Influence of Nano-Alumina and Mullite on the Sintering Behavior of Hotpressed Silicon Carbide

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Abstract

Sintering of Silicon Carbide with nano-sized alumina as well as mullite as an additive has been studied. Nano-sized alumina produced by several routes were first analyzed and then investigated. This alumina along with yittria as well as mullite was then added to SiC powder in different proportions and sintered under ambient pressure of argon and then also hotpressed under 20 MPa uniaxial pressure using a graphite mold. The microstructure of the sintered pellets obtained from the two techniques shows interesting difference in the distribution and morphology of the different grains and phases. The shrinkage curves plotted for the hotpressed SiC also predict the presence of a very small amount of liquid phase

Introduction

Silicon carbide (*SiC*) is a very promising ceramic material due to its high hardness, low bulk density, high creep resistance which makes *SiC* useful for a wide range of industrial applications[1,2,3]. The main application of silicon carbide as structural material is in automotive engines, cutting tools, heat exchange and mechanical seals. These applications are possible because of the unique properties of silicon carbide based materials, including high temperature strength and low density, as compared to conventional steel, and excellent thermal shock and wear resistance[4]. Recently whisker reinforced composites based on *SiC* and *SiC* coated nano wires have also generated new interest in special applications[5,6,7,8.]

All these properties are inherent to silicon carbide due to highly covalent bonding. However, this covalent feature causes complications with sintering of *SiC* based ceramics to high densities. Silicon carbide can be densified by solid-state sintering process at high temperatures above *1900°C* with the aid of boron and carbon, but liquid-phase sintering of *SiC* can be achieved at lower temperatures *(1800-1900 °C)* with the aid of metal oxides, such as Al_2O_3, Y_2O_3, and other rare-earth oxides. The densification of *SiC* by liquid-phase sintering lately draws more attention because the materials processed by this method are cheaper and with adequate mechanical properties. Liden[9] *et al* have used a novel technique of sol adsorption to add metallic oxides. This not only stabilized the slurry but also reduced to a greater extent the total amount of additives because of proper homogeneous distribution. The oxide sintering aids react with SiO_2, present at the surface of *SiC* particles in more or less quantity depending upon the history of the powder, forming a silicate melt and enhancing densification. Addition of other oxides changes the equilibrium, but sintering dynamics has to be very carefully adjusted in each case. These reactions can be to

some extent suppressed by the application of the high external partial pressure of *CO* and/or application of reactive powder beds[10,11.] Hotpressing or hot Isostatic Pressing (HIP) was also used to sinter pure *SiC* but complete densification at usual hotpressing conditions is difficult to achieve[12.] Use of mullite as a second phase as well as a re-enforcement to increase mechanical properties has also been suggested at several places[13,14]

The aim of this paper is to contribute to the previous works[15,16] and compare naturally sintered with hotpressed SiC pellets having similar additives, in terms of their microstructure and sintering properties. Three SiC powder mixtures with similar amounts of additives were prepared and sintering was carried out under pressureless conditions as well as hotpressing.

Experimental work

Commercially available β-SiC, Al_2O_3 (Baikalox, France), Y_2O_3 (Fine Grade, H. C. Starck, Germany), Al2O3 produced by Sol-Gel method and Mullite (Fine Grade, H, C, Starck, Germany) were used (Table 1). The locally produced alumina through sol-gel process when analyzed through TEM exhibited highly agglomerated structure (Fig. 1). Individual agglomerates varied in size from about 20 nm to almost 200 150 nm. Figure 2 shows XRD of the Sol Gel and classical alumina. The noise level is high and the peaks are broader in the Sol Gel powder, which depicts the presence of residual molecules and extremely fine particle size. The TEM result confirms the same. Thermal analysis conducted gives about 16% weight loss between 25°C to 800°C. The simultaneous TGA/DSC analysis carried out, given in Figure 3, also shows two endothermic peaks, one at low temperature (50°C) and another at relatively high temperature (760°C). The weight losses are

