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Variations of physical properties in pellets containing alumina/carbon powder mixtures during reduction and nitridation

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Surface area and porosity of pellets containing alumina/carbon powder mixtures during reduction and nitridation were determined. The experimental results indicated that surface area and porosity of solid samples were decreased by increasing the reaction temperature, grain size, forming pressure and the amount of catalyst. Increasing the molar ratio of C/Al_2O_3 and gas flow rate could decrease the surface area and increase the porosity of the solid sample.

1. Introduction

The carbothermic nitridation of aluminium oxide has received much attention [1–8]

$$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3CO(g) \quad (1)$$

Most of the works focused on the effects of operating variables on the final yield of aluminium nitride. Chen and Lin [9] examined the kinetics of this reaction system. Additionally, the mechanism of this reaction was discussed by Wang [4], Cho and Charles [7], Chen and Lin [9] and Lefort and Billy [10].

A thorough understanding of the change of the physical properties during the reaction would facilitate an understanding of the reaction itself. Hence, an investigation of the effects of gas flow rate, reaction temperature, molar ratio of C/Al_2O_3, grains sizes, forming pressure and the amount of catalyst on the variations of surface area and porosity of the solid sample during reduction and nitridation, will be reported.

2. Experimental procedure

Nitrogen (Lien-Hwa) with a minimum purity of 99.99% was employed. Reagent-grade aluminium oxide and graphite were supplied by Cerac Incorporated and Johnson Matthey Electronics, respectively.

Powders of aluminium oxide and graphite were separately dried and screened. Next the powders with known sizes and predetermined proportions were mixed in a V-blender for 43 200 s with ethanol employed as a dispersing medium. The mixed samples were then dried in a nitrogen stream at 323 K. Pellets of solid sample were prepared using a die and an hydraulic press. The pellets were in disc-form of 0.0055 m radius, 0.001 m thick and 1.7×10^{-4} kg in weight. The disc was held in an alumina holder during reduction and nitridation.

Reactions were carried out in a horizontal alumina tube heated by a tubular furnace. The solid sample was placed in the cold end of the tube during the heat-up period, during which nitrogen was continuously flowed through the tube. The solid sample was pushed by an alumina rod to the reaction zone for reaction as a response to the temperature, thereby reaching the predetermined value and remaining stable for about 300 s. The pressure in the reaction tube was maintained at 0.005–0.015 m H_2O higher than atmospheric. The solid sample was removed and quenched in argon gas once the predetermined reaction time had been reached.

Surface area and porosity of the solid samples were measured by a surface area meter of Micromeritics (model ASAP2000).

The experimental conditions employed in the present study are summarized in Table I. The italicized values are the standard operating variables. That is,

TABLE I Experimental conditions used in this study

Condition	
Gas flow rate (10^{-6} $m^3 s^{-1}$)	1.67, 5.00, 8.33, 11.7
Reaction temperature (K)	1700, 1750, 1773, 1798
Molar ratio of C/Al_2O_3	2.13, 4.25, 6.38
Alumina grain diameter (10^{-6} m)	5, 39, 414
Carbon grain diameter (10^{-6} m)	5, 39, 414
Forming pressure (10^{-5} Pa)	1773, 3106, 4436
Amount of AlN added (%)	0, 5, 10

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when the effect of that variable is not examined, its value is held at the italicized value in that series of experiments. Further experimental details are available in the report [11] on which this paper is based.

3. Results and discussion

3.1. Effect of gas flow rate

The measurements of surface area and porosity of the solid pellet are shown in Figs 1 and 2. These figures indicate that the pore surface area is decreased

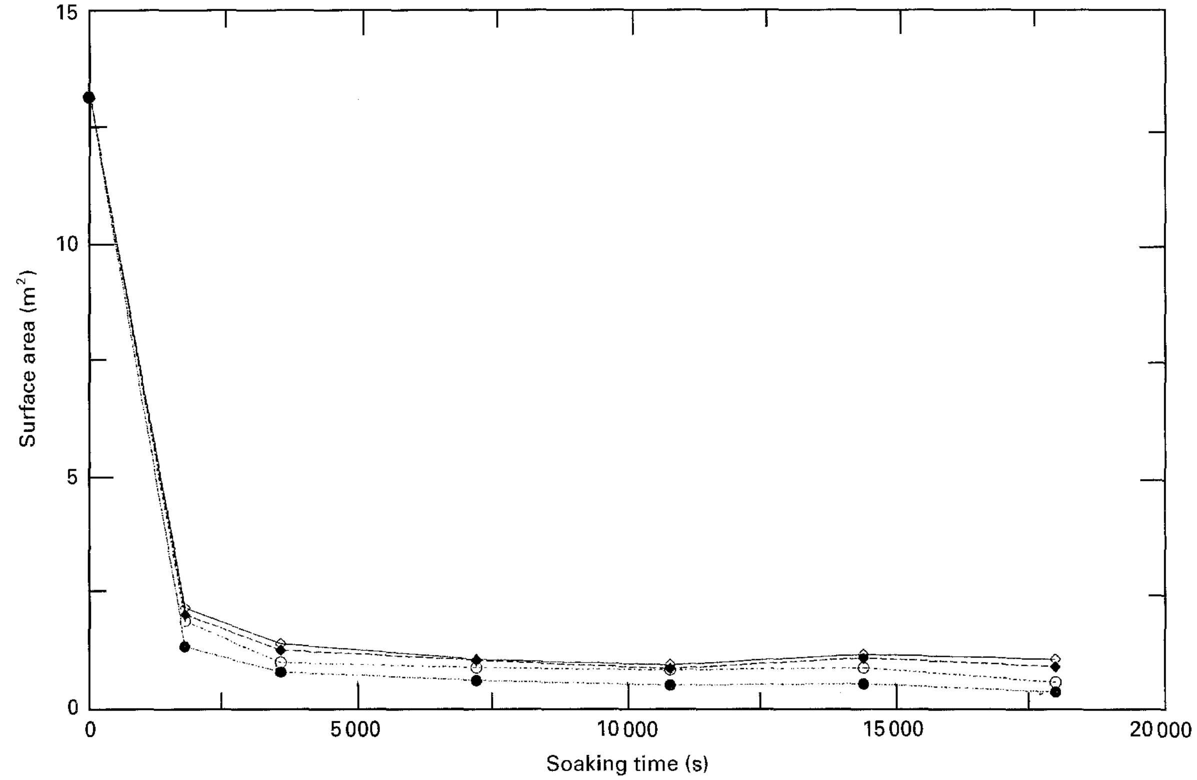

Figure 1 The effect of gas flow rate on the variation of surface area of the solid sample with soaking time. Gas flow rate ($m^3 s^{-1}$): (◇) 1.67×10^{-6}, (◆) 5.00×10^{-6}, (○) 8.33×10^{-6}, (●) 1.17×10^{-5}.

