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Effect of the Addition of La_2O_3 on the Properties of ZrO_2-Al_2O_3 Ceramic Composites for Coatings in Aerospace Turbines

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ABSTRACT: Ceramic matrix composites have attracted the interest of turbine manufacturers for use in coating hot sections because of their higher capacity to withstand high temperatures and because they have a lower requirement for air cooling. One of the most commonly used ceramic coatings is zirconia-yttria. However, its main disadvantage is the inherent fragility of ceramics, which limits the use of these materials in mechanical structures and industrial applications. Ceramics are generally reinforced with the incorporation of additives to reduce their brittleness and increase their mechanical strength and toughness. It is known that La_2O_3 which are potential source for stabilization of zirconia composites. In this context, ZrO_2-Al_2O_3-La_2O_3 based ceramic matrix composites were developed for deposition of a thermal barrier coating on the substrate of exhaust nozzles of aerospace turbines varying the content of La_2O_3 by 5, 7 and 10 wt%. The composites were produced by a thermomechanical process and sintered at 1385 °C. The properties of these composites were studied by X-ray diffraction, relative density, scanning electron microscopy, and Vickers microhardness tests. The results indicate that the composite with 10% La_2O_3 has great potential for use as ceramic coatings of turbine exhaust nozzles in the aerospace industry.

KEYWORDS: Ceramic matrix composites; Ceramic coatings; ZrO_2-Al_2O_3-La_2O_3; Turbine exhaust Nozzles.

INTRODUCTION

The Brazilian aerospace industry, comprised of the aeronautical, space, and defense industries, is responsible for producing goods, generating highly qualified jobs and improving the quality of several other products by incorporating new technologies and procedures, with a consequent increase in the competitiveness of Brazilian industry as a whole (Dieese CNM-CUT 2005).

The development of this sector has primarily occurred due to the use of gas turbines, which are responsible for the propulsion of airplanes and aircraft. They are able to generate higher power than other machines of same weight, resulting in greater efficiency and load capacity (Pereira and Benegra 2011).

Gas turbines used in the aerospace industry currently consist of nickel-based superalloys due to their high strength and stability at high operating temperatures. Particularly in the case of rockets, during propulsion, a combustion reaction between

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the propellants generates a gas at high temperature and pressure in a combustion chamber and is, then, accelerated through a convergent-divergent nozzle (Sutton and Biblarz 2001; Oliveira 2013).

Gas turbines are equipped with sophisticated refrigeration systems and thermal barrier coatings that are used as superalloys in the turbine components and are capable of responding to the mechanical and thermal needs during their operation. The use of thermal barrier coatings together with anchoring systems allows this equipment to be subjected to temperatures as high as the melting temperature of some of the metals in the superalloys, which are on the order of 1080 °C. The use of thermal barrier coatings reduces metal temperature and increases the lifespan of turbine components (Schloesser *et al.* 2010; Gleeson 2006).

In recent decades, there has been greater interest in the use of ceramic matrix composites such as thermal barrier coatings for hot sections due to their higher capacity to withstand high temperatures and a lower requirement of air cooling in order to reduce fuel consumption and improve efficiency (Mecham 2012; Christian *et al.* 2011; Zawada *et al.* 2003).

The use of ceramic materials in aerospace applications has been rather limited due to the intrinsic fragility of this type of material, but efforts have been made to improve its properties in order to benefit from its use.

Due to their characteristics, high temperature ceramic materials have become a promising class for aerospace applications (Opeka *et al.* 2004; Fahrenholtz *et al.* 2007). The refractory nature of this class of carbides, borides, nitrides, and oxides make them attractive candidates for greater heat flow in hot sections. However, the relatively high density of these materials and the challenges involved in processing large components are difficult to overcome. Reinforcements using particles, whiskers and fibers are helping to improve their mechanical performance, such as their resistance to thermal shock and fracture resistance (Dichiara *et al.* 2005).