Table 1. Different powders utilized for fabrication of compacts

| Powder	Particle Size Range	Source
Alumina (Baikalox)	200 - 350 nm	Baikalox, France
Alumina (Sol gel)	27 - 100 nm	Local Research Lab
SiC (S)	1.7 μm	H. C. Starck, Germany
Mullite	200 − 500 nm	H. C. Starck, Germany
Yittria	200 − 500 nm	H. C. Starck, Germany
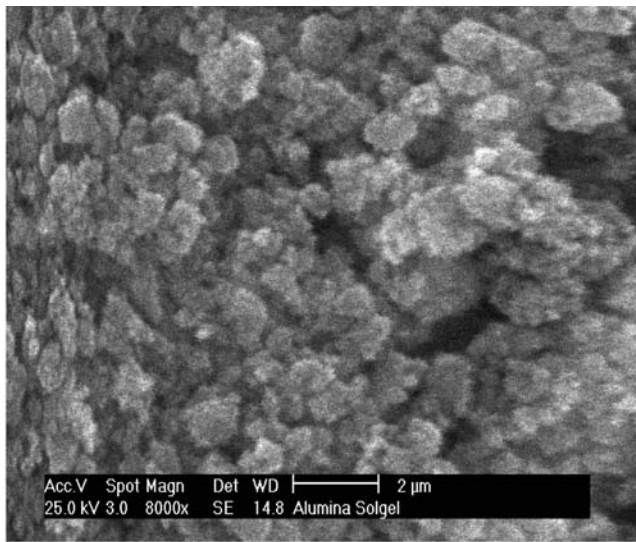
(a)
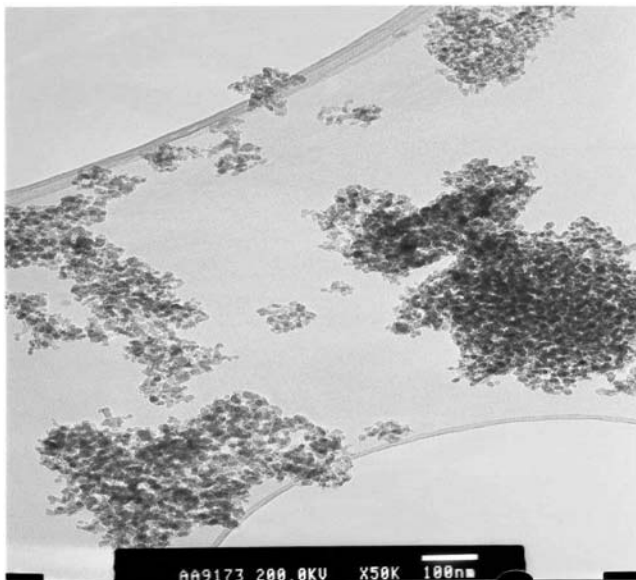
(b)

Fig. 1. (a) Scanning Electron Microscope (SEM) and (b) Transmission Electron Microscope (TEM) images of locally produced Sol-Gel alumina

presumed to be due to the following; (i) loss of water (free water and condensed from hydroxide) at lower temperatures and, (ii) possibly loss of residual hydroxyl groups. The first endotherm corresponds to a well defined weight loss region observed in the TGA. The latter peak at *760 °C* could be attributed to the phase changes (may be due to very minute presence of γ- phase which could not be detected by XRD). The powder mixtures of SiC containing 12 wt% Al_2O_3 and 8 wt% Y_2O_3 as sintering additives were ball milled in ethanol for 22 h. The ratio of Al_2O_3:Y_2O_3 was fixed at 6:4 by weight. Another mixture was prepared adding 4 wt% mullite under similar conditions. Batch compositions are shown in Table 2. The milled slurry was dried and was compacted by uniaxial pressing. The batch of compacts was then sintered under ambient pressure at 1900 °C for half an hour. The same compositions were also hot pressed at 1830 °C for three hours under argon atmosphere. Hot pressing was carried out in a graphite mould also provided with a shrinkage probe. The rate of shrinkage as a function of temperature was measured in real time. Densities were measured using size calculation method. The hot-pressed and pressureless sintered samples were cut and polished. The microstructures were observed by Scanning Electron Microscope (PHILIPS XL30).

Results

The sintering cycles for ambient pressure sintering were all kept the same, a 25 °C/min heating till a temperature of 1250 °C is reached and then a reduced heating rate of 10 °C/min heating rate till the final sintering temperature of 1900 °C is reached. A 30 minute dwell time was given at this sintering temperature. All samples were then cooled under a cooling rate of 5 °C/min to a temperature where furnace cooling takes over. The Horpressing cycles were different in a sense that lower temperature (1830 °C) was required to achieve a good densification. A particular point of interest in the sintering cycles adopted for hot pressing is that these cycles are coupled with shrinkage curves thus giving us real time progress on sintering. These sintering curves give very useful information regarding sintering kinetics, although a load of 20 MPa is applied at the same time as temperature increases, putting this shrinkage at early stages similar to a creep process. A more useful effort would be to try to match these curves with the eventual microstructures. It should also be mentioned here that an absolute shrinkage value cannot be quoted here as the shrinkage curves are plotted only above 1100 °C and also because the load is applied on loose powder thus shrinkage also includes the effect of re-arrangement of initially loose powder under load. These values can only be effectively used for a comparative purpose as all samples were treated under same conditions.

