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Magnetic-resonance study of the transformation γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$

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The transformation γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ has been investigated by magnetic resonance. The residual fraction of γ-Fe_2O_3 was measured for several aging times and temperatures, in the range 450–550 °C. The experimental data show that the transformation can be described by a first-order kinetic equation and that the activation energy is 47 kcal/mol. This value is found to be independent of aging temperature and particle size. The results suggest that the reaction is growth controlled and that nucleation occurs preferentially at the particle surface.

I. INTRODUCTION

The transformation of γ-Fe_2O_3 to α-Fe_2O_3 has been studied by several researchers, using different techniques.[1–5] The reported values for the activation energy show a large spread, from a minimum of 36.6 kcal/mol (Ref. 1) to a maximum of 86 kcal/mol.[5] This failure to obtain consistent results has been attributed, among other factors, to the presence of impurities[1] and to the influence of particle size.[4] The purpose of this investigation is threefold: first, to measure the activation energy for the transformation with a technique that gives unambiguous results, so that reliable data can be obtained; second, to investigate the influence of particle size on the transformation kinetics; and third, to develop a model for the transformation which is compatible with the experimental results.

The method used in the present study is based on the fact that, since the saturation magnetization for the γ phase is about 180 times larger than for the α phase,[6] in a mixture of the γ and α phases the absorption intensity (area under the magnetic-resonance curve) is linear with the mass of the γ phase. Magnetic-resonance measurements in heat-treated samples thus provide an accurate determination of the residual fraction of the γ phase.

II. EXPERIMENTAL PROCEDURE AND RESULTS

A. Sample preparation and identification

The samples used in this work were prepared using the method described by Coey and Khalafalla.[7] The material was examined in the electron microscope, and consists of particles in two different size ranges (see Fig. 1): 100–200 Å (group *A*) and 1000–2000 Å (group *B*). The particle shape is approximately equiaxial in both groups.

The compound was identified as γ-Fe_2O_3 by x-ray diffraction and Mössbauer spectrometry.

Isothermal treatments were performed in air at several temperatures and for several aging times. The samples were quenched in cool water after each treatment.

B. Magnetic-resonance measurements

All magnetic-resonance measurements were performed at room temperature and 9.25 GHz. The area under the absorption curve was determined by numerical integration from the first-derivative spectrum, using an algorithm due to Alger[8] that corrects automatically for base line drift. Four runs, using different samples, were performed for each aging temperature. The average results for each temperature are shown in Fig. 2. The data for the four runs were remarkably consistent for all temperatures, except 490 °C, where a large spread was found (the dashed lines in Fig. 2 are for the two extreme runs). The data for the runs at 490 °C were not used in the

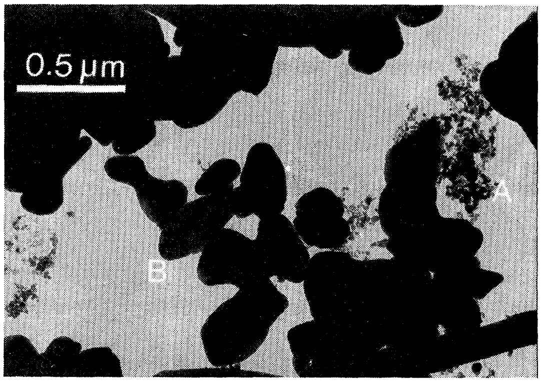

FIG. 1. Transmission electron micrograph of unaged sample.

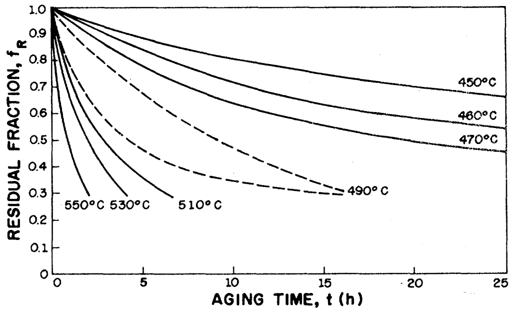

FIG. 2. Residual fraction of γ-Fe_2O_3 as a function of aging time for several aging temperatures.