Zirconium dioxide (ZrO_2) is an interesting material for various engineering applications. In comparison to other ceramics, it has superior mechanical properties such as a high mechanical strength, chemical stability, and fracture resistance combined with good wear resistance and a coefficient of thermal expansion close to that of iron and iron-based alloys. These characteristics make it favorable for use in ceramic hardening and coating (Wu *et al.* 2004). Zirconium dioxide shows excellent mechanical properties through a highly refined microstructure, consisting of a metastable tetragonal phase maintained at room temperature known as tetragonal-zirconia polycrystals (TZP) (Denry 2008).

However, the fragility inherent in ceramics is still a limiting factor for the use of these materials in mechanical structures and industrial applications. To reduce this brittleness and increase their mechanical strength and fracture resistance, the ceramics are usually reinforced by the incorporation of one or more ceramic additives (Rêgo *et al.* 2012). Studies have been carried out on the stabilization of zirconia polycrystals through the additions of other oxides. Several binary and ternary oxide systems such as ZrO_2-yttria (Y_2O_3), ZrO_2-ceria (CeO_2), ZrO_2-calcium (CaO), and ZrO_2-Y_2O_3-magnesia (MgO) were found to be potential sources of high zirconia polycrystals (TZP), showing that these systems are useful for the preparation of these types of materials (Santos 2011; Rêgo *et al.* 2012).

The main limitation of ceramics is the fact that they are brittle, that is, they tend to fail suddenly due to their lack of plastic deformation. This is of particular relevance when the material is used in structural applications. In metals, the characteristics of the metallic bonds in which the nonlocalized electrons allow the atoms to change their neighborhood without completely breaking the bond structure allow them to deform when under tension. The bonds simply slide during deformation. In ceramics, due to the combined mechanisms of ionic and covalent bonds, the particles cannot slide easily. Ceramics break down when a lot of force is applied and the breakage of bonds creates new breaking surfaces. A brittle fracture occurs through the formation and rapid propagation of cracks. In crystalline solids the cracks grow through the grains (transgranular) and along planes of cleavage in the crystal. For the manufacture of ceramic products, it is very important to start with high purity ceramics with a uniform and homogeneous particle morphology. In ceramic processing, its microstructural characteristics play a vital role in the quality of the final product. The development of the microstructure is also strongly dependent on the sintering behavior of these ceramics.

Currently, aerospace research has as one of its challenges to reduce mission costs. The need for cost reduction in launching rockets is paramount in increasing the frequency of access to space. Considering that approximately 90% of the weight of a launch vehicle is composed of propellant storage tanks, small improvements in the propulsion system can result in significant cost reduction. Thus, the performance enhancement of hot sections, such as exhaust nozzles, can help in achieving current industry needs (Germer 2014).

In this context, this work aimed the development of a zirconia-alumina ceramic matrix (ZrO_2-Al_2O_3) reinforced with a rare earth oxide (La_2O_3) for nonindustrial gas turbine exhaust applications in the aerospace sector varying the content of La_2O_3 by 5, 7 and

10 wt%. Since the composites are experimental, initially, it is necessary to evaluate their physical, mechanical, and microstructural properties and to verify the percentage of additive that presents better results and cost-benefits.

MATERIALS AND METHODS

For the production of La_2O_3 reinforced ZrO_2-Al_2O_3 ceramic composites, Al_2O_3 was added to ZrO_2 in 5 wt% ratios, and La_2O_3 was added at 5, 7 and 10%. Table 1 presents the phase compositions of the composites to be tested.

Table 1. Components of the ceramics to be tested.

Ceramics	ZrO_2 (wt%)	Al_2O_3 (wt%)	La_2O_3 (wt%)
C1	90	5	5
C2	88	5	7
C3	85	5	10

The final weight of each composition was fixed in batches of 100 g. Each batch of ceramic mixtures was thoroughly mixed and homogenized separately in a ball mill (Equipment Marconi MA-50, São Paulo, Brazil) with a stainless-steel milling chamber and high purity aluminum balls for a period of 24 h. In this type of ball milling process, the number of balls required for milling under general conditions is 50–55% of the net capacity of the milling chamber. However, occupation of this volume is not effective, given the gaps between the balls, so the actual volume occupied is approximately 60%. Particle size and particle size distribution of the ceramics before and after grinding were determined by a laser particle size analyzer model MASTERSIZE 2000, Malvern Instruments.

