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SIZE- AND SURFACE-DEPENDENCE OF ENTHALPY OF OXIDATION OF SUBMICRONIC MAGNETITES*

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Submicronic magnetites prepared by two different methods were studied between 30 and 280°, using a fluxmetric microcalorimeter to investigate the size- and surface-dependence of ΔH, the enthalpy of oxidation of magnetite to γ-Fe_2O_3.

For the particles with mean diameters ranging from 95 to 950 Å and specific surfaces of the order of 100.0 to 10.0 m^2/g, ΔH varied from -77.3 ± 2.5 to -61.0 ± 2.5 kJ/mol, and is identified as a linear function of the size of the particles, as depicted by the relationship $\Delta H = \Delta H_{\text{intrinsic}} + \Delta H_D$, where ΔH_D represents the particle size-dependent part of the enthalpy of oxidation.

From the viewpoints of the structure, reactivity and application properties of pure, substituted and doped spinel ferrites and related lacunar spinel systems, studies on the kinetics, mechanism and thermodynamics of the oxidation of synthetic magnetite to γ-Fe_2O_3 are deemed to be of great practical and theoretical interest [1–3]. In particular, the dependence of the oxidation of magnetite on the conditions of preparation, the details of the composition, the particle profiles and the strains and defects associated with the magnetite crystallites has been examined by several workers.

David and Welch [4] showed that specimens of magnetites which gave γ-Fe_2O_3 on oxidation, invariably contained appreciable amounts of water, while specimens prepared under dry conditions oxidized with great difficulty, never yielding γ-Fe_2O_3. Elder [5] reported that dry magnetite can also be oxidized to γ-Fe_2O_3 by grinding the samples in a wet ball-mill so as to yield crystallites of submicronic size and carrying out oxidation in an atmosphere of water vapour and oxygen. Egger and Feitknecht [6] stated that the particle size determines not only the rate of oxidation, but also whether the α or the γ form of Fe_2O_3 is obtained. In magnetites

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having water removable at a temperature above 600°, Gazzarini and Lanzavecchia [7] found that the water exists in a form where its protons occupy lattice positions, thereby replacing iron ions to maintain electrical neutrality. It was shown that in these water acts as a lattice defect and favours the stabilization of a lacunar structure easily oxidizable to γ-Fe_2O_3.

For the transformation $Fe_3O_4 \rightarrow \gamma$-$Fe_2O_3$, a model based on the cationic diffusion of Fe^{2+} ions was presented by Gallagher et al. [8]. In their studies it was shown that the particles smaller than 3000 Å were oxidized to γ-Fe_2O_3, whereas in the larger particles the spontaneous nucleation of α-Fe_2O_3 occurred, because of lattice strains, and the oxidation proceeded to yield hematite. A reinterpretation of the part played by the grain size in the mechanism proposed by Gallagher et al. was warranted by the studies carried out by Colombo et al. [9]. They concluded that stoichiometric magnetite is oxidizable to γ-Fe_2O_3, even when its particle size is larger than 3000 Å, while magnetite containing stacking faults and/or a trace of α-Fe_2O_3 is oxidized partially to α-Fe_2O_3, even when the particle size is smaller than 3000 Å. Thus, the reaction rate is shown to depend on the grain size and even more on the degree of lattice order. The grain size itself therefore plays a purely kinetic part in the process of oxidation. It is the stacking faults present in the form of hexagonal sequences of (111) oxygen planes in magnetite that behave as nuclei of α-Fe_2O_3, or crystals of α-Fe_2O_3 that determine the low-temperature oxidation of magnetite to hematite [9].

In our previous investigations [3] on magnetites with a large size variation, ranging from 100 to 15,000 Å, it was found that for sizes less than 5000 Å the oxidation yields the lacunar phase γ-Fe_2O_3, while for sizes above 10,000 Å the rhombohedral α-Fe_2O_3 phase is formed. For intermediate sizes, the γ-Fe_2O_3 phase is formed at the beginning of the reaction; this is followed by the formation of α-Fe_2O_3 from γ-Fe_2O_3, and afterwards directly from the remaining unoxidized magnetite. The influence of size was accounted for in terms of the structures and stresses that prevailed in the crystal lattice [3]. As a continuation of our previous work and as part of our programme on the thermodynamic and structural aspects of iron oxide systems, the present study deals with an initial calorimetric investigation of the oxidation behaviour of submicronic magnetites.

Experimental

Submicronic magnetites were prepared by the following two different routes.

In the first route, Fe_3O_4 was directly precipitated by neutralization of mixed solutions of one part of iron(II) chloride and two parts of iron(III) chloride with aqueous ammonia solution under an inert atmosphere of N_2 gas. Except for sample

1, which was not subjected to further heat treatment, all the precipitated and dried magnetites were heated at temperatures ranging from 175 to 300° in a H_2—H_2O atmosphere, to obtain single-phase magnetites.

The second route involved the thermal decomposition of iron(II) oxalate in air, followed by reduction of the decomposition product to Fe_3O_4 in a controlled atmosphere of H_2—H_2O. The temperature of decomposition of iron(II) oxalate was varied from 300 to 600°, while that of reduction was from 280 to 320°.

