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Influence of the milling environment on the reaction progress in the Si–Al_2O_3 system

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Abstract

In the solid-state reaction of alumina and silicon in nitrogen the value of the surface area seems to be the most important factor. Agglomerates formed during the milling process can exhibit unfavourable effect on the reaction progress: non-homogenous distribution of both kinds of particles and limited nitrogen access to the surface of silicon particles during subsequent nitridation. The milling process was performed in the attritor mill using two different environments: polar and non-polar with addition of surfactant. For non-polar environment an additional mixing of fine powders on a roller bench was applied. Surface area of powders was examined by BET. Mass changes and shrinkage of the tablets were measured after nitridation at 1250 °C. Thermal properties of the samples were determined by dilatometry and TG measurements. The nitrogen content was measured by mass gain whereas the sample homogeneity was verified by SEM studies.

Keywords: Surface area; Sialon; Al_2O_3; Porosity

1. Introduction

One of the best-known high performance engineering materials is the Si_3N_4-based ceramic. Simultaneous equivalent substitution of Si–N by Al–O in the Si_3N_4 lattice results in a solid solution called sialon, with general formula $Si_{6-z}Al_zO_zN_{8-z}$.[1] Sialon is a compound of silicon, aluminium, oxygen and nitrogen. The material was discovered in the early 1970[2–4] and since that time has been actively developed. It found wide applications as an advanced engineering ceramics or as cutting tool and refractory material.

Sintering reaction of silicon and aluminium oxide compacts in nitrogen is one of methods of sialon ceramics production.[5–8] This method offers low cost of manufacturing, no shrinkage and the absence of liquid phase during sintering, so it results in porous but high strength material. The main role in this process plays the surface area of both powders and a direct contact between particles of both compounds because apart from a reaction of silicon with gaseous nitrogen, the reaction of the relevant sialon formation takes place in a solid state.

Agglomerates formed during the milling process could exhibit a critical effect on the reaction progress with respect to the non-homogenous spatial distribution of both kinds of particles, limited access of nitrogen to the silicon particles surface. The recent studies showed that application of a proper solvent–dispersant couple in the Al_2O_3–Si_3N_4–AlN system resulted in a correct dispersion and stability of the suspension.[9–12] Surface properties of alumina and silicon can be similar to those of the relevant nitrides since the thin oxide film is formed at the nitride particles surface. Thus, it was expected that agglomerates present in the polar environment could be split if a less polar solvent was applied and a proper dispersant was selected.

The aim of this work was to determine the effect of milling environment on the alumina–silicon mixture reaction progress during nitridation at elevated temperature.

2. Experimental

The cation ratio Al:Si in the initial batch was chosen as 1:1. It should permit to obtain sialon ceramics with composition of β-sialon–X-sialon. In this work silicon (Aldrich, specific surface area of 1.2 $m^2\,g^{-1}$) and aluminium oxide (Martinswerk, specific surface area of 9.1 $m^2\,g^{-1}$) were used as starting raw materials. The milling process was performed in the attritor mill in a polar

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environment and the second experiment was performed on a roller bench in the non-polar environment with a dispersant addition. Powders in attritor were milled in the isopropyl alcohol (99.7) with Si_3N_4 balls for 4 h. In the 2 h mixing process, the methyl ethyl ketone (MEK 2-Butanone 99.5% Aldrich) and ethanol (99.8) were used as the solvent and the phosphate ester (triethyl phosphate 99.8% Sigma–Aldrich) as dispersant. The composition of the solvent was constant (66% MEK + 34% ethanol) in all the experiments. Silicon powder after milling for 4 hrs in attritor with specyfic surface area of 13.4 $m^2 g^{-1}$ and aluminium oxide powders were dispersed in this solvent by adding phosphate ester. In order to find an optimum amount of phosphate ester the volume of dispersant was varied from 0.5 wt.% up to 5 wt.% of ceramic powder. The effect of dispersant addition was observed by the sedimentation behaviour and the influence on the subsequent nitridation process. After the solvent removal the batches were dried at 105 °C. Specific surface area of the powders was examined by BET method. Specific surface area of the silicon powder after milling in attritor in isopropanol for 4 h was also examined. Dried powders were uni-axially pressed into the form of cylinders with diameter of 10 mm and of 6 mm height. The applied pressure had the value of 80 MPa. Powder sample resulted from attritor milling was examined by TG and dilatometric test (SetaRam). The specimens were heated at the rate of 10 °C/min up to 1350 °C without any holding time in nitrogen flow (150 cm^3/h). The dilatometric plot of alumina compact was also recorded as the reference. The tablets were embedded in a BN crucible with Si_3N_4 + BN powder bed and placed into the graphite resistance vacuum furnace (Thermal Technology). The furnace was flushed with nitrogen twice then the nitrogen flow was fixed to 3 l/h. The specimens were heated at the rate of 10 °C/min up to 1250 °C and held for 4 h and changes of their mass, height and diameter were measured. Their density after sintering was calculated and measured by Archimedes methods. The samples homogeneity was examined by SEM studies. XRD measurements were performed on the outer surface of sintered specimens and 2 mm below the outer surface. X-ray tube with the copper anode (Cu Kα) was applied as the radiation source and the diffraction patterns were plotted for 2θ Bragg angle in the range of 10°–90° (Philips E'XPERT).

