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EFFECTS OF DIFFERENT REINFORCING PHASE IN CORDIERITE MATRIX COMPOSITES

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Abstract: *This paper proposes a comparison between the effects of reinforcing cordierite matrix with three different types of reinforcing materials: ZrO_2, TiC and SiC. All samples were made following the same processing steps. The technological process adopted was intended to be easily repeated on an industrial scale and therefore we tried to use methods and equipments that are easily accessible. The volume fraction of the reinforcing phase was set at 15% for all three types of composites. Shaping the samples was done by uniaxial pressing at 40MPa. Sintering was performed for one hour at 1375°C in air - for ZrO_2 addition, and in vacuum – for the reinforcement with TiC and SiC. Current work focuses on the effects on porosity and elastic properties.*
Keywords: *cordierite, particulate reinforcement,*

1. INTRODUCTION

Cordierite is a ceramic material which due to its properties is found in many technical applications, especially in the manufacture of structural materials, refractories, electrical and thermal insulation etc. However, the use of cordierite is limited by its poor mechanical properties. To overcome this obstacle the best solution found is mixing cordierite with powders made from a diverse variety of materials such as diamond [1], mullite ($3Al2O_3$ • $2SiO_2$ and $2Al_2O_3$ • SiO_2) [2], Si_3N_4 [3], ZrO_2 [4], SiC etc. Of the reinforcement materials listed above, probably the most common example is ZrO_2 because it allows the use of two strengthening mechanisms: residual stresses caused by the thermal expansion mismatch and phase transformation mechanism (transformation toughening). However, is very difficult to obtain significant strengthening results by normal processing technology, mainly due to the natural tendency of ZrO_2 to react with SiO_2 to form zircon (Zr_2SO_3). This compound, as has been observed in several studies, allows poor improvement of mechanical performance of the composite [5].
The present study is intended to follow the global trends of developing advanced materials using techniques that are simple an easy to be reproduced at an industrial scale. Thus we propose a comparative study between the effects of reinforcing cordierite with different compounds: ZrO_2, TiC and SiC.
TiC reinforcements are commonly found in a variety of matrices (Al_2O_3, Si_3N_4, SiC, TiB_2, $MoSi_2$ and so on). However, at the date on which this paper was written we did not found any studies focused on using TiC as reinforcement in a cordierite matrix. The situation is similar to that of SiC additions: they are rarely used in cordierite matrices, mainly as fibers reinforcement (whiskers).
The concerning of the present paper are the effects of the additions over the porosity and Young's modulus.

2. SAMPLE'S PREPARATION

The whole process of sample's preparation was conducted at National Laboratory of Energy and Geology - LNEG (Lisbon, Portugal). The raw materials used were: Cordierite - BALCO SPA (Italy), ZrO_2 + 3% mol.Y_2O_3 (UNITEC CERAMICS LIMITED - England), TiC (Alfa Aesar GmbH & Co.Co.KG - Germany) and SiC (Arendal Smelteverk AS - Norway). Powder characterization consisted in measurements of the particle size (laser diffractometer - Cillas 1064) and density (pycnometer AccuPyc 1330). The results are presented in Table 1.

Table 1: Average particle size of the starting powders

Starting powder	cordierite	ZrO_2	TiC	SiC
Average diameter [μm]	7.11	1.21	2.03	3.31
Density [g/cm^3]	2.63	5.40	4.89	3.24

After consulting much of the existing publications concerning cordierite composites, the addition of ZrO_2 was set at 15% vol. This value has been adopted for other types of composites in order to make direct comparisons between the three types of additions,

The step of mixing the starting powders was made by ball milling for an hour at a speed of 1400rpm. Mixing medium consisted of distilled water and ZrO_2 balls (for the addition with ZrO_2) and Al_2O_3 (for the additions with TiC and SiC). Particle size measurement was repeated after mixing raw materials and we obtained average values between 3.03 and 5.2μm.

The shaping of samples was done by uniaxial pressing using a pressure of 40 MPa. In order to maintain a low level of contamination we didn't used lubricants. Samples were uniaxial pressed in two geometries: cylindrical (Φ = 30 mm, h = 3.3 mm) and rectangular (50 x 4.5 x 3.3 mm). In order to have reference samples, besides composite green-bodies we have also pressed a batch of pure cordierite samples. The cordierite and cordierite+ZrO_2 samples were sintered air in an electrically heated furnace at a temperature of 1375ºC for one hour. In order to avoid oxidation of TiC and SiC, the cordierite+TiC and cordierite +SiC samples were sintered in vacuum using the same temperature and duration.

