JOURNAL OF MATERIALS SCIENCE 15 (1980) 3081–3090

Energetics of formation of lamellar porous microstructures in γ-Al_2O_3

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The formation of a lamellar porous microstructure in γ-Al_2O_3 during the dehydration of boehmite (γ-AlOOH) has been studied as a function of the temperature and water vapour pressure conditions under which the dehydration was performed. The γ-Al_2O_3 samples were characterized by transmission electron microscopy and nitrogen adsorption. A marked dependence of the scale of the microstructure, and of the adsorption characteristics, on water vapour pressure was observed. This pressure dependence of scale and surface area has been discussed in terms of a model, similar to those derived for cellular growth of lamellar microstructures during eutectic and eutectoid reactions, in which the dehydration mechanism is diffusion controlled. The inter-lamellar spacing is determined by the energy available for the formation of a new surface, and an estimate of surface energy for γ-Al_2O_3 has been made. The partial pressure, p_{H_2O}, dependence observed has important implications for the possibility of tailoring pore structures.

1. Introduction

The dehydration of boehmite (γ-AlOOH) to γ-Al_2O_3 in air is a topotactic reaction giving a product having a lamellar porous microstructure of uniform spacing and orientation [1, 2]. This porous microstructure has similarities with the lamellar microstructures produced by cellular growth during eutectic and eutectoid reactions. In line with these similarities a diffusion-controlled mechanism has been proposed for the dehydration of boehmite, involving counter-diffusion of protons and Al cations in the plane of the reaction interface and in a direction perpendicular to the lamellae [2].

Treatment of the energetics of cellular growth, as e.g. by Christian [3], suggests that the spacing of the lamellae is dependent on the overall free energy change for the reaction. For the precipitation of lamellar pearlite in the Fe/C system, a variation of scale of the microstructure with temperature has been observed [4]. The aim of the present work is to examine the appropriateness of such a treatment for a thermal decomposition reaction, by studying the dependence of the scale of the lamellar porous microstructure in γ-Al_2O_3 on the free energy change, by varying the temperature and water vapour pressure at which the dehydration is performed.

2. Experimental procedure

The starting material for this study was CERA hydrate, supplied by the British Aluminium Company Ltd, which is boehmite with a maximum crystal size of about 5 μm.

A variety of methods were used to set up the dehydration conditions shown in Table I. Furnaces and thermal balances in which the atmosphere could be controlled were used. The conditions for Samples 2 and 3 were produced by dynamic pumping with a rotary pump and liquid nitrogen trap with or without a diffusion pump. For Samples 4 and 6 the furnaces were pre-evacuated and then allowed to equilibrate with reservoirs containing

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TABLE I

Sample	Conditions	P_{total} (torr)	p_{H_2O} (torr)	λ (Å)	d_p (Å)	S_{geom} ($m^2\,g^{-1}$ Al_2O_3)	S_{BET} ($m^2\,g^{-1}$ Al_2O_3)	V_p ($ml\,g^{-1}$ Al_2O_3)
1	*in situ* in e^-m	10^{-5}	–	22	(< 4.6)	(> 315)	–	–
2	vacuum furnace 380–450° C 3½ h	0.015	–	25	5.25	277	negligible	negligible
3	vacuum furnace 400° C 1 h	~ 1	–	28	5.9	248	7	~ 0.01
4	H_2SO_4 reservoir 450° C 1 h	8	8	30	6.3	231	69	0.051
5	in air 450° C 1 day	760	~ 15	38	8.0	183	107	0.080
6	H_2O reservoir 450° C 1 day	25	25	36	7.6	193	–	–
7	steam flow 480° C 3 h	760	~ 760	50	10.5	139	86	0.077
8	hydrothermal 500° C 1 day	~ 15000	~ 15000	–	α-Al_2O_3	α-Al_2O_3	α-Al_2O_3	–

H_2SO_4 (specific gravity (SG) = 1.46) or H_2O. Sample 7 was prepared in a thermal balance dynamically purged with steam from a boiler. For Sample 8 a hydrothermal bomb was used. Knowledge of the atmospheric conditions, particularly those experienced at the reaction interface, is rather imprecise, but in the present context this is less important than the preparation of samples over a large range of water vapour pressures. Where it is only possible to quote a total pressure in Table I, this, because of the continuous evolution of H_2O from the dehydrating sample, should approximate to p_{H_2O}.

