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PHYSICAL, MECHANICAL AND MICROSTRUCTURAL CHARACTERIZATION OF ZTM CERAMICS AS A TBC PROSPECTIVE MATERIAL

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Abstract. *Thermal barrier coatings are widely used as thermal protection of heated parts of metal components of gas turbines. Currently, ZrO_2 ceramics play an important role in this technological field. The addition of amounts of yttria, magnesia and other oxides supports the stabilization of the tetragonal phase after cooling, improving the ceramic behavior. In this study, a Zr-based material was produced as a candidate of TBC material. The influence of titanium oxide in a magnesia partially stabilized zirconia (Mg-PSZ) matrix was investigated on the physical, mechanical and microstructural characteristics, as a candidate of TBC material. TiO_2 was incorporated into the ZrO_2 matrix, whose tetragonal phase was stabilized by the addition of magnesium oxide (24% by weight). The ceramics were formed by cold uniaxial compaction and consolidate through solid-phase sintering, at different temperatures – 1250 and 1350 ºC for 24 hours. The ceramics were evaluated using scanning X-ray diffraction, electron microscopy, Vickers microhardness and physical tests (density and porosity). The analysis indicate that the addition of titania improved the sintering, resulting in better densification, while decreased porosity.*

Keywords: *MgO, TiO_2, phase composition, thermal barrier coatings, zirconia-based ceramic*

1. INTRODUCTION

Higher thermal efficiency, according to Carnot Cycle, is expected by increasing the inlet temperature of advanced gas turbines. However, the augment of operation temperature imposes more thermal loads to hot-section components and makes the thermal environment more severe (Han *et al.*, 2020). In general, the efficiency of gas turbines is determined by the pressure ratio of the compressor stage and by the inlet temperature of the high-pressure turbine (Mack *et al.*, 2019).

Thermal barrier coatings (TBCs) are frequently used to protect metallic substrates exposed to high temperature environments, such as power plants and jet engine gas turbine parts. TBCs are mostly composed of two layers. The first one, called bond coat, is directly applied to substrate, in order to increase the oxidation resistance of it and to improve the adhesion strength of the ceramic layer, the top coat (Lavasani *et al.*, 2017).

Zirconia-based ceramics are widely used as top coat of thermal barrier coating, which purpose is to provide insulation to metals components that operates at high temperature. Zirconia is among the most studied ceramic materials. It has three crystalline phases: monoclinic (m), tetragonal (t) and cubic (c), while the transformation during heating is related the temperature (Li *et al.*, 2019).

Partially stabilized zirconia-yttria (YSZ) is widely used in the TBC industry (Viswanathan *et al.*, 2020). Mechnich *et al.* (2011) studied the high-temperature corrosion of yttria partially stabilized zirconia thermal barrier coatings. Other oxides are well known as effective stabilizers materials, such as CaO and MgO, among others, the massive recent studies involve YSZ ceramics (Maridurai *et al.*, 2016; Fan *et al.*, 2018; Wang *et al.*, 2018).

Doleker et al. (2018) have compared microstructures and oxidation behaviors of ytria and magnesia stabilized zirconia for thermal barrier coating's purpose. They suggest that the coatings produced with magnesia may be more suitable for lower-temperature applications (<900 °C) due to its lower production cost.

In this context, this work aims the production of the ceramic Zirconia-Magnesia-Titania as a prospective ceramic material for high temperature coatings that aims to protect metal substrates. The effects of TiO_2 on sintering and physical and mechanical behaviour, phase content and microstructure of the well know Mg-PSZ materials were also studied.

The phase diagram of the ZrO_2–MgO–TiO_2 system provided by Saenko *et al.* (2019) and Saenko *et al.* (2020) provided a background a background on the phase transitions expected for this system.

2. EXPERIMENTAL

High purity chemicals commercially available monoclinic zirconia (99%, Sigma-Aldrich), magnesium oxide (95%, Vetec) and titanium oxide (99%, Sigma-Aldrich) were used. The ceramic samples were prepared by a thermo mechanical process.

First, 24 wt.% of magnesium oxide was incorporated to the ceramic mass to stabilize the tetragonal phase (24MgO:76ZrO_2), this is reference composition, labeled ZM. Then, another formulation containing 7.5 (wt.%) of titania was prepared and labeled ZTM. Since the proportion of 24% of magnesia doped on zirconia is also found as a powder commercially available used for the purpose of thermal protection, it allowed us to evaluate the influence of titania into this ceramic.