Figures 4, 5, and 6 give us the sintering/shrinkage curves for SiC(B), SiC(S) and SiC(Mu) samples respectively. A constant pressure of 20 MPa is applied on the graphite mould after the sample reaches 1050 °C. It can be seen on each curve that a systematic re-arrangement and thermal expansion is observed just after this load is applied for the first half hour, this is basically the compacting of the loose powder as well as normal thermal expansion after
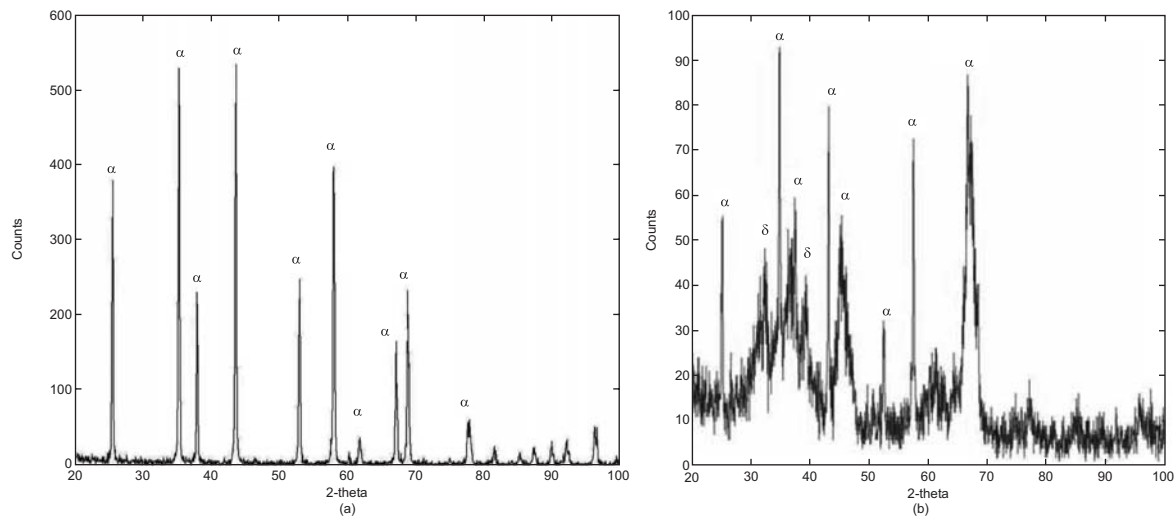
Fig. 2. (a) XRD spectra of Al_2O_3 (Baikalox) and (b) XRD spectra of AlN (Sol Gel)

Table 2. Batch compositions and relative treatment being carried out on the samples

No	Sample		Composition	Temperature ^oC	Time (min)
SC1	SiC (B)	Pressurless sintering	SiC 80 wt%+Al_2O_3 12wt %+Y_2O_3 8wt%	1900	30
SC2	SiC (S)		SiC 80 wt%+Al_2O_3 12wt %+Y_2O_3 8wt%	1900	30
SC3	SiC (M)		SiC+Y_2O_3 2wt%+Mullite 4wt%	1900	30
SC 4	SiC (B)	Hot pressing	SiC 80 wt%+Al_2O_3 12wt %+Y_2O_3 8wt%	1830	180
SC 5	SiC (S)		SiC 80 wt%+Al_2O_3 12wt %+Y_2O_3 8wt%	1830	180
SC 6	SiC (M)		SiC+Y_2O_3 2wt%+Mullite 4wt%	1830	180
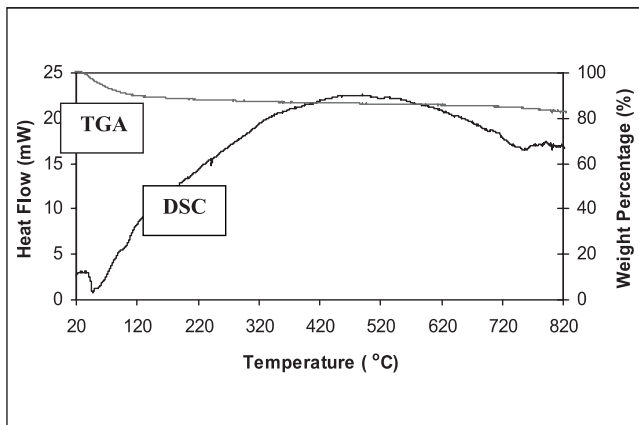
Fig. 3. Simultaneous Thermal Analysis of alumina (Sol Gel)

re-arrangement typically observed during hotpressing before the actual sintering starts.

