

## Influence of addition of polymeric precursors of ceramics on sintering of Al<sub>2</sub>O<sub>3</sub>

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**Abstract.** The effects of adding polymer precursor on the sintering behavior, microstructure and hardness of alumina ceramics have been studied. Polymer sintering aid polymethylhydrogensiloxane were used for alumina based ceramics sintered at 1650° C. The sintered materials were characterized using: (a) helium pycnometry to determine apparent density; (b) x-ray diffraction analysis, scanning electron microscopy, transmission electron microscopy and energy dispersive x-ray spectrometry to determine the microstructure and composition; (c) Vickers indentation analysis to determine the hardness and fracture toughness. The addition of polymethylhydrogensiloxane yielded alumina/mullite composites. The preparation of ceramic composites using small amounts of polymer precursors is suited for alumina based ceramics. The processing route being simple, it has the potential to enable the manufacture of complex shaped pieces.

### 1. Introduction

Inorganic polymers have found many applications in the processing of ceramic materials and include forming aids for pieces and as ceramic precursors. As precursors and with adequate heat treatment, polymers can be used to obtain ceramics pertaining to different systems.

The development of new inorganic polymers or organo-metallics has enabled new ceramic materials to be produced and these have found applications in many areas, especially in high temperature chemically aggressive environments [1-4].

The use of ceramic polymer precursors has been reported in many papers [2,3,5]. The synthesis of Si based ceramics using polymeric precursors and in the form of fibres, thin films, foams, nanocomposites, nanofibers, coatings, glasses and compacted materials has received much attention [6-13]. The route to obtain ceramic materials using polymer precursors generally involves various steps [14] and consists basically of synthesizing polymers from monomers or oligomers to obtain the polymer precursor. In recent years many inorganic polymers have been developed. Silicon based polymers are used more often and include [15] polysiloxanes, polysilazanes, polysilanes and polycarbosilanes. Polysiloxanes and silicones are terms used to describe a family of compounds based on molecular chains with alternating silicon and oxygen atoms [16]. The bond between the Si and O atoms in silicone is strong and sufficiently flexible to impart high heat resistance to the material, without undergoing decomposition. The angle between the Si and O bonds can open and close, enabling the whole chain to be quite flexible [17,18]. Depending on the length of the chain and the organic groups bonded with the silicon atoms, it is possible to obtain a range of products, from low viscosity oils to greases, gels, rubbers, solid resins, sealing agents, lubricating oils, hydraulic fluids, biomaterials, cosmetics etc [16].

The structure of the materials produced from polymer precursors can vary from amorphous to nanocrystalline, depending on the raw materials and the heat treatment temperatures during processing. Both, the chemical composition and the microstructure of the final product are dictated by the composition of the polymer used, by the heat treatment environment and by the temperature [19,20]. According to Hörz [21], the polymer-ceramic conversion generally takes place with shrinkage and volatilization of organic compounds, resulting thereby in mass loss.

In this investigation, alumina was the material under study. Alumina is widely used as a ceramic material due to an excellent combination of physical and chemical properties such as high heat, wear and oxidation resistance. Alumina has high chemical stability and is therefore used as a refractory oxide because of its capacity to resist heat without undergoing any significant change in its chemical nature [22]. Besides these properties, alumina has a low thermal expansion coefficient and therefore, high thermal shock resistance [23-25]. Alumina has been widely used as ceramic coatings, a grinding agent, for furnace parts, as cutting tools, in medical and dental components, besides its use as a biomaterial [26]. Sternitzke et al. [27] studied the microstructure and mechanical properties of Al<sub>2</sub>O<sub>3</sub>/SiC nanocomposites prepared with polycarbosilane (PCS). They prepared Al<sub>2</sub>O<sub>3</sub> specimens with different SiC concentrations (2.5, 5.0 and 7.5 vol%) using polycarbosilane. The alumina powder was coated with PCS, cured, pyrolyzed (1500 °C for 2 h in argon) and hot pressed (1700 °C for 1 h at 25 MPa in Ar). The average density achieved was  $3.9 \pm 0.04 \text{ g/m}^3$ , with Vickers hardness of  $18.4 \pm 0.5 \text{ GPa}$  and fracture toughness of  $2.99 \pm 0.05 \text{ MPa}\cdot\text{m}^{1/2}$ . Variation in SiC content did not markedly alter the density, hardness and fracture toughness values.