The raw materials were ground in a ball mill (Marconi, model MA-500), 200 rpm, during 24 hours, using steel cylinder and alumina balls as milling media in a dry process. The mixtures powders were shaped into pallets of 15 mm in diameter and 3mm thickness in a hydraulic press machine (SCHWING SIWA, ART6500089) at 600MPa.

Then, the green bodies were sintered in a muffle furnace in two different thermal cycles. The obtained specimens and respective heating parameters are described as follows Table 1. The sintering conditions were stablished empirically and based in our previous studies.

Table 1. Description of the specimen's composition and sintering parameters.

Specimen	Composition (wt.%)	Sintering parameters
ZM1	24%MgO – 76% ZrO_2	1250 ºC for 24 h
ZTM1	92.5% (24MgO:76ZrO_2) - 7.5% TiO_2	
ZM2	24%MgO – 76% ZrO_2	1350 ºC for 24 h
ZTM2	92.5% (24MgO:76ZrO_2) - 7.5% TiO_2	

The magnesia partially-stabilized zirconia ceramics reinforced with titanium oxide were characterized by means X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Vickers microhardness.

Physical indices were measured, at room temperature, by Archimedes' principle.

Phase analysis was carried out by Shimadzu XRD 7000 diffractometer, equipped with Cu – Kα radiation (λ = 1.5406Å), 40.0 kV acceleration voltage, 30.0 mA current, scan speed of 1.00 deg/min, in ranges from 2 *theta* from 0 to 90º. Phases were identified based on International Centre for Diffraction Data (ICDD) and American Mineralogist Crystal Structure Database (AMCSD) databases.

The samples were previously metallographic prepared by using SiC sandpapers and mechanical polishing, then the Vickers microhardness test was performed. For the hardness tests, a Vickers's microhardness indenter Importecnica, model HVS-5 was used. It was performed ten indentations in the polished surfaces of two samples of each composition, under a load of 1 kgf and 10s dwell time, as recommended by JIS R 1610-91 standard. The Vickers micro - hardness (MHV) is given by Equation 1.

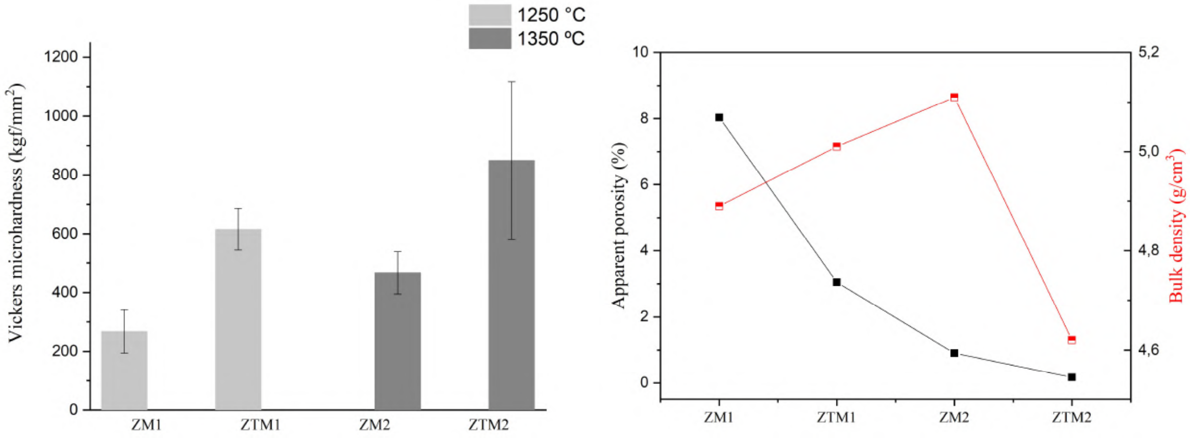
$$MHV = 1.8544P/d^2 \quad (1)$$

Where P is the applied load and d is the average diagonal of the indentation produced by the diamond pyramidal indenter in the sample.

Microstructural analysis of the sintered ceramics was carried out by scanning electron microscopy Tescan (model Mira 3), using backscattered electrons. But, first, the ceramics were polished and metalized with a thin layer of gold.