Irrespective of the sintering atmosphere used, both types of samples had deviations from the original geometry (bending) that can be attributed to density gradients introduced during uniaxial pressing. For this reason it was necessary to include a mechanical machining step to correct the sample geometry.

In the case of vacuum sintering was found that residual vapors emanated from the furnace residual substances formed precipitates in the surface layers of the samples. We tried to remove the contaminated layer by mechanical machining, but this process could not be completed for all samples because it was quite difficult to determine the boundary between contaminated and uncontaminated layer (both of them had the same shade of color).

3. EVALUATION OF APPARENT POROSITY AND YOUNG'S MODULUS

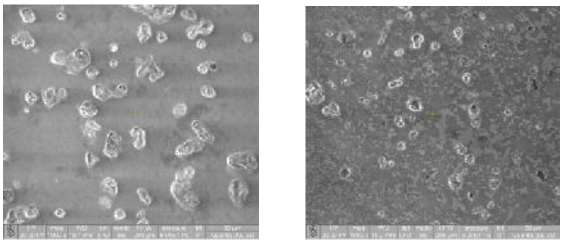
Given the fact that the samples placed near the oven walls had variations of porosity greater than those placed in the center, for further evaluations were used only samples placed in the center of the sintering chamber.

Porosity evaluation was made using a technique based on Archimedes principle, which is described in detail in ASTM B962 [7]. According to it, density and apparent porosity can be calculated from values obtained by weighing the dry sample in dry, soaked and immersed state. In this study, wetting the samples was done through boiling for one hour in distilled water. Weighing samples was performed using a hydrostatic balance which allows a resolution of 10^{-4} [g]. Each sample was evaluated twice and we couldn't notice significant differences between the obtained values.

Determination of Young's modulus. It was performed using the method of mechanical resonance, using the regulations found in ASTM C 1198 [8]. All samples analyzed were previously mechanically machined in order to reduce geometric deviations. Before testing, the samples were dehumidified by drying for one hour at a temperature of 85°C. The evaluation was repeated at least twice for each sample and we found that the difference between the results is negligible (below 0.1%).

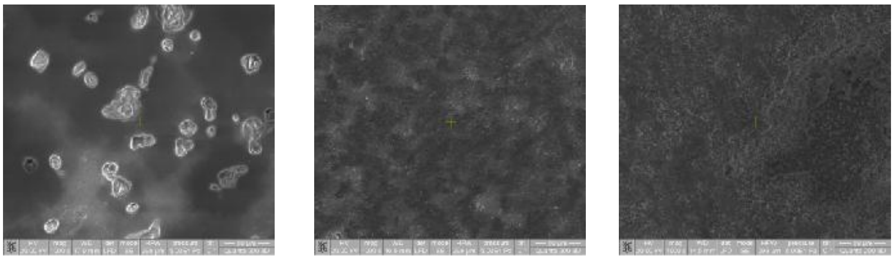
4. RESULTS AND DISCUSSIONS

As shown in figure 3, the conditions adopted for sintering in air allowed reaching of apparent porosities of less than 1%. There were no means of determining the closed porosity, but using SEM analysis (figure 1) one can conclude that the addition of ZrO_2 allows a closed porosities lower than the base material (pure cordierite). The causes are multiple: increased surface contact between particles (ZrO_2 powders are much finer than those of cordierite), the appearance of a small amount of vitreous phase due to presence of Y_2O_3 etc. Consequently, the difference in porosity of the composite material confirms the efficiency and ZrO_2 as sintering additive



a) b)

Figure 1: SEM microstructure analysis: a) cordierite b) cordierite+ZrO_2



a) b) c)

Figure 2: SEM microstructure analysis: a) cordierite (vacuum), b) cordierite + TiC and c) cordierite + SiC

For a given material, sample geometry has a negligible influence on apparent porosity values of samples sintered in air. In contrast, in samples sintered in vacuum was found that bars (rectangular shaped samples) shows porosities higher than those found in the discs (cylindrical shaped samples). This difference is due to the fact that removal of the contaminated layers of the bar samples could not be performed with the same efficiency as in the case of disc samples.