3. Results

The dilatometric curve (Fig. 1.) shows that shrinkage process of the alumina–silicon compact starts at about 1000 °C. Shrinkage of the sample was below 1% up to 1350 °C. The tablet prepared from pure alumina starts to sinter at the same temperature of 1050 °C but the shrinkage is considerably higher −7%.

TG results show the mass gain starts over 800 °C (Fig. 2.). This process could be attributed to the nitrogen and silicon reaction. Formation of the reaction product is limited by the specimen densification process. If the entire silicon would react with nitrogen and to form silicon nitride then the mass gain of 23.3 wt.% is expected. The nitridation effect observed on the TG plot was much lower than the expected value because the atmosphere was different from that in the graphite furnace.

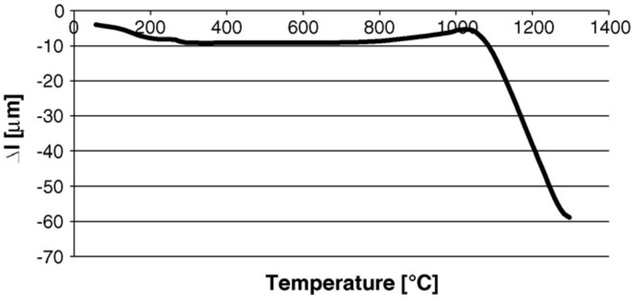

Fig. 1. Dilatometric curve of the sample after attrition milling without ester addition.

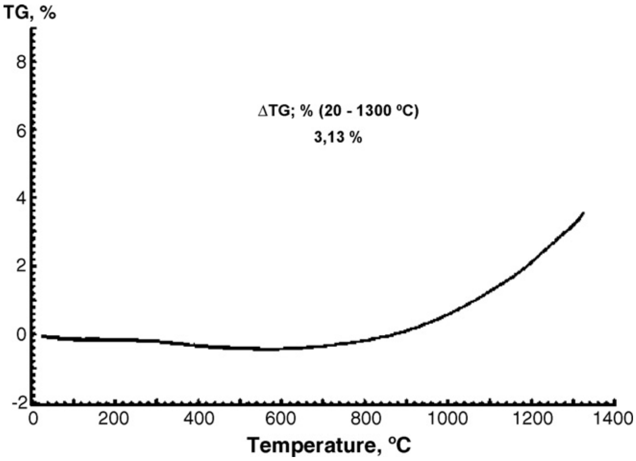

Fig. 2. TG of silica–alumina sample after attritor milling without ester addition (up to 1350 °C).

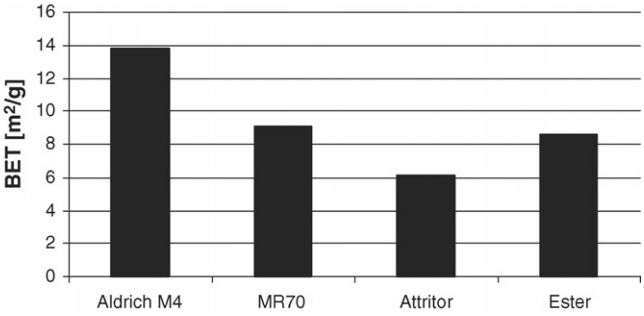

Fig. 3. Specific surface area of the initial powders and after milling or mixing process; *Aldrich M4* – Si powder after separate milling (4h), *MR70* – commercial alumina, *Attritor* and *Ester* – Si/Al_2O_3 mixtures after milling in attritor or mixing with dispersant.

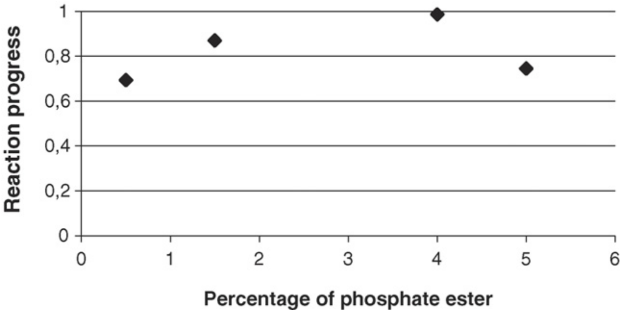

Fig. 4. Relationship between reaction progress and amount of dispersant additive.