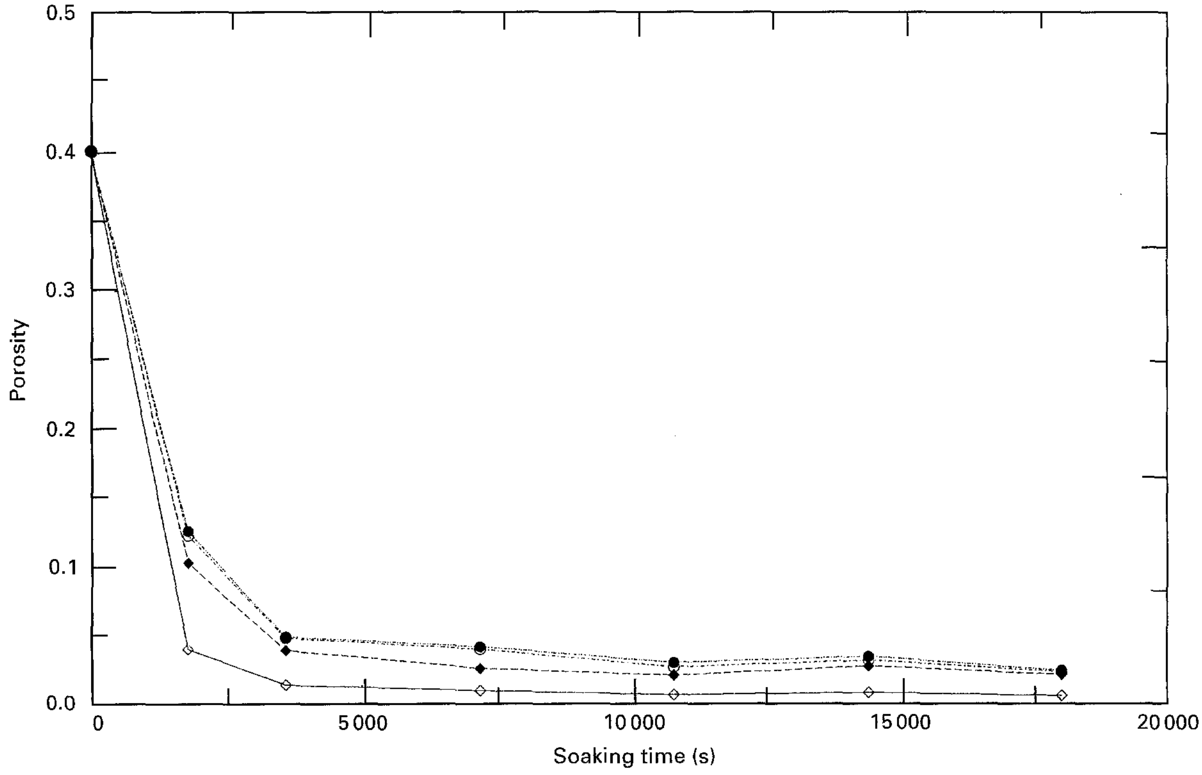

Figure 2 The effect of gas flow rate on the variation of porosity of solid sample with soaking time. For key, see Fig. 1.

drastically and then decreased moderately with increasing reaction time. As time proceeds, chemical reaction and sintering take place simultaneously. Because the surface area of reactant Al_2O_3 is $5.18\ m^2\ kg - mol^{-1}$ and that of product AlN is $0.30\ m^2\ kg - mol^{-1}$, the reaction is known to reduce the surface area. Sintering also decreases the surface area. Both reaction and sintering render the reduction of surface area with time. As the reaction proceeds, carbon is vaporized as shown in Equation 1 which increases the porosity. Sintering, however, reduces the porosity as it proceeds. Fig. 2 reveals that with time, the porosity of the pellet is reduced, thereby leading to the conclusion that the effect of sintering on the porosity is much more severe than that of the reaction.

The influence of gas flow rate on the surface area and porosity can also be determined by comparing the curves in Figs 1 and 2, respectively. The effect of sintering for the different curves is the same; the only difference is the chemical reaction: the higher the gas flow rate the faster is the reaction [8]. The faster the reaction, the faster Al_2O_3 is converted to AlN, such that the surface area becomes lower as shown in Fig. 1. The faster the reaction implies that the faster the vaporization of graphite, the larger the porosity would become. This expectation has been verified by the experiments, as shown in Fig. 2.

3.2. Effect of reaction temperature

Experiments in this series were conducted at four temperatures within the range 1700–1789 K and these results are shown in Figs 3 and 4. These figures reveal that surface area and porosity of the pellet are low when the reaction temperature is high, at which point both sintering and reaction are fast. Both factors reduce the surface area. This event accounts for the results obtained in Fig. 3. While sintering reduces the porosity, reaction increases the porosity. The influence of sintering is stronger than that of reaction, such that porosity is low when the reaction temperature is high.

3.3. Effect of molar ratio of C/Al_2O_3

The effect of the molar ratio of C/Al_2O_3 on surface area can be seen in Fig. 5. Because the specific surface area of carbon ($1.03 \times 10^{-1}\ m^2\ kg^{-1}$) is higher than that of aluminium oxide ($5.08 \times 10^{-2}\ m^2\ kg^{-1}$), the higher the molar ratio of C/Al_2O_3, the higher is the surface area at $t = 0$, as shown in Fig. 5. The reduction rate of the surface area for high C/Al_2O_3 ratio is faster than that of low C/Al_2O_3 ratio. During the final stage, the surface area of high C/Al_2O_3 is smaller than that of low C/Al_2O_3. The reason is that the higher the C/Al_2O_3 ratio, the faster is the reaction [8], thereby causing the reduction rate of surface area to be higher.

While Al_2O_3 is a dense powder, carbon is a porous material. The increase of C/Al_2O_3 ratio may increase the initial porosity of the pellet as shown in Fig. 6. In addition to this, when the molar ratio of C/Al_2O_3 is high, the reaction is fast, which gives a high porosity of the pellet. Both of these factors result in the final porosity for high C/Al_2O_3 ratio being larger than that for low C/Al_2O_3 ratio.

