Sintering Characteristics and Microstructures of Colloidally Processed

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ABSTRACT

High-purity (99.99 %) fine-grained alumina samples were prepared using the colloidal processing method to minimise the formation of agglomerates during powder consolidation. In this research, the soft agglomerates were broken down by ultrasonic agitation whereas sedimentation at pH = 2.0 successfully stabilised the suspension and separated it from the unwanted hard agglomerates. Consolidation was achieved through slip casting directly from the suspension to avoid the reflocculation of the powders. The removal of the agglomerates from the initial starting material resulted in the increase of packing density during compaction and led to a higher green density. A dense homogeneous microstructure was thus achieved with a uniform, fine grain size generated at low sintering temperatures. Submicron-grained alumina of about 0.5 μm in grain size was produced at the lowest sintering temperature of 1310 °C.

ABSTRAK

Sampel alumina yang mempunyai ketulenan tinggi (99.99 %) dan berira halus telah disediakan dengan menggunakan kaedah pemprosesan berkoloid untuk meminimumkan pembentukan aglomerat semasa pengukuhan serbuk. Dalam penyelidikan ini, aglomerat lembut telah dihuraikan secara pengadukan ultrabunyi manakala pengendapan pada pH = 2,0 telah berjaya menstabilkan ampaian dan memisahkannya dari aglomerat kuat yang tidak dikehendaki. Setelah pemeraian, pengukuhan dilaksanakan melalui kaedah penuangan terus dari buburan untuk mengelakkan pemeraian semula serbuk. Penyingkiran aglomerat dari bahan permulaan meningkatkan ketumpatan padatan semasa pemadatan dan seterusnya meninggikan ketumpatan hijau. Dengan demikian, sebuah mikrostruktur yang tumpat dan homogen berjaya dihasilkan dengan saiz ira yang seragam dan halus pada suhu pensinteran yang rendah. Alumina submikron dengan saiz ira sekitar 0.5 μm telah dihasilkan pada suhu pensinteran terendah iaitu 1310 °C.

INTRODUCTION

Current consolidation technology has confirmed the ruinous effects ofagglomerates on the end products of ceramic articles especially those meant for engineering applications (Lange 1984; Rhodes 1981; Evans 1982; Raj and Bordia 1984; Hsueh et al. 1986; Inada et al. 1990). The presence of agglomerates creates density variations leading to differential sintering that

produces crack-like voids which are detrimental to the overall mechanical properties of the final ceramic products. The agglomerates also limit the densification process which means higher sintering temperatures and longer sintering times, hence, a very uneconomical mass production approach to say the least. In view of this, the current trend in powder processing science and technology is to identify techniques that are able to solve problems caused primarily by agglomerates.

In 1984, Kumagai and Messing described a method in which relatively high density (98 %) alumina samples were fabricated at low sintering temperatures of between 1200 °C and 1400 °C. The sample preparation involved seeding boehmite sol-gel samples with α-Al_2O_3 seed particles. These seed particles acted as nucleation sites for the δ- to α-Al_2O_3 phase transformation, resulting in a significant increase in the rate of nucleation. This in turn suppressed the growth of the α-alumina particles. Hence, upon transformation, a uniform, fine-grained alumina microstructure was developed. However, apart from the difficulty of preparing boehmite sol-gel samples, it was reported in later works (Kumagai and Messing 1985; Messing et al. 1986) that the gels tended to undergo large shrinkages during drying and cracks were prone to occur.

Alternatively, a promising method in this line of research is known as the colloidal processing technique (Aksay 1984; Pober et al. 1984; Aksay 1985). In the consolidation of ceramic powders, colloidal processing serves as an efficient means to eliminate agglomerates from the main body to produce a homogeneous raw material. Working with TiO_2 powders, Barringer and Bowen (1982) demonstrated how colloidal processing was successfully used to properly disperse the powders such that agglomeration did not occur. This resulted in uniform, dense packing in the green compacts, allowing them to sinter to greater than 99 % of theoretical density at temperatures far less than conventional sintering temperatures. Furthermore, the elimination of the agglomerates has lessened the occurrences of large pores that require very high temperatures and long sintering times to rid off, both of which may also cause excess excessive grain growth (Sacks and Pack 1982; Lange 1984; Kimura et al. 1987).

