

Densification Study of SiC:Al₂O₃:Y₂O₃ with Polymer Additions

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Abstract: The influence of polymer precursor additions on liquid phase sintering of SiC:Al₂O₃:Y₂O₃ has been evaluated. Two polymer precursors were used: polymethylhydrogen-siloxane and D₄V_i (1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane). The ceramic phase had the following composition in wt%: 91.6 SiC, 4.2 Al₂O₃ and 4.2 Y₂O₃. The composites were prepared using the following ceramic phase to polymer ratios in wt%: 82.7: 17.3; 74.0: 26.0 and 71.5: 28.5. Density measurements were carried out using a helium pycnometry and the Archimedes method. The crystalline phases were identified by X-ray diffraction analysis and the microstructures were observed by optical and scanning electron microscopy.

I. Introduction

Silicon carbide is an important structural ceramic material. Besides high hardness, it has excellent oxidation resistance, high thermal conductivity, good wear and thermal shock resistance and good high temperature mechanical strength^[1,2]. This combination of properties is due mostly to the strong covalent type chemical bond (up to 88%), between the silicon and carbon atoms. This type of bonding also makes its densification difficult^[3]. One of the most important applications of this material is as a refractory^[4], due to its relatively high thermal stability and oxidation resistance^[5]. Presently, SiC based materials are widely used as furnace parts in the porcelain industry, for hard metal sintering, abrasive wheels, abrasive powders, heat exchanger piping and automotive industry components^[6,7].

An important characteristic of SiC is its polytypism. A large number of polytypes are known; the cubic polytype is referred to as β -SiC and the other non-cubic structures (hexagonal and rhombohedral) as α -SiC^[3]. It has been suggested that the type of SiC formed is controlled by the impurities present in it^[8]. The impurities that exercise the most influence on the type of SiC formed are those with elements from groups III and V of the periodic table, that is, the electronic acceptors (Al, B, etc.) and the electronic donors (N, P).

Solid state densification of covalent structural ceramics like SiC is difficult, even at high temperatures. Hence, they are often liquid phase sintered with oxide additions, which upon cooling form secondary glass phases of silicon oxynitride or silicon oxycarbide.

In liquid phase sintering, a viscous liquid forms at the sintering temperature and this is very important for the densification of various materials^[9]. It is important to have complete wetting of

the solid by the liquid for the liquid phase sintering process to take place. Another important factor in liquid phase sintering is dissolution of the solid in the liquid and its re-precipitation.

In this process, the pressed powder is heated to a temperature at which there is liquid formation, normally made possible by an eutectic composition. The quantity, the viscosity of the liquid phase formed, the wettability and the solubility of the solid in the liquid determine the degree of sintering^[10].

Synthesis of Si based ceramics from polymeric precursors in the form of fibers, foams, glasses, and pressed materials has been the focus of much attention among researchers^[11-14].

This new type of ceramic processing can be understood by making an analogy with processing of carbon based materials, which often involves polymer pyrolysis^[12]. These materials, made up of C and H, are heat treated to several hundred degrees centigrade, during which the hydrogen atoms are released leaving behind only the carbon structure of the original polymer. The knowledge that a variety of polymers can be made by adding Si, B and N atoms, opens the possibility of producing ceramic materials using an analogous process to processing carbon based materials through polymer pyrolysis. These has a lot of promising applications like binders, fibers and coatings that are very difficult or almost impossible to obtain through conventional routes.

In 1975 Yajima et. al.^[13] published a paper on thermal conversion of polysilanes to SiC starting research in this area. The production of ceramic materials from polymer precursors generally involves various steps^[14].

- synthesis of the polymer from monomers or oligomers;
- molding and curing with a catalyst to obtain lattice polymers; before curing, the material is in the form of a viscous liquid or powder;
- pyrolysis (generally between 400 and 900°C); and
- crystallization.

A number of inorganic polymers has been developed. The silicon based polymers often used are: polysiloxanes $[-R_2Si-O-]_n$, polysilanes $[-R_2Si-]_n$, polycarbosilanes $[-R_2Si-CH_2-]_n$ and polysilazanes $[-R_2Si-NH-]_n$.^[15]

The chemical behavior of the polymer depends on the nature of the functional group R that is bound to the silicon atoms, which could belong to the alkyl or aryl groups or even hydrogen. For example: the chlorosilanes, used as the starting material to obtain silicones are precursors of polysiloxanes, and these have been used in this investigation.

The microstructure of materials produced from polymeric precursors can vary from the amorphous to nanocrystalline, depending on the temperature used. The chemical composition depends on strongly the composition of the polymer used^[16].

Ceramics prepared from polymeric precursors have been studied in detail and new ideas for the use of precursors continue to appear. Mixtures containing powders and pre-ceramic polymers constitute systems with significant advantages and potential for preparing composites^[17].