3.4. Effect of grain sizes

If the alumina grain diameter is increased from 5×10^{-6} m to 3.9×10^{-5} or 4.14×10^{-4} m, the initial surface area or the initial porosity of the pellet is

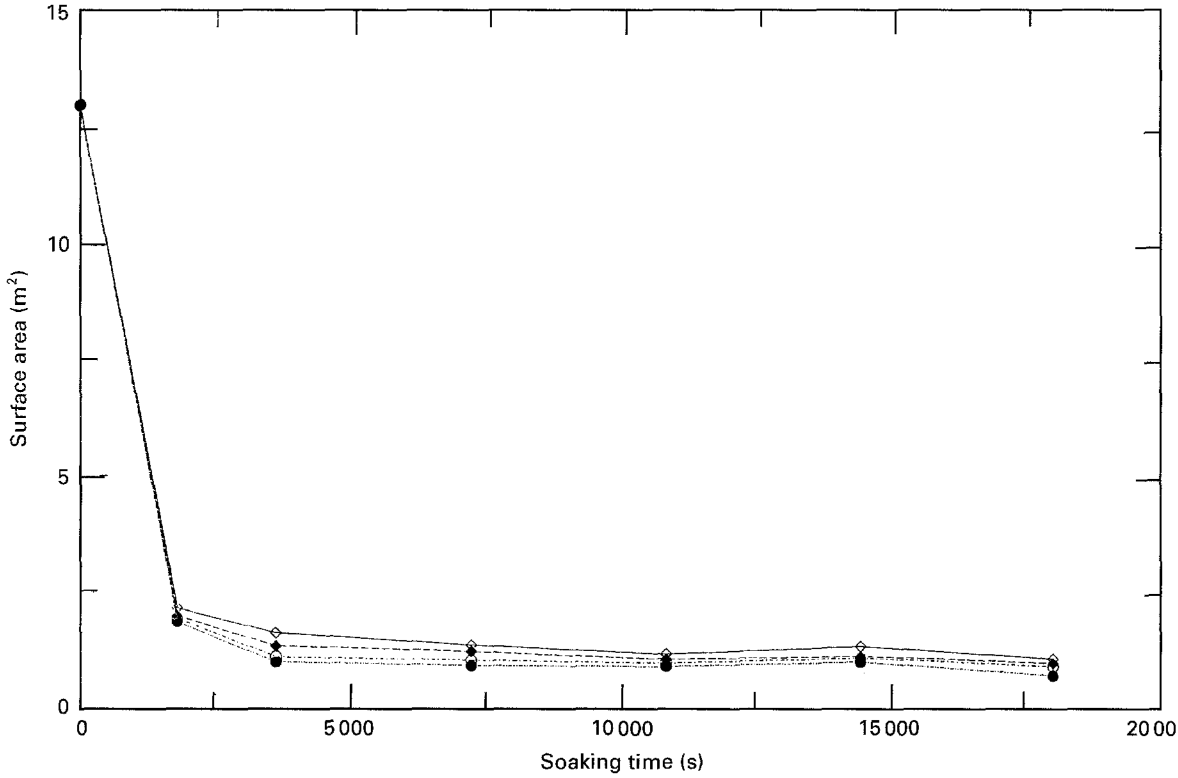

Figure 3 The effect of reaction temperature on the variation of surface area of solid sample with soaking time. (◇) 1700 K, (◆) 1750 K, (○) 1773 K, (●) 1798 K.

drastically reduced, as shown in Figs 7 and 8, respectively. Because the initial surface areas and initial porosities are very small for larger grain sizes, experimental results indicate that no more space is available for the reduction of surface area and porosity during reaction and sintering.

The effect of carbon grain size on the surface area and porosity of the pellet is quite different from that of

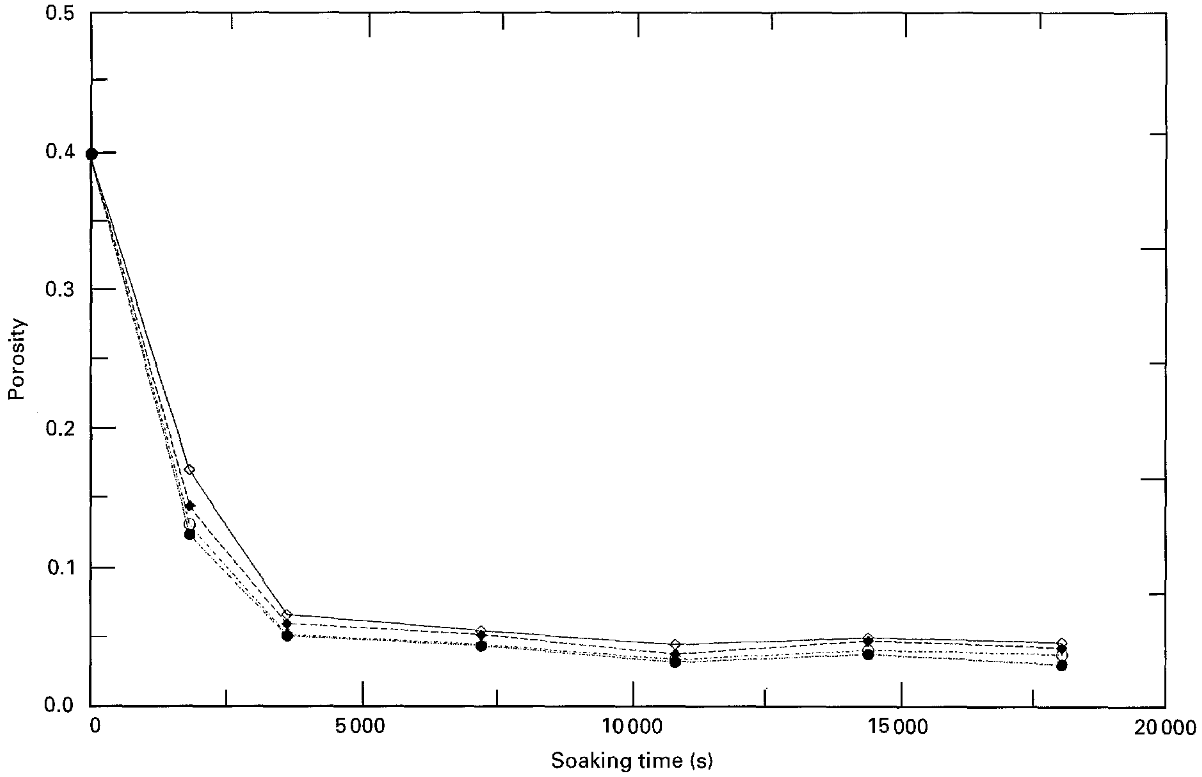

Figure 4 The effect of reaction temperature on the variation of porosity of solid sample with soaking time. For key, see Fig. 3.