In both the above methods, the samples were reduced in the H_2—H_2O atmosphere for 2 hours each at different temperatures, followed by quenching in air.

The average size of the crystallites was obtained from X-ray line-broadening measurements on powder diffraction patterns of samples, employing the Scherrer method. BET measurements were used to determine the specific areas of the samples. Table 1 summarizes the conditions of preparation of the samples. Our conditions of preparation permitted us to obtain samples having crystallite sizes from 95 to 950 Å and specific surface areas from 100 to 10 m^2/g.

A preliminary characterization of the samples was carried out by means of powder XRD, IR spectroscopy, DTA and TG methods.

Table 1 Conditions of preparation of submicronic magnetites

Sample no.	Precursor	Temperature of decomposition and reduction, in °C		Composition of oxidn./redn. atmosphere	
				H_2, l/h	H_2O, %
1	Magnetite precipitated from aqueous ammonia solution	—	—		
2	Magnetite precipitated from aqueous ammonia solution	—	175	6	5
3	Magnetite precipitated from aqueous ammonia solution	—	210	6	5
4	Magnetite precipitated from aqueous ammonia solution	—	250	6	5
5	Magnetite precipitated from aqueous ammonia solution	—	300	6	5
6	Iron(II) oxalate dihydrate	300	280	6	5
7	Iron(II) oxalate dihydrate	400	300	6	6
8	Iron(II) oxalate dihydrate	600	320	6	7

Enthalpy measurements were made with about 50 mg of the sample in the temperature range between 30 and 280°, using a SETARAM–C80 fluxmetric microcalorimeter, with a rate of temperature increase of 0.5 deg/minute.

The partial oxidation of the submicronic magnetites during storage and handling was analyzed by a wet chemical method. The weight percentages of the γ-Fe_2O_3 phase present in samples 1 to 8 prior to the calorimetric measurements were thus found to be 19.0, 28.5, 26.3, 33.6, 20.3, 20.4, 15.7 and 24.4, respectively. The ΔH of the oxidation was calculated by taking into account the actual Fe_3O_4 contents of the samples.

Results and discussion

The enthalpies of oxidation and the temperatures of the onset and the maximum of the low-temperature oxidation are listed in Table 2, along with the particle sizes and specific surface areas of the samples. The temperature corresponding to the maximum in the oxidation is observed to depend strongly on the specific surface area of the sample. Thus, for specific areas from 10 to 100 m^2/g, the oxidation temperature varies from 90 to 160° (see Fig. 1). On the other hand, the temperature of oxidation onset is less sensitive to the specific surface area. Figure 2 splots the variation of the enthalpy of oxidation for the reaction $2Fe_3O_4+\frac{1}{2}O_2 \rightarrow 3\gamma\text{-}Fe_2O_3$. For samples 1, 2 and 3, possessing higher specific areas, the enthalpy of oxidation is -77.3 ± 2.5 kJ/mol and the variation in the enthalpy is very small. Samples with lower specific surfaces exhibit a regular rise in ΔH with decreasing specific surface area, and for a sample with Sw = 10 m^2/g, $\Delta H_{\text{oxidation}}$ of -61.0 ± 2.5 kJ/mol is obtained.

Table 2 Microcalorimetric and microstructural data on submicronic magnetites

S.N.	Temperature of oxidation, °C, ±2.5 °C		$\Delta H_{\text{oxidation}}$, kJ/mol (±2.5 kJ/mol)	Crystallite size, Å (±10%)	Specific surface, Sw, m^2/g (±10%)
	onset temperature	peak temperature			
1	65	85	−77.3	95	100
2	60	105	−76.1	160	59.4
3	60	115	−76.1	300	31.7
4	65	125	−72.3	440	21.1
5	65	160	−69	600	19.8
6	70	145	−66.9	480	15.8
7	75	160	−62.3	800	11.9
8	75	165	−61.0	950	10.0

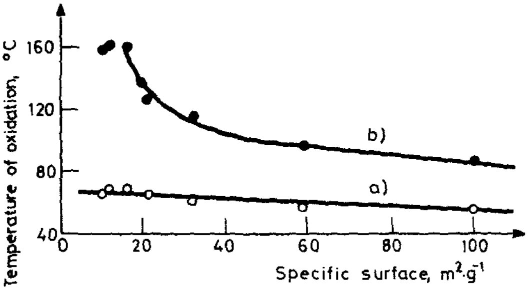

Fig. 1 Temperatures of oxidation of samples as a function of their specific surface. Curve a, indicates the temperature at which oxidation just starts. Curve b, refers to temperatures at which oxidation attains its maximum

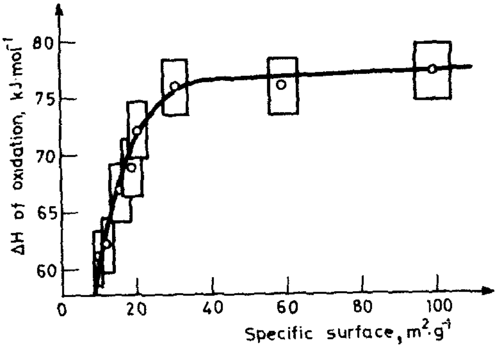

Fig. 2 Variation of enthalpy of oxidation, $\Delta H_{oxidation}$, with the particle size of the samples