3. RESULTS AND DISCUSSION

The average Vickers micro - hardness results are shown in Figure 1a.



(a) (b)

Figure 1. Vickers microhardness values (a) and physical indices (b).

Small amounts of titania added to the mass contributed to raise the Vickers microhardness of the ceramics. Once the sintering temperature increases to 1350 °C there is also hardness enhancement. Thus, the maximum value of HV was obtained for the sample sintered at 1350ºC and doped with titania (ZTM2), average value equal to HV849,5, and the lowest value found in the sample ZM1, equal to HV267.7.

Figure 1b illustrates the influence of the addition of TiO_2 in the physical indexes. The bulk density of samples sintered at 1250 ºC raised by adding titania. This can also be noted in SEM images. However, the opposite was evidenced in samples sintered at 1350 ºC.

The apparent porosity is also temperature and composition dependent. Samples prepared at 1350ºC showed lower apparent porosity than ceramics, of the same composition, sintered at 1250ºC. Porosity was also reduced in samples doped with titania, produced by both thermal cycles. The correspondent value for sample ZTM2 is equal to 0.18%.

Figures 2-5 demonstrate the XRD of the as-sintered ceramics.

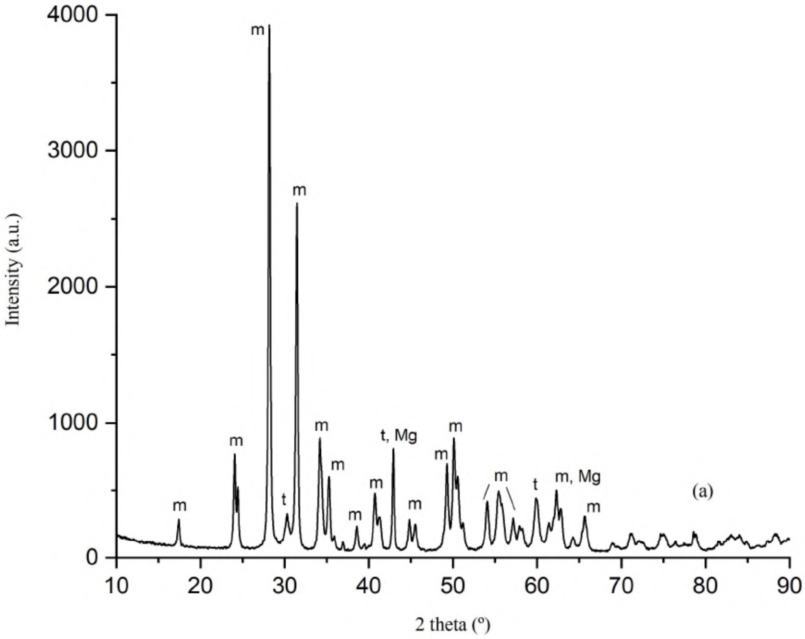


Figure 2. Diffractogram of the ceramic ZM1 – sintered at 1250 ºC.

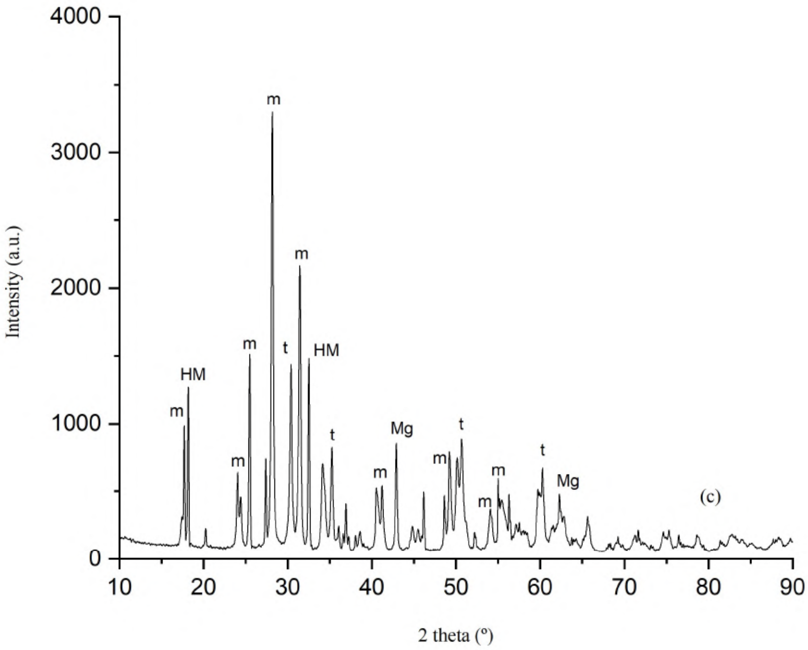


Figure 3. Diffractogram of the ceramic ZM2 – sintered at 1350 ºC.