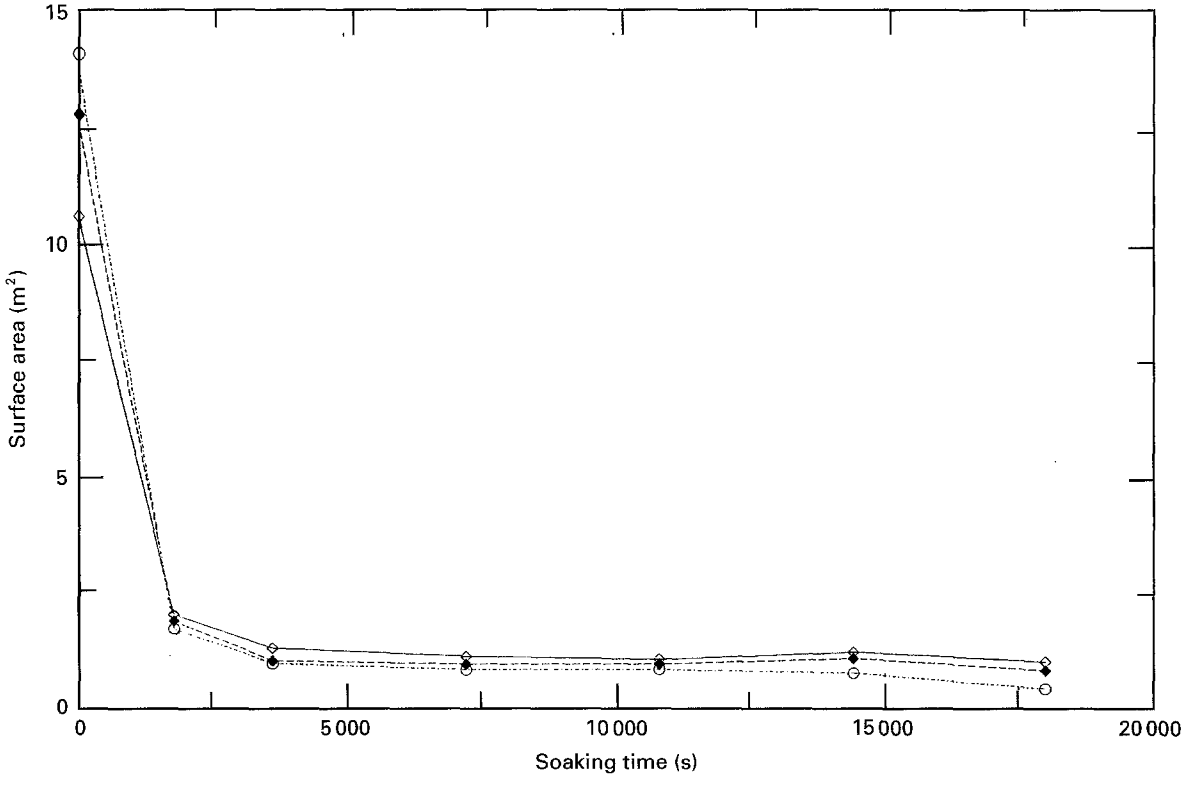

Figure 5 Variation of surface area of solid sample with soaking time, showing the effect of molar ratio of C/Al_2O_3: (◇) 2.13, (◆) 4.25, (○) 6.38.

alumina grain size. The influence of carbon size on the initial surface area and final surface area is rather moderate. Instead of a drastic reduction, the initial porosity is increased when the carbon grain size is increased. When the carbon grain size is large, the reaction is slow such that the porosity is low. Hence, after some reaction time, the porosity of the large carbon grain size is lower than that of small carbon grain size.

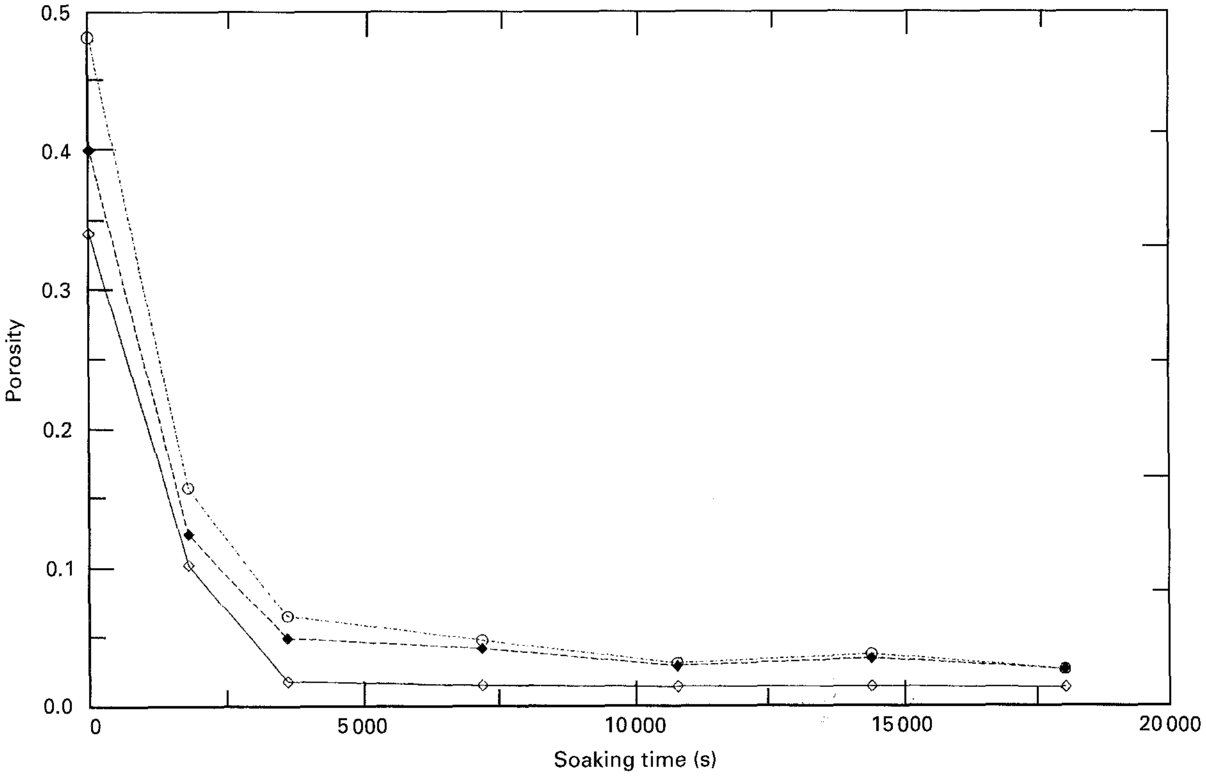

Figure 6 Variation of porosity of solid sample with soaking time, showing the effect of molar ratio of C/Al_2O_3: (◇) 2.13, (◆) 4.25, (○) 6.38.

