3Y-TZP/Si$_2$N$_2$O COMPOSITE OBTAINED BY PRESSURELESS SINTERING

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Abstract: Y-TZP presents excellent properties at room temperature but these properties decrease as the temperature increases. This paper studies the behavior $20_{vol}\%$Si$_3$N$_4$-SiC when added in YTZP matrix and heated under no pressure system. Al$_2$O$_3$ and Y$_2$O$_3$ were used to maintain the stability of the matrix and as sintering aids. The addition of Si$_3$N$_4$ and SiC in a Y-TZP matrix leads to formation of silicon oxynitride and it increases the mechanical properties like toughness and hardness. The mixture was milled and molded by CIP. Samples were heated at 1500ºC, 1600ºC and 1700ºC for 2h without pressure under atmospheric conditions in bed-powders of Si$_3$N$_4$. Samples were characterized by XRD. Density, hardness, toughness, bending strength were measured. The structure of the material was observed in SEM/EPMA to verify the distribution of the materials in the composite. The formation of Si$_2$N$_2$O was observed in the sintered material and it showed an increment of both hardness and toughness as temperature increases. The samples presented considerable resistance of oxidation at 1000ºC.

Introduction

The addition of some ceramic materials, as silicon carbide and silicon nitride, in a Y-TZP matrix has been extensively studied because Y-TZP has excellent properties in a room temperature but they decrease as the temperature increases because high temperature acts negatively over the stress induced transformation toughening in the matrix (1, 2, 3). The addition of Si$_3$N$_4$ and SiC in a Y-TZP matrix is very interesting because it increases the mechanical properties like toughness and hardness (4). Moreover, both Si$_3$N$_4$ and SiC exhibit very interesting characteristics owing to thermal stability under high temperatures and it can shows some advantages like mechanical modulus improvement because α-β Si$_3$N$_4$ transformation. The elongated morphology permits to obtain better contact between these materials surface and the matrix(5). There is also the formation of Si$_2$N$_2$O as a product from the reaction between Si$_3$N$_4$ and SiO$_2$ present in the sample. It is formed a liquid in a second phase because all constituents react amongst themselves and this liquid promotes densification and formation of Si$_2$N$_2$O (6). Y$_2$O$_3$ and Al$_2$O$_3$ additions form a ternary eutectic with SiO$_2$ at about 1300ºC and this ternary silicate which contains variable amounts of nitrogen is the basis for liquid phase sintering in materials of the Si-Al-O-N system. This ternary eutectic presents good densification at 1600-1700ºC (7). The characteristics of this material are so good as Si$_3$N$_4$ to apply in structural ceramic materials such as cutting tools, wear parts and others (8). Composites made from Si$_3$N$_4$ and Si$_2$N$_2$O exhibit high toughness, high thermal shock resistance, low rate of oxidation and high strength even after relative oxidation. Besides Si$_2$N$_2$O has not been discussed so much, the term "Silicon Oxynitride" is used by some researchers to describe several combinations of silicon, oxygen and nitrogen (9, 10). Some of them suggest that Si$_2$N$_2$O corresponds to a solid solution of SiO$_2$ and Si$_3$N$_4$, although ceramists understand it as a crystalline ceramic produced by oxidation of the system SiO$_2$/Si$_3$N$_4$ (11). Certainly the mechanical properties increment is limited by several difficulties which have appeared during processing and heating of these high covalent materials (6). Pressureless sintering seems to be an interesting way to obtain this compound due to

low cost, high volume of production and possibility to get complex shapes. This paper studies the behavior of the Si_2N_2O in a YTZP matrix, produced by reaction of Si_3N_4-SiC under different conditions of processing and sintering without pressure.