After a further detailed look on the shrinkage behavior of the three samples we can separate the two SiC(B) and SiC(S) from the third sample SiC(Mu) containing mullite. A small peak due to change in slope of the curve is observed in the first two cases, for a very short period of time, after about 40 minutes. This creep effect can be attributed to a low melting phase. This has been reported[17] that silicon, if present or produced through a reaction at these temperatures, can be responsible for such a behavior.

The SEM images of samples sintered under ambient pressure and argon atmosphere as well as samples hotpressed under 20 MPa are shown in Figures 7 to 12. The following important observations can be considered after looking at these images

- Apart from the sample containing mullite, sintered under ambient conditions, all samples possess a dense microstructure, depicting that the sintering in these cases has reached its final stages.
- The hotpressed samples SiC(B) and SiC(S) have a better distribution of the secondary phase compared to the same samples sintered under ambient conditions. This underlines a liquid phase migration along grain boundaries when no external pressure is applied.
- The sample containing mullite, where the additives concentration is much lower, doesn't achieve full densification unless external pressure is applied.
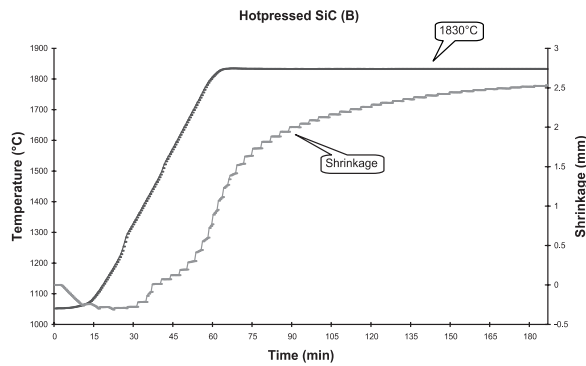
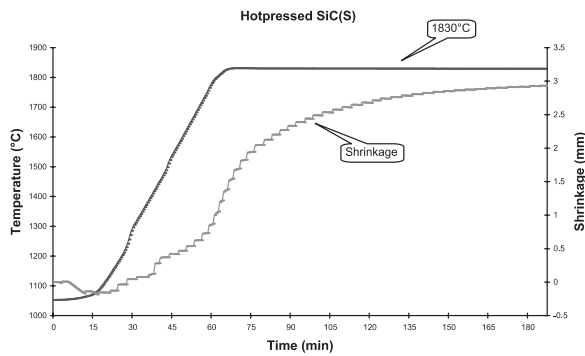**Fig. 4.** Heating cycle and shrinkage curve for SiC(B)

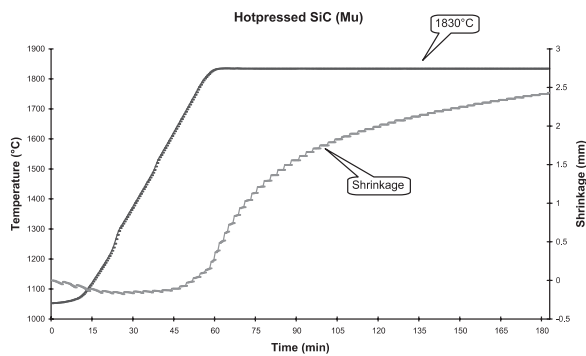**Fig. 5.** Heating cycle and shrinkage curve for SiC(S)

Fig. 6. Heating cycle and shrinkage curve for SiC(Mu)
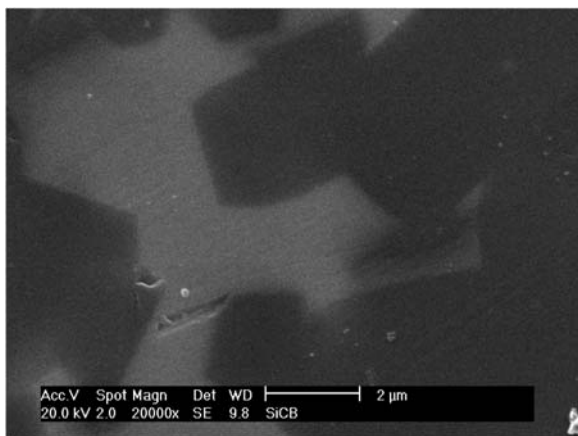