In this study, an attempt is made to study the sintering characteristics and microstructures of colloidally processed alumina. The raw material was a commercially available alumina powder (TM-5D, Taimei Chemicals Co., Ltd., Japan) of 99.99 % purity with an average particle size of 0.25 μm.

METHODOLOGY

The alumina powder was first mixed in an ultrasonic bath (Ney 300 Ultrasonik, USA) with pH = 2.00 distilled water (adjusted with the addition of HCl) at 20 % volume. In forming a system of deflocculated powder particles, a repulsive force among the particles is desirable. In this study, an electrostatic repulsive force was generated by the careful addition of HCl. The deflocculation of the soft agglomerates was further assisted by ultrasonic agitation. The strong hydrodynamic forces created by ultrasonification are able to break (Dooher et al. 1977) apart weakly bonded particles i.e. the soft agglomerates. As for the

hard agglomerates, these were not as easily deflocculated. They were heavier though and as such, under gravity soon settled to the bottom after a sedimentation period of 24 hours. Once deflocculated, consolidation was achieved through the slip casting method directly from the slurry. This was to avoid the re-flocculation of the powders.

The green compacts were subsequently dried for at least 72 hours. It was important to ensure total removal of moisture from the compacts else they cracked during prefiring. Prefiring served to impart some strength onto the samples allowing a certain amount of bonds to form between the powder particles. To do this, the fully dried specimens were heated to 800 °C for 45 minutes in a box furnace (Carbolite, England). Once prefired, the specimens were sufficiently strong to allow for handling (for instance, when taking green density measurements). Sintering was accomplished in a vacuum furnace (Centorr Vacuum Furnace M60-3x8-W-D-VPO-A-20, Vacuum Industries, USA) in vacuum better than 10^{-5} Pa to avoid contamination. The sintering temperature used was varied from 1310 °C to 1550 °C with a hold time of 1 hour.

To study the microstructure under scanning electron microscope, SEM (JEOL JSM-T330A Scanning Microscope), the samples were first polished to mirror finish quality, followed by thermal etching in the same high vacuum furnace used for sintering. The specimens were heated to 1200 °C and soaked for 180 minutes. After thermal etching, the specimens were ultrasonically cleaned in an acetone bath and gold coated before examination under the SEM. Grain size measurements were done using the linear intercept method.

RESULTS

GREEN AND SINTERED DENSITIES

The colloidal sedimentation process was found to be effective in the elimination of agglomerates in the starting powder material. This yielded a high green density of 65.8 % th (% th is defined as the density of the specimen divided by the crystal density of the material). This compared favourably with the green density achievable from the conventional compaction techniques which registered around 55 % th (Wong 1991; Lim et al. 1997). Note also that the green density measured compared well with the theoretical estimate of 64 % th for dense random compact of equal-sized spheres (Bordia 1984). Subsequently, the high green density lowered both the sintering temperature and sintering period required to reach full densification. The high green density also means that less shrinkage is expected during sintering, hence a better dimensional control of the finished products.

The final sintered density, obtained by Archimedes Immersion Technique, is plotted against the sintering temperature in Figure 1 whereas the primary data on actual green and sintered densities is given in Table 1. Note that a high sintered density of 99.4 % was registered at the highest sintering temperature used, i.e. 1550°C. It was anticipated that if even higher sintering temperatures were used, the final density would increase accordingly. However, it was suspected that higher temperatures would also promote grain growth

