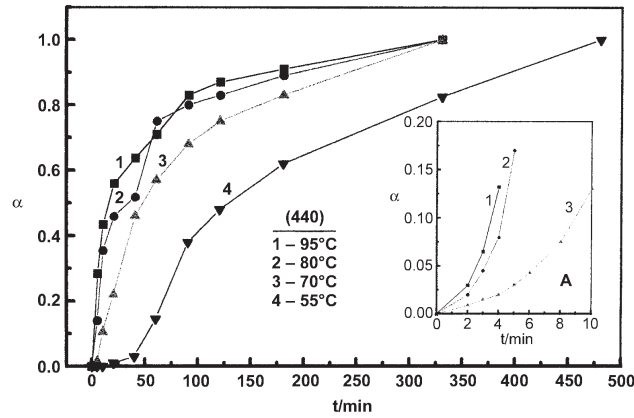


Fig. 2 The maturation (α, t) curves, corresponding to the formation of the (440) plane of the ferrite phase, at different temperatures in static conditions

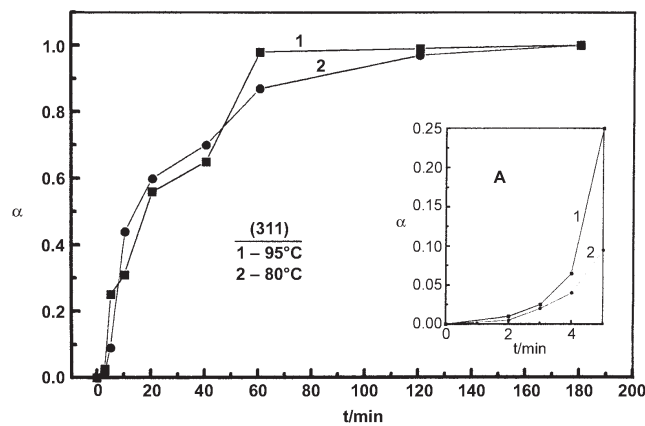


Fig. 3 The maturation (α, t) curves, corresponding to the formation of the (311) plane of the ferrite phase, at different temperatures in well-stirring conditions

The kinetics of the growth of the ferrite phase amount

In order to identify the ferrite phase formation mechanism in solution, we determined the slope of the straight lines ($\ln\alpha, \ln t$) for $\alpha \leq 0.2$, for the experimental curves given in detail A from Figs 1–4. The obtained values as well as the mechanisms corresponding to them, according to the equations (I)–(III) and (IX)–(XI) from Appendix, are given in Table 1.

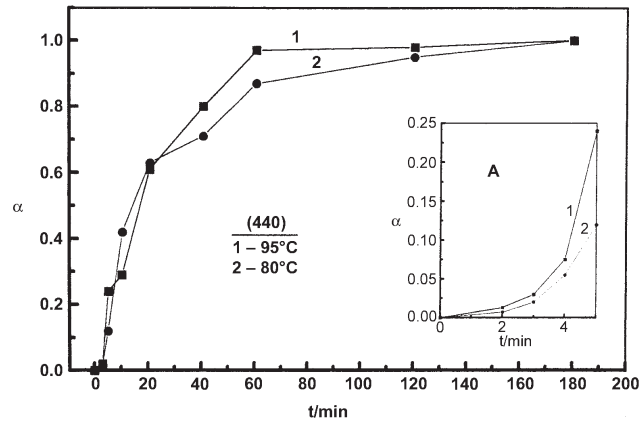


Fig. 4 The maturation (α , t) curves, corresponding to the formation of the (440) plane of the ferrite phase, at different temperatures in well-stirring conditions

Table 1 The slopes of the linear dependencies ($\ln\alpha$, $\ln t$) for $\alpha \leq 0.2$, corresponding to the formation of (311) and (440) planes of the ferrite phase for various maturation temperatures and regimes

Maturation regime	Crystalline plane	$T/^\circ\text{C}$	Slope of the linear dependence/ $\ln\alpha$, $\ln t$	r^*	Ferrite formation mechanism
Static (without stirring) regime	(311)	95	2.58	0.9954	Precipitation with homogeneous nucleation and diffusion controlled growth
		80	2.53	0.9865	
		70	2.49	0.9949	
		55	2.49	0.9996	
	(440)	95	2.40	0.9913	
		80	2.39	0.9893	
		70	2.45	0.9947	
		55	2.49	0.9963	
Well-stirring regime	(311)	95	3.87	0.9909	Precipitation with homogeneous nucleation and polynuclear layer formation controlled growth
		80	4.02	0.9950	
	(440)	95	4.08	0.9953	
		80	3.90	0.9917	