The relation for the enthalpy of oxidation of a submicronic magnetite and its dependence on the surface area can be given by the equation $\Delta H_{measured} = \Delta H_{intrinsic} + \Delta H_D$, where $\Delta H_{intrinsic}$ is the enthalpy that is independent of the specific surface area, while ΔH_D denotes the ΔH dependent on the specific surface area, such that $\Delta H_D = k \cdot S^{-n}$. From Fig. 3, linearity is observed between ΔH_S and the size of the crystallites, thus giving n, a value close to unity. This gives $\Delta H_{intrinsic} = -80.7$ kJ/mol; $k = 155$ kJ · m²/mol · g, and therefore $\Delta H_{measured} = -80.7 + 155\ S^{-1}$ kJ/mol.

In an attempt to estimate the contributions of size and surface effects to the vacancy ordering in γ-Fe_2O_3, Haneda and Morrish [10] showed that the vacancy distribution is highly disordered within three or four layers of the surface, independently of the particle size, and that the vacancies are disordered in γ-Fe_2O_3 particles with diameters of less than about 200 Å. Indeed, in our study of γ-Fe_2O_3 derived from magnetite, the lines of the superstructure characteristic of the ordering of the vacancies at octahedral sites appear only for magnetite samples whose

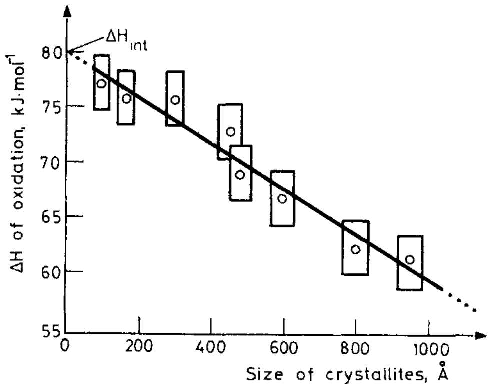

Fig. 3 Variation of enthalpy of oxidation, $\Delta H_{\text{oxidation}}$, with the specific surface area of the samples

precursors have specific areas as low as 20 mg^2/g. A detailed mechanism of the size and surface-dependences of the enthalpy of oxidation of magnetites is not possible, in want of a rigorous analysis of the distribution of crystallite size and specific surface area in magnetites, and the extent of the ordering of vacancies in the reaction products. However, it is suggested that the growth in particle size results in an increased number of Fe^{2+} and vacancy neighbour exchange interactions and an increase in distance of cationic migrations. These variations, along with the fluctuations in concentration and ordering of the vacancies in the γ-Fe_2O_3 formed, contribute differently to the $\Delta H_{\text{oxidation}}$ of submicronic magnetites, depending on the differences in their particle profiles. A further analysis of the calorimetric curve profiles, correlating the surface and interface effects involved and their contributions to the enthalpy of oxidation of submicronic magnetites, is to be reported in a future publication.

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Zusammenfassung — Nach zwei verschiedenen Methoden hergestellte, submikrone Magnetite werden zwischen 30 und 280° mittels eines fluxometrischen Mikrokalorimeters untersucht, um die Abhängigkeit der Enthalpie ΔH der Oxydation von Magnetit zu γ-Fe_2O_3 von der Partikelgröße und -oberfläche zu ermitteln. Für Partikel mit mittleren Durchmessern im Bereich von 95 Å bis 950 Å bzw. spezifischen Oberflächen in der Größenordnung von 100–10 m^2/g variieren die ΔH-Werte von $-77{,}3 \pm 2{,}5$ kJ/mol bis $-61{,}0 \pm 2{,}5$ kJ/mol. Die Enthalpie korreliert linear mit der Partikelgröße, was durch die Beziehung $\Delta H = \Delta H_{\text{intrinsic}} + \Delta H_D$ ausgedrückt werden kann, worin ΔH_D den von der Partikelgröße abhängigen Teil der Oxydationsenthalpie repräsentiert.

Резюме — Магнетиты, полученные двумя разными методами, были изучены в интервале температур 30–280° с помощью микрокалориметра теплового потока с целью определения зависимости ΔH от равмера и поверхности частиц, а также энтальпии окисления магнетита до γ-Fe_2O_3. Для частиц со средним диаметром от 95 до 950 Å и с удельной поверхностью, соответственно, от 100,0 до 10,0 $м^2/г$, значения ΔH изменялись от $-77{,}3 \pm 2{,}5$ до $-61{,}0 \pm 2{,}5$ кдж/моль. Параметр ΔH является линейной функцией размера частиц и описывается соотношением $\Delta H = \Delta H_{\text{внутр.}} + \Delta H_{\text{д}}$, где $\Delta H_{\text{д}}$ — представляет часть энтальпии окисления, зависящей от размера частиц.