considerably (Lange 1989). Since the emphasis of the study was to analyse the properties of fine-grained alumina, it was decided that the present range of sintering temperatures was sufficient.
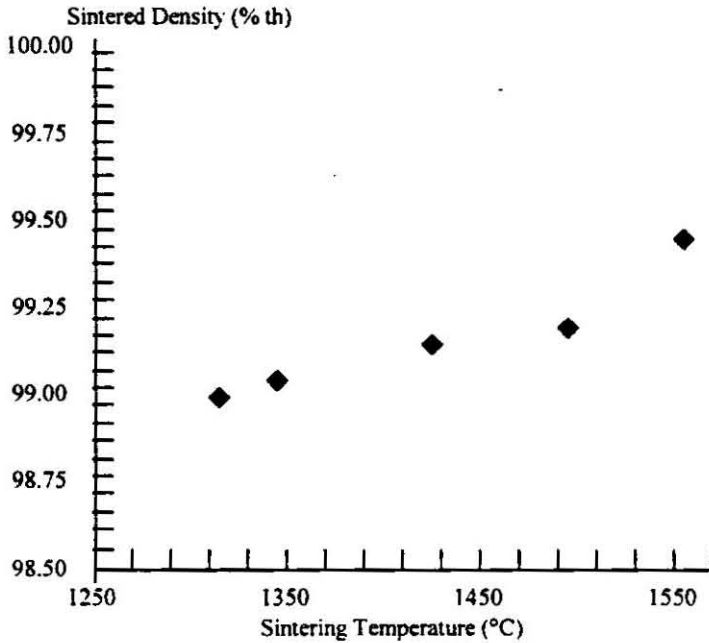

FIGURE 1. The sintered densities of the fabricated alumina specimens

TABLE 1. Actual green and sintered densities of the fabricated alumina specimens

Theoretical Density	Green Density	Sintered Density
3.99 g/cm^3 (value for corundum)	2.625 g/cm^3	1310°C 3.950 g/cm^3 1350°C 3.952 g/cm^3 1425°C 3.955 g/cm^3 1500°C 3.956 g/cm^3 1550°C 3.966 g/cm^3

MICROSTRUCTURAL CONSIDERATIONS

SEM micrographs indicated fairly equiaxed grains of uniform size. Porosity was low with voids being scarcely but homogeneously distributed throughout the specimens. For the coarser-grained samples, the pores were mostly trapped within grains whilst a handful few were lodged in grain boundary junctions. The opposite was noticed for the smaller-grained specimens. As expected, the elimination of the agglomerates resulted in a narrow grain size distribution. The average final grain size, measured using the linear intercept technique, was about 0.5 μm for the lowest temperature and about 4.5 μm for the highest temperature used, as shown in Figure 2.
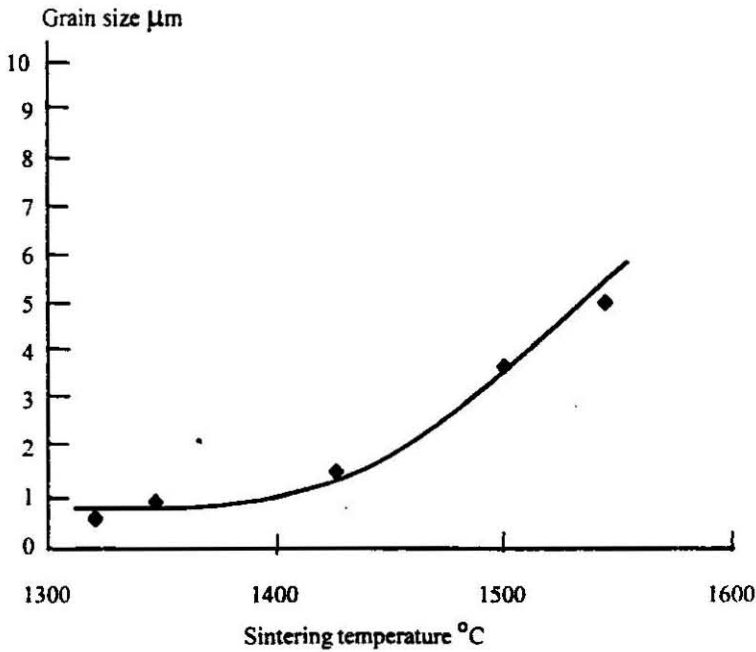
FIGURE 2. Grain sizes of high purity alumina specimens
sintered at different temperatures