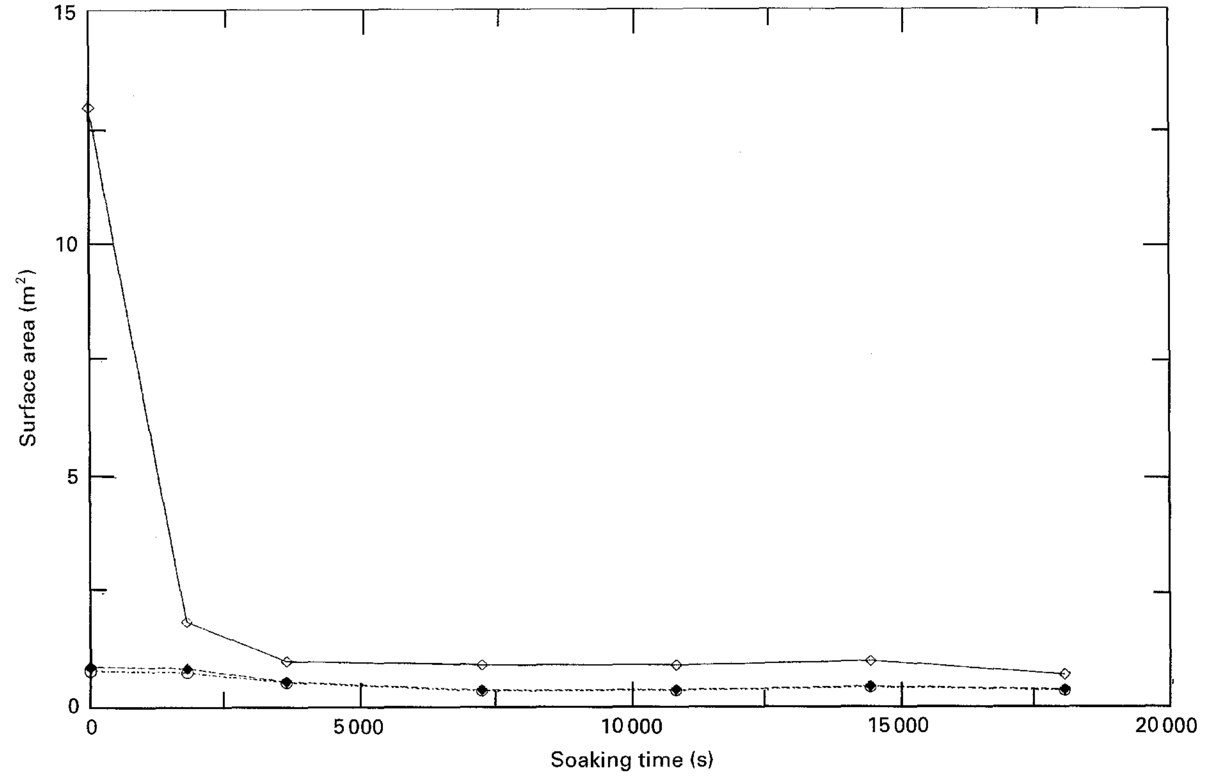

Figure 7 Variation of surface area of solid sample with soaking time, showing the effect of alumina grain diameter (10^{-6} m): (◇) 5, (◆) 39, (○) 414.

3.5. Effect of forming pressure

Experimental results designed to examine the effect of forming pressure on the surface area and porosity of the solid sample are shown in Figs 11 and 12, respectively. These figures indicate that the higher the forming pressure, the larger is the surface area and the porosity. However, the effect on the surface area is very mild.

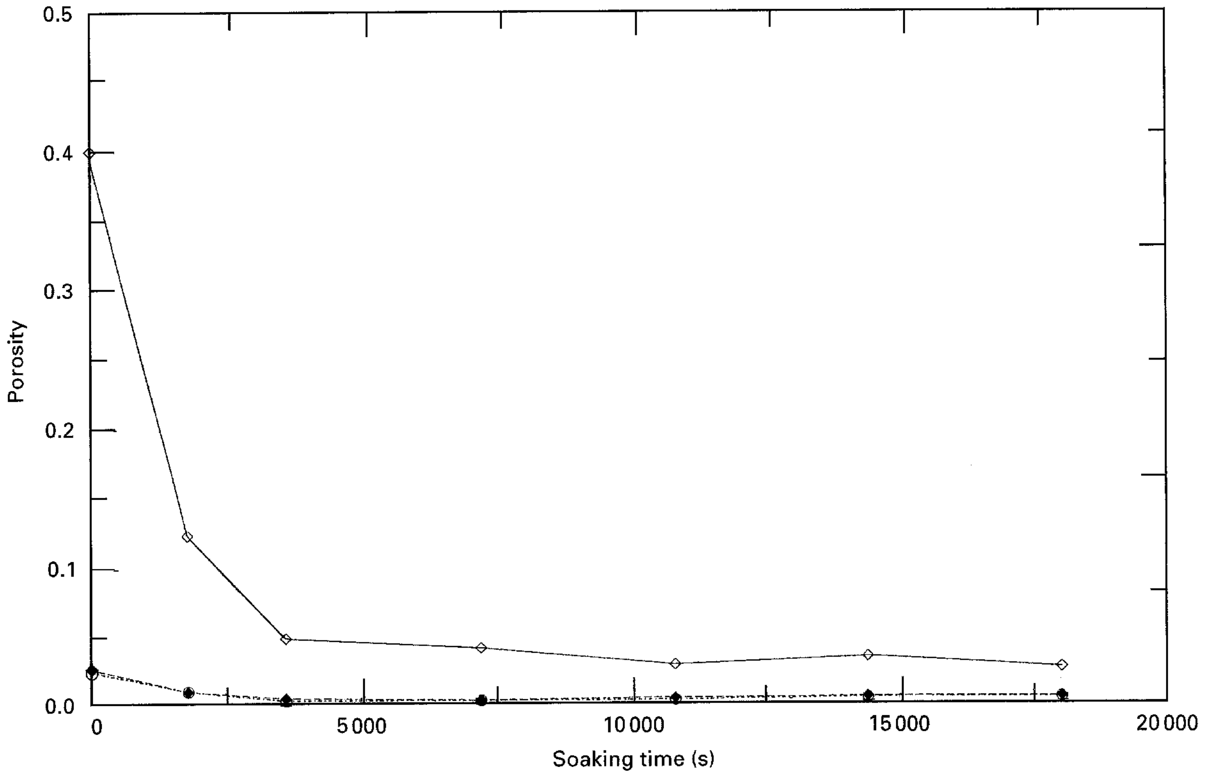

Figure 8 Variation of porosity of solid sample with soaking time, showing the effect of alumina grain diameter. For key, see Fig. 7.