TABLE I. Activation energy E_A for several values of the residual fraction f_R.

f_R	E_A (kcal/mol)
0.9	44
0.8	46
0.7	48
0.6	49
0.5	49
0.4	49

analysis that follows. Notice also from Fig. 2 that the incubation time, if it exists, is very small.

III. ANALYSIS AND DISCUSSION

A. Activation energy

The activation energy was obtained from the data shown in Fig. 2 by two different methods. The first is based on the equation[9]

$$t_f = Ce^{E_A/RT} , \qquad (1)$$

where t_f is the aging time corresponding to a given residual fraction f_R, C is a constant, E_A is the activation energy, and T is the aging temperature. The advantage of this method over the more usual Arrhenius method[9] described below, is that it is not necessary to assume a specific form for the kinetic equation. The only condition for Eq. (1) to be valid is that the process be isokinetic.

The results obtained by applying Eq. (1) to the data in Fig. 2 are shown in Fig. 3 and Table I.

The other method that can be used to analyze the data of Fig. 2 is to try to fit to the experimental points for each isothermal run, a first-order equation

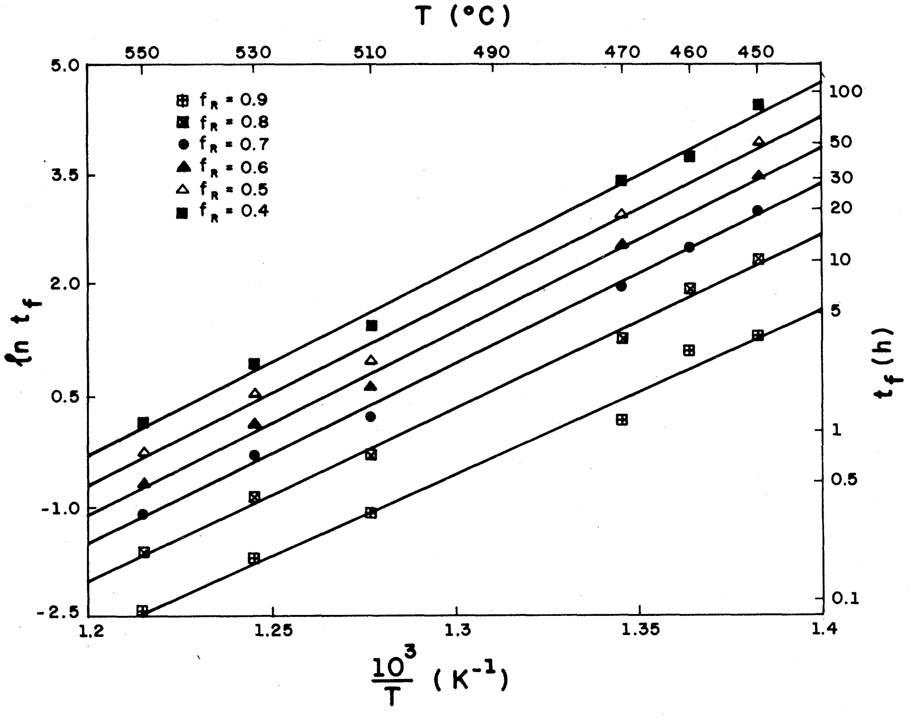

FIG. 3. Aging time for a given residual fraction of γ-Fe_2O_3, f_R, as a function of the inverse absolute temperature. The solid lines are least-squares fits to the experimental points.