For each atmosphere, heating conditions, so as to produce as nearly complete dehydration as possible, were chosen to obtain γ-Al_2O_3 phases prior to the onset of the subsequent transformations in the γ-AlOOH/Al_2O_3 system [5, 6]. Heating conditions approximated to isothermal, except for Sample 2 which was heated so as to maintain a constant rate of weight loss. The progress of the dehydration reaction was followed where possible by weight loss, and (in all cases) by examination of products by X-ray powder and electron diffraction methods.

The samples of porous γ-Al_2O_3 prepared were characterized by nitrogen adsorption at − 197° C (after outgassing at 250° C), using a gravimetric technique, and by electron microscopy. Samples for electron microscopy were prepared by crushing, dispersing in alcohol and depositing on perforated carbon films on copper support grids. Transmission electron microscopy (TEM) was performed on a Siemens 102 instrument equipped with a double-tilting stage and operated at 100 kV.

3. Results

Fig. 1c shows the microstructure developed during the dehydration of a boehmite single crystal at 450° C in air. The micrograph represents a view parallel to a regular series of fine lamellar pores. The direction of the electron beam also coincides with the direction of growth of the pore system which is perpendicular to the surface of the plate-like boehmite crystal. Each boehmite crystal is transformed on dehydration to an essentially single crystal of γ-Al_2O_3 (with a tetragonally distorted defect spinel structure) with a uniquely orientated lamellar pore system of regular spacing. A precise description of the orientational relationships has been given elsewhere [1, 2, 5] and is not necessary here: the micrographs of Fig. 1 are, however, all presented in equivalent orientations.

The average lamellar repeat distance for this air-fired sample (Sample 5) was found to be 38 Å. No significant variation of this figure was found for samples of boehmite heated at 350° C for 36 days or at 550° C for ½ h (times chosen to obtain equivalent degrees of dehydration). The scale of the microstructure is thus apparently insensitive to temperature, although the range studied is of necessity relatively small. The time–temperature behaviour of the boehmite dehydration [6] does not allow convenient study of a larger temperature range.