For the composite formation by normal solid-state sintering, finely ground and homogenized ceramic mixtures were uniaxially compacted in a metallic mold fabricated from abrasion resistant AISI A2 steel (HRC 58) to form circular discs 30 mm in diameter and 2 to 3 mm thickness. A pressing load of 10 ton/cm² was applied for powder compaction, using a hydraulic press (SCHIWING Siwa, model ART6500089). Every compaction process pressure was applied for 10 min to stabilize the pressure load distribution in the pressed compact. Fig. 1 shows the metallic matrix and hydraulic press used for processing.

Fig 1. Metallic matrix and hydraulic press (SCHWWING SIWA, ART6500089 model).

The compacted ceramic mixtures were subjected to the normal solid-state sintering process at a temperature of 1385 °C for 24 h at ambient atmosphere. Sintering was carried out at ambient atmosphere in high purity alumina crucibles using a high temperature muffle furnace muffler (Jung 0614) as shown in Fig. 2, followed by furnace cooling until it reached the ambient temperature.

Fig 2. Muffle furnace muffler (Jung 0614), maximum temperature of 1400 °C.

Structural characteristics and identification of the phases were investigated by X-ray powder diffractometry (XRD) using a Shimadzu X-ray diffractometer equipped with Cu-Kα radiation (λ = 1.5406 Å). After composite formation was confirmed through X-ray diffractometry, the bulk density, mechanical properties, and microstructural features of the sintered ATY ceramics were analyzed in order to evaluate their potential as toughened ceramic coatings for the aerospace industry.

Sintered densities of the composites were determined by the Archimedes method using distilled water. The mechanical behavior of the sintered ceramic composites was studied by measuring Vickers microhardness using a Vickers hardness indenter model HVS-5 No. 0021.

The microstructure of the sintered composite ceramics was studied by scanning electron microscope (JEOL JSM-5900) using back-scattered electrons. As these composites are electrically nonconducting, samples were covered with thin gold coating using a sputtering unit (Coater BAL-TEC SCD050) to observe the microstructure.

RESULTS AND DISCUSSION

The milling step of the powders aims to reduce their particle size in order to increase the reaction rate of the components, to aid in densification during sintering, and improve the mechanical properties of the finished product.

Particle size analysis was performed on the ceramic powders before and after mixing the precursor powders in order to verify the effect of the milling process. The analysis yielded particle size distribution curves from which it was possible to obtain parameter D50, which corresponds to the median of the distribution in micrometers (μm).

According to the values of D50, shown in Table 2, the particle size of the ceramic composites formed was between 4.51 and 13.13 μm, lower results than those presented by the oxides separately before the milling process, which obtained values between 20.95 and 54.16 μm. With this analysis, it can be verified that the milling process promoted the reduction of the particle size of the powders, favoring the densification of the samples.

Table 2. Granulometric distribution before and after milling.

Samples		Before	After	Reduction (%)
		D_{50} (μm)	D_{50} (μm)	
C1	$90ZrO_2$-$5Al_2O_3$-$5La_2O_3$	17.07	3.39	80.1
C2	$88ZrO_2$-$5Al_2O_3$-$7La_2O_3$	9.94	4.21	57.6
C3	$85ZrO_2$-$5Al_2O_3$-$10La_2O_3$	9.45	8.35	11.6

The X-ray diffraction technique was performed on the ceramic samples produced after sintering at 1385 °C for 24 h. The obtained images are illustrated in Figs. 3-5, where the characteristic peaks of the raw materials used can observed. It is possible to perceive the similarity across their compositions, considering that all are formed with the same oxides, having only some variation in the content of each one of them. A small variation in the intensity of the peaks, justified by the percentage variation in the composites, can also be observed.