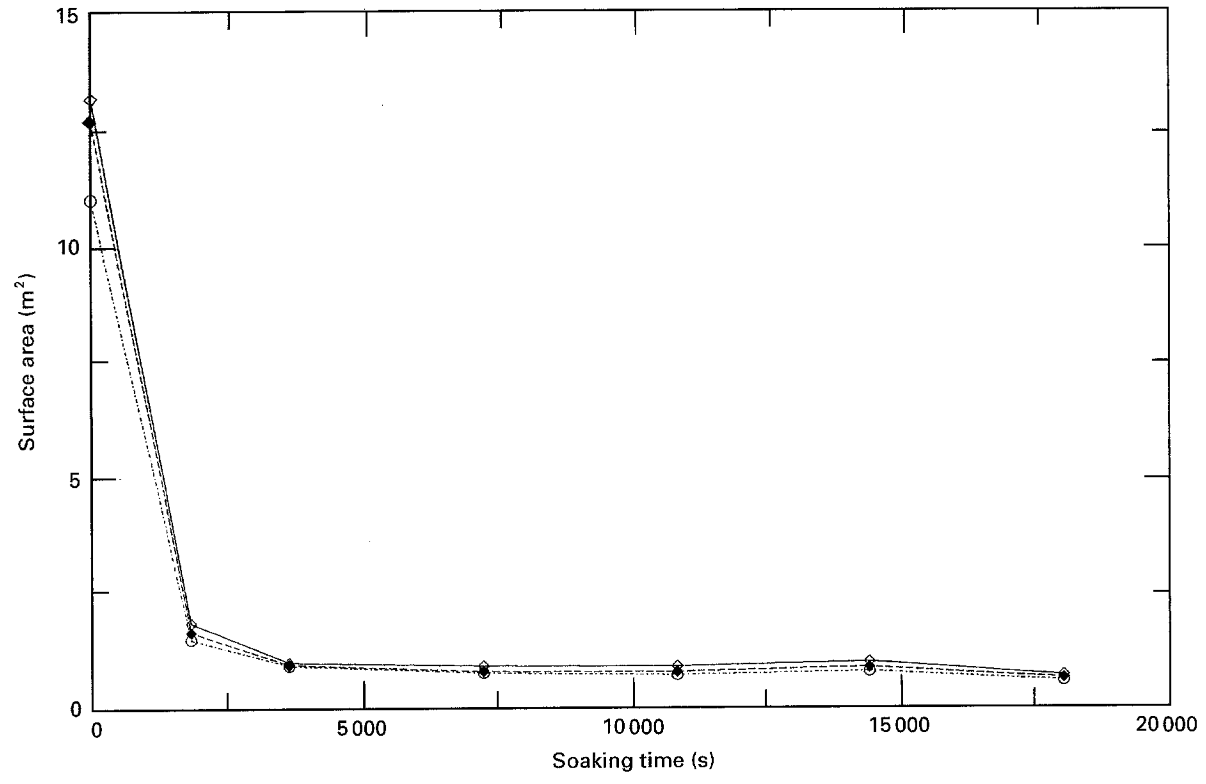

Figure 9 Variation of surface area of solid sample with soaking time, showing the effect of carbon grain diameter (10^{-6} m): (◇) 5, (◆) 39, (○) 414.

3.6. Effect of addition of AlN

Results obtained from this series of experiments are shown in Figs 13 and 14; which results reveal that an increase in the amount of catalyst AlN added leads towards a decrease in the initial and final surface area and porosity. However, the influence on the surface area is moderate.

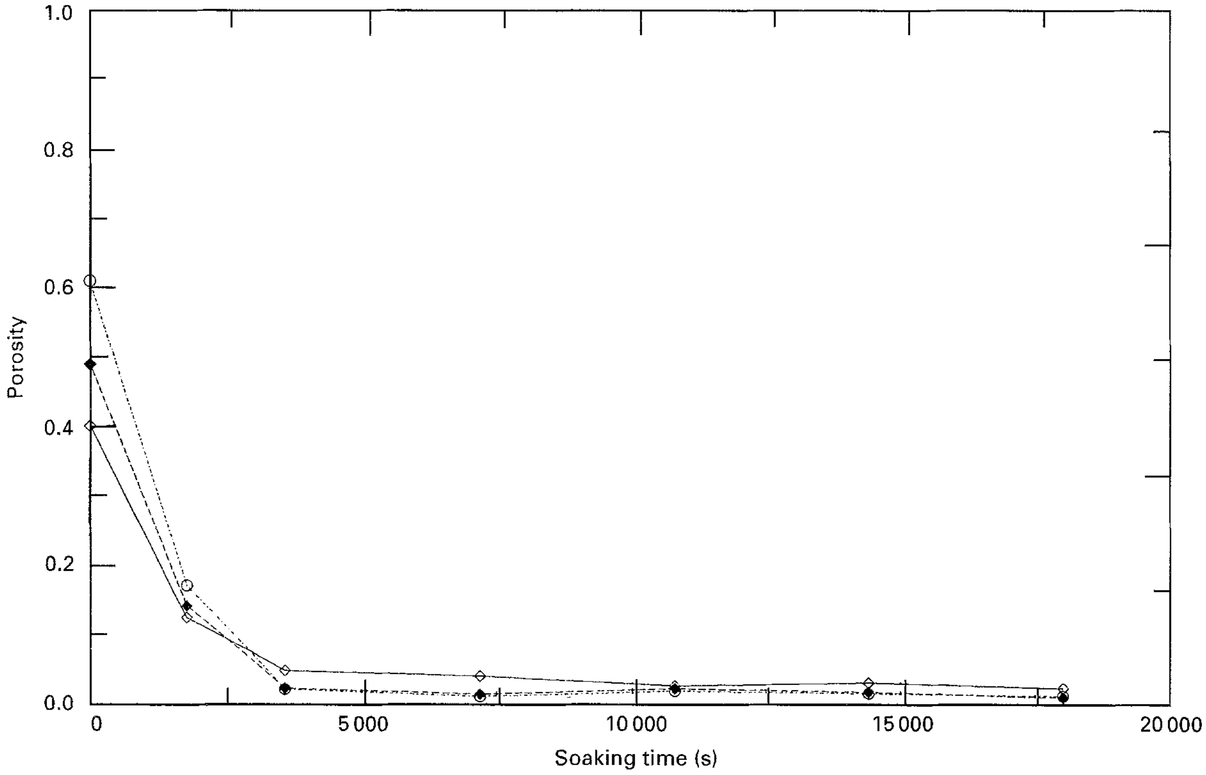

Figure 10 Variation of porosity of solid sample with soaking time, showing the effect of carbon grain diameter. For key, see Fig. 9.