In studying the effect of variations in water

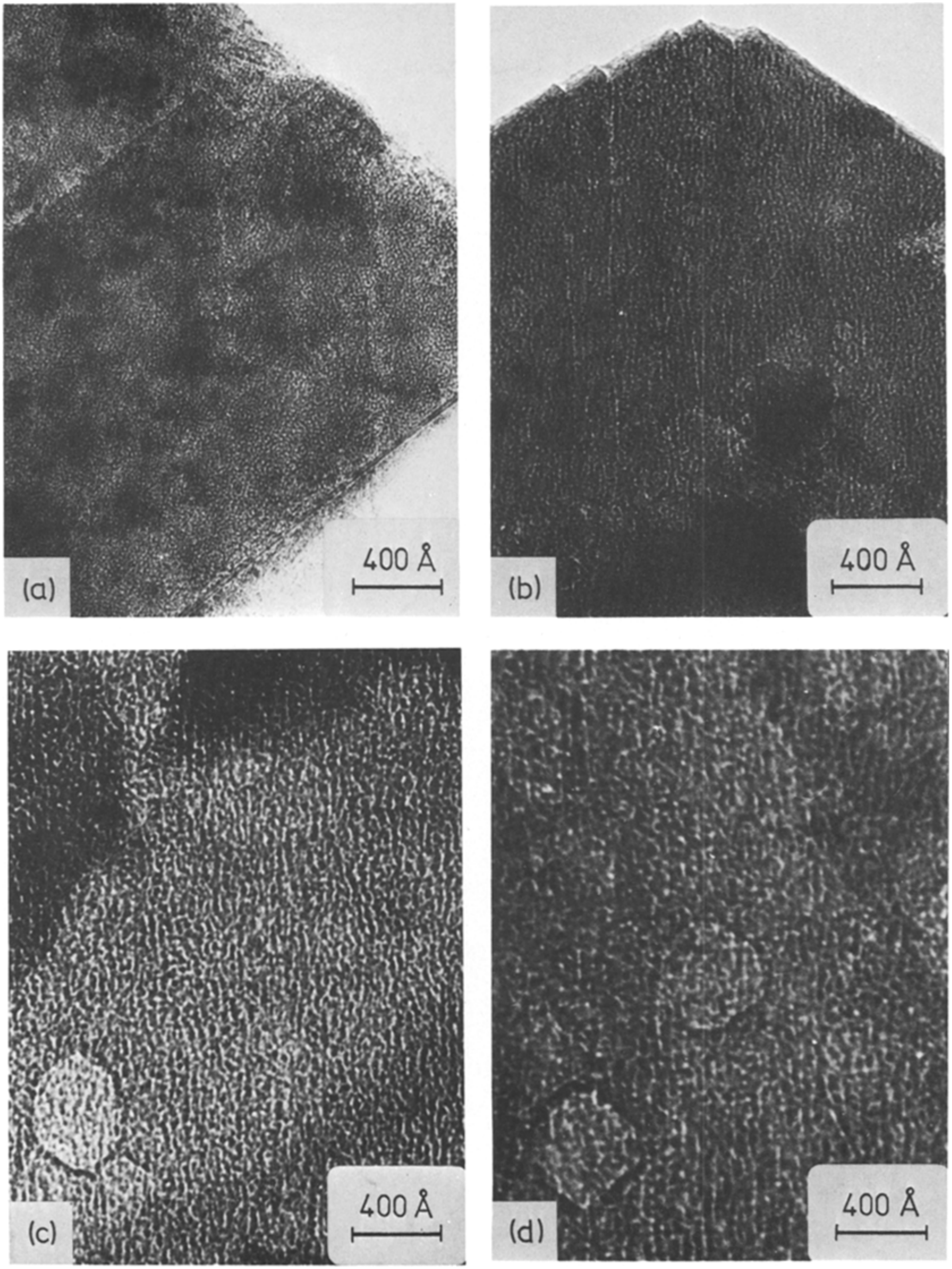

Figure 1 Transmission electron micrographs of γ-Al_2O_3 from (a) Sample 1, (b) Sample 2, (c) Sample 5, (d) Sample 7. The γ-Al_2O_3 *c*-axis is horizontal.

vapour pressure on microstructure, ideally a constant temperature should be used, and as far as possible this was attempted. However the general effect on time–temperature behaviour is such that for higher pressures, higher temperatures or longer times are required to reach equivalent stages in the dehydration sequence. For the pressure range studied it was necessary to use temperatures in the

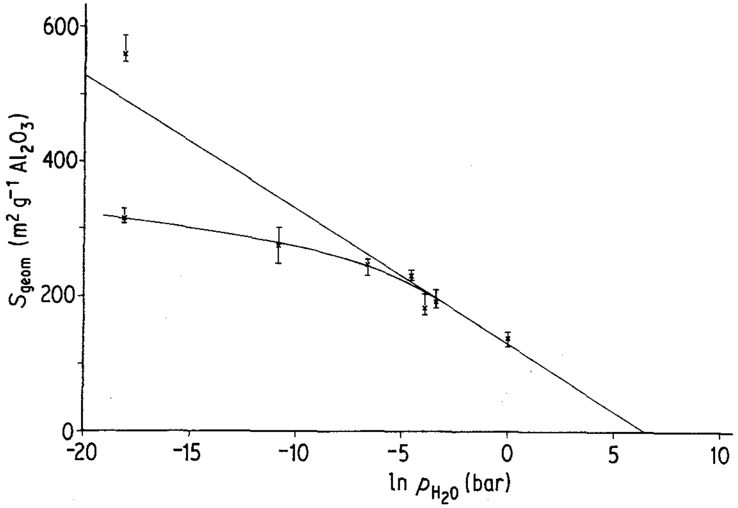

Figure 2 Variation of S_{geom} with ln p_{H_2O}.

range 380 to 500° C, but, given the apparent insensitivity of microstructure to temperature variations at constant pressure, this should not detract from the analysis of any pressure dependence.