This paper presents the effects of adding polymethylhydrogensiloxane on microstructure, hardness and fracture toughness of Al<sub>2</sub>O<sub>3</sub>.

## 2. Methods and Materials

The raw materials used were: aluminium oxide – Al<sub>2</sub>O<sub>3</sub>-A16 SG-Alcoa; polymethylhydrogensiloxane (PMHS) – 1107, liquid, general formula [(CH<sub>3</sub>)(H)SiO]<sub>n</sub> - Dow Corning; catalyst with platinum - Hüll. The polymer additions to Al<sub>2</sub>O<sub>3</sub> were 1, 5 and 10 wt%. Specimen processing consisted of milling Al<sub>2</sub>O<sub>3</sub> with isopropyl alcohol for 4 hours in an attrition mill with a central rod, a jar and alumina balls. The milled material was dried, de-aggregated in an agate mortar with pestle and then sieved (100 Mesh). The standard specimen without any polymer additions, denominated A0, was axially compacted and then isostatically pressed at 200 MPa and sintered in nitrogen atmosphere at 1650 °C in a (Astro) furnace with graphite heating elements. To the other specimens, Pt catalyst dilute in isopropyl alcohol was added to the polymer and this mixture in turn to Al<sub>2</sub>O<sub>3</sub>. The material was homogenized in a mechanical mixer (Turbula, model T2C), dried at 50 °C for 30 min and then compacted axially in a hot press at 200 °C for 2 hours. The specimens were then pyrolyzed in a tube furnace in nitrogen atmosphere at 900 °C for 1 hour. The sintering of these specimens was done in a furnace (Astro) with graphite heating elements for 1 hour under nitrogen. This heat treatment was carried out in a graphite closed crucible. The heating rate was 5 °C/min up to 400 °C and 20 °C/min from 400 °C to the sintering temperature.

The apparent density of the sintered specimens was obtained with a He picnometer (Micromeritics, model 1330). Mass losses of the specimens were also determined ( $\Delta M$ ). X-ray diffraction analysis (Rigaku, model Multiflex), with CuK <sub>$\alpha$</sub>  was used to determine the crystalline phases in the sintered specimens. The specimens were examined in a scanning electron microscope, SEM (Philips XL30). The specimens were also examined in a transmission electron microscope (Jeol, 200C) to identify the phases from the electron diffraction patterns and by chemical analysis using EDS (EDAX). Standard specimen preparation procedures were used [28]. Identification of the crystalline phases and the crystallographic orientations was done using the DIFPAT program [29]. The Vickers hardness measurements were done in a Buehler VMT-7 machine. On each specimen, 10 indentations were made with adequate distance between indentations, as suggested by Ponton and Rawlings [30]. To determine the type of crack emanating from the Vickers indentations, the specimens were polished with 6  $\mu\text{m}$  diamond paste for 2 min. The equation [31] used to determine fracture toughness with radial cracks was

$$K_{Ic} = 0,0154 (E / H_v)^{1/2} (P/c^{3/2}). \quad (1)$$

Where  $K_{Ic}$  is fracture toughness ( $\text{MPa}\cdot\text{m}^{1/2}$ ),  $E$  the elastic modulus (GPa),  $H_v$  the Vickers hardness (MPa),  $P$  the applied load (N) and  $c$  the crack length ( $\mu\text{m}$ ).

The specimens were identified. A0 was the specimen without polymer additions and AXH represented alumina specimens with additives ( $X = 1, 5$  or  $10 \text{ wt}\%$ ) of polymer PMHS.

### 3. Results and discussion

#### 3.1. Al<sub>2</sub>O<sub>3</sub> with PMHS addition

The X-ray spectra of the specimens A1H, A5H and A10H are shown in Fig. 1. The X-ray spectra of Al<sub>2</sub>O<sub>3</sub>-PMHS specimens revealed the presence of alumina and mullite (PDF 73-1389) in the specimens, considering that the Si and O from the polymer had reacted with the Al<sub>2</sub>O<sub>3</sub>. According to Su and Sternitzke [32], the oxidation of Si in the polymer precursor results in the formation of mullite. Michalet et al. [33] reported in their paper related to addition of polysiloxane to Al<sub>2</sub>O<sub>3</sub> that mullite formation started at 1400 °C. Harshe et al. in their work on addition of polysiloxane to Al<sub>2</sub>O<sub>3</sub>, achieved densification when the SiO<sub>2</sub> turned viscous [34].