Fig. 7. SEM image of SiC(B) sample at 20000x, sintered under pressureless conditions. The image is focused at a region where secondary phase is visible
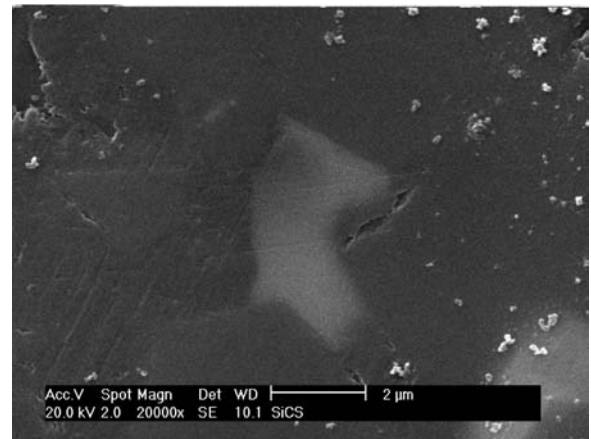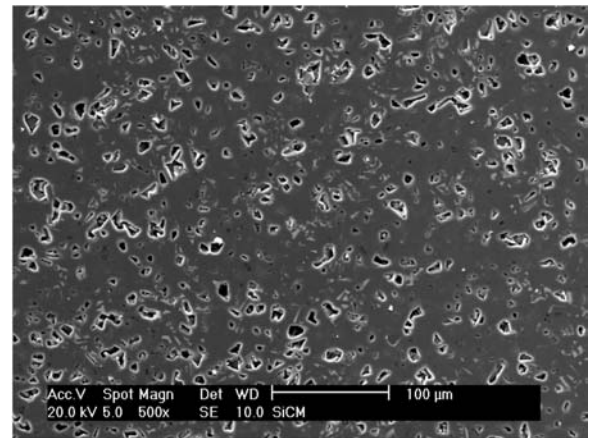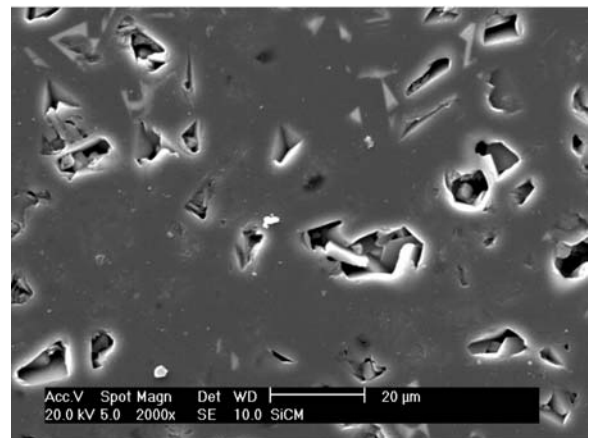

Fig. 8. SEM image of SiC(S) sample at 20000x, sintered under pressureless conditions. White regions show the presence of a secondary liquid phase
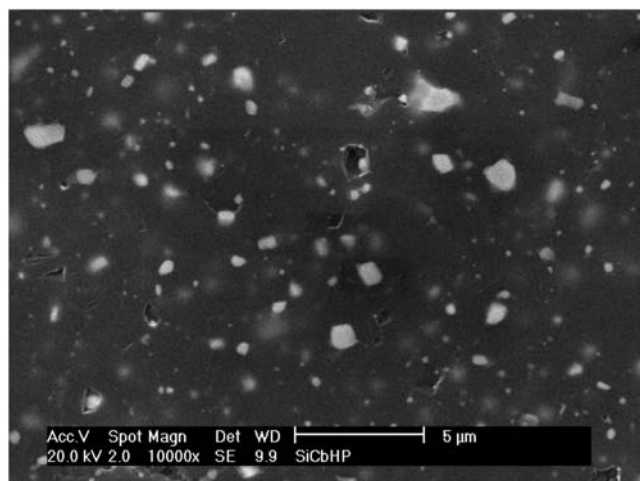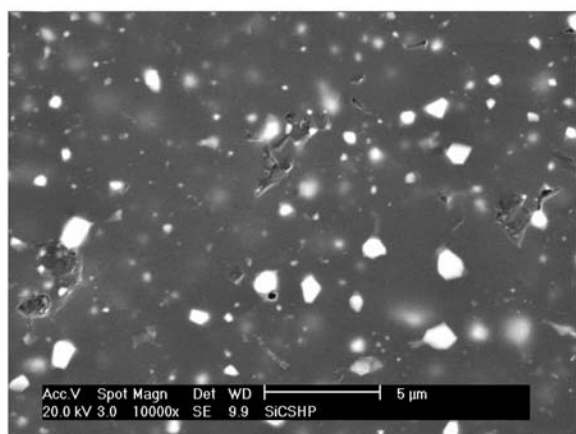