The sample prepared at the highest water vapour pressure (~ 20 atm) was found to consist solely of α-Al_2O_3. This suggests that, as has been found previously [7, 8], boehmite dehydrates directly to α-Al_2O_3 (corundum) under such conditions.

The effect of water vapour pressure on the scale of the porous microstructure is clearly shown by the micrographs of Fig. 1, an increase in p_{H_2O} results in an increase in pore spacing. In an attempt to quantify this, a large number of measurements were made on micrographs of a number of crystalline fragments, carefully tilted to within a few degrees of $[1\,1\,0]_\gamma$, for each sample. The figure thus obtained is an average pore repeat distance, λ, measured perpendicular to the lamellae, and is quoted in Table I. For any one sample some spread in λ was observed, probably due to imprecise control of p_{H_2O}, or to variations in pressure experienced at different parts of the sample. The extent of this spread is indicated by the error bars in Fig. 2. The scale itself is very much smaller than that observed for eutectic and eutectoid lamellar microstructures, which are commonly at the micron level. The other microstructural features visible in Fig. 1c and d are relics of relatively large isolated pores which have been observed to develop, probably from defects in the boehmite structure, prior to the onset of dehydration [1].

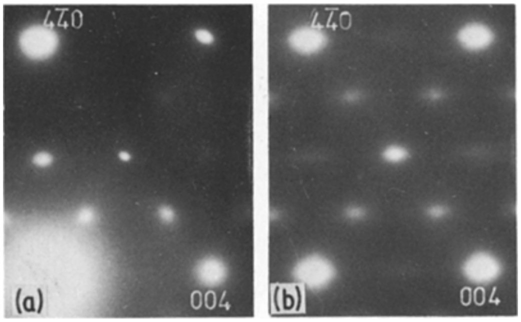

Figure 3 Electron diffraction patterns showing [1 1 0] γ-Al_2O_3 zones from (a) Sample 1, (b) Sample 5.

The regularity of the lamellar microstructure, in terms of orientation and spacing, was in general observed to be quite good with the exception of Sample 1, for which a much more random microstructure was observed (Fig. 1a). This sample was dehydrated *in situ* in the electron microscope under conditions of electron bombardment which produced a very fast reaction, taking of the order of a few minutes rather than hours. Presumably in such a fast reaction the same degree of mechanistic organization as in the more controlled dehydrations cannot be achieved. This loss of the regular lamellar nature of the microstructure is apparent also in the electron diffraction patterns of Fig. 3. The pattern from Sample 5 shows a degree of streaking in the c^*-direction, perpendicular to the lamellae, while that from Sample 1, with the random microstructure, shows no such streaking.

The stoicheiometry of the reaction

$$2\gamma\text{-AlOOH} \rightarrow \gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O} \qquad (1)$$

shows that one quarter of the boehmite oxygen lattice is lost during dehydration, and, thus, that for a mechanism in which the total crystal volume is conserved, the pore volume should constitute