The tetragonal zirconia phase (t) - ICDD 79-1769, in addition to monoclinic zirconia peaks (m) - ICDD 65-1023, were observed in the XRD results of all samples. The ZM2 sample showed more intense t-phase peaks, indicating that its stabilization was benefited by the increase in temperature. The studies by Saenko *et al.* (2019), in turn, did not indicate the stabilization of the tetragonal phase.

Peaks of magnesia (Mg) - AMCSD 501, were also found in all compositions. The reference samples Residual peaks of magnesium hydroxide (HM) - AMCSD 1637, were diffracted in sample ZM2. That is probably a response to a magnesium hydration process with atmospheric moisture.

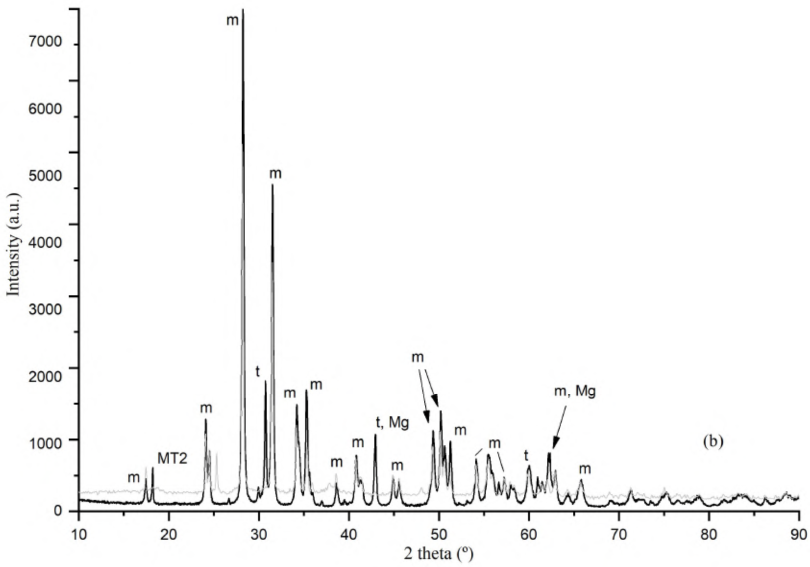


Figure 4. Diffractogram of the ceramic ZTM1 – sintered at 1250 ºC

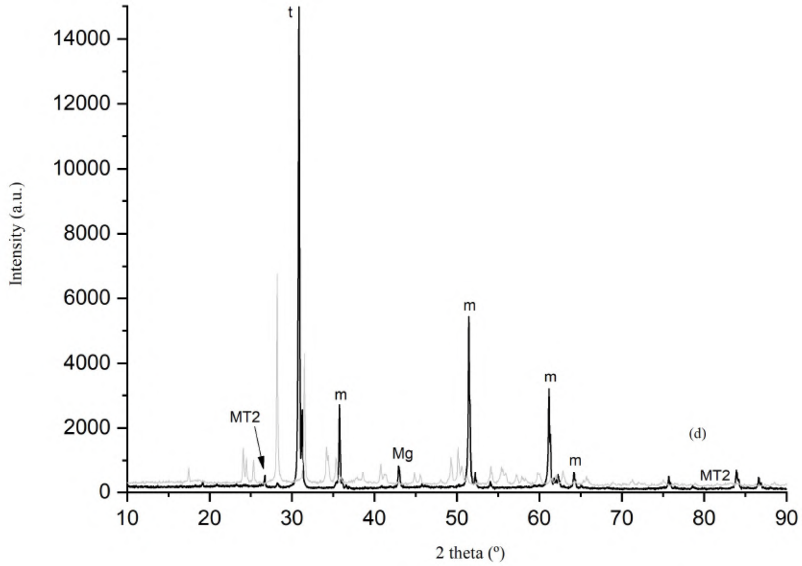


Figure 5. Diffractogram of the ceramic ZTM2 – sintered at 1250 ºC.