(a)

(b)

Fig. 9. SEM images of SiC(Mu) at 500x (a) and 2000x (b), sintered under pressureless conditions. Evenly dispersed pores are visible in both images

Fig. 10. SEM image of SiC(B) sample at 10000x, hotpressed under 20 MPa. White regions showing the presence of a secondary liquid phase are more evenly distributed in this case

Fig. 11. SEM image of SiC(S) sample at 10000x, hotpressed under 20 MPa. The microstructure is practically the same as shown in Figure 9
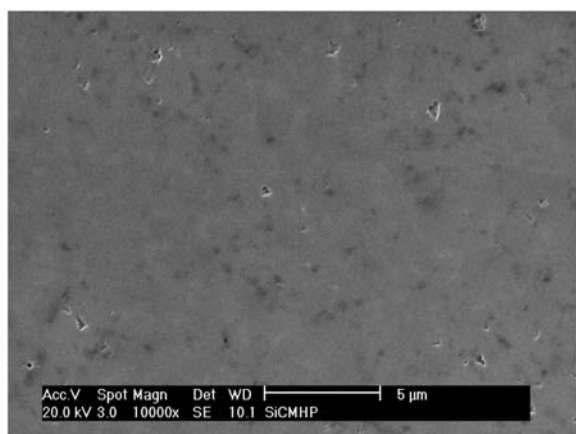
Fig. 12. SEM image of SiC(Mu) sample at 10000x, hotpressed under 20 MPa. Very small quantities of secondary phase is visible, but no porosity

Discussion and conclusion

Silicon carbide was sintered in the presence of alumina and yittria at 1900ºC under pressureless conditions and with yittria and mullite at 1830ºC under 20 MPa pressure. The sintering cycles of hotpressed samples were also coupled with the shrinkage/creep curves which gave a useful insight of the sintering behavior. The microstructures were studied under SEM at high resolutions.

The sintering curves of hotpressed samples manifest a shrinkage/creep behavior at low temperature (1130ºC) for samples having large concentrations of alumina and yittria (SiC(B) and SiC(S) samples). This may be attributed either to the presence of free silicon, or a semi liquid eutectic which creeps under 20 MPa pressure at this temperature. The phenomenon is nevertheless short living as the normal shrinkage starts afterwards. This does not exist in the SiC(Mu). The reason for a much uniform shrinkage during hotpressing in SiC(Mu) is related to both, absence of free alumina and much lesser amount of secondary phase produced as a result of lower quantity of additives.

The sintering carried out resulted in fully dense ceramic at 1900ºC under ambient conditions. The liquid phase thus produced not only densifies the structure but also grows in size and migrates along SiC grain boundaries thus creating relatively larger zones of amorphous secondary phase. This may help in improving the properties at low temperature but the creep properties of such a material would be low.

Samples hotpressed with similar composition (alumina and yittria) also densified to their maximum density but in this case the second phase distribution was relatively evenly dispersed compared to the one obtained in pressureless sintered samples. This is understandable knowing that high pressure applied during sintering fixed the secondary phase at the triple points, not allowing it to migrate along grain boundaries.

The microstructure of SiC(Mu) sintered with and without pressure does show an important difference of densification as apparent from the presence of a large number of small size pores in the pressureless sintered sample (Figure 9). It is so concluded that the amount of secondary phase is not enough to be able to sinter it without applying pressure. The pore structure is very angular but still showing small amount of evaporation at some places, may be due to the fact that sintering temperature of 1900ºC is achieved in this case before densification is completed. Under pressure, the process of diffusion coupled with creep of semi-solid second phase gives a much improved dense microstructure. High temperature creep behavior of such a sintered sample can be anticipated to be much higher than the previous samples.

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