II. Materials and Method

To develop this research it were used YTZP (3mol%Y_2O_3, 0,42μm particles average, Daiichi Kigen Kagaku Co., Japan); α-Si_3N_4 (0,58μm particles average, Shin-Etsu Co., Japan); β-SiC (0,28μm particles average, Ebiden, Japan). As sintering additives were used α-Al_2O_3 (99,99%, TaiMei Co., Japan) and Y_2O_3 (99,9%, Shin-Etsu Co., Japan). Si_3N_4 was mixed with 20_{vol}%SiC and after added in a proportion of 20_{vol}% in a YTZP matrix with 4_{wt}% Al_2O_3 and 1_{wt}% Y_2O_3 as a sintering aids. Materials were milled in a Zirconia ball-mill for 2 hours under ethanol solution. The mix was dried, passed through a 100 meshes sieve and cold isostatically pressed (CIP) under a pressure of 200MPa. Samples were sintered at 1500ºC, 1600º and 1700ºC for 2 hours. Sintering was lead under atmospheric conditions, using a bed-powder of Si_3N_4 involving all samples to avoid oxidation. Samples were characterized by XRD (Cu-α radiation) and investigated by Scanning Electron Microscopy/Electron Probe Microscopy Analyzer - SEM/EPMA - to observe the structure and the kind of intergranular/intragranular phase. Polished surface were observed with a SEM after chemical etching with HF for 2 hours. Mechanical properties were studied: hardness were measured by a Vickers indentor using a load of 2.000g for 10s. Toughness was calculated by indentation microfracture method (JIS - R1607). Bulk density was measured using picnometer's method. Four point flexural strength was measured at room temperature using bars (3x4x40)mm. A span of 30mm was used with a crosshead of 0.5mm/min. The oxidation experiments were conducted in air at 1000ºC for 2, 4 and 8 hours. The weight variations of the specimens were measured after cooling to room temperature using a microbalance.

III. Results and Discussion

XRD

Using a bed-powder as a support, α-Si_3N_4, SiC and Si_3N_4-20_{vol}%SiC were heated, separately, at 1700ºC in a bed powder of Si_3N_4 with the addition of Al_2O_3 and Y_2O_3 (Figure 1). Figure 1b presents a α-Si_3N_4 - β-Si_3N_4 transformation that occurs via solution-precipitation mechanism where particles slowly dissolves in the liquid silicate at high temperatures and it precipitates as β-Si_3N_4 after saturation. As a result of this precipitation there is the formation of a secondary phase, intergranular, retained during cooling. The liquid is formed because metallic oxides combine with the coating surface of silica presents in the material and form a low melting point of Si-O-N liquid at high temperatures. During cooling there is a formation of a glass bonding of β-Si_3N_4 and, depending on the concentration of SiO_2, simultaneous formation of Si_2N_2O. Figure 1c shows the XRD of a mixture of Si_3N_4-20_{vol}%SiC heated at 1700ºC in bed-powder.
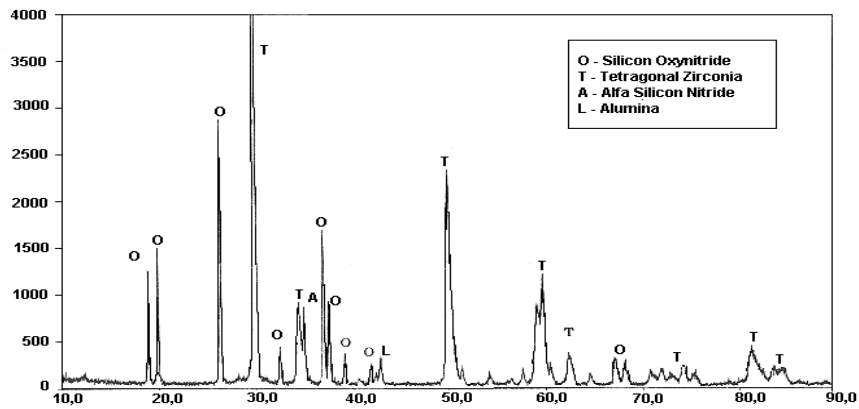
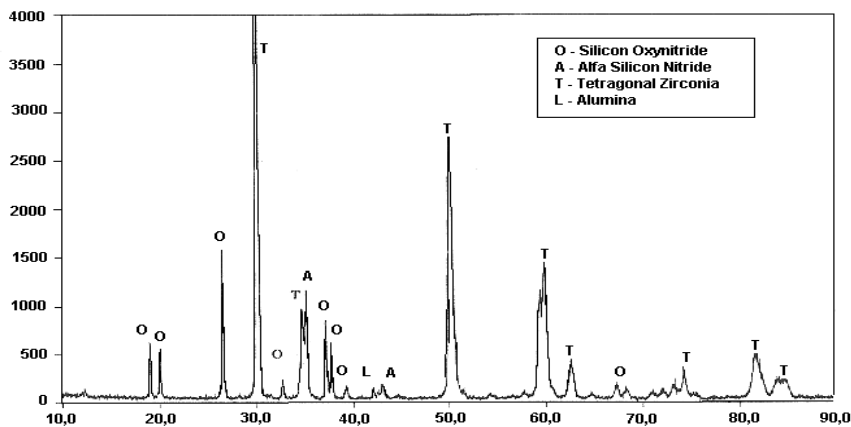**Figure 1** – XRD of materials heated at 1700° C in a bed-powder:
a) SiC; b) Si_3N_4 and c) Si_3N_4-20_{vol}%SiC.