It can be noticed the intensity of the main peak of t-phase, at 2 *theta* approximately 30º, increased in samples containing titania (Figures 3 and 5), if compared with the respective reference samples. It was also improved by raising the temperature of the process. Although, it was observed some peaks related to $MgTi_2O_5$ (MT2) - ICDD 35-0792, as a result of reactions between magnesium and titanium oxides.

According to the literature, it is expected that in magnesia-titania systems, three intermediate compounds can be formed - magnesium dititanate ($MgTi_2O_5$), magnesium orthotitanate (Mg_2TiO_4) and magnesium metatitanate ($MgTiO_3$). They are formed depending on the mutual quantitative proportions of the initial oxides (Kusiorowski, 2020).

SEM images and XRD diffractograms were associated in the microstructure identification. As shown in Figure 6, the ceramics presented well distributed particles.

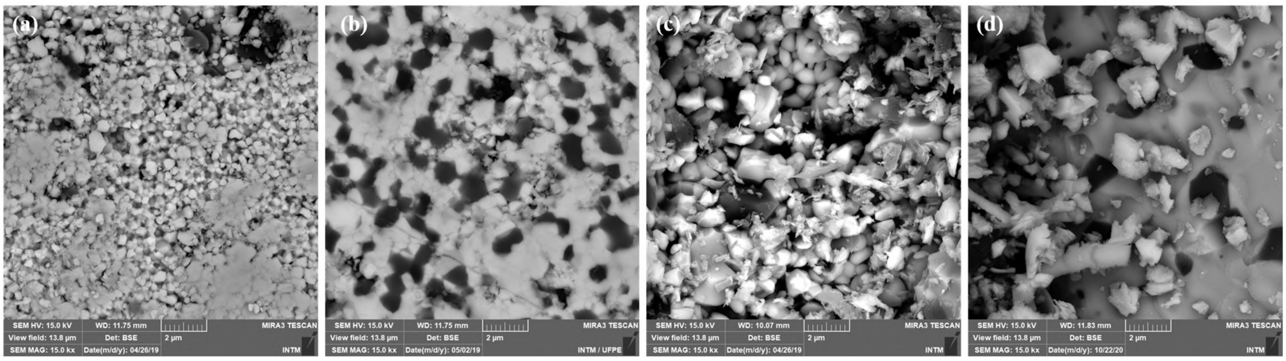


Figure 6. SEM micrographs (15kx) of ZM1 (a) ZTM1 (b) ZM2 (c) and ZTM2 (d).

Sample ZM1 is made of fine grains of zirconia in an early stage of sintering, while the ZTM1 sample shows less residual porosity and grains better connected. Similar behavior can be observed in the samples sintered at 1350 ºC. Ceramics doped with titania presented black regions, Figures 6a-b, which have been attributed to $MgTi_2O_5$ particles.

4. CONCLUSIONS

In the present work we have produced a zirconia-based ceramics doped with titania and studied their mechanical, physical and microstructure features. It was possible to partially stabilized by adding 24 wt.% of magnesia, which directly influenced in the behavior of ceramics.

Higher Vickers microhardness values were obtained by the addition of titanium oxide. The hardness of the samples sintered at 1350 ºC T also were be increased. Sample ZTM2 has 849,5 HV.

In general, physical indices were refined by increasing the sintering temperature from 1250 ºC to 1350 ºC. So that, the ceramics presented lower porosity and better densification. Sample ZM2 density has 5.11 g/cm^3. The porosity also decreased with the addition of titania. Although the density of the ZTM2 sample was lower than the others.

The XRD results showed refracted peaks of tetragonal and monoclinic zirconia phases, in addition to those of magnesium oxide and hydroxide. No peaks related to titanium oxide were observed. However, peaks referring to the compound magnesium dititanate ($MgTi_2O_5$, MT2) were indexed. The appearance of MT2 suggests that the starting oxides reacted in the thermoactivated process. Due to the low titanium oxide content in the compositions, the MT2 peaks are of low intensity.

Based on this, we can infer titanium oxide was, in general, beneficial to physical and mechanical characteristics of the ceramics developed on this paper.

5. ACKNOWLEDGEMENTS

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7. RESPONSIBILITY NOTICE

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