Composites Obtained from Alumina and Polymer Derived Ceramic

Glauson A.F. Machado[1,a], Rosa M. Rocha[2,b] and Ana H.A. Bressiani[1,c]

[1]Instituto de Pesquisas Energéticas e Nucleares- IPEN- Av.Prof. Lineu Prestes, 2242, 05508-000, São Paulo- SP, Brazil

[2]Instituto de Aeronáutica e Espaço- IAE-Praça Marechal do ar Eduardo Gomes, 50 12228-904, São José dos Campos- SP, Brazil

[a]gmachado@ipen.br, [b]rosa.rocha11@gmail.com, [c]abressia@ipen.br

Abstract. Alumina-mullite composites with low shrinkage can be made by reaction bond using mixtures of alumina, aluminum and silicon carbide. In this work, an alternative route is used to produce alumina composites with low shrinkage. Here alumina samples containing additions of 10 and 20 wt% of a preceramic polymer were warm-pressed and treated in the range of 900 -1500°C to produce alumina based composites. The obtained composites were analyzed by linear shrinkage and compared to pure alumina samples sintered at the same temperature range. It were also evaluated the density variation and crystalline phases formed during heat treatment of alumina composites. Results showed that alumina-silicon oxycarbide and alumina-mullite composites were obtained with lower shrinkage than pure alumina samples.

Introduction

Polymers are broadly used in shaping ceramic parts in process involving cast (e.g. tape casting) or plastic forming (e.g. extrusion, injection molding) [1-2]. Warm pressing or plastic forming is traditionally used as the method of forming ceramic green bodies, using mixtures of ceramic powder (e.g., alumina) and thermoplastic or thermosetting organic polymers. After decreasing the temperature the polymer hardens and provides the green body with desired handling strength. Usually the polymer is not intended as a permanent additive and is completely removed (burnt out) before sintering. On the other hand the discovery of preceramic polymers, i.e., polymers which upon suitable thermal treatment (pyrolysis) convert to ceramics with high yield, opened new possibilities for warm pressing. These polymers can provide advantages as: lower temperatures relating to conventional processes, possibility of control of composition through molecular design and use of near-net shape technology [3]. In this case the warm pressing is used as a means of shaping the preceramic polymer by heating them to temperatures where particles of the polymer can be deformed by viscous flow, or above their melting point, and pressing them to a die of desired geometry [4-5]. After cooling down to ambient temperature, the polymer green body obtained is converted to ceramic by pyrolysis in controlled atmosphere. The method has been successfully applied for preceramic polymers precursors of silicon nitride and silicon-boron carbonitride [4-5]. Commercially available polysiloxanes and polysilsesquioxanes can be used for such application.

These polymers when pyrolysed above 600°C under inert atmosphere leads to silicon oxycarbide glasses (SiOC) [6⁻[8]. SiOC is a class of amorphous materials with a similar silica glass structure, in which oxygen atoms are partially replaced by tetracoordinated carbon atoms. The presence of carbon atoms covalently bound to the silicon atoms creates a more interconnected structure with better strength and chemical stability than conventional silica. This material can potentially be implemented in several technological applications that require high temperatures [9]. The SiOC glass heat treated up to 1200°C is completely amorphous to x-ray. At temperatures greater than 1200°C the amorphous phase starts to decompose into SiC nanocrystals and β-cristobalite [10].

In the present work a polysilsesquioxane is added to alumina in two different proportions. Alumina-polymer samples were warm pressed for shaping and polymer crosslinking. Shaped green compacts obtained were heat treated in a range 900-1500°C under inert atmosphere. The aim of the

study is to obtain near-net shape alumina based composites controlling the shrinkage by varying the polymer amount added to alumina. It was also compared the shrinkage behavior of alumina samples produced by conventional compacting and sintering method to warm-pressed alumina based composites produced by pyrolysis and heat treatments. Beyond linear dimensional changes, alumina composites were analyzed to determine density variation, structural changes and phases formed during pyrolysis and heat treatments.