It is possible to verify the formation of Si_2N_2O according to:

(1) $SiC + O_2 \rightarrow SiO + CO$

(2) $Si_3N_4 + 3SiO + N_2 \rightarrow 3Si_2N_2O$

(3) $2Si_3N_4 + \frac{1}{2}O_2 \rightarrow 2Si_2N_2O$

(4) $Si_3N_4 + SiO_2 \rightarrow 2Si_2N_2O$

Figure 2 permits to observe the behavior of composite when sintering temperature increases. In the XRD for 1500ºC (figure 2a) there is a presence of β-Si_3N_4, product of the transformation observed during sintering of Si_3N_4 ceramics and that occurs after solution of fine grains in a liquid formed with the sintering aids and posterior precipitation as nuclei (12). At 1500ºC can be observed also the formation of Si_2N_2O that increases as the sintering temperature increases, as observed for 1600ºC and 1700ºC (figure 2b and 2c). As temperature increases also the fluidity of the glass silicate increases. Then, the mobility of oxygen and others elements is faster and enhances the reaction to produce Si_2N_2O formation. Si_2ON_2 is a product of a reaction that occurs in a liquid phase under the presence of a metal oxide, as Y_2O_3 and Al_2O_3 in this case (13, 14, 15).

Figure 2a – XRD of the sample heated at 1500ºC

Figure 2b – XRD of the sample heated at 1600ºC

Figure 2c – XRD of the sample heated at 1700ºC

SEM/EPMA

Observing the samples sintered in different temperatures it is possible to verify a considerable grain growth and a reduction of the secundary intergranular phase. The reduction of the intergranulary phase volume can be explained by Si_2N_2O formation that occurs in the second phase: a Y-Si-Al-O-N glass. During the process Si_3N_4 is dissolved in the liquid and reacts with the SiO_2 from the vitreous net. At 1500ºC, it is possible to verify the β-Si_3N_4 because of its elongated morphology (Figure 3a).
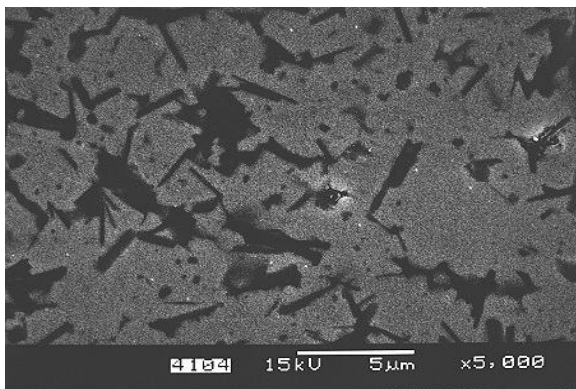
Figure 3a – SEM of the sample heated at 1500ºC
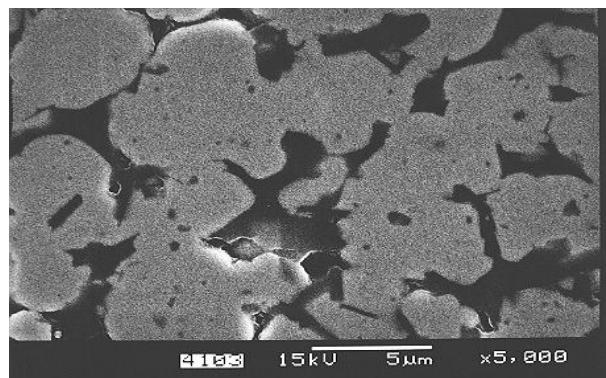
Figure 3b – SEM of the sample heated at 1600ºC
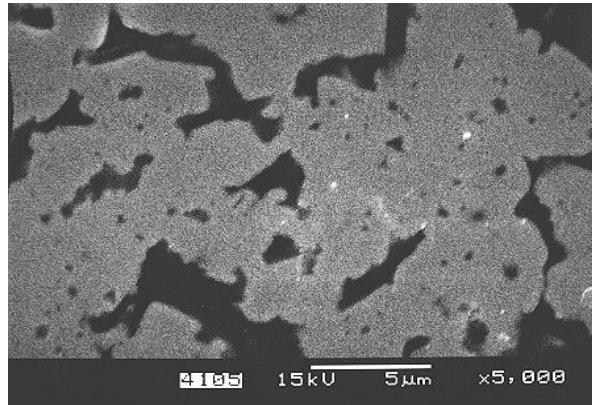
Figure 3c – SEM of the sample heated at 1700ºC

