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SINTERING AND MICROSTRUCTURE OF $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ PRODUCED FROM KAOLIN

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Résumé - Le frittage d'une poudre de $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ est discuté comme une alternative au frittage réactif plus usuel d'un mélange de poudres de Si_3N_4 , Al_2O_3 et AlN . Comme la poudre de $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ est produite à partir du kaolin, la présence d'impuretés dans le kaolin est considérée avec attention. Les propriétés finales du matériau fritté sont indiquées.

Abstract - The sintering of $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ powder is discussed as an alternative for the more usual reaction sintering of a mixture of Si_3N_4 , Al_2O_3 and AlN powders. As the $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ powder is produced from kaolin, attention is paid to impurities which are present in the kaolin. Finally properties of the sintered material are given.

I - INTRODUCTION

The aim of the study is to obtain an economic production route for sintered, non oxide ceramic articles. Fine non oxide ceramic powders can be obtained by carbo-thermal reduction of oxides. When minerals are used instead of synthetic oxides this method is supposed to be very economic. However minerals will contain more impurities than synthetic oxides. When the non oxide powders, produced by the carbothermal production method, are shaped and pressureless sintered the overall route to produce ceramic articles seems promising. In this article the authors discuss the sintering of a $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ powder, which is produced from the mineral kaolin. A β' -sialon material with such a high content of Al/O is not commercially produced at the moment. We will show that this material has a unique combination of properties and therefore is worth being developed.

II - POWDER PREPARATION

$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ was produced from kaolin and carbon black using the carbothermal production method described by Lee and Cutler /1/ and van Dijen et al /2/. Details of the production method are given in /2/. The composition of the kaolin used was (in wt.%): 45.6 SiO_2 , 38.6 Al_2O_3 , 14.0 H_2O , 0.34 Fe_2O_3 , 1.37 TiO_2 , 0.06 K_2O , rest adsorbed H_2O . This corresponds to a molar ratio Si:Al=1.00. As confirmed by lattice constant measurements the resulting β' -sialon powder has the composition $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$. When the pellets are taken from the reactor the powder is strongly agglomerated. Therefore they have to be milled. The $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ pellets, with a specific surface area of $8 \text{ m}^2/\text{g}$ according to the BET method, were ball milled in a polyethene flask. Alumina balls (95% alumina) were used. The pellets were wet milled in propanone for 50 hours. Fig. 1 shows the particle size distribution of the powder. A Micromeritics SediGraph was used.

According to the formula: $S = 6/(\rho dp)$, one can calculate the specific surface area S from the average particle diameter dp . The density of the powder, ρ , is taken as 3.15 g/cm^3 . The x-ray density for $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ is 3.1 g/cm^3 , but we corrected for the impurities TiN and FeSi_x . The calculated specific surface area is $1.3 \text{ m}^2/\text{g}$. The difference with the measured specific surface area is explained by assuming agglomerates. Mill wear was about 2%. To compensate for the mill wear the sialon powder is produced with a slight nitrogen excess. This is achieved by using a carbon black: kaolin mass ratio of 0.26 instead of the theoretical 0.24 ratio. As a result some 15R phase can be detected in the powder by XRD.

In this way the composition of the milled powder falls within the region of β' -sialon solid solutions and the formation of glassy phases in the sintered product is prevented (apart from those due to sintering aids). However, impurities which originate from the kaolin starting powder do lead to impurities like TiN and FeSi_x in the sialon powder.

Fig. 1 - Particle size distribution of a $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ powder after 50 hours ball milling.