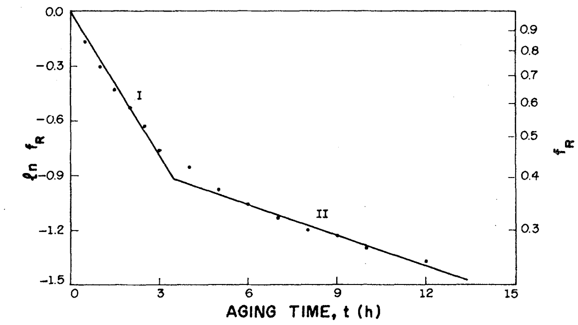

FIG. 4. Logarithm of the residual fraction of γ-Fe_2O_3 as a function of aging time at 510 °C. The solid lines are least-squares fits to the experimental points.

of the form

$$f_R = e^{-kt} , \qquad (2)$$

where k is the reaction constant and t is the aging time. The reaction constant is related to the activation energy through the Arrhenius equation[9]

$$k(T) = Se^{-E_A/RT} , \qquad (3)$$

where S is the frequency factor.

When Eq. (2) is applied to the experimental data in Fig. 2 it is found that for each aging temperature, the reaction occurs in two stages and that both can be described by first-order equations. The transition from the first to the second stage occurs at about $f_r = 0.4$ for all aging temperatures. A typical plot is shown in Fig. 4. The reaction constants k obtained as the slopes of the straight lines, can then be used to determine the activation energy, using an Arrhenius plot (Fig. 5). The results for stages I and II are shown in Table II. The activation energy for the two stages is found to be the same, within experimental error. The results also agree with those obtained by the first method. The agreement between the two methods of mathematical analysis confirms the observed value for the activation energy but great caution should be exercised before accepting all the implications of the simple first-order rate model. It is well known that a variety of rate laws each having its own distinct mechanistic model, will yield nearly identical values of activation energy when applied to the same set of experimental data. The average of the values obtained using the two methods yields 47 kcal/mol as the most probable value for the activation energy.

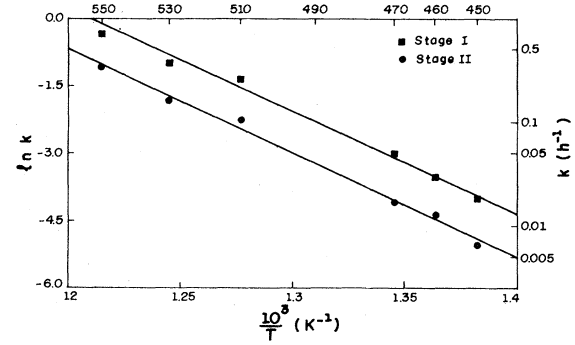

FIG. 5. Logarithm of the reaction constant as a function of the inverse absolute temperature. The solid lines are least-squares fits to the experimental points.

TABLE II. Activation energy E_A and frequency factor S for stages I and II of the transformation.

Stage	E_A (kcal/mol)	S ($10^{11} h^{-1}$)
I	45	5.3
II	46	5.3

B. Influence of particle size

The shape of the magnetic-resonance curves is not constant along each run; they become less symmetric for long aging times. This is attributed to the fact that the reaction rate is larger for the smaller particles (group A). In effect, the particles in this group are superparamagnetic, and the magnetic-resonance curves of superparamagnetic powders are symmetric,[10,11] while the curves of ferromagnetic

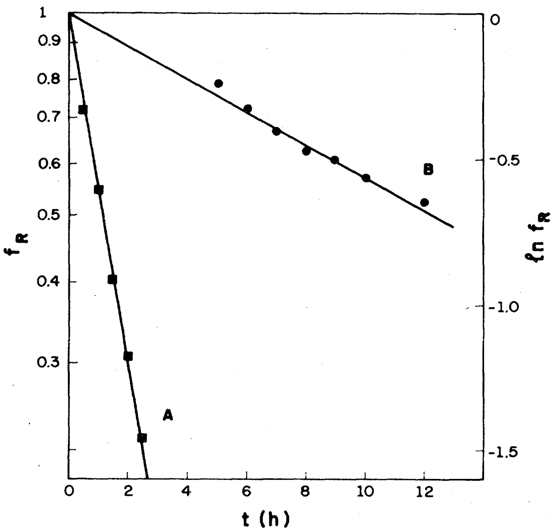

FIG. 6. Logarithm of the residual fraction of γ-Fe_2O_3 as a function of aging time at 510 °C, for the two groups of particles. The solid lines are least-squares fits to the experimental points.