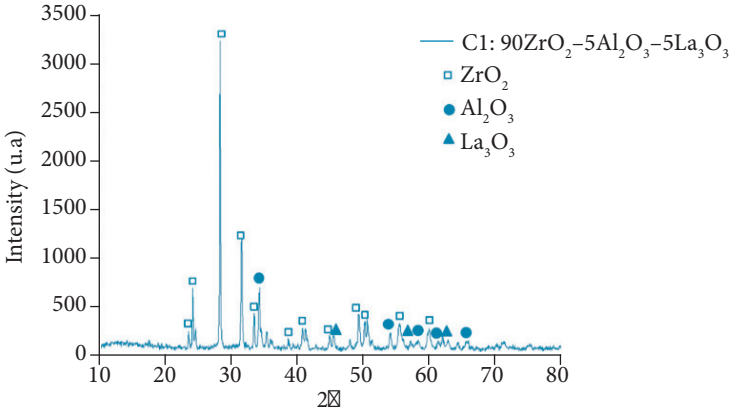

Fig 3. XRD for the samples with 5 wt% La_2O_3.

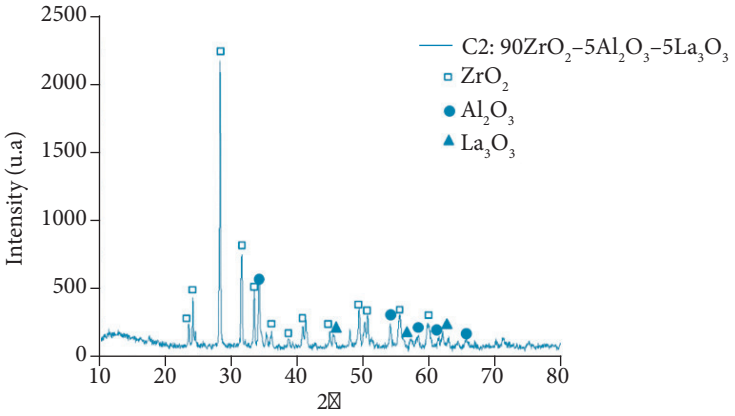

Fig 4. XRD for the samples with 7 wt% La_2O_3.

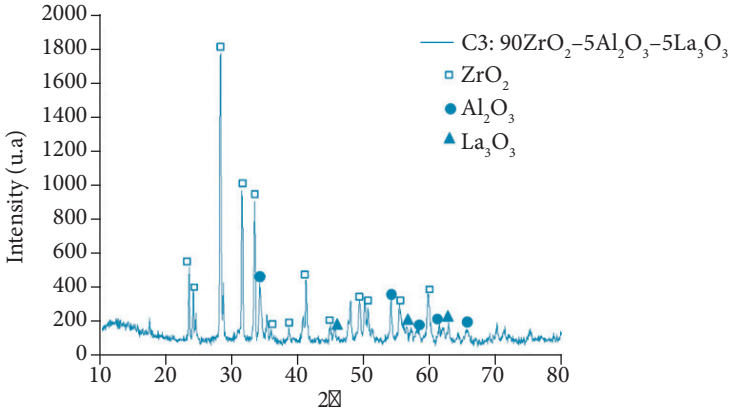

Fig 5. XRD for the samples with 10 wt% La_2O_3.

The relative density of the samples, determined by the Archimedes immersion method with distilled water, using a 50 ml pycnometer, analytical balance of 0.0001 g, and controlled ambient temperature (22 °C), presented results between 4 and 5 g/cm^3, with the composition of C1 being the densest with a density equal to 4.72 g/cm^3, which corresponds more or less to the average densities of the precursor oxides, according to the values shown in Table 3.

Table 3. Density of the ceramic composites samples.

Samples		Density (g/cm^3)
	ZrO_2	5.68
	Al_2O_3	3.95
	La_2O_3	6.51
C1	$90ZrO_2$-$5Al_2O_3$-$5La_2O_3$	4.72
C2	$88ZrO_2$-$5Al_2O_3$-$7La_2O_3$	4.02
C3	$85ZrO_2$-$5Al_2O_3$-$10La_2O_3$	4.34

The microstructure of the ceramic composites was analyzed by the MEV. The technique was used to verify the presence of the phases, already shown in the XRD, as well as to observe the changes caused by increases of the La_2O_3 percentage.