The present work showed that with the colloidal technique and a starting powder of submicron particle sizes, the compacts can be sintered to near full densification at relatively low temperatures producing a resultant submicron-grained structure. Figure 3 shows typical SEM images of the as-sintered high-purity fine-grained alumina.
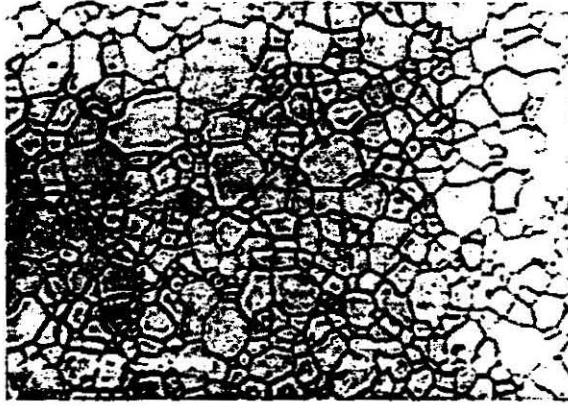
GRAIN GROWTH

To study the grain growth kinetics during sintering, one may present the sintering data based on the grain growth law (Kingery et al. 1976),
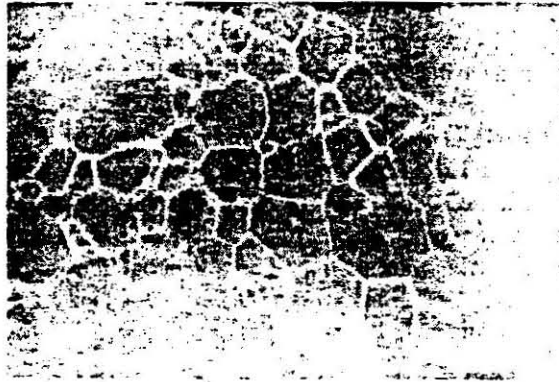
$$d^n - d_0^n = K.exp(-\frac{Q}{RT})t \tag{1}$$

where n is the grain growth exponent, Q the grain growth activation energy. K the grain growth constant, R the universal gas constant, T the sintering temperature and, t the time for sintering. The symbol d and the subscript o represents the grain size and its initial value respectively. The value of n is generally taken as equal to 3 for alumina (Coble, 1961) and d_0 is 0.25 µm in the present work. A plot of ln $(d^3 - d_0^3)$ versus $\leftarrow$ is given in Figure 4. A straight line was obtained, giving an activation energy of 643 kJ mol^{-1}, which compares well with values obtained by previous researchers (Coble 1961; Bae and Baik 1993).
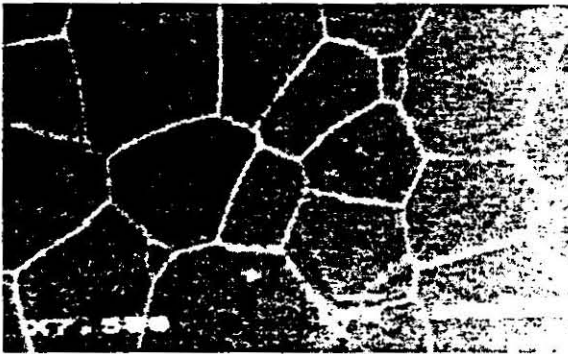
(a)

(b)

(c)