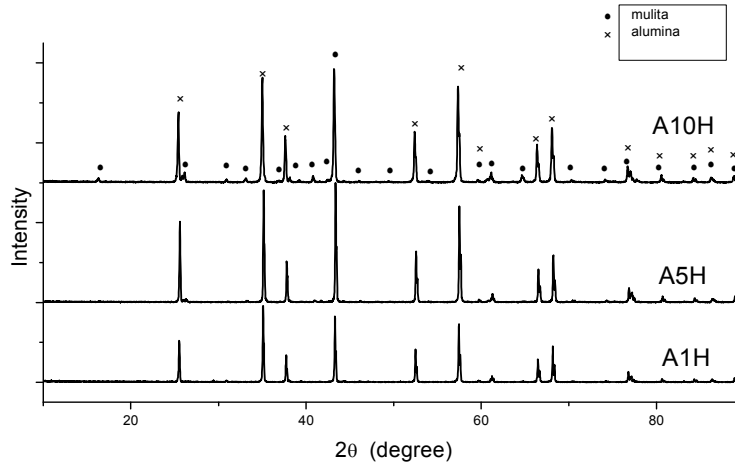


Fig. 1- X-Ray diffraction patterns of specimens A1H, A5H and A10H after pyrolysis and sintering.

The apparent density values (as % of T.D.) of PMHS containing specimens sintered in the graphite furnace and the mass losses are given in Table 1. To calculate the relative density (% T.D.), the theoretical density of alumina was taken as 3.98 g/cm<sup>3</sup>.

Table 1- Apparent densities, %T.D. and mass loss of Al<sub>2</sub>O<sub>3</sub>-PMHS samples.

Samples	$\rho_{\text{apparent}}$ (g/cm <sup>3</sup> )	T.D. (%)	$\Delta M$ (%)
A0	3,96 ± 0,03	99,5	1,2
A1H	3,77 ± 0,01	94,7	1,9
A5H	3,66 ± 0,01	92,0	3,6
A10H	3,76 ± 0,01	94,5	6,9

The density of the standard specimen was higher than that of specimens with polymer precursors. This was due probably to formation of mullite, which has a lower density than alumina. The densities of the specimens with PMHS were close to one another, with the exception of A5H. Overall, the mass losses were relatively low.

The microstructure of specimen A10H in Fig. 2 consists of alumina and mullite grains that are uniformly distributed as shown in the X-ray maps [28]. The micrograph shows a heterogeneous microstructure, intergranular fracture and grain size varying between 1 - 7  $\mu\text{m}$ .

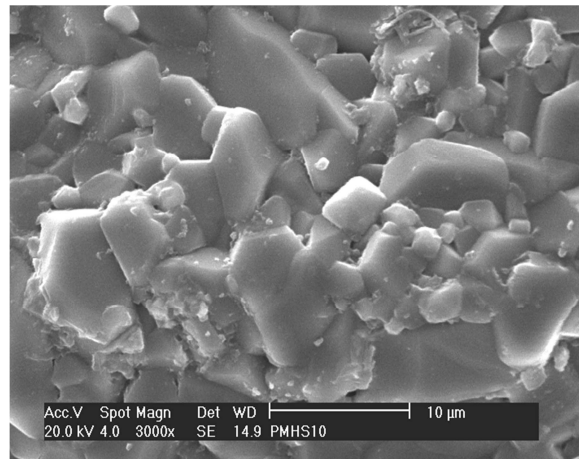


Fig. 2 - Intergranular fracture of sample A10H.

To determine the phase composition, the A10H specimen was examined in a TEM. Many grains were analyzed and Fig.3a is a typical micrograph. The EDS spectrum shown in Fig. 3b with the Al and O peaks corresponds to the alumina matrix grains in Fig. 3a. The EDS spectrum in Fig.3c of the bright region of Fig.3a, which was more abraded by the ion beam, revealed Al, O and Si, indicating the possible presence of mullite (light grain). These observations are in agreement with the X-ray spectra in Fig.1.