TABLE III. Initial fraction $f(0)$ and reaction constant k at 510 °C for particle groups A and B.

Group	$f(0)$	k (h^{-1})
A	0.52	0.606
B	0.48	0.054

powders are usually asymmetric.[12] The Mössbauer spectra of samples aged for different times also shows that the fraction of superparamagnetic particles decreases faster than the total fraction of γ-Fe_2O_3. According to this interpretation, the first stage of the reaction (stage I) corresponds to the simultaneous transformation of particles in groups A and B, while in the second stage (stage II) almost all the particles in group A have already been transformed to α-Fe_2O_3. Therefore, the intercept of the straight line that corresponds to stage II in Fig. 4 with the ordinate axis is the logarithm of the fraction of group B particles in the untreated sample $f_B(0)$. Knowing $f_B(0)$, and with the help of the data of Fig. 4, it is possible to determine the residual fraction of γ-Fe_2O_3 in each group as a function of aging time. The results are shown in Fig. 6 and Table III.

The results in Tables II and III, when taken together, show that: (a) the activation energy is the same for particles in groups A and B; (b) the reaction constant is about 11 times larger for particles in group A.

C. Control mechanism

The control mechanism for the γ-α reaction must be consistent with four experimental facts observed in this work: (1) for each group of particles, the transformation should be described by a first-order reaction; (2) the incubation time should be small, certainly less than 30 min (see Fig. 2); (3) the activation energy should be independent of particle size, in the range 100–2000 Å; (4) the reaction constant for particles in the size range 100–200 Å (group A) should be about 11 times larger than for particles in the size range 1000–2000 Å (group B).

A model that is consistent with all the facts above is that of surface nucleation with site saturation.[13] According to this model, the residual fraction after an aging time t is

$$f_R = e^{-S_v Y t} , \qquad (4)$$

where S_v is the particle surface area per unit volume and Y is the interface propagation velocity.

As Eq. (4) shows, the kinetic equation associated with this model describes a first-order process. Moreover, the saturation of nucleation sites in the beginning of the reaction leads to small incubation times. The activation energy is independent of particle size. Finally, the reaction constant is proportional to the constant S_v, so that, taking the average sizes of the particles in groups A and B and assuming spherical shapes, we have

$$k_A/k_B = S_v(A)/S_v(B) = d_B/d_A = 1500/150 = 10 \ . \qquad (5)$$

This ratio is close to the experimental value $k_A/k_B = 11$ (see Table III).

According to the proposed model, the reaction probably proceeds by diffusion of the iron ions, since the activation energy for the process (47 kcal/mol) is quite close to the activation energy for diffusion of iron in magnetite[14] (45–48.8 kcal/mol) a material that has a similar structure.

ACKNOWLEDGMENT

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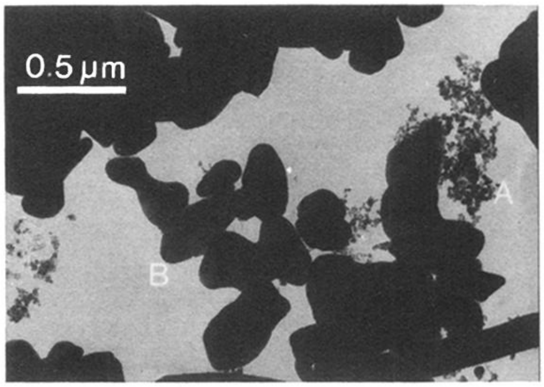

FIG. 1. Transmission electron micrograph of unaged sample.