As the formation of SiO_2 was not enough to form Si_2N_2O, the saturation of β-Si_3N_4 leads to its precipitation in the intergranular phase. In the image is verified that elongated β-Si3N4 occurs in the intergranular phase similar a needles but, as the liquid silicate has so heavy elements than Si_3N_4, the images of the intragranular phase are dark due to absorption contrast. Then, as the temperature increases also the formation of Si_2ON_2 increases and, consequently, bigger grain growth and lower volume of vitreous phase (Figure 3b and 3c)(16). Moreover, the grain growth of the matrix surrounding Si_3N_4 remaining grains of the composite shows a character of intragranular composite. According Niihara (17), that incorporation by the matrix increases mechanical properties as toughness, hardness and bending in both room temperature and high temperature. Besides that, the reduction of vitreous phase also promotes a refractory increment. Figure 4 presents a SEM of the sample after etching to verify the zirconia and the silicon oxynitride grain. The grain of silicon oxynitride has a needle aspect.
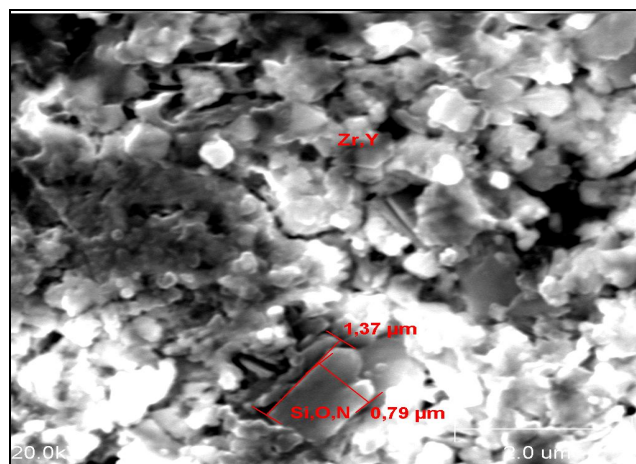

Figure 4 – SEM of the composite sintered at 1700ºC and etched for 2h with HF.