*correlation coefficient of the linear regression

Over the inflection points of the curves, the pairs of values (α, t) are described by Eq. (3) and the corresponding values of the parameters k and n are listed in Table 2:

$$\alpha = 1 - \exp(-kt_n) \quad (3)$$

Table 2 The values of the kinetic parameter k and n for the ferrite phase formation at various maturation temperatures and regimes

Maturation regime	Crystalline plane/hkl	$T/^\circ\text{C}$	Conversion range	n	k/s^{-1}	r^*
Static (without stirring) regime	(311) $d=2.56 \text{ \AA}$	95	$0.17 < \alpha \leq 0.72$	0.89	$1.57 \cdot 10^{-3}$	0.9936
		80	$0.15 < \alpha \leq 0.69$	0.87	$0.91 \cdot 10^{-3}$	0.9889
		70	$0.10 < \alpha \leq 0.78$	0.90	$0.25 \cdot 10^{-3}$	0.9997
		55	$0.13 < \alpha \leq 0.72$	1.03	$0.60 \cdot 10^{-4}$	0.9961
	(440) $d=1.50 \text{ \AA}$	95	$0.18 < \alpha < 0.70$	0.88	$2.52 \cdot 10^{-3}$	0.9962
		80	$0.16 < \alpha < 0.82$	0.94	$1.51 \cdot 10^{-3}$	0.9888
		70	$0.10 < \alpha < 0.75$	0.98	$0.53 \cdot 10^{-3}$	0.9901
		55	$0.15 < \alpha < 0.70$	1.1	$0.15 \cdot 10^{-3}$	0.9943
Well-stirring regime	(311) $d=2.56 \text{ \AA}$	95	$0.23 < \alpha < 0.25$	1.05	$0.37 \cdot 10^{-3}$	0.9879
		80	$0.10 < \alpha < 0.70$	1.10	$0.47 \cdot 10^{-3}$	0.9916
	(440) $d=1.50 \text{ \AA}$	95	$0.23 < \alpha < 0.70$	1.15	$0.33 \cdot 10^{-3}$	0.9929
		80	$0.10 < \alpha < 0.70$	1.17	$0.37 \cdot 10^{-3}$	0.9925

*correlation coefficient of the linear regression

The values of the apparent rate constant, k , obtained for the maturation in static conditions are greater than the corresponding ones for the maturation in well-stirring regime. In the same time, in the case of the well-stirring maturation, the value of k obtained at 80°C is greater than those for 95°C . These results may be explained by the influence of the temperature on the value of the solution supersaturation ratio and by the cumulate influence of the temperature and stirring on the critical value of the ferrite nuclei radius in equilibrium with the solution.

For $n=1$, the Eq. (3) is similar to the Eqs (IV), (VI) and (VIII) from Appendix. Taking also into account the data from Table 1, the values $n \cong 1$ from Table 2 confirm that the formation of the ferrite phase in static conditions occurs through homogeneous nucleation and diffusion controlled growth, and under well-stirred regime it occurs through precipitation with homogeneous nucleation and growth controlled by the generation of the polynuclear layer.

The Eq. (3) is known as J.M.A.Y.K. equation [12]. For $n=1$, the J.M.A.Y.K. equation is specific to the formation of crystalline planes in high dispersed systems. As far as the growth is concerned, this is controlled by surface phenomenon with nuclei mutual inclusion and overlap. Under such conditions, the growth mechanism of polynuclear layer and that described by J.M.A.Y.K. equation could be considered as similar.

According to the mechanism of precipitation with homogeneous nucleation, the formation of the ferrite nuclei occurs spontaneously in solution and their growth occurs through the deposition of the ions from the solution in successive layers. This phenomenon occurs as long as through dissolution of the amorphous or weakly crystallised phases from the initial precipitates, the solution has the supersaturation necessary for homogeneous nucleation.

From the change of constant k (from Table 2) with temperature, we obtained the values of the apparent activation energy and preexponential factor, which are listed in Table 3. Taking into account that $n \cong 1$ (Table 2), the preexponential factor is expressed in s^{-1} .