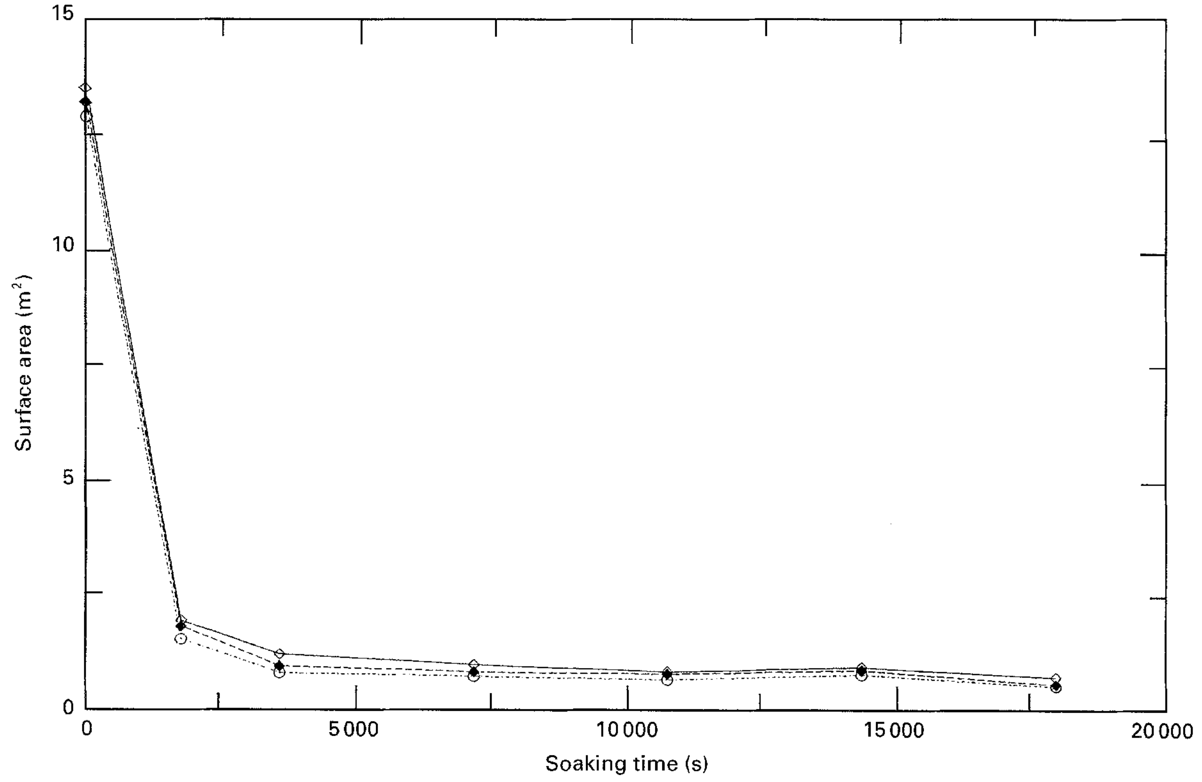

Figure 11 Variation of surface area of solid sample with soaking time, showing the effect of forming pressure (10^{-5} Pa): (◇) 1773, (◆) 3106, (○) 4436.

4. Conclusion

The surface area and the porosity of the solid sample are decreased as the reaction proceeds due to sintering and the reaction itself. The surface area and the porosity of the pellet are low when the reaction temperature, grain size, forming pressure or the amount of AlN added are low. The surface area is low and the porosity is high when the molar ratio of C/Al_2O_3 and gas flow rate are high.

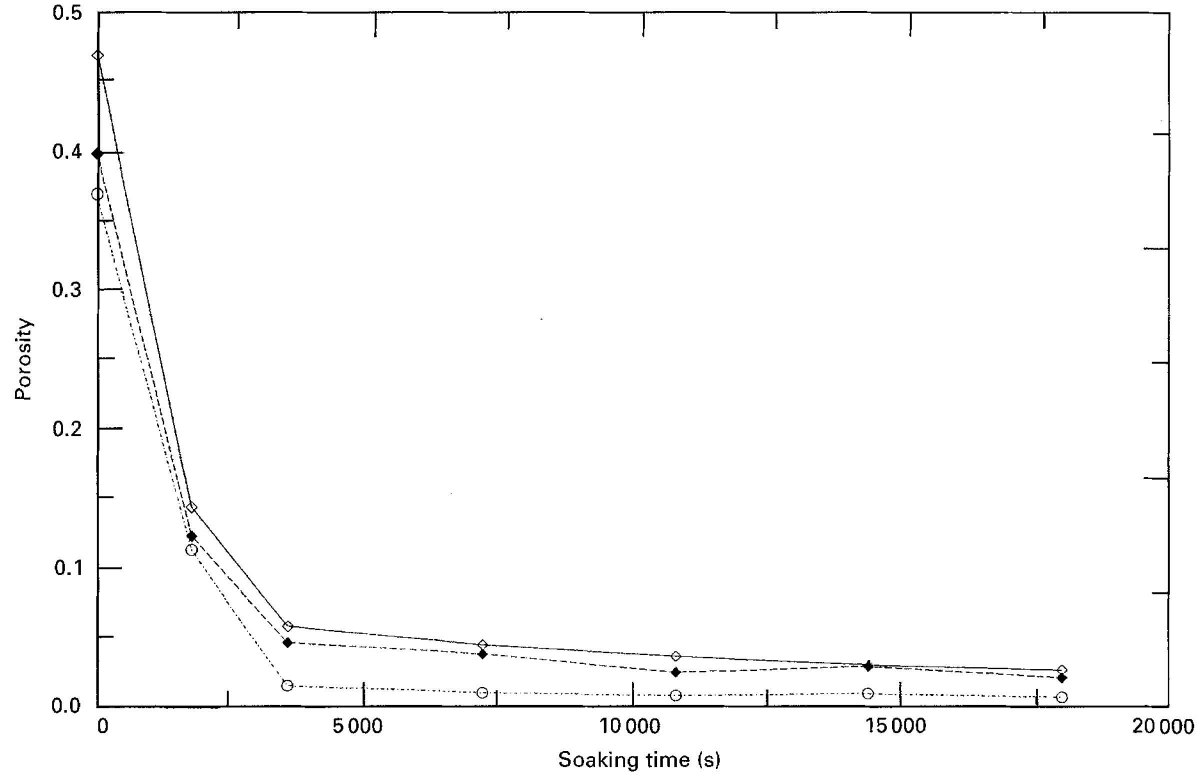

Figure 12 Variation of porosity of the solid sample with soaking time, showing the effect of forming pressure. For key, see Fig. 11.