Experimental

The raw materials used in this experiment were: i) α-alumina A-16 SG, fabricated by Alcoa; ii) commercially available poly(methylsilsesquixane), MK powder resin produced by Wacker Chemie. Two compositions were produced, containing 10 and 20 wt% of polymer added to alumina.

To manufacturing the composites the polymer was dissolved in isopropanol, α-alumina powder was gradually added to the solution and stirred vigorously. The obtained suspension was dried at 60°C/24h in a muffle furnace. Powders obtained after drying were crushed in a mortar and passed through 100 Mesh sieve. The powders were uniaxially die pressed in a 25 mm diameter cylindrical matrix at a pressure of 43 MPa and kept at 200°C/2h to crosslinking the polymer. Alumina samples with no polymer addition were also die pressed in the same conditions except the crosslinking stage. Alumina samples were sintered at 900, 1100, 1300 and 1500°C/1h, in a tube furnace (Lindberg blue) with heating rate of 5°C/min. Treatments were carried out in N_2 atmosphere. Alumina-polymer samples were pyrolyzed at 900°C and after heat treated at 1100, 1300 and 1500°C. Pyrolysis and heat treatment were done at the same conditions used for alumina samples with no polymer addition. Samples were coded according to polymer mass percentage and heat treatment temperature. For example: A10-1300 means alumina with 10% wt of polymer, heat treated at 1300°C.

Fourier transformed infrared (FTIR) analysis were carried out in the range 4000-400 cm^{-1} to evaluate structural changes in the alumina-polymer samples after each heat treatment stage. Samples were powdered and mixed with potassium bromide and shaped as discs. X ray diffraction was used to identify crystalline phases formed after heat treatments, using CuKα radiation (Rigaku-Multiflex). Dilatometric analysis (Netzsch 402E) was performed with a heating rate of 5°C/min until 1600°C/30min, under N_2 atmosphere. Bulk densities and apparent porosity were measured by Archimedes principle using distilled water as fluid. It was also performed scanning electron microscope images (Jeol JSM 6701F) from fractured surfaces of A0, A10 and A20 samples heat treated at 1500°C.

Results and Discussion

Infrared spectroscopy (FTIR). The infrared spectra of A10 and A20 samples heat treated at different temperatures are shown in Fig.1 a and b respectively. The same absorption bands are present for both samples. In a 1500 - 400cm^{-1} range, Si –O absorption bands can be observed. Absorption at ~1065 cm^{-1} is related to asymmetric vibrations of Si - O - C bonds while those at ~454 and ~608 cm^{-1} can be assigned to Si - O – Si symmetric vibrations. A vibration band related to AlO_4 tetrahedral units of alumina is also present ~ 643 cm^{-1} [11].

It can be observed that as the heat treatment temperature increases these absorption bands become less intense. The Si - O - C bonds indicate the presence of amorphous SiOC formed during polymer pyrolysis [11]. It is observed that as the heat treatment temperature increases, these absorption bands become less intense which indicates the decomposition of the amorphous phase [8]. Decomposition of SiOC results in SiC and SiO_2 crystalline phases. Silica formation is confirmed in samples heat treated at 1500°C by a Si – O absorption band ~1086cm^{-1} characteristic of SiO_4 units [12]. Absorption bands of stretching and bending vibrations of OH groups are present at ~3436 and 1635 cm^{-1}, respectively. It probably can be related to incomplete crosslinking. An absorption band ~2363 cm^{-1} related to Si – H bonds is present and decreases its intensity as the heat

