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VARIATION OF SURFACE AREA DURING ISOTHERMAL SINTERING OF MESOPOROUS GAMMA-ALUMINA

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ABSTRACT

Mesoporous gamma-alumina ($S_{BET} = 149$ m^2 g^{-1}), prepared by thermal decomposition of hydrated aluminium sulphate, was heat-treated under various gas conditions in order to study the influence of the surrounding atmosphere on sintering rate. This was monitored by the reduction in specific surface area, $\Delta S/S_0$, as a function of calcination time, t. A kinetic equation of the type $(\Delta S/S_0)^\gamma = Kt$ was found to describe the experimental results adequately. Oxygen and water vapour were both found to enhance sintering, when compared with the results obtained in an inert atmosphere.

INTRODUCTION

Sintering is a thermally activated process which leads to a reduction in surface area by smoothing of surface roughness, grain-boundary formation, neck growth between individual particles and coalescence of small micelles to form larger particles. When the initial solid is of a porous nature, the progressive elimination of porosity is also an important factor to consider. Mass transport mechanisms responsible for sintering include surface and grain-boundary diffusion, bulk diffusion, evaporation–condensation, plastic flow, or any combination of these individual mechanisms.

Several authors [1–5] have pointed out that the rate of thermal sintering of a powdered solid can be determined by monitoring the reduction in surface area during thermal treatment. The decrease in surface area on isothermal heating tends towards a final equilibrium value determined by the initial physical condition of the material and the temperature of the experiment [5]. For the initial steps of sintering in an ensemble of spherical particles of homogeneous size, and in the absence of porosity (i.e., without internal surface) it has been shown [2,3,6] that the sintering kinetics follow an equation of the form

$$(\Delta S/S_0)^\gamma = Kt \tag{1}$$

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where ΔS is the loss in surface area from the initial value S_0, K a constant and γ an exponent dependent on the diffusion mechanism.

A number of studies [4,7–11] have also dealt with the role of the surrounding atmosphere on the sintering behaviour of different metal oxides. The results, however, are rather fragmental and inconclusive.

The present paper reports on a study of the isothermal sintering of mesoporous gamma-alumina in the presence of either an inert atmosphere (dry argon), dry oxygen or oxygen saturated with water vapour. The aim is two-fold: (i) to test whether an empirical equation type (1) can still describe the sintering kinetics when porosity contributes substantially to specific surface area, and (ii) to study the influence of different atmospheres on the sintering rate of gamma-alumina. This last aspect is of considerable relevance to many applications of gamma-alumina in technology.

EXPERIMENTAL

The starting gamma-alumina was obtained by thermolysis of hydrated aluminium sulphate, $Al_2(SO_4)_3 \cdot 18\ H_2O$ (T. Schuchardt, 99.9%), at 1173 K. Full characterization of this material has been reported elsewhere [12]. For the purpose of the present work, it suffices to say that the solid had a BET surface area of 149 $m^2\ g^{-1}$ (average of three determinations by nitrogen adsorption at 77 K) and was mesoporous, with a pore volume of 0.723 $cm^3\ g^{-1}$ and most frequent pore radius of 7 nm.

Separate portions of the starting material were given isothermal heat treatments at different temperatures (in the range 1073–1273 K) under a flow of dry argon (N45), dry oxygen (N48) or oxygen saturated with water vapour at room temperature. A temperature controller ensured that temperature fluctuations never exceeded ±10 K. Samples were removed from the furnace at increasing time periods, and the corresponding BET surface areas were determined by nitrogen adsorption at 77 K, using a volumetric apparatus of conventional design. X-ray diffraction at the end of each run showed that no phase transformation of the initial gamma-alumina had occurred.

RESULTS AND DISCUSSION

Figure 1 shows the variation of BET surface area, as a function of calcination time, during each isothermal run. These were: dry argon at 1173, 1223 and 1273 K; dry oxygen at 1073, 1173 and 1273 K; and water vapour-saturated oxygen at 1273 K.

It is seen that, in each run, there is an initial decrease of specific surface area which then tends towards a final equilibrium value, as the time of the heat treatment is increased. Figure 1 also shows that, for any given tempera-

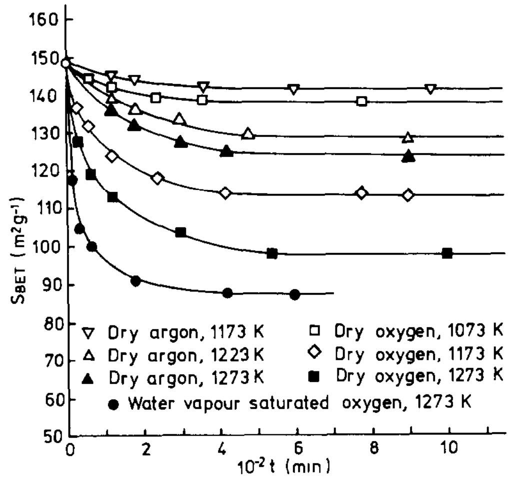

Fig. 1. Surface area as a function of calcination time for the different atmospheres and temperatures.

