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Abstract

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PHYSICAL CHEMISTRY

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ON THE QUESTION OF THE MAXIMUM RATE OF DECOMPOSITION OF WÜSTITE

The rate of decomposition of wüstite, as is known (see, for example, [1,2]), increases with increasing temperature up to 400°, and then decreases appreciably. The latter might have been explained by a change in the metastability of the wüstite phase on approaching the equilibrium temperature (570°); however, the investigation we carried out made it possible to suggest that the cause of the rate maximum is the mechanism of the process itself. As has already been reported ([3]), in the course of the decomposition process microscopic pores about 0.1μ in size appeared. On specimens from the same batch, decomposition was studied at temperatures of 500 and 400°. The same methods of X-ray structural and magnetic analysis and electron microscopy were used as in the previous work ([3]).

The curves of the dependence of the specific saturation magnetization σ_s of the specimens on annealing time revealed the kinetics of the processes (Fig. 1). From the very beginning of decomposition at 500° the rate was small and decreased monotonically with annealing time. The constancy of the parameter of the decomposing wüstite indicated that the decomposition proceeded according to the reaction

$$4\mathrm{Fe}_{1-x}\mathrm{O} \rightarrow \mathrm{Fe}_3\mathrm{O}_4 + (1-4x)\mathrm{Fe} \quad (x = 0.093).$$

Fig. 1. Dependence of the specific saturation magnetization of specimens of decomposing wüstite on annealing time at 350, 400, and 500°.

Meanwhile, examination of the surface of the specimens did not reveal any slowing in the change of structure in comparison with experiments at 350°. After 15 min of annealing, both large dense formations, similar to primary magnetite at 350°, and porous regions characteristic of the eutectoid were already visible (Fig. 2a, see insert, p. 456). After holding for 30 min, the pore walls and large formations acquired faceting (Fig. 2b); some regions (at the lower right in 2b) were already without pores, with small recrystallized crystallites. Subsequently such regions grew and occupied the entire surface, with the exception of large crystals (Fig. 2c). The structure was analogous to the surface structure of a specimen completely decomposed at 350° and additionally recrystallized at 500° ([3]). Thus, as before, there were two stages of transformation, but they proceeded very rapidly in each region and therefore were not separated radiographically. The further growth of σ_s could be explained by the same process of decomposition at grain boundaries, blocks, and other defects. Decomposition at 400° was of the same type as at 350°. Its distinctive features were the increased decomposition rate (Fig. 1) and the recrystallization and elimination of pores beginning at the end of the transformation.

In general, the change in the character of the entire process with increasing temperature may be represented as follows. The pre-eutectoid precipitation of mag-

···of magnetite and, especially, eutectoid decomposition are associated with the diffusion (to the emerging metastable wüstite and iron) of iron ions from the lattice sites of wüstite and with the coagulation of the remaining vacancies into pores, which do not have time to become filled with magnetite formed from iron-depleted wüstite.

The presence of porosity facilitates the transformation in the undecomposed regions adjoining the pores both through an increase in the free energy of the surface particles of these regions and, indirectly, through acceleration of diffusion along the pore surface. As the temperature rises, these elementary processes are accelerated, but the recrystallization of the decomposition products is also accelerated. The pores become overgrown, which leads to a decrease in the overall rate of the process.

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