treatment temperature increases. It means that hydrogen atoms are still present in the SiOC structure, not having been fully eliminated during pyrolysis [13].
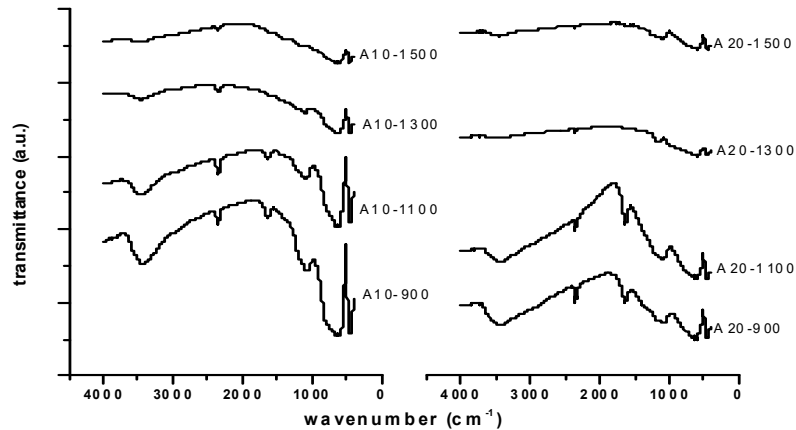

Fig. 1. Infrared spectra of A10 and A20 samples heat treated at different temperatures.

X-ray diffraction analysis. Fig.2a and b show the X-ray diffractograms taken from A10 and A-20 samples, respectively, after heat treatment to the indicated temperatures. Both samples present the same crystalline phases at all tested temperatures. Until 1100°C, the unique crystalline phase detected is alumina, indicating that SiOC phase, evidenced by FTIR, is still amorphous. At 1300°C, cristobalite peak is detected. It means that amorphous SiOC phase has started to decompose into cristobalite and SiC nanocrystals [8]. Mullite and alumina are the crystalline phases present at 1500°C. Mullite formation takes place by the reactions between alumina and cristobalite [14].
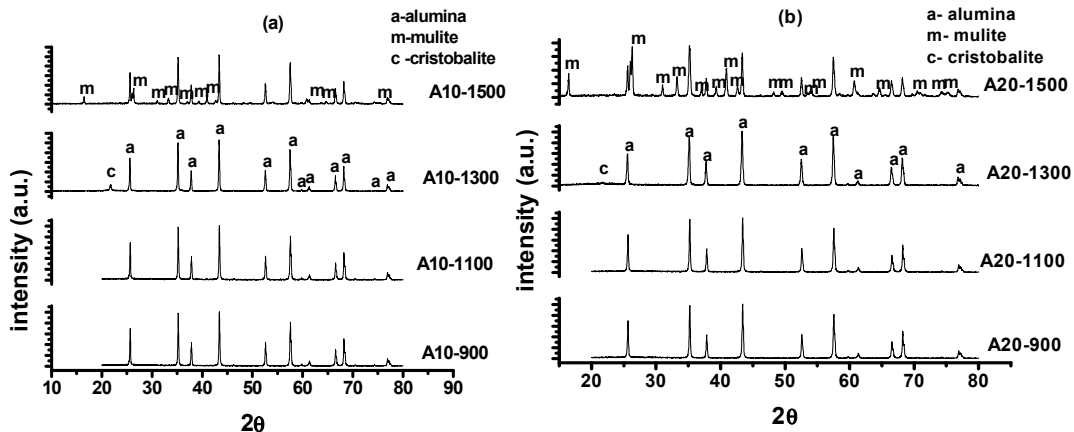

Fig. 2. X-Ray diffractograms from A10 (a) and A20 (b) samples heat treated at different temperatures.

Dilatometric studies. Fig.3a and b show dilatometric and derivative curves of A0, A10- and A20 samples, respectively. It is observed from Fig.3a that A0 sample shrinks ~16% and densification starts around 1000°C. From derivative curves (Fig.3b) it can be observed that A0 maximum shrinkage rate is between 1350 -1450°C and occurs in single step; by solid state reaction [15]. A10 sample starts to densify ~1200°C and shrinks ~13,5% (Fig 3a). Two peaks of higher rates between1200 -1300°C and 1400 -1500°C are observed (Fig.3b). Studies on SiOC obtained by sol-gel process show that its viscosity decreases at the temperature range of the first peak, which can cause shrinkage by viscous flow [16]. The second peak can be caused by the reaction between alumina and crystalline silica: XRD analysis detected cristobalita present at 1300°C and in accordance with experiments on reaction sintering of Al_2O_3 with different silica sources, it is reported that alumina reacts with cristobalite forming a metastable alumino-silicate viscous phase. According to this, the second step of shrinkage probably is also caused by viscous flow [17]. It is observed from Fig.3a that A20 sample presents expansion at temperatures lower than 600°C, shrinkage starts ~700°C and the final shrinkage obtained is ~8%. SiOC glasses obtained from sol-