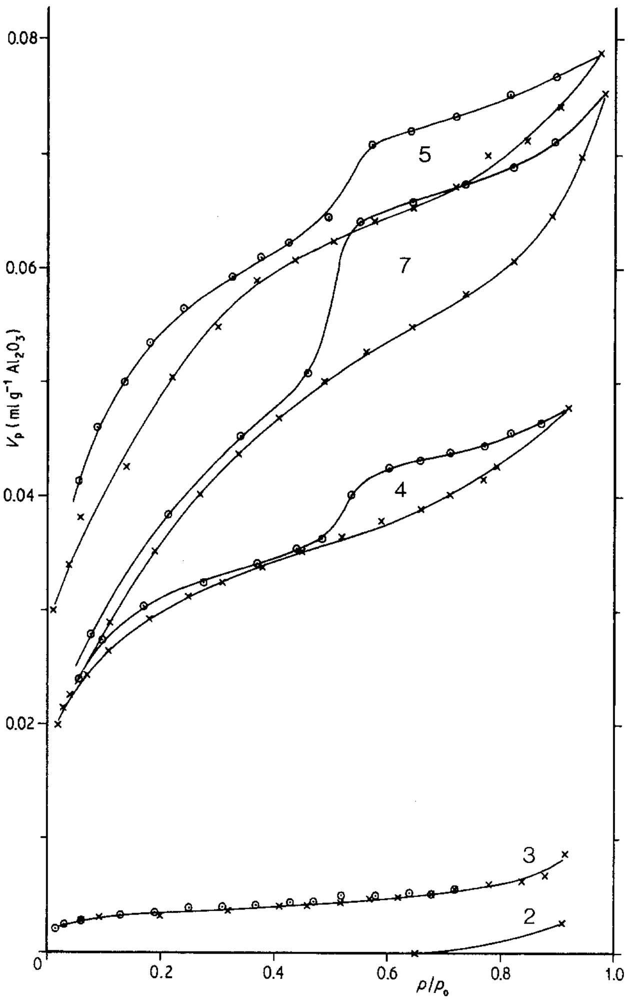

Figure 4 Nitrogen adsorption (X) and desorption (O) isotherms for Samples 2, 3, 4, 5 and 7.

one quarter of that total. The micrographs of Fig. 1 are consistent with this. In fact if the slight expansion (~ 6%) in the lattice vector perpendicular to the lamellae, which occurs during the transformation of boehmite to tetragonally distorted γ-Al_2O_3, is taken up by the pores, the ratio of pore width to the lamellar repeat distance is reduced to about 0.21 [2]. Pore widths, d_p, calculated on this basis (strictly valid only for a regular lamellar microstructure) have been included in Table I. Accurate measurement of d_p from micrographs is difficult as contrast is so much a function of electron microscope focus position. Also included in the table is a calculated geometric internal surface area,

$$S_{\text{geom}} = \frac{2V}{0.79M\lambda}, \tag{2}$$

where M is the molecular weight, and $V = 27.93\,\text{cm}^3$ is the molar volume of γ-Al_2O_3. Again this is only correct for a strictly lamellar microstructure: any degree of randomness, such as observed for Sample 1, will increase surface area substantially over that calculated.

The nitrogen adsorption behaviour of five of the samples was investigated and adsorption and desorption isotherms are shown in Fig. 4. Those for Samples 4, 5 and 7 exhibit typical microporous behaviour. A more complete analysis of the adsorption behaviour of such porous alumina materials is presented elsewhere [9]: here, the data derived from the nitrogen adsorption studies is restricted to the BET surface area, S_{BET}, and the total pore volume accessible to nitrogen, V_p (obtained by extrapolating the isotherms to $p/p_0 = 1$), and these two functions are quoted in the table. Variations in these values reflect variations in the scale of the microstructure and the pore width. Thus Samples 5 and 7, which have pore widths allowing essentially unhindered access to nitrogen, have similar pore volumes, which correspond well with a calculated geometric pore volume $(S_{\text{geom}} \cdot d_p)/2 = 0.073\,\text{ml}\,\text{g}^{-1}$, but very different surface areas. These two facts are indicative of the increase in both λ and d_p from Sample 5 to Sample 7. For these two samples the BET surface areas measured are smaller than those calculated, and this is to be expected since BET theory assumes multi-layer adsorption, while the narrow pore widths do not allow access by more than two molecular nitrogen layers. However the ratios of S_{BET} and S_{geom} for the two samples are similar. The trend towards a decrease in both V_p and S_{BET} for Samples 4, 3 and 2 may be attributed to the decrease in pore width hindering access by nitrogen molecules to the pore system. The extent of adsorption exhibited by Sample 2 is essentially negligible and the pore width for this sample may be compared with the commonly accepted cross-sectional area of the N_2 molecule of 16.2 Å^2 [10].