Table 3 The values of the activation parameters for the formation and growth of the ferrite phase in static regime

Crystalline plane/ hkl	$E/kJ\ mol^{-1}$	A/s^{-1}	r^*
(311)	85.2	$2.4 \cdot 10^9$	0.9823
(440)	72.9	$6.8 \cdot 10^7$	0.9882
(511)	79.2	$6.7 \cdot 10^8$	0.9913
(400)	91.1	$4.2 \cdot 10^9$	0.9905
(220)	90.6	$3.5 \cdot 10^9$	0.9937

*correlation coefficient of the linear regression

The kinetics of the increase of the ferrite crystallites linear sizes

The change in time of the conversion degree, β , corresponding to the formation of (311) and (440) planes of the spinell $MnFe_2O_4$ in static conditions at various maturation temperatures, is shown in Figs 5 and 6. For the region of the curves located over

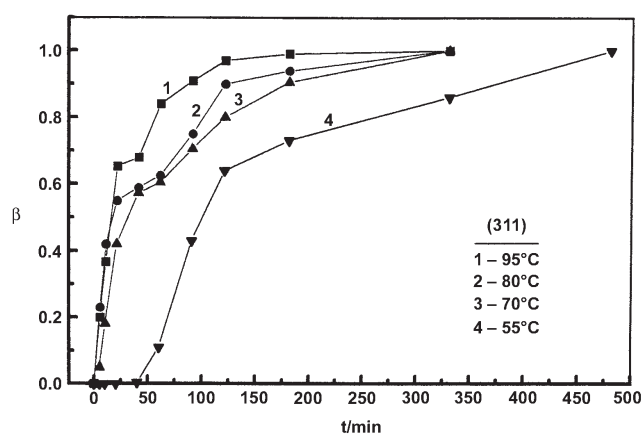


Fig. 5 The maturation (β, t) curves, corresponding to the formation of the (311) plane of the ferrite phase, at different temperatures in static conditions

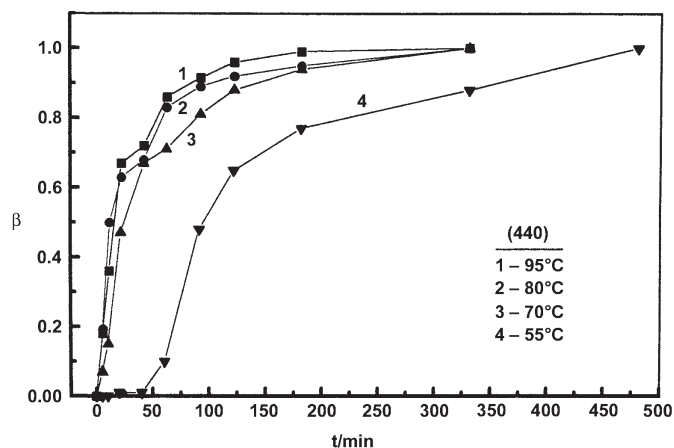


Fig. 6 The maturation (β , t) curves, corresponding to the formation of the (440) plane of the ferrite phase, at different temperatures in static conditions

the inflection point, the pairs of values (β , t) corresponding to these curves are also described by Eq. (3). The corresponding value of the parameters n and k are given in Table 4. These values are characteristic of the growth of the primary particles of manganese ferrite in the original solution. From the linear dependence ($\ln k$, $\ln t$) we obtained the values of the apparent activation energy and preexponential factor, is listed in Table 5.

Table 4 The values of the kinetic parameter k and n for growth of the ferrite particles linear sizes at various maturation temperatures in static regime

Crystalline plane/hkl	$T/^\circ\text{C}$	Conversion range	n	k/s^{-1}	r^*
(311) $d=2.56 \text{ \AA}$	95	$0.20 \leq \alpha \leq 0.69$	1.08	$0.82 \cdot 10^{-3}$	0.9936
	80	$0.22 \leq \alpha \leq 0.62$	1.10	$0.61 \cdot 10^{-3}$	0.9858
	70	$0.17 \leq \alpha \leq 0.57$	0.92	$0.45 \cdot 10^{-3}$	0.9902
	55	$0.10 \leq \alpha \leq 0.63$	1.12	$0.31 \cdot 10^{-3}$	0.9903
(440) $d=1.50 \text{ \AA}$	95	$0.17 \leq \alpha \leq 0.72$	1.03	$0.79 \cdot 10^{-3}$	0.9971
	80	$0.19 \leq \alpha \leq 0.69$	1.16	$0.62 \cdot 10^{-3}$	0.9882
	70	$0.15 \leq \alpha \leq 0.67$	1.14	$0.46 \cdot 10^{-3}$	0.9916
	55	$0.11 \leq \alpha \leq 0.76$	0.98	$0.33 \cdot 10^{-3}$	0.9921

* correlation coefficient of the linear regression

The obtained values of E are close to those obtained by Tang (25 kJ mol^{-1} [5]) for the maturation of the coprecipitates obtained from solutions of Fe^{3+} and Mn^{2+} ions. These values, characteristic of the reaction with the diffusion of ions in solution as rate limiting step, confirms the growth mechanism of the ferrite particles in static maturation regime as evidenced at point 1.

