Physical Chemistry

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1963

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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KINETICS OF THE DECOMPOSITION OF WÜSTITE

The kinetics of the decomposition of wüstite was studied, by means of magnetic analysis as in ([1,2]), on samples with lattice parameter 4.032 Å. The isothermal decomposition of wüstite was carried out in vacuum at various temperatures in the range 200–500°. The specific saturation magnetization of the samples σ_s as a function of time t clearly reflected the existence of two consecutive reactions (I—pre-eutectoid precipitation of magnetite and II—eutectoid decomposition of metastable wüstite) at temperatures not exceeding 400°, and one reaction (III —overall eutectoid decomposition of the initial wüstite) at temperatures above 400° (Fig. 1a and b). From the curves $\sigma_s(t)$, the kinetic curves $\alpha(t)$ were calculated for reactions I, II, and III, where α is the fraction of substance transformed by time t. The most complete and accurate data were obtained for the kinetics of reaction II; therefore this process was considered first.

The decomposition of wüstite is accompanied by the appearance of diffusion porosity ([1,2]), which apparently is what mainly determines the kinetics of the transformation. At first, decomposition occurs at certain initial defects in the wüstite crystals, but very soon the numerous newly appearing defects—pores —become reaction centers, and the rate of the whole process $d\alpha/dt$ becomes substantially dependent on their number N.

Fig. 1. Dependence of the specific saturation magnetization of samples of decomposing wüstite on the time of isothermal annealing at temperatures: *a*— not exceeding 400°, *b*—above 400°

Since $N \sim \alpha$, then, to a first approximation, $d\alpha/dt \sim N \sim \alpha$. In addition, $d\alpha/dt$ is proportional to the number of unreacted regions, i.e., to the fraction of unreacted substance $(1-\alpha)$. We obtain

$$\frac{d\alpha}{dt} = k\alpha(1-\alpha), \qquad (1)$$

Fig. 2

Figure 2: Fig. 2

whence

$$\frac{\alpha}{1-\alpha} = e^{kt-b_1} \tag{1'}$$

(k and b_1 are constants).

The experimental data for reaction II satisfy (1′), but only up to $\alpha \approx 1/2$ (Fig. 2a).

The decomposition of wüstite is followed by processes of pore growth and recrystallization ([2]). It may be assumed that these processes occur even

Fig. 2. Verification of the kinetic equations for the decomposition of wüstite using the experimental data for reaction II:
a—equation (1′) in the form

$$\lg \frac{\alpha}{1-\alpha} = (k_{\mathrm{II}} \lg e)t - (d_1)_{\mathrm{II}} \lg e,$$

b—equation (2′) in the form

$$\lg \frac{\alpha}{1-\alpha} = (b_2)_{\mathrm{II}} \lg e - (2n_{\mathrm{II}} \lg e)t^{-1/2}$$

at low temperatures (in the temperature range studied), since the specimen is in a state of increased free energy owing to its considerable porosity. The influence of these secondary processes on the overall course of the reaction evidently appears only after substantial development of the reaction ($\alpha \approx 1/2$). Treating a micropore as a nonstationary source of diffusion (vacancies), we obtain ([3]) that the pore loses vacancies and decreases (grows) with time proportionally to $1/(Dt)^{3/2}$, where D is the diffusion coefficient. If it is assumed that the number of pores N in the decomposed regions in the second half of the reaction changes with time approximately according to the same law, i.e., $N \sim \alpha/(Dt)^{3/2}$, then for the overall rate of the process we have

$$\frac{d\alpha}{dt} = \frac{k'}{(Dt)^{3/2}}\,\alpha(1-\alpha) = \frac{n}{t^{3/2}}(1-\alpha), \tag{2}$$

whence

$$\frac{\alpha}{1-\alpha} = e^{b_2 - 2nt^{1/2}}, \quad \text{where } n = \frac{k'}{D^{3/2}} \tag{2'}$$

Fig. 3. Temperature changes in the kinetic parameters k and n

Figure 3: Fig. 3. Temperature changes in the kinetic parameters k and n

(k', n, b_2 are constants).

The experimental data satisfy (2′) for $\alpha \gtrsim 1/2$ (Fig. 2b). Reactions I and III are very close in mechanism to reaction II; therefore equations (1′) and (2′) also describe these transformations well ((1′)—for $\alpha \lesssim 1/2$, (2′)—for $\alpha \gtrsim 1/2$).

Temperature changes in the kinetic parameters k, n, b_1, b_2 are regular (Fig. 3) and can be explained on the basis of the same ideas about the role of diffusional porosity in the decomposition of wüstite.

The parameter k characterizes the rate in the first stage. For reactions I and II, the corresponding quantities k_{I} and k_{II} increase with temperature, since the mobility of ions in the wüstite lattice increases, which facilitates the crystallochemical transformation. As the temperature approaches 400°, the increase in k_{I} and k_{II} slows down, while for reaction III, proceeding at still higher temperatures, the corresponding quantity k_{III} already decreases (Fig. 3). The latter is probably explained by the fact that at elevated temperatures (above 400°) there may be a larger number of vacancies in the crystal lattice (of wüstite, magnetite), and consequently fewer micropores are formed, i.e., a given value of α already corresponds to a smaller number N (see the justification of equation (1)).

Fig. 3. Temperature changes in the kinetic parameters k and n

The parameter n characterizes the rate in the second stage and, by definition (equation (2)), $n = k'/D^{3/2}$, where k' has approximately the same meaning as k, and D is the diffusion coefficient. The value of n for all three reactions changes hardly at all (Fig. 3). Assuming that k' changes with temperature in the same way as k, we find that D also first increases with temperature and then decreases. The reason for this is that diffusion takes place mainly along the pore surface, while above 400° the porosity begins to decrease noticeably.

The parameter b_1 characterizes the initial degree of decomposition

$$\left(\frac{\alpha}{1-\alpha} \to e^{-b_1} \text{ as } t \to 0\right),$$

i.e., the degree of decomposition of wüstite at the initial defects; after this degree is reached, the kinetics is already determined by new defects—pores. The changes in this quantity with temperature are insignificant and, given the low accuracy of the present investigation, cannot be discussed.

The parameter b_2 characterizes the final degree of decomposition

$$\left(\frac{\alpha}{1-\alpha} \to e^{b_2} \text{ as } t \to \infty\right),$$

i.e., the maximum amount of decomposition that could be attained if only one mechanism operated—the one associated with porosity. With increasing temperature this quantity naturally increases, since the mobility of the particles of the decomposing substance increases, and then decreases, since the number of pores (reaction sites for this decomposition mechanism) becomes ever smaller.

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Received
1 X 1962

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Note: Figure translations are in progress. See original paper for figures.