gel process as well as silicone resin present expansion from 40°C up to ~800°C [16]. It is more noticeable in A20 sample because of its greater amount of polymer added. From Fig.3b it can be seen that A20 sample presents three peaks of higher rates in the following temperature ranges: 600-800°C; 1200-1300°C and 1400-1500°C. The first can be attributed to the beginning of retraction after initial expansion. The two other peaks can be assigned to the same causes of the A10 sample.
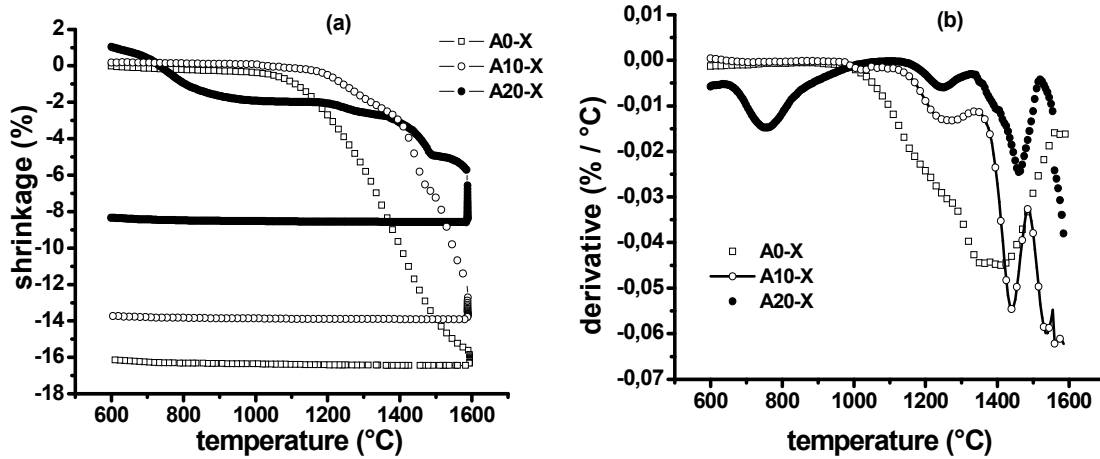
Fig. 3. Dilatometric curves (a) and derivatives (b) of A0, A10 and A20 samples.

Density analysis. Table 1 shows the density and apparent porosity values of A0, A10 and A20 samples heat treated at different temperatures. It is observed that until 1100°C A0 samples presents no significant density increase and apparent porosity values almost not change. Samples heat treated in the1300-1500°C temperature range show increase in density values and decreased porosity. Dilatometric analysis shows that from 1100°C densification is more intense, although theoretical density value of 3,98g/cm³ is not reached even for samples heat treated at 1500°C. For A10 sample, density values do not change in the 900-1100°C range as well as porosity and it is observed by its dilatometric curve that no densification occurs. From 1100 to 1300°C it is observed an increase in density values and decrease in porosity. This behavior is also observed from 1300 until 1500°C. The density increase from 1200°C is confirmed by dilatometric analysis. It is possible that alumina densification has the greater contribution for density increasing. A20 samples present a decrease in density values and increased porosity in the range 900-1100°C although its dilatometric curve shows no variation. It can occur because SiOC is an unstable compound. As the heat treatment temperatures are higher, a rearrangement occurs between Si-C and Si-O bonds in its structure which can cause these variations [18]. From 1100 until 1300°C density values reach its higher values and it is observed an intense porosity decrease. From 1300°C until 1500°C, density values decreases although the amount of porosity not changes. It can be related to lower density of mullite which starts to form ~1500°C.