Table 5 The values of the activation parameters for the growth of the ferrite particles linear sizes in static regime

Crystalline plane/ hkl	$E/\text{kJ mol}^{-1}$	A/s^{-1}	r^*
(311)	24.5	2.5	0.9983
(440)	22.4	1.2	0.9959
(511)	24.9	2.6	0.9928
(400)	23.7	2.2	0.9971
(220)	24.7	2.5	0.9953

*correlation coefficient of the linear regression

The obtained values of E are close to those obtained by Tang (25 kJ mol⁻¹ [5]) for the maturation of the coprecipitates obtained from solutions of Fe³⁺ and Mn²⁺ ions. These values, characteristic of the reaction with the diffusion of ions in solution as rate limiting step, confirms the growth mechanism of the ferrite particles in static maturation regime as evidenced at point 1.

The shift of the origin of the curves from Fig. 1, in their inflection points, corresponding to the beginning of the critical nuclei growth, and the reevaluation of the kinetic parameter leads to $E=30$ kJ mol⁻¹.

Conclusions

1. Under static regime conditions, the formation of the ferrite phase occurs through precipitation with homogeneous nucleation and diffusion of the ions in solution. The rate and the activation energy of various crystalline planes formation are characterised by different values, the fastest plane to develop being (440).
2. Under well-stirring conditions, the formation of the ferrite phase occurs through precipitation with homogeneous nucleation and growth controlled by the formation of the polynuclear layer. The rate of various crystalline planes formation are characterised by close values.

Appendix

A. If the crystalline phase grows through the simultaneous increase of the particles number and size, we speak about a homogeneous nucleation mechanism described by the following kinetic equations [2]:

– for $0 < \alpha \ll 1$:

$$A_1: \alpha \cong [(1-t)^{-2} - 1]^m \quad (\text{I})$$

if the grain growth is controlled by the mononuclear layer formation,

$$A_2: \alpha \cong \text{const. } t^4 \quad (\text{II})$$

if the grain growth is controlled by the polynuclear layer formation (as a result of the inclusion of several surface nuclei into the growing process),

$$A_3: \alpha \cong \text{const.} \cdot t^{5/2} \quad (\text{III})$$

if the grain growth is controlled by the ion diffusion from the solution to the particle surface;

– for $\alpha \rightarrow 1$, the equations corresponding to the three growing mechanisms above mentioned are:

$$A_1: \alpha \cong 1 - \exp(-\text{const.} \cdot t), \text{ for } m=1 \quad (\text{IV})$$

$$\alpha \cong 1 - \text{const.} \cdot t^{-1/(m-1)}, \text{ for } m>1 \quad (\text{V})$$

$$A_2: \alpha \cong 1 - \exp(-\text{const.} \cdot t), \text{ for } p=1 \quad (\text{VI})$$

$$\alpha \cong 1 - \text{const.} \cdot t^{-1/(p-1)}, \text{ for } p>1 \quad (\text{VII})$$

$$A_3: \alpha \cong 1 - \exp(-\text{const.} \cdot t), \quad (\text{VIII})$$

B. If the amount of crystalline phase grows by increase of the sizes of a constant number of particles, the following kinetic equations should be considered [2]:

– for $0 < \alpha < 1$:

$$B_1: \alpha \cong (\alpha_{\text{om}}^{-1/3} - t/\text{const.})^{-3} \quad (\text{IX})$$

when the grain growth is controlled by the mononuclear layer formation,

$$B_2: \alpha \cong (t/\text{const.})^3 \quad (\text{X})$$

when the grain growth is controlled by the polynuclear layer formation (as a result of the inclusion of several surface nuclei into the growing process),

$$B_3: \alpha \cong (t/\text{const.})^{3/2} \quad (\text{XI})$$

when the grain growth is controlled by the ion diffusion from the solution to the particle surface;

– for $\alpha \rightarrow 1$, the equations corresponding to the three growing mechanisms above mentioned are:

$$B_1: \alpha \cong 1 - [\text{const.}/(m-1)t]^{1/(m-1)} \quad (\text{XII})$$

$$B_2: \alpha \cong 1 - [\text{const.}/(p-1)t]^{1/(p-1)} \quad (\text{XIII})$$

$$B_3: \alpha \cong 1 - \exp(-\text{const.} \cdot t) \quad (\text{XIV})$$

In the relations (I)–(XIV), m stands for the kinetic order of the formation of the mononuclear layer, having the physical significance of the number of ions from the stable surface nucleus and p is the kinetic order of the formation of the polynuclear layer [2].

The relations (I)–(XIV) describe conversion curves of sigmoid type, approximated under the inflexion point by the equations (I)–(III) and (IX)–(XI) and over this point by the equations (IV)–(VIII) and (XII)–(XIV) which tend asymptotically to 1.

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