ture, the sintering rate in flowing dry oxygen is considerably greater than in dry argon. When the results obtained at 1273 K are compared, it is also seen that the presence of water vapour causes a further increase in the sintering rate. Previous studies [13] have already indicated that in the temperature range 1073–1273 K surface diffusion is the main mechanism responsible for the textural changes of gamma-alumina, with bulk diffusion becoming dominant above 1473 K [13,14]. The present work conclusively proves that oxygen and water vapour favour diffusion. Small amounts of water vapour have also been found [11,15,16] to enhance the sintering of magnesium oxide. The role of water vapour in the sintering of metal oxides has been assigned by Anderson and Morgan [15] to an increased surface mobility brought about by adsorption–desorption of the water molecule. This would facilitate transport of the anion, as could also be the case with free oxygen.

The experimental surface area reductions with isothermal sintering time are plotted on a log–log basis in Figs. 2 and 3. The experimental points corresponding to initial sintering are seen to fit straight lines. This is the behaviour predicted from eqn. (1) in the introduction which, even in its original derivation, can only be applied to the initial stages of sintering [2,4].

It should be pointed out that eqn. (1) was derived for a physical model in which interparticle neck growth is responsible for surface area reduction [2,6]. Under these conditions, the value of the γ-exponent to be expected when surface diffusion is the dominant sintering mechanism is $\gamma \approx 3.5$ [2,4]. The inverse slope of the straight lines in Figs. 2 and 3 gives the following values of γ: dry argon, 2.1; dry oxygen, 2.2; oxygen saturated with water vapour, 2.4. This last value, however, does not have good precision, owing to the scarcity of experimental points. From the whole set of experimental runs a value of $\gamma \approx 2.2$ may be established.

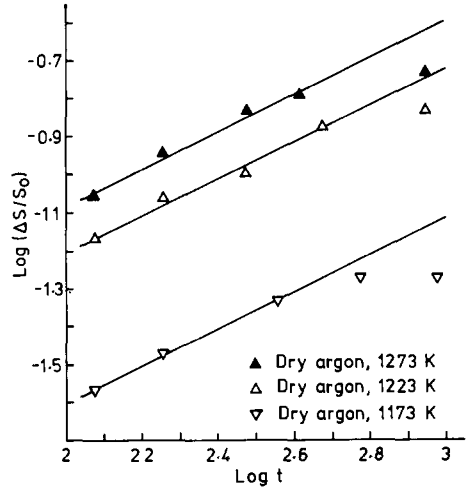

Fig. 2. Kinetics of the reduction of specific surface area for samples calcined in dry argon.

It may be concluded that eqn. (1) can provide a good phenomenological description of the surface area reduction during isothermal sintering, even in cases where the experimental conditions do not fit the physical model used to derive the equation. However, internal surface area (and probably also

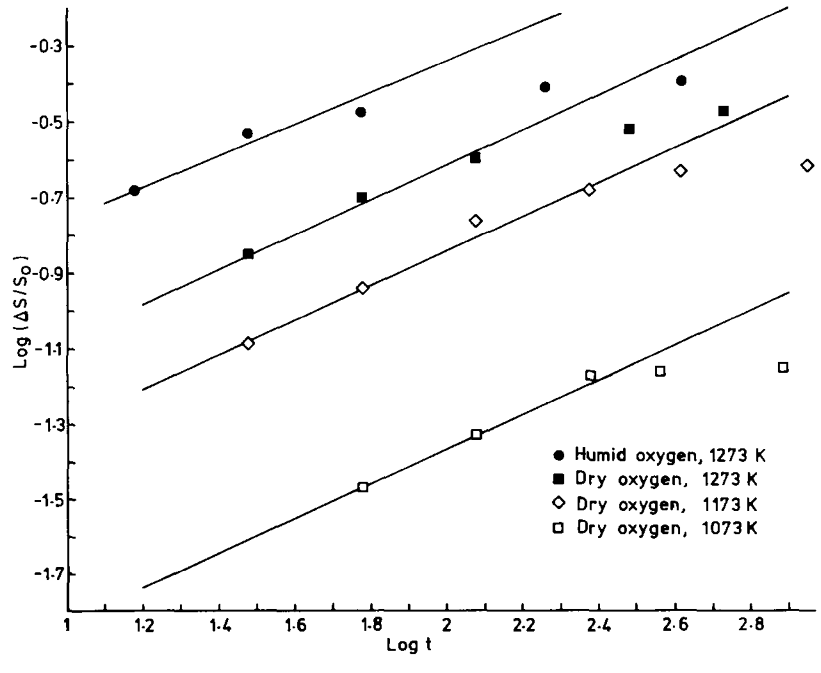

Fig. 3. Kinetics of the reduction of specific surface area for samples calcined in dry and in humid oxygen.

particle heterogeneity) have the effect of a decrease in the γ-exponent. This should not be surprising, since consideration of eqn. (1) shows that a decrease of γ results in an increase of the rate constant, K. The presence of porosity in the starting material would precisely be expected to cause a faster rate of surface area reduction.

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