Table 1. Density and apparent porosity values of A0, A10 and A20 heat treated at different temperatures.

Temperature [°C]	A0		A10		A20	
	Density [g/cm³]	Apparent porosity [%]	Density [g/cm³]	Apparent porosity [%]	Density [g/cm³]	Apparent porosity [%]
900	2,15 ± 0,05	44,0 ± 2,0	2,39 ± 0,02	32,8 ± 0,4	2,85 ± 0,01	7,3 ± 0,4
1100	2,18 ± 0,06	43,5 ± 0,7	2,41 ± 0,01	33,0 ± 1,0	2,79 ± 0,01	15,0 ± 1,0
1300	2,60 ± 0,06	33,0 ± 1,0	2,78 ± 0,02	22,8 ± 0,8	2,93 ± 0,02	4,0 ± 1,0
1500	3,50 ± 0,04	10,5 ± 0,7	3,15 ± 0,02	9,2 ± 0,9	2,95 ± 0,01	1,8 ± 0,9

Microstructural analysis. Fig. 4 shows scanning electron microscope images of fractured surfaces from A0, A10 and A20 samples heat treated at 1500°C, respectively (a), (b) and (c). When compared A0 and A10 samples concerning to porosity, it can be seen that both present porosity. Although they have the same porosity percentage, A10 sample is less dense (Tab.1) and show lower

shrinkage (Fig3a). It can be related to the polymer addition [19]. On the other hand, the micrograph of A20 sample presents less porosity than A0 sample. Here the polymer addition was high enough to reduce porosity although the density values are even lower than A10 sample (Tab.1).
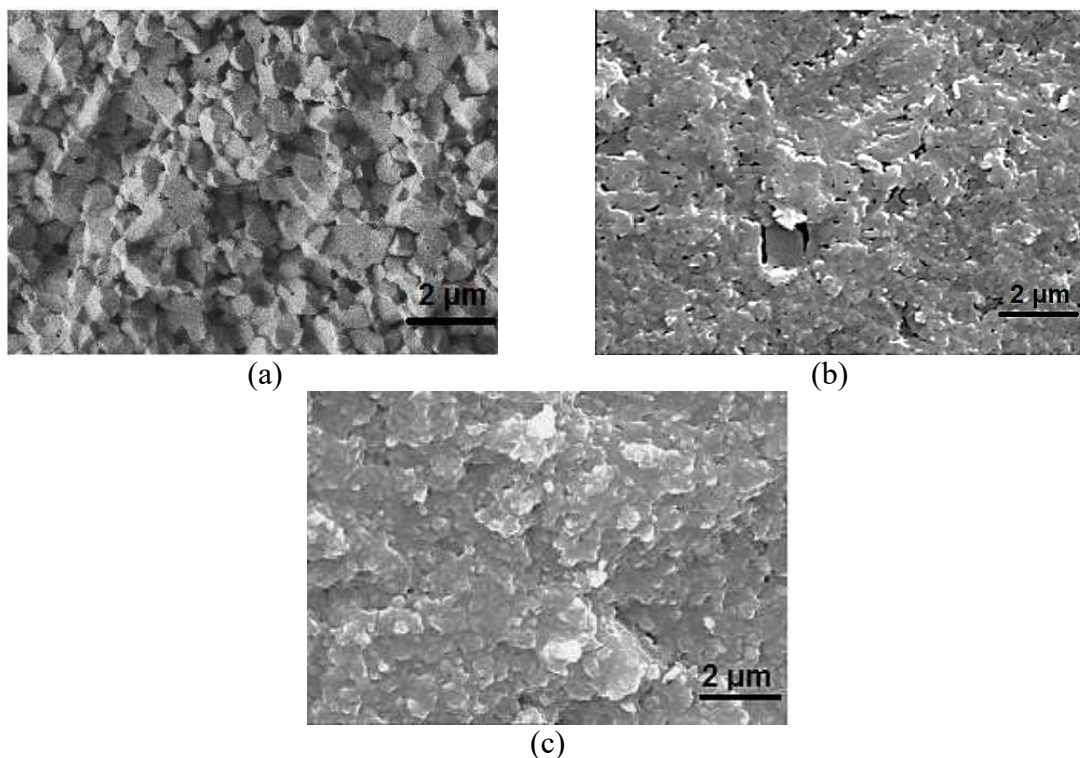