III - SINTERING OF $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ ACCORDING TO THE LITERATURE

Usually β' -sialon is produced by mixing powders, for instance Si_3N_4 , Al_2O_3 and AlN or Si_3N_4 and polytypes. Often sintering aids are added. The powder mixture is then shaped, often by isostatic pressing, into a tablet form. Next this tablet is sintered and reacted for 1/2 to 2 hours at about 1700 to 1800°C. The cooling and heating of the sample usually takes half an hour. This reaction sintering technique is similar to that of Si_3N_4 . Descriptions of this technique are given by several authors /3,4,5/. Sintering of β' -sialon powder itself instead of reaction sintering is scarcely described, however Mitomo et al published some work on this subject /6/. Whether pure β' -sialon powder sinters without a liquid phase at the grain boundaries is not clear, see Boskovic /3/ and Mitomo /6/. Such a liquid phase gives enhanced sintering rates and can be provided by the use of stable oxides which form low melting eutectics. Usually oxides of high melting points are used. The resulting glassy phase at the grain boundaries influences the mechanical properties of the product in a negative way /7/. Sometimes the glassy phase between the grain boundaries can be crystallised at the triple points /8/.

Oxides which function as sintering aids are, for example: MgO , CaO , Y_2O_3 , CeO_2 , La_2O_3 , Sc_2O_3 , BeO etcetera. CaO is usually rejected due to its bad influence on high

temperature properties. For industrial purposes BeO is rejected because of its poisonousness.

IV - ASPECTS OF SINTERING $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$

$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ powder or without sintering aid was dry pressed into a tablet of 13 mm diameter and a weight of 1 gram. The pressure was 3000 kg/cm². After isostatically pressing with a pressure of 4000 kg/cm² the density of the tablet was 1.8 g/cm³. During the sintering of the pellet in an alumina crucible weight loss occurs due to the reaction: $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5 \rightarrow 3\text{SiO} + 3\text{AlN} + \text{N}_2$. The SiO pressure as a function of the temperature can be calculated, assuming that the total pressure is 1 atmosphere. Data from Turkdogan /9/ and Döner et al /10/ was used. See table 1. A calculation shows that this SiO pressure is similar to that caused by the reaction:

Table 1 - Calculated SiO pressure as a function of the temperature for the reaction $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5 \rightarrow 3\text{SiO} + 3\text{AlN} + \text{N}_2$.

Temperature (K)	P _{SiO} (atm)
1673	2.7×10^{-4}
1773	1.9×10^{-3}
1873	1.1×10^{-2}
1973	5.3×10^{-2}
2073	2.3×10^{-1}

$\text{Si}_3\text{N}_4 + \text{Al}_2\text{O}_3 \rightarrow 3\text{SiO} + 2\text{AlN} + \text{N}_2$. So this mixture as well as $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ powder can be used to generate an SiO pressure in a powder bed.

Weight loss can be prevented by a high nitrogen pressure, an SiO pressure or a high sintering rate as there will be a competition between sintering and SiO loss. An atmosphere containing SiO can be obtained by use of the powder bed technique /11/. BN powder is added by many authors to prevent sintering of the bed. According to Jack /12/ packing the sample in pure BN is also effective. In this work $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ powder was used to generate an SiO pressure.

In kaolins CaO and MgO are common impurities. Therefore, in our sintering studies we investigated the influence of 1 wt% additions of these oxides. Na and K evaporate during processing /13/ and are therefore not of interest. The oxides Fe_2O_3 and TiO_2 in our kaolin lead to the formation of FeSi_x and TiN in the sialon powder. Figure 2 shows that these impurities are present as inclusions in the sintered pellets. Therefore it is not likely that they act as sintering aids. When the

Fig. 2 - Photomicrograph of a sintered sialon sample, showing pores and FeSi_x inclusions.

inclusions are small and dispersed homogeneously in the matrix they also do not deteriorate the properties of the final product /14/. Apart from CaO and MgO we also investigated the influence of 1 wt% of Y_2O_3 , CeO_2 and La_2O_3 on the sintering properties. In literature often higher concentrations of Y_2O_3 (e.g. 5 wt%) are mentioned. However, since our sialon powder is supposed to be cheap, the use of such large amounts of an expensive sintering aid was not considered. The heating and the cooling rates of the samples was 175°C per hour. The results for two sintering times and two sintering temperatures are presented in table 2. The weight loss was less than 3 wt%. The theoretical density for $Si_3Al_3O_3N_5$ is 3.10 g/cm³. Due to impurities and sintering aids a somewhat higher density for samples without porosity might be expected.