Figure 5 and 6 show a chemical mapping of samples by EPMA that exhibit a high concentration of N_2 in the intergranular phase due to Y-Si-Al-O-N glass formation. This phase is rich in nitrogen. High concentration of each element is represented by the white color. Dark color means absence of the element. Figure 6 presents a large concentration of alumina in the intergranular phase. It is due to Al_2O_3 added and do not reacted to form a liquid phase.
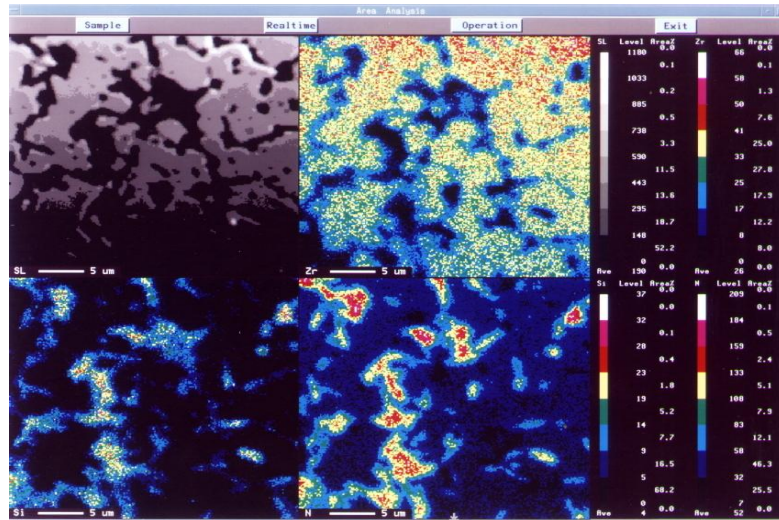
Figure 5 – EPMA of the sample heated at 1600ºC for Zr, Si and N.
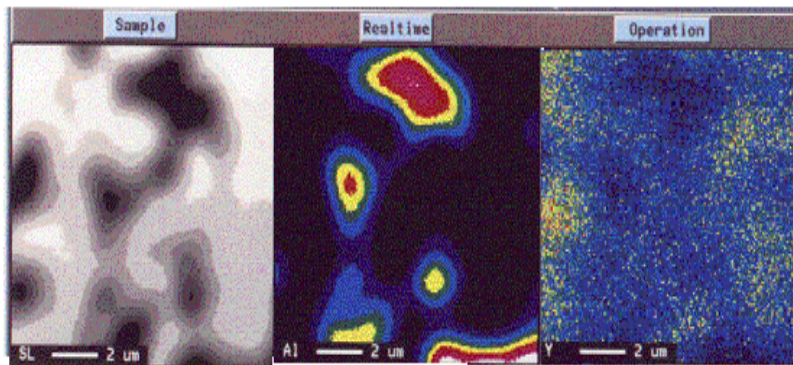

Figure 6 - EPMA of the sample heated at 1600ºC for Al and Y.

Density

Samples were densified about 97% of theoretical density that was calculated based on starting powders (5,26g/cm^3) (Figure 7)**.** The composite presented a green density of 3,41g/cm^3. With the temperature increasing, new phases are formed . The zirconia matrix presented a density of 6,08 g/cm^3 after sintering at 1450ºC for 2 hours.
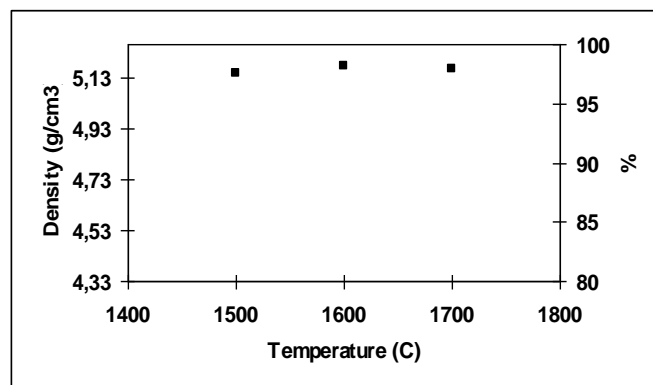

Figure 7 - Density of the samples heated in different temperatures.

Mechanical Properties

As matrix parameters were used the mechanical properties of the same YTZP heated at 1450ºC for 2h. The material presented the follow characteristics: Hardness Vickers = 1350; K_{IC} = 5 MPa/m$^{1/2}$ and Flexural bending = 700MPa.
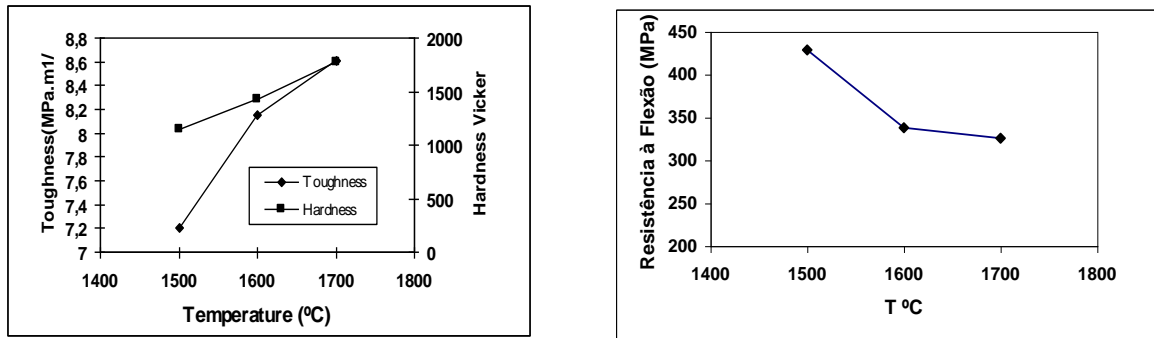
Figure 8 - Mechanical properties at room temperature