FIGURE 3. Microstructures of high-purity fine-grained alumina at sintering
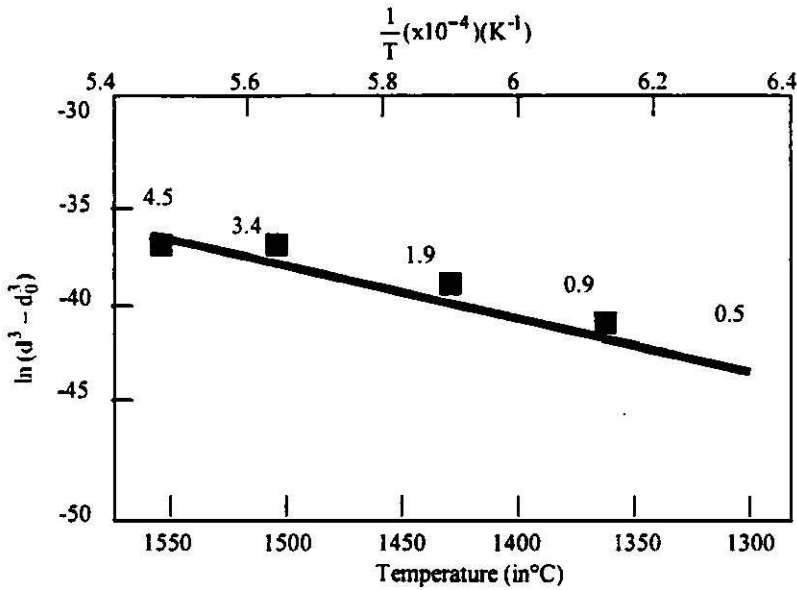temperatures   (a) 1310°C   (b) 1350°C   (c) 1425°C

$$\frac{1}{T}(\times 10^{-4})(K^{-1})$$

FIGURE 4. Grain growth of high-purity alumina with initial particle size of 0.25 μm. Activation energy is found to be 643 kJ mol⁻¹. Data labels indicate grain size inμm.

OTHER OBSERVATION

In an earlier publication (Muchtar and Lim 1998), the fracture toughness (K_c) of the present alumina samples prepared by the colloidal processing technique was determined via the indentation test method. The K_c was found to decrease with increasing grain size, being about 3.9 MPa√m for the submicron-grained samples and about 3.3 MPa√m for specimens with a grain size of 3 - 5 μm.

A wide variation in K_c values exists in the literature (Mussler et al. 1982) and it appears that the test results are method dependent. Coarse-grained products tend to microcrack in a zone in advance of the main crack and hence the toughness value will be dependent on this zone size relative to the crack length. Hence the K_c value registered of between 3 and 4 MPa√m compared well with alumina samples prepared using conventional processing techniques.

DISCUSSION

As recently reviewed by Lange (1989), colloidal processing serves as a means to produce reliable and improved engineering ceramics. Removal of heterogeneities from the initial starting material has yielded a well dispersed particle distribution in the green compact. In this research, sedimentation at pH = 2.0 successfully stabilised the suspension and separated it from the unwanted agglomerates. A dense homogeneous microstructure was achieved with a uniform, fine grain size generated at low sintering temperatures. Abnormal grain growth was not apparent in any of the micrographs taken under SEM even with the absence of sintering additives like those required in other works (Bae and Baik 1994). All

in all, the results were most encouraging since the production of fine-grained alumina compacts of ultra pure compositions and of narrow size distribution at low temperatures of sintering without the use of sintering aids is rarely accomplished except under strict laboratory conditions. As it is, colloidal processing reflects potential in the fabrication of a more reliable ceramic material although it is not commercially viable at present due mainly to it being time consuming. It is also noted however, that the present work is less time consuming as compared to that proposed by Kumagai and Messing (1984). In their work, it took a minimum of 10 days from the consolidation stage to the firing of the compacts whereas with the present colloidal technique, the drying time was about 72 hours.

Finally, it is noted that to facilitate submicron grain size, a first priority would be to obtain a small initial particle size of the alumina powder such that when this is processed using the colloidal technique, a uniform green microstructure with no agglomerates is achieved which, in turn, will allow the compacts to be sintered to full density at relatively low temperatures.

CONCLUSIONS

1. Colloidal processing was successfully employed to produce dense alumina samples from ultra purity (99.99 %) alumina powder at relatively lower sintering temperatures compared to other processing techniques.
2. Fine-grained alumina of grain sizes ranging between 0.5 μm and 4.5 μm were produced by such a technique.
3. The activation energy for grain growth during sintering of alumina was found to be 643 kJ mol^{-1}, which compares well with values obtained by previous researchers.

ACKNOWLEDGEMENT

NOTATIONS

d = Grain size
d_o = Initial grain size
K = Grain growth constant
K_c = Fracture toughness
n = Grain growth exponent
Q = Grain growth activation energy
R = Universal gas constant
T = Sintering temperature
t = Sintering time

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