Table 2 shows that $Si_3Al_3O_3N_5$ sinters, although full density is not obtained. It is also shown that MgO is not a very effective sintering aid, which is in accordance with the results of Lowell /15/.

Table 2 - The influence of sintering time, temperature and sintering aid on the sintering of a $Si_3Al_3O_3N_5$ powder. The apparent density is given in g/cm³.

Sintering aid (1 wt%)	15 hour 1675°C	20 hour 1675°C	15 hour 1700°C	20 hour 1700°C
none	2.4	2.6	2.8	2.5
MgO	2.7	2.8	2.8	2.8
CaO	2.9	3.0	2.9	3.0
Y_2O_3	3.0	2.9	2.9	3.1
La_2O_3	2.9	3.0	2.8	3.0
CeO_2	2.9	2.9	3.1	3.0

Compared with the density measured on samples which were sintered for 15 hours at 1675°C, an increase in density for the other samples is expected. However, often a decrease of the density is observed. This is due to loss of SiO, which results either in a decrease of the sintering rate, or in the development of a surface layer on the sample. This surface layer may be short in SiO, in which case it consists mainly of the 15R phase. However, this layer may also be rich in SiO. This extra SiO originates from the bed. An example of the latter case was observed on the samples which were sintered with Y_2O_3 .

Sintering can be improved by the use of larger amounts of sintering aids. It can also be improved by further milling of the powder, which not only decreases the size of the agglomerates but also increases the oxygen content of the powder due to wear losses of the alumina balls.

When these results are compared with those of Lee and Gutler /1/, who found that $Si_3Al_3O_3N_5$ powders made from kaolin were easily sintered, it seems probable that their powder contained a higher oxygen content and or a higher calcium content.

V - PROPERTIES OF $Si_3Al_3O_3N_5$

Properties of samples which were sintered for 20 hours at 1700°C were measured. 1 wt% CeO_2 was used as a sintering aid. The powder was made from a carbon black-kaolin mixture with a ratio of 0.25. The powder was milled for 48 hours which yielded an average particle size of 1.5 μm . The density was 3.16 g/cm³ as measured by Archimedes' method. The size of the pores and of the FeSi_x and TiN inclusions was less than 10 μm . The average crystallite size was estimated to be about 5 μm . We shall briefly discuss some properties of these ceria doped sialons and compare these with literature data. We measured a Rockwell hardness 92 Hra, which indicates a higher value than for Si_3N_4 in agreement with Lumby /16/, but in disagreement with Gauckler et al /17/. According to Gauckler et al /17/ and Glandus and Boch /18/ a Youngs modulus of 225 GPa can be expected, which is close to our observation of 230 GPa*. Using a resonance technique a Poisson ratio of 0.285 was obtained. From the indentation method /19/ we found a K_{IC} value of 5 MPa m^{1/2}, which is higher than the value reported by Gauckler et al /17/. The same holds for our value of the bend strength of 550 MPa as obtained by using the diametral compression method. These data

* Measured by Dr. G. de With, Philips Research Laboratories, Eindhoven

show that the $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ material produced from kaolin is of a rather good mechanical quality, despite the presence of impurities. However, further improvement seems possible after further sintering studies. The room temperature electrical resistivity exceeds $3 \cdot 10^{12} \Omega\text{cm}$, in accordance with literature /20/.

It should be remarked that the thermal conductivity is also rather low, about $7 \text{ Wm}^{-1}\text{K}^{-1}$ /17,21/ and therefore the thermal shock resistance will be lower than of Si_3N_4 .

VI - CONCLUSIONS

$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ powder can be sintered to about 90% of theoretical density without sintering aids. When the powder is made from kaolin CaO is the only impurity which acts as an effective sintering aid. The other impurities which are usually present in a kaolin hardly influence the sintering behaviour. Despite the presence of impurities the $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ material is not a second class material.

Most striking properties of the material are its low thermal conductivity and its low Youngs modulus compared with those of Si_3N_4 .

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