(a)   (b)

(c)

Fig. 4. Scanning electron microscope images from fractured surface of A0 (a), A10 (b) and A20 (c) samples heat treated at 1500°C.

Conclusions

For both compositions, containing 10 and 20 %wt of polymer, alumina-SiOC composites were obtained in the range of 900-1100°C. Cristobalite was identified in samples heat treated at 1300°C and alumina-mullite composite was formed at 1500°C. The polymer addition causes an increase in density values and decreasing of porosity percentage until 1300°C. It is also observed that shrinkage is reduced as the polymer amount is higher. It can make possible to obtain near-net shape components by controlling of shrinkage as function of polymer amount.

References

[1]   D.W. Richerson: *Modern Ceramic Engineering*. (Marcell Drekker New York, 1992).

[2]   R.M. Rocha, M. Scheffler, J.C. Bressiani, A.H.A. Bressiani: Cerâmica Vol. 51 (2005), p. 42.

[3]   P. Colombo, G. Mera, R. Riedel, G.D. Soraru: J. am. Cer. Soc. Vol. 93 (2010), p. 1805.

[4]   R. Haug, M. Weinmann, J. Bill, F. Aldinger: J. Eur. Ceram. Soc. Vol. 19 (1) (1999), p. 1.

[5]   C. Konetschny, D. Galusek, S. Reschke, C. Fasel, R. Riedel: J. Eur. Ceram. Soc. Vol. 19 (16) (1999), p. 2789.

[6]   C.G. Pantano, A. K. Singh, H. X. Zang: J. Am. Cer. Vol. 71 (1987), p. 386.

[7]   G.D. Soraru: Sol-gel Sci. Tech. Vol. 2 (1994), p. 843.

[8]   H. Brequel, J.Parmentier, G.D. Soraru, L. Schiffini, S. Enzo: NanoStructured Materials Vol. 11 (1999), p. 721.

[9]   M.A. Schiavon, J.L. Ferrari, M. Hojamberdiev, I.V.P Yoshida: Quim. Nova Vol. 387 (2015), p. 972.

[10] F.I. Hurwitz, P. Heimann, S.C. Farmer: J. Mat. Sci. Vol. 28 (1993), p. 6622.

[11] D. Chomel, P. Dempsey, J. D. Latournerie, Hourlier-Bahloul, U.A. Jayasoorya: Chem. Mater. Vol. 17 (2005), p. 4468.

[12] P. Coloban: J. Mater. Sci. 24 (1989), p. 3011.

[13] M. Monthioux, O. Delvedier: J. Eur. Cer. Soc. Vol. 16 (1996), p. 721.

[14] H. Schneider, S. Komarneni: *Mullite*. (Willey-VHC Weinhein, 2005).

[15] E. Dörre, H. Hübner: *Alumina Processing and Properties*. (Springer-Verlag New York, 1984).

[16] T. Rouxel, S. Gian-Domenico, J. Vicens: J. Am. Ceram. Soc. Vol. 84 (5) (2001), p. 1052.

[17] H.J. Kleebe, F. Siegelin, T. Straubinger, G. Ziegler: J. Eur. Cer. Soc. Vol. 21 (2001), p. 2521.

[18] J. Brus, F. Kolar, V. Machovitz, J. Svitlová: J. Non-Cryst. Solids Vol. 89 (2001), p. 62.

[19] A.L.E. Godoy, J.C. Bressiani, A.H.A. Bressiani: Cerâmica Vol. 56 (2010), p. 97.