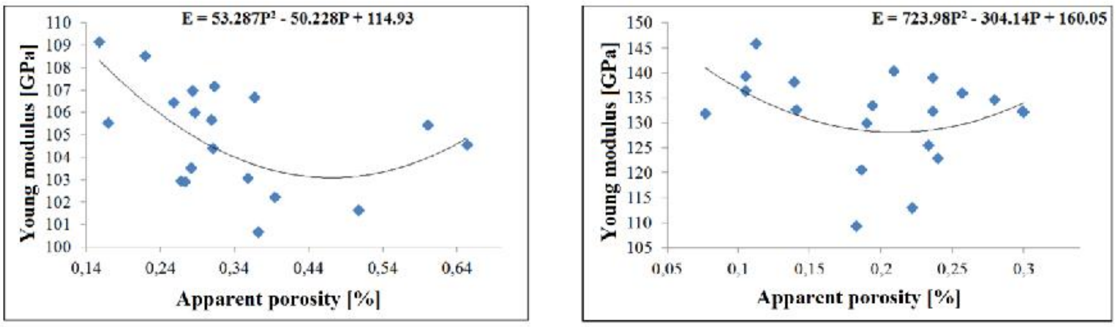
As shown in figure 2, of all the samples sintered in vacuum only cordierite samples could be completely decontaminated.

For the TiC and SiC composites was found that contaminating vapors formed precipitates deep in the sample's body (figure 2.b and 2.c), so that the complete removal of contaminated layer was impossible. Infiltration of contaminants throughout the sample volume is probably the main cause for the fact that composites sintered in vacuum shows high values of apparent porosity.

In this paper are discussed only the results obtained from the samples. The reasons behind this choice are:

- in the case of sintering in air, the results do not depend on sample's geometry;
- in the case of sintering in vacuum, the most efficient decontamination was obtained for the disc samples and thus. This means that the results obtained on the disc samples are closest to reality.

It is important to note that regardless of the sintering medium used, cordierite samples shows always the same range of apparent porosities. This suggests that, if we avoid the sample's contamination, composites sintered in vacuum and those sintered in air may have similar porosities.

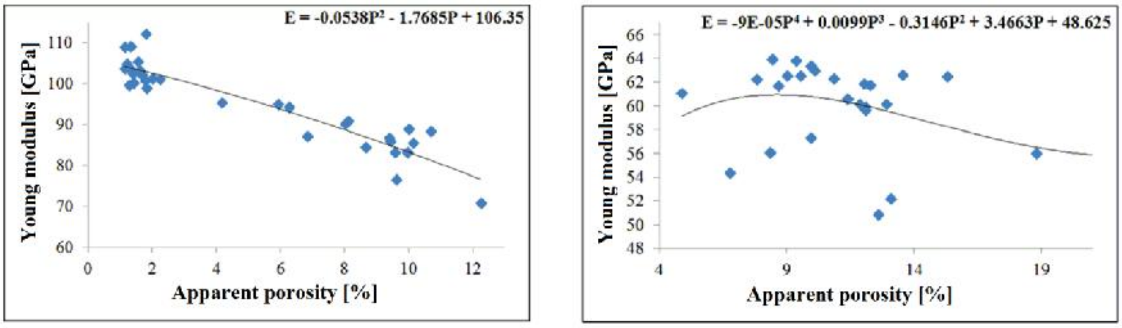


a) b)

Figure 3: Young's modulus as a function of apparent porosity for air sintered samples:
a) cordierite; b) cordierite + ZrO_2

Young's modulus values obtained for samples made of cordierite (figure 3.a) are within the range of 95-110 GPa and are about 20-25% higher than those that can be found in similar works. This discrepancy can be attributed to the fact that, in general, the values found in the literature were determined on cordierite synthesized from different mixtures of powders which, besides the constituent phases (Al_2O_3, SiO_2 and MgO) presents a certain amount of impurities. In contrast, in this study the raw materials used were of high purity.