Table 1
Green density, density after sintering, Archimedes density, mass gain, height and diameter and open porosity of the samples after sintering the compacts of powders from attritor milling and roller bench mixing

Sample	Green density (g/cc)	Density after sintering (g/cc)	Archimedes density (g/cc)	Mass changes (%)	Height changes (%)	Diameter changes (%)	Open porosity (vol.%)
4% Ester	1.68	2.24	2.26	23	−1.5	−2.4	29.4
Attritor	1.73	2.22	2.26	17.9	−3.7	−2.3	30

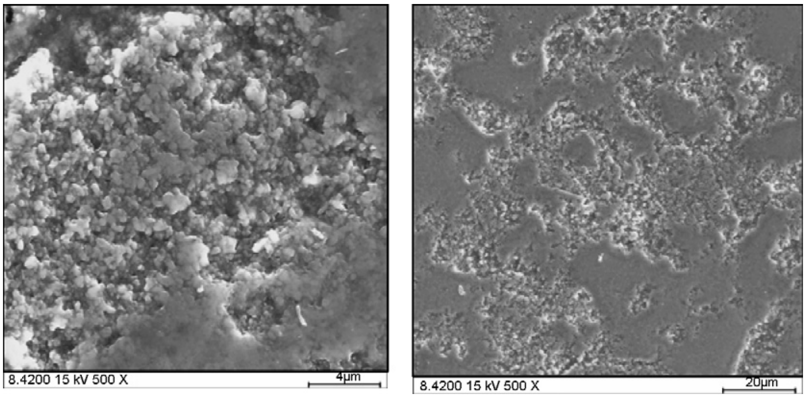

Fig. 5. Microstructure of the sample with 4% of phosphate ester after nitridation at 1250 °C.

The results of the silicon and aluminium oxide powders sedimentation test with different dispersant addition showed various behaviour of suspensions. The suspension with 0.5% ester separated very quickly. For solvent containing 4% of the phosphate ester powders settled very slowly in comparison to the other samples. The amount of 5% addition was too high and powders separated faster than in the sample with 4% addition. The sedimentation test showed that the non-polar solvent with 4% of the phosphate ester gives the most stable suspension.

Changes of the silicon and alumina powders surface area (Fig. 3.) after attrition milling and mixing on a roller bench were studied by BET. It was found that the surface area of the batch after attrition milling in isopropanol is lower than the surface area of the initial powders. Such the effect results from the formation of agglomerates. Surface area of the batch after mixing in the non-polar solvent with the dispersant was higher than after attrition milling. This result suggests that the number of agglomerates was reduced by dispersant addition. This should facilitate nitrogen access to the surface of silicon particles.

The measurement of the mass gain was used for calculation of the reaction progress (Fig. 4):

$$\text{reaction progress} = \frac{\text{mass gain after nitridation}}{23.3} \qquad (1)$$

where the value of 23.3 was calculated from the reaction balance: $3\text{Si} + 2\text{N}_2 = \text{Si}_3\text{N}_4$ under the assumption that silicon content in the mixture was equal to 35 wt.%.

Addition of the dispersant caused the mass gain growth after nitridation at 1250 °C. The lowest mass gain was observed for the sample with the ester content of 0.5%. The best results were obtained for the sample with 4% of dispersant addition and the reaction progress measured by mass gain reached the value of 1. For the other ester amounts the reaction progress was similar to that for the sample after attrition milling in polar environment. The sample sintered after attritor milling in polar solvent exhibited lower mass gain and higher shrinkage than the sample after mixing in non-polar solvent with ester addition (Table 1).

The samples after nitridation at 1250 °C with 4% of ester showed the fine-grained and homogeneous microstructure (Fig. 5.). The XRD studies confirmed formation of β-sialon ($z = 2$) apart from alumina in the dispersant–non-polar suspension-derived tablets. In contrary, silicon oxynitride and residual silicon besides alumina were present in the tablets prepared from attrition-milled batches.

4. Summary

The differences between the mass gain after a TG experiment and after the isothermal nitridation at 1250 °C in the graphite furnace come from the use of different furnaces and from the powder bed absence in the case of TG studies. It results in the different atmosphere and affects the heterogeneous reaction.

The main role in nitridation of silica and alumina compacts plays homogeneity of the particles size distribution of the both powders. Formation of the agglomerates and changes in the green compacts microstructure had affected the reaction progress in the nitrogen atmosphere. The homogeneity improvement was achieved by the non-polar solvent application and the dispersant addition.

Shrinkage of the attritor-milled samples indicates that the sintering process of the original alumina and silicon particles predominates over nitridation of silicon.

Mixing process with phosphate ester addition was a proper method to attain the good homogeneity and consequently to take the increase of the nitridation reaction progress up to the theoretical value.

However, lower surface area of the batch with the surfactant addition in comparison to that of the original powders as well as high porosity of the resulted specimens indicate that agglomerates splitting process was not completed.

Acknowledgement

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