In the work carried out by M. Sternitzke, B. Derby and R. Brook^[18], the microstructure and mechanical properties of Al₂O₃/SiC nanocomposites prepared by conventional processing and from polymeric precursors were studied. Specimens of Al₂O₃ with different concentrations of SiC (2.5, 5.0 and 7.5 vol%) were prepared. A silicon based polymer (polycarbosilane, PCS) was mixed with Al₂O₃ powder, cured, pyrolyzed and sintered. Ceramic composites with SiC nanoparticles in an Al₂O₃ matrix, using polymeric precursors were obtained at the same sintering temperature.

Recent work carried out by Schiavon^[19] involved the preparation of different pre-ceramic polymers, polysiloxane and polysilazane, and their conversion by controlled atmosphere pyrolysis to silicon oxycarbide (SiOC) and silicon carbonitride glasses, respectively. The polysiloxane performed as a powder particle binder and as a precursor of the SiC rich ceramic phase. These materials had good mechanical properties and wear resistance.

In this investigation the effect of polymeric precursor additions on liquid phase sintering of SiC has been studied. The polymeric precursors are expected to react with the oxide additives or crystallize at high temperatures forming silicon based phases.

II. Materials and methods

The raw materials used in this investigation were:

- Silicon carbide – SiC grade BF 17 – H. C.Starck, containing 91.1wt% of β -SiC and 1.45% oxygen
- Aluminium oxide - Al_2O_3 – A – 16 SG – Alcoa, 99.8% purity
- Rare earth oxide – Y_2O_3 – Aldrich
- Polimethylhidrogensiloxane – Dow Corning – liquid 1107 (liquid phase)
- D_4V_i – Dow Corning – (liquid phase)
- Platinum Catalyst – Dow Corning

The ceramic phase had the following composition in wt%: 91.6 SiC, 4.2 Al_2O_3 and 4.2 Y_2O_3 . The polymers weight percent are:

SAY5: PMHS: 9,1 and **D₄V** 8,2

SAY8: PMHS: 13,6 and **D₄V** 12,3

SAY9: PMHS: 15,0 and **D₄V** 13,5

The mixtures of the different powders ($\text{SiC}:\text{Y}_2\text{O}_3:\text{Al}_2\text{O}_3$) in wt% and the polymers (PMHS: D_4V_i) are shown in table I.

Table I. Weight percent of the materials used in this investigation

Specimen code	Powders $\text{SiC}:\text{Al}_2\text{O}_3:\text{Y}_2\text{O}_3$ (wt%)	Polymers (PMHS: D_4V_i) (wt%)
SAYP / (standard)	100	-----
SAY5	82,7	17,3
SAY8	74,0	26,0
SAY9	71,5	28,5

The powders of Al_2O_3 , Y_2O_3 and SiC, mixed in the above mentioned proportions and the base composition $\text{SiC}:\text{Y}_2\text{O}_3:\text{Al}_2\text{O}_3$, were milled in an attritor for four hours. The mixed and milled materials were dried in a rotoevaporator, de-agglomerated in a mortar and sieved (325 mesh). The platinum catalyst was added to the polymers (PMHS + D_4V_i) and this solution was stirred for 5 minutes before it was added to the powders. These material with the polymer additives were compacted uniaxially in a hydraulic press (Marconi, 098/A) at 70°C. A rectangular steel mold was used and a pressure of 10 ton was applied for 2 hours. The standard specimen were uniaxial pressed

at low pressure and cold isostatically pressed at 200 MPa. The polymer containing specimens were pyrolyzed at 900° C in a tube furnace under a flowing argon atmosphere. Sintering was carried out in a furnace with graphite heating elements (Astro) under a protective bed of SiC:Y₂O₃:Al₂O₃, at 1950°C for 1 hour. A slight overpressure of argon atmosphere and heating rate of 15°C.min⁻¹ were used.

After sintering, the apparent densities of the specimens were determined using the Archimedes method and with the helium picnometry (Micromeritics). X-ray diffractometry (Rigaku) was used to identify the crystalline phases. The microstructures were observed in an optical microscope (Leitz) and in a scanning electron microscope (Philips-XL30). In the latter, back scattered electrons were used.

III. Results and discussion

Table II presents the apparent densities of the sintered specimens determined using the two methods.

Table II – Apparent densities of specimens determined using the Archimedes method and helium picnometry.

Specimens	Hydrostatic density (g.cm ⁻³)	He Picnometry density (g.cm ⁻³)
Standard	3,08	3,13
SAY5	2,93	2,95
SAY8	2,87	2,84
SAY9	2,77	2,71

Comparison of specimen densities determined by the two methods shows that the values are close. The density decreases with increase in quantity of polymeric precursor. This is due to the difference in the densities of the different components. These results are in agreement with data presented by Schiavon^[19].

Calculation of the theoretical density of the different materials is quite complex as the polymers release various elements during pyrolysis. Some of these elements probably react with the oxides that form the liquid phase during the heat treatment, and some probably crystallize at high temperatures forming silicon carbide.

Figure 1 shows the diffraction spectra of the standard, SAY5, SAY8 and SAY9 specimens after sintering.