4. Thermodynamic control of inter-lamellar spacing

A schematic illustration of the mechanism envisaged for the dehydration of boehmite is presented in Fig. 5. The possibility of similar mechanisms operating in other hydroxide dehydration reactions has been discussed [11, 12, 13]. The low temperature reduction of hematite to magnetite has also been described in a similar fashion [14] but in this case the pores are cylindrical, probably because of the small fractional pore volume created. The lamellar morphology observed for γ-Al_2O_3 will be due to the higher pore volume and to the highly anisotropic atomic mobilities in boehmite. An easy path for proton diffusion is provided by the hydrogen bond chains in the boehmite structure which are uniquely orientated perpendicular to the lamellar pores [2].

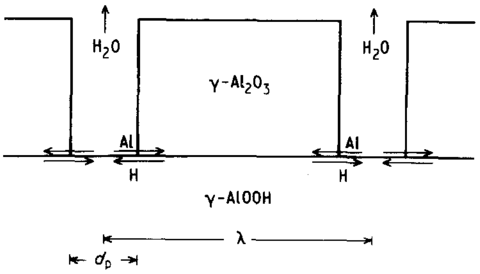

Figure 5 Schematic illustration of the dehydration mechanism.

Fig. 5 emphasizes the mechanistic similarities between the dehydration of boehmite and the formation of lamellar microstructures during eutectic solidification and eutectoid reactions (such as the pearlite reaction in the Fe/C system). However there are a number of basic differences. The dehydration of boehmite is a thermal decomposition rather than a solute segregation reaction and as such the free energy change increases in magnitude with increasing temperature. Thus a substantially different time–temperature behaviour is observed for the γ-AlOOH/γ-Al_2O_3 system [6] than for eutectoid systems. Eutectic and eutectoid reactions proceed by cellular growth, i.e. the lamellae are propagated simultaneously from a number of nuclei. However, in the case of boehmite dehydration, the orientational characteristics of the mechanism are so rigidly controlled [2] that each boehmite crystal is effectively a single cell. The topotactic character of the reaction means further that the boehmite/γ-Al_2O_3 interface cannot be considered as incoherent. Finally, the very fine scale of the γ-Al_2O_3 pore system is virtually at the unit cell level, in fact, ideally, the spacing would be an integral multiple of twice the boehmite a_0 parameter (2 x 3.7 = 7.4 Å). Despite these differences it should be possible to develop a model for boehmite dehydration along similar lines to those suggested for cellular growth [3].

The underlying principle of the treatment is that the inter-lamellar spacing is governed by the amount of energy available for the formation of new surface. For the dehydration of boehmite to γ-Al_2O_3

$$\Delta G = \Delta G_0 + \frac{2\sigma V}{0.79\lambda}, \tag{3}$$

where σ is the surface energy per unit area, $(2V/0.79\lambda)$ is the surface area per mole and ΔG_0 (a function of temperature and pressure) is the free energy change for the reaction producing non-porous γ-Al_2O_3 (i.e. for $\lambda = \infty$). There exists a limiting minimum value of the spacing, $\lambda^* = -(2\sigma V/0.79\Delta G_0)$, for which ΔG becomes zero and all the available free energy would be used in creating surface. Thus

$$\Delta G = \Delta G_0 - \frac{\lambda^*}{\lambda}\Delta G_0 = \Delta G_0\left(1 - \frac{\lambda^*}{\lambda}\right). \tag{4}$$