The addition of ZrO_2 leads to an increase of Young's modulus by about 25% compared with the base material (figures 3.a and 3.b). The possible reasons are multiple: modulus of ZrO_2 which is about two times higher than that of cordierite, increasing of the surface contact between particles as a result of mixing the base material with a much finer powder (15% vol. ZrO_2), accumulation of residual stresses due to the difference of thermal expansion coefficients of the composite compounds etc. The XRD analysis revealed that most of the ZrO_2 reacted to zircon, so in this case the influence of the transformation toughening mechanism can be neglected.
Unlike pure cordierite samples, those mixed with ZrO_2 are characterized by a higher dispersion values. This is probably because mixing of starting powders wasn't enough efficient in order to avoid powder agglomeration (figure 1.b).



a) b)

Figure 4: Young's modulus as a function of apparent porosity for vacuum sintered samples:
a) cordierite; b) cordierite + TiC

From the graphs shown in figures 3 and 4 it can be seen that, irrespective of the sintering medium used (air or vacuum) the Young's modulus of cordierite most often falls in about the same range (95-110 MPa).
In the case of cordierite+TiC results shows that, in comparison with pure cordierite samples, the high levels of apparent porosity are reflected in low values of Young's modulus. The value's scatter follows quite closely the apparent porosity values, which means that the porosity is predominantly of open type and the initial surface contact between the particles did not increase significantly after sintering. The most common values are found in the range of 55-65 GPa.

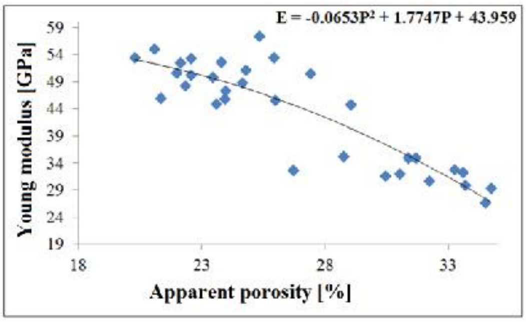


Figure 5: Young's modulus as a function of apparent porosity for air sintered samples.
The case of SiC addition

The high degree of apparent porosity that can be seen in figure 5 shows that the samples of cordierite + SiC have the highest sensitivity to the action of contaminants. In addition, major differences of measured values were observed between disc and bar samples of SiC composites. The main reason for this was the fact that this type of composites had the lowest strength, which made the decontamination machining to be particularly difficult.
It is noted that although the most common values that can be seen in figure 5 are similar to those found in figure 4.b, the difference between the apparent porosity of the two materials is significant. This suggests that in case of some technological improvements that would allow a full densification of the two types of materials, cordierite+SiC samples would have a much greater Young's modulus that that of cordierite+TiC composites.
Irrespective of the sintering medium used it is found that the samples sintered in vacuum shows a clear dependence of Young's modulus with apparent porosity. In contrast, samples that were sintered in air shows values that don't have a clear dependence with the apparent porosity, because in their case the total porosity consist mainly in closed pores, whose volume could not be taken into account.

5. CONCLUSIONS

Methods that were used in this work are nondestructive, which allowed testing of samples several times. The results showed that testing conditions allowed a good reproducibility of the results.
The sintering condition used does not avoid formation of zircon, mainly due to lower heating rates used. However the addition of ZrO_2 allows increased Young's modulus of base material by improving densification.
The addition of TiC and SiC fail to exceed the elastic performance of the base material because the contamination occurred during the sintering step greatly reduced the densification rate. However, there is a huge difference between porosity of the composites sintered in vacuum and base material and a little difference between their Young's modulus. This fact suggests that by reducing the sample's porosity, the Young's modulus of these composites could easily have superior values compared with the base material.
So, in qualitative terms, we can say that all the reinforcements used are able to increase the Young's modulus of the base material. It is found that all the values obtained are in close touch with the sample's apparent porosity. All of this remarks suggests that by improving the sintering parameters while keeping the initial phase composition, would allow the discussed composites to reach a much higher range of Young's modulus values.
In the case of TiC and SiC additions, this optimization could consists in prolonging sintering time and avoid contamination of samples during sintering (e.g. using sintering in inert atmosphere instead of vacuum).
In the care of ZrO_2 additions, much better results would be possible by using higher heating rates (>10K/min) in order to quickly overcome the thermal range in which the reaction rate of zircon formation has maximum values (~ 1200-1250 ° C) [6].

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