Figure 8 shows an improvement for both hardness and toughness when sintering temperature increases, maintaining the stability of YTZP matrix. This increment can be associated to Si_2N_2O formation. As observed in the XRD graphics, there is an increasing in the formation of Si_2N_2O but there is also a higher accomodation of grains in the intergranular phase, producing a low stress. In the case of toughness measurement, the crack propagated transgranularly due to surface interaction and it must be concluded that YTZP and Y-Si-Al-O-N glass phase have a strong interfacial bonding that does not affect the crack propagation. Thus, the presented values are higher than those presented by the matrix. Comparing with the YTZP matrix (700MPa), the low strength can be attributed to the residual glass of the intergranular phase produced by cooling from sintering temperature. The bonding between vitreous phase and matrix grains requires also higher interfacial energy and flexibility. The loss in strength can also be attributed to a residual Y-Si-Al-O-N glass phase rich in nitrogen as verified in EPMA mapping. Sun et al (11) studied such mechanism. Mechanical properties as hardness and toughness increase as nitrogen level present in the phase also increases. That behavior is due to O substitution by N in the coordination system. The S-N bonding is stronger than Si-O because of its covalent character.

Annealing

Samples were annealed at 1000 for 2h, 4h and 8h. XRD did not present any crystalline phase alteration or oxidation of the material. Figure 9 presents a weight variation after annealing.
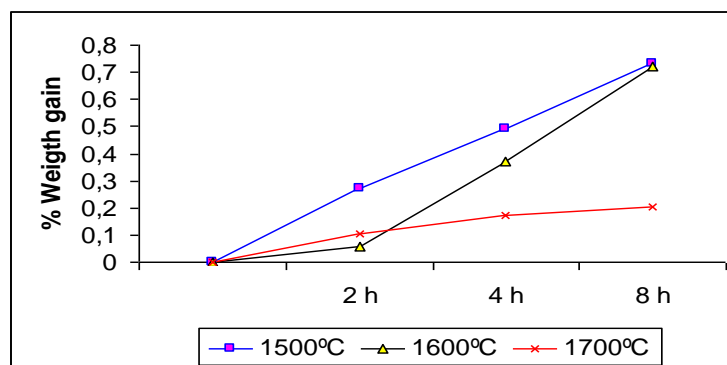
Figure 9 – Weight Gain after annealing at 1000ºC

Samples annealed at 1000ºC presented 0,7% of weight gain. Sample sintered at 1700ºC present the smallest value. It seems evident that oxidation is connected with the formation and increasing of Si_2N_2O. Furthermore, even so Si_3N_4 sintered with a metallic additive produces a continuous

intergranular vitreous phase acting as a diffuse way to transport the ions from the bulk to the surface and vice-versa, the formed Si_2N_2O layer on the surface of the material avoids the O_2 penetration. Then, the material with Si_2N_2O becomes resistant to oxidation.

Conclusions

20_{vol}% Si_3N_4/SiC was added in a YTZP matrix and heated in different temperatures without pressure and using Al_2O_3 and Y_2O_3 as sintering additives. Crystalline phase was investigated and mechanical properties was measured at room temperature. The addition of Silicon Nitride and Silicon Carbide in a Stabilized Zirconia matrix can improve some mechanical properties as hardness, even if heated in atmosphere using bed powder, due to Si_2N_2O formation. Si_2N_2O is a product of the reaction between starting powders since heating in bed-powder has demonstrated to be effective in avoiding the oxidation of the starting materials. The compound is stable when heated at 1000ºC in normal atmosphere. The addition of 1% of Y_2O_3 can lead to matrix stability when heated in high temperatures.

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