The spacing λ is not however variable between the limits λ^* and ∞, but is fixed for a particular set of reaction conditions. For the eutectic and eutectoid cases a number of models have been proposed to describe how λ is determined, and these are described by Christian [3]. The main assumptions of the models are (a) that the overall rate of the reaction is dependent on the velocity of diffusion processes parallel to the interface rather than on the inherent mobility of the interface itself, and (b) that the interface represents a situation not far removed from equilibrium. Since the models attempt to describe what are essentially solute segregation reactions, they have been derived by consideration of processes of mass transport along concentration gradients. It would seem inappropriate to treat the thermal decomposition of boehmite in a similar fashion. The following treatment has been derived by considering diffusion in the plane of the reaction interface along a free energy gradient. For a free energy gradient ($2\Delta G/\lambda$), the average velocity of diffusing species is ($2M\Delta G/\lambda$) where M is a mobility term. The time taken for the diffusion processes to be complete in one layer of the boehmite structure is proportional to ($\lambda^2/M\Delta G$) and the interface velocity, R, is thus proportional to ($M\Delta G/\lambda^2$), or, $R \propto (M\Delta G_0/\lambda^2)(1-\lambda^*/\lambda)$. Zener [15] assumed that this function R, which is proportional to overall reaction rate, would be maximized, in which case $\lambda = 3/2\lambda^*$, although it is not obvious why this should necessarily be the case. It might be more fundamentally important to maximize the rate of decrease of free energy of the system or the rate of entropy production. Both these functions are maximized with $R \cdot \Delta G$ or $(M\Delta G_0^2/\lambda^2)(1-\lambda^*/\lambda)^2$ which is a maximum for $\lambda = 2\lambda^*$. The treatment presented here parallels the treatment of cellular growth, in terms of concentration gradients, due to Turnbull [16].

The thermodynamic data available for γ-Al_2O_3 [17] undoubtedly includes a surface energy contribution which is variable dependent on the method of preparation of the γ-Al_2O_3. In the absence of data as a function of internal surface area, no independent measure of (λ^*/λ) is possible. However the treatment presented here suggests that (λ^*/λ) is a constant, i.e. that a fixed proportion of ΔG_0 is used for the formation of new surface. In the treatment of cellular growth due to Cahn [18] (λ^*/λ) is held to be a variable, but the model requires that the compositions of the lamellae should also be variable, a proviso which seems inappropriate in the present case.

So this gives

$$\frac{2\sigma V}{0.79\lambda} = -\frac{\lambda^*}{\lambda}\Delta G_0\,; \tag{5}$$

thus, λ and surface area should be sensitive to variations in ΔG_0. In the present study we have attempted to vary ΔG_0 by control of the temperature and water vapour pressure at which the dehydration takes place.

For variation of temperature, the approximation that $\Delta G_0 \propto \Delta T$ (the degree of superheating) suggests that $\lambda \propto (\Delta T)^{-1}$. However in the present study no dependence of λ on T was observed. The reasons for this insensitivity are not clear, although it may be that we are operating in a limited temperature range very far removed from equilibrium conditions. This insensitivity to temperature has however been observed in other studies. Thus, in studies of the pearlite eutectoid [4], Pb–Sn alloys [18, 19, 20] and Fe–Zn alloys [21] a dependence of λ on T was observed, but in all cases the sensitivity is lower than expected. This relative insensitivity is revealed either by the calculation of unreasonably high values of σ or, assuming reasonable values for σ, by the calculation of very low values for (λ^*/λ). In a study of the dehydration of gibbsite [22] the development of surface area, and presumably also pore size, was found to be more sensitive to changes in water vapour pressure than to changes in temperature, and this has also been found to be the case in the present study of the dehydration of boehmite. Despite lack of precision in the pressure data, a marked dependence of λ on p_{H_2O} over a large pressure range has been demonstrated.