Besides the presence of various polytypes of SiC, which indicates that the specimen contains α -SiC and β -SiC, other compounds like Al₂Y₄O₉ (aluminum yttrium oxide) and YAG (Al₅Y₃O₉) are also present in all the specimens. The precursors addition (siloxane) just forms amorphous phase or

SiC. It was not possible to determine the degree of formation of secondary phase from the polymeric precursor addition.

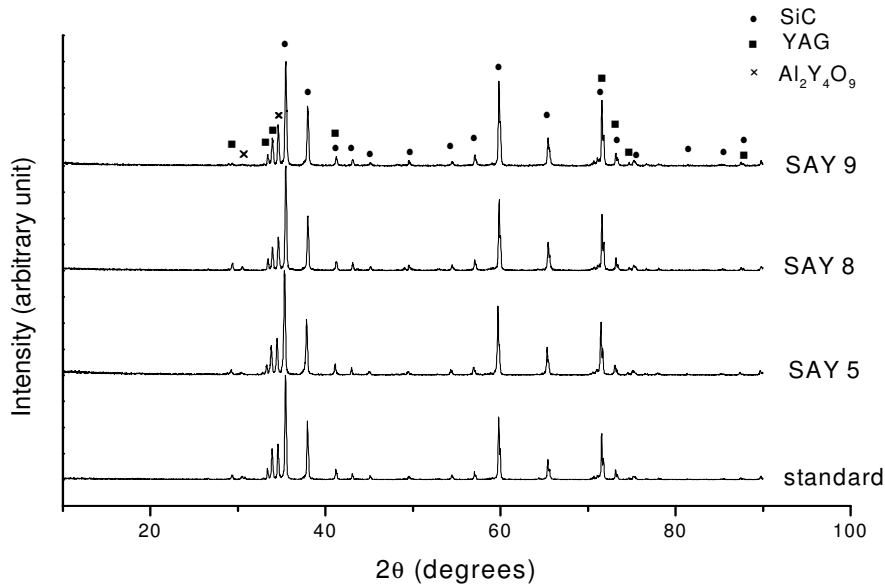
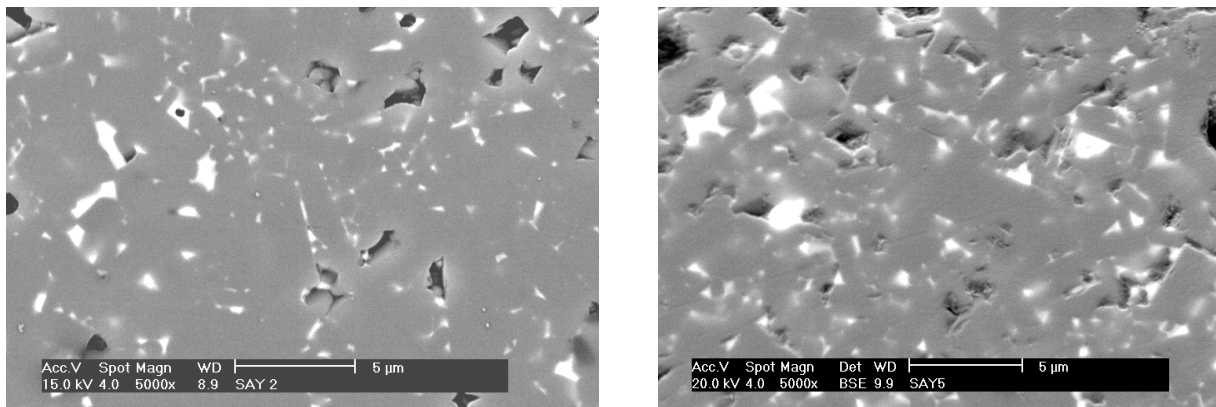


Figure 1. X-ray diffraction spectra of the different specimens.

Scanning electron micrographs obtained with back scattered electrons of a standard specimen $SiC:Y_2O_3:Al_2O_3$ and that of a representative polymer precursor containing specimen (SAY5) are shown in figures 2 (a) and (b).



(a)

(b)

Figure 2. Scanning electron micrographs. (a) Standard specimen (b) SAY5 specimen.

The microstructures of the standard and the polymer additive containing specimens are similar. They are homogeneous with elongated grains. Yttrium containing secondary phases in grain boundary, grain triple points and intergranular pores can also be seen. These microstructures are typical of liquid phase sintered SiC based specimens. Transmission electron microscopy and EDS techniques will be used to further characterize the different phases.

IV. Conclusions

Addition of a mixture of polymer precursors (PMHS) polymethylhydrogensiloxane and D_4V_i (1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane), siloxanes, along with a platinum catalyst to the $SiC:Al_2O_3:Y_2O_3$ powder mixture permitted liquid phase sintering of $SiC:Al_2O_3:Y_2O_3$. Further studies will be carried out to optimize the sintering temperature and the quantity of polymer added.

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