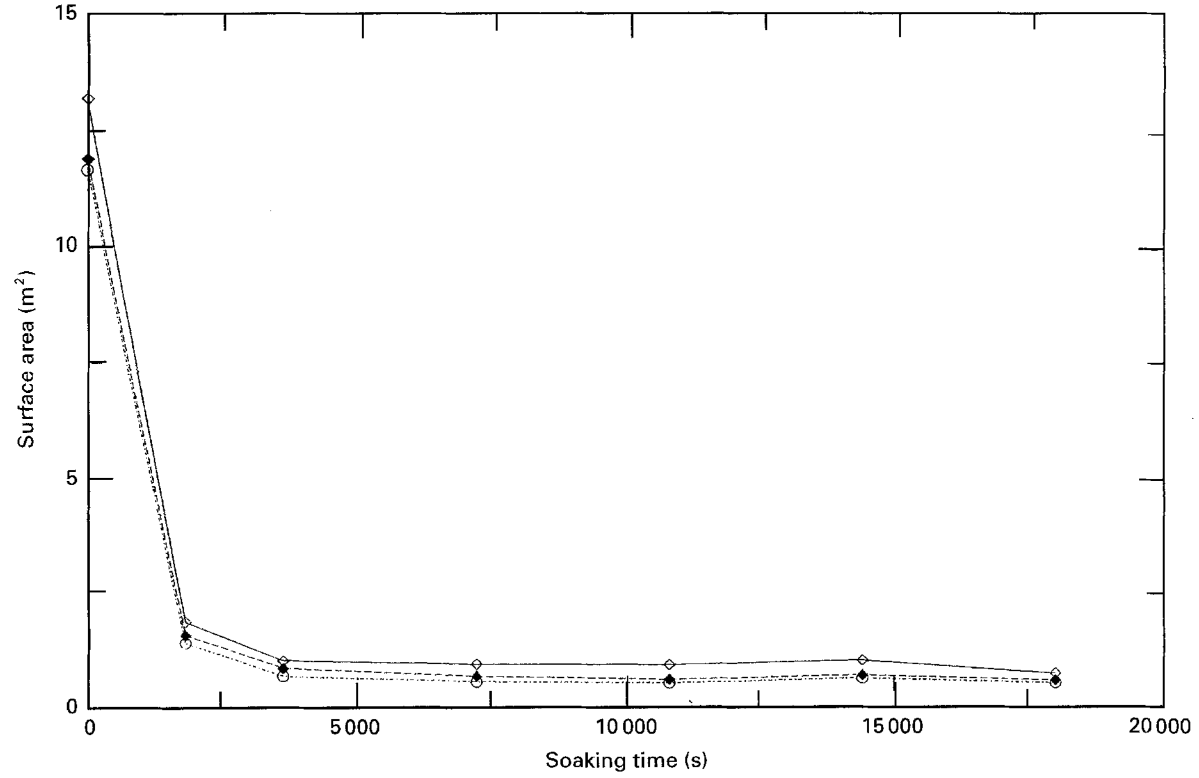

Figure 13 The effect of addition of catalyst on the variation of surface area of a solid sample with soaking time. (◇) No addition, (◆) 5 mass % AlN, (○) 10 mass % AlN.

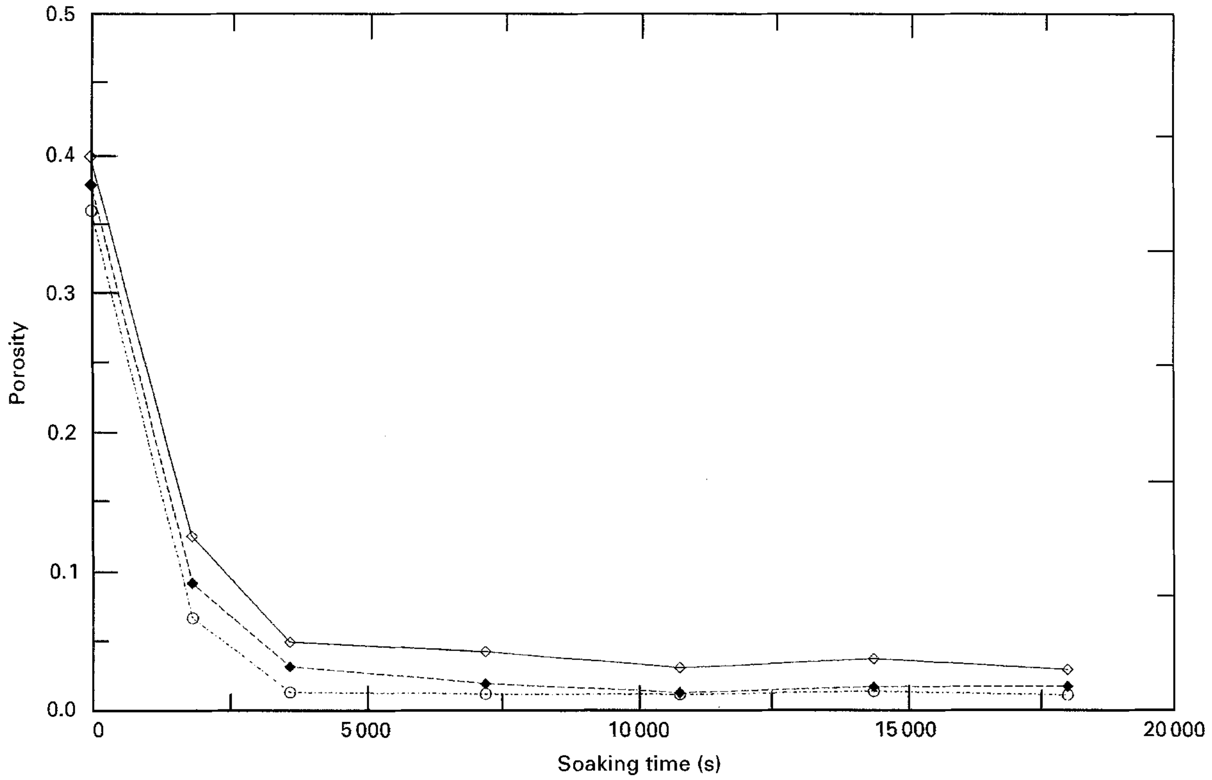

Figure 14 The effect of addition of catalyst on the variation of porosity of a solid sample with soaking time. For key, see Fig. 13.

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References

1. N. KURAMOTO and H. TANIGUCHI, US Pat. 4618 592 (1986).
2. T. SAKAI and M. IWATA, *Yogyo-Kyokais-Shi* **82** (3) (1974) 181.
3. T. YA. KOSOLAPOVA, D. S. YAKOVLEVA, G. S. OLEINIK, T. S. BARTNITSKAYA, N. P. TEL'NIKOVA and I. I. TIMOFEEVA, *Sov. Powder Metall. Metal Ceram.* **11** (263) (1984) 829.
4. H. L. WANG, MS thesis, Department of Mineral Metallurgy and Materials Science, National Cheng Kung University, Tainan, Taiwan (1988).
5. S. HIRAI, T. MIWA, T. IWATA, M. OZAWA and H. G. KATAYAMA, *J. Jpn Inst. Metals* **53** (1989) 1035.
6. H.INOUE, A. TSUGE and M. KASORI, *J. Mater. Sci.* **25** (1990) 2359.
7. Y. W. CHO and T. A. CHARLES, *Mater. Sci. Technol.* **7** (1991) 495.
8. H. K. CHEN, C. I. LIN and C. LEE, *J. Am. Ceram. Soc.* **77** (1994) 1753.
9. H. K. CHEN and C. I. LIN, *J. Mater. Sci.* **29** (1994) 1352.
10. P. LEFORT and M. BILLY, *J. Am. Ceram. Soc.* **76** (1993) 2295.
11. C. I. LIN, Technical Report to National Science Council of Taiwan, NSC 83-0402-E-011-035 (1994).

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