For the variation of ΔG_0 by control of p_{H_2O}

$$\frac{2\sigma V}{0.79\lambda} = -\frac{\lambda^*}{\lambda}RT\ln p_{H_2O} + c. \tag{6}$$

In Fig. 2, S_{geom} is plotted against $\ln p_{H_2O}$. The deviation from linearity is due to the increase in randomness of the microstructure as pressure decreases. As explained above, the calculation of S_{geom} is only valid for a perfectly lamellar microstructure, any degree of randomness leading to an increase in surface area. For Sample 1 (Fig. 1a) the degree of randomness is high and the deviation of true surface area from S_{geom} is large. For this sample a calculation on the basis of a pore network delineating hexagonally-packed hexagonal rods of γ-Al_2O_3 gives a geometric internal surface area of $560\,m^2\,g^{-1}$ and this value is included in Fig. 2. The true surface area will undoubtedly approach this value.

Extrapolation of Fig. 2 to the pressure conditions used for the preparation of Sample 8 predicts that γ-Al_2O_3 formed under such conditions would have $S_{geom} \sim 70\,m^2\,g^{-1}$ and $\lambda \sim 100\,Å$. Evidently, because of the requirement of such a large inter-lamellar spacing, a different dehydration mechanism, that of direct nucleation of α-Al_2O_3, becomes easier and is kinetically preferred. Extrapolation to $S_{geom} = 0$ gives a pressure of about 700 bars, which should correspond to the equilibrium pressure between boehmite and non-porous alumina.

From the slope of the straight line drawn in Fig. 2 an estimate of surface energy per unit area can be made. Thus for a temperature of 700 K, assumption of $(\lambda^*/\lambda) = 1/2$ or $2/3$ gives, respectively, values for σ of 1.43 and $1.91\,J\,m^{-2}$. There is little surface energy data available for oxide materials for direct comparison with these results. A few experimental results have however been obtained for MgO and CaO, reviewed by Benson and Yun[23], and these lie in the range 1.0 to $1.3\,J\,m^{-2}$, showing that the values obtained here are credible for the more covalent oxide, γ-Al_2O_3. All the samples of γ-Al_2O_3 prepared here, then, possess a substantial total internal surface energy: for example, for the air-fired Sample 5 values of 26.8 and $35.7\,kJ\,mol^{-1}$ (for $\lambda^*/\lambda) = 1/2$ and $2/3$ respectively) may be calculated. Again there is little data to compare these values with. Yokokawa and Kleppa [24] obtained, using a calorimetric method, values of enthalpy of solution for γ-Al_2O_3 samples with a variety of preparative and thermal histories, although with unspecified surface areas. The enthalpy difference between γ-Al_2O_3 samples with relatively high and low surface areas is of the order of $11\,kJ\,mol^{-1}$.

5. Discussion and conclusion

Previous studies of the growth of lamellar microstructures during eutectic and eutectoid reactions have allowed the derivation of models which assume that the reactions are controlled by the velocity of diffusion processes parallel to the reaction interface but perpendicular to the lamellae. Detailed predictions of the models, for example the nature of the dependence of λ on T, are, however, not closely obeyed. Here, for the first time, a similar model, derived in terms of diffusion along a free energy gradient, has been applied to a thermal decomposition reaction, in which the lamellar microstructure is in fact a pore system. The model is successful in explaining the observed p_{H_2O} dependence of λ and surface area, and in allowing the derivation of reasonable estimates of surface energy. The ideas that the mechanism of the dehydration of boehmite is diffusion controlled, and that the inter-lamellar spacing is dependent on the free energy available for the formation of new surface, are thus substantiated.

Previous observations of the sensitivity of the surface area of porous oxides to the p_{H_2O} conditions under which they were formed [22, 25] suggest that the treatment presented here may be of quite general application to hydroxide dehydration reactions. More particularly the results described here outline a method for the strict control of pore spacing, pore width and surface area in lamellar porous γ-Al_2O_3. Thus by close control of p_{H_2O} conditions it may be possible to tailor the porosity of such materials to within quite close tolerances.

Acknowledgements

The receipt by S. J. Wilson of an award under the ICI Joint Research Scheme, and the use of the SRC funded Siemens 102 instrument in the Cavendish Laboratory, Cambridge, are gratefully acknowledged.

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Received 27 March and accepted 1 May 1980.