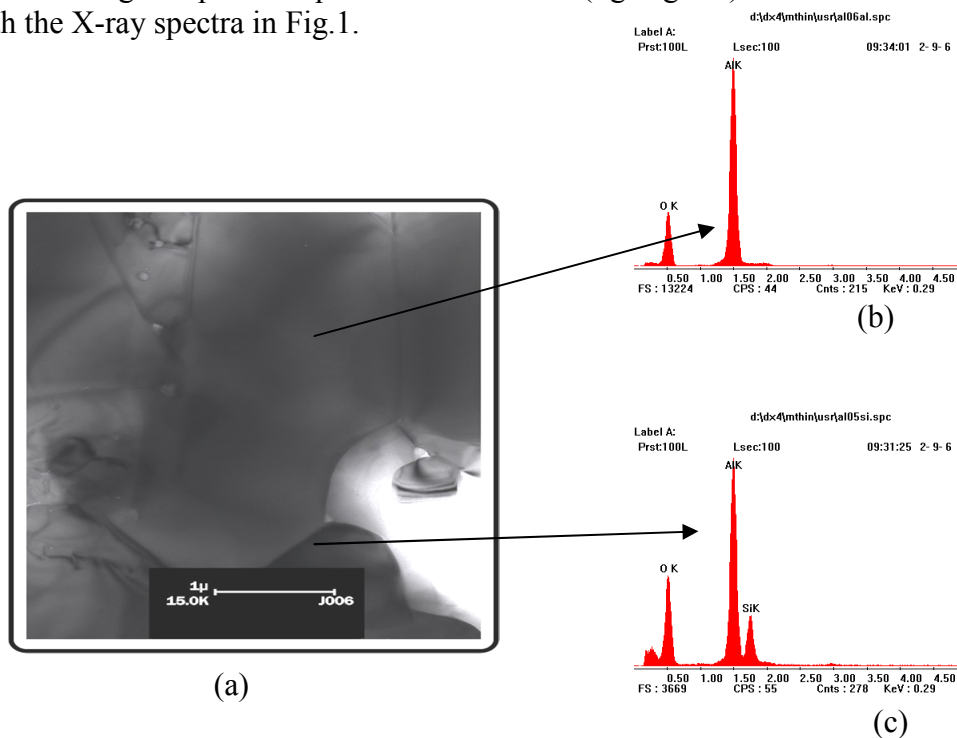


Fig. 3- Bright field TEM image (a) and EDS spectra showing O, Al (b) and showing O, Al and Si (c) of sample A10H.

The Vickers hardness values (Table 2) are within the range 14.9-16.3 GPa, considering that materials prepared from polymer precursors have slightly higher hardness than the standard specimen. The measured fracture toughness values varied from  $3.45 \text{ MPa}\cdot\text{m}^{1/2}$  to  $3.72 \text{ MPa}\cdot\text{m}^{1/2}$ , as shown in Table 2. These results demonstrate that the use of PMHS polymer enabled hardness increase even though the same polymer caused the fracture toughness of alumina to decrease.

Table 2- Vickers hardness ( $H_v$ ) and fracture toughness of A1H, A5H and A10H samples.

Sample	$H_v$ (GPa)	$K_{Ic}$ (MPa.m <sup>1/2</sup> )
A0	14,9 ± 0,6	3,72 ± 0,18
A1H	15,9 ± 0,3	3,47 ± 0,10
A5H	15,7 ± 0,6	3,48 ± 0,10
A10H	16,3 ± 0,6	3,45 ± 0,11

#### 4. Conclusions

PMHS additions to alumina resulted in mullite phase formation.

This investigation revealed that the addition of PMHS to alumina reduced the density of the sintered material.

The microstructure of Al<sub>2</sub>O<sub>3</sub>-PMHS was heterogeneous.

The materials prepared with ceramic polymer precursors had higher hardness than the standard specimen.

The preparation of ceramic composites using small additions of ceramic polymer precursors has been shown to be viable for alumina based materials. It is a simple forming route with a large potential for obtaining pieces with complex shapes.

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**Advanced Powder Technology VIII**

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**Influence of Addition of Polymeric Precursors of Ceramics on Sintering of**

**Al<sub>2</sub>O<sub>3</sub>**

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