A good homogeneity can be verified in the distribution of the constituents on the entire surface of the three ceramic samples (Figs. 6 to 8). In the samples with 5 and 10 wt% of La_2O_3, as shown in Fig. 6 and Fig. 8, respectively, the three components of the composite, ZrO_2, Al_2O_3, and La_2O_3, can be seen more clearly.

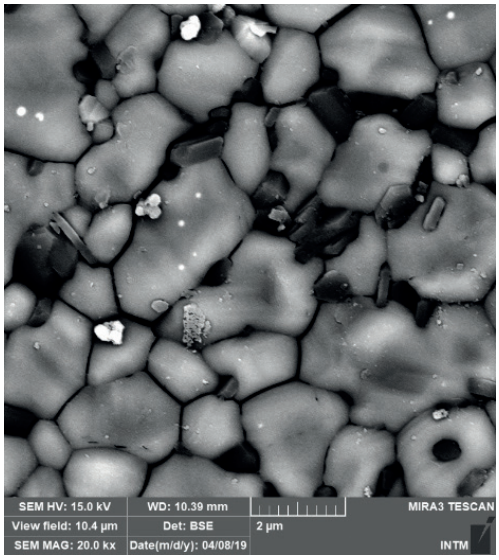

Fig 6. SEM of the sample with 5 wt% La_2O_3.

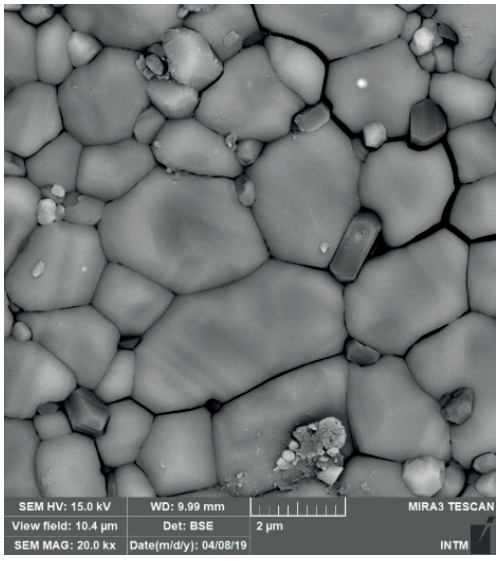

Fig 7. SEM of the sample with 7 wt% La_2O_3.

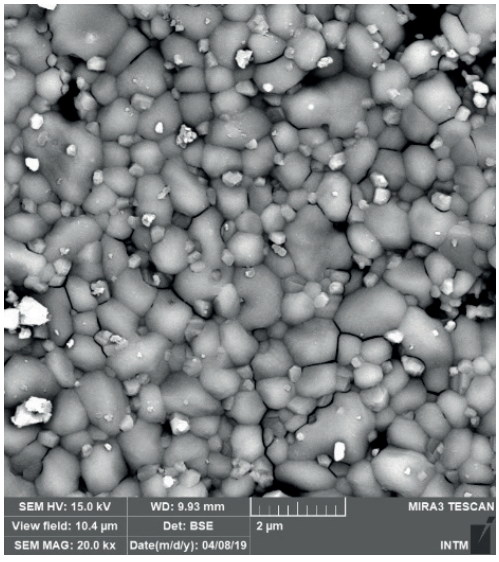

Fig 8. SEM of the sample with 10 wt% La_2O_3.

La_2O_3 acted in the compositions as a grain refinement agent, so the addition of this rare earth oxide at a higher percentage resulted in more refined grains. Besides the indication of a homogeneous distribution of the grains, the images confirm the material densification, indicating that the sintering process was efficient. There are defects, such as pores, but they are expected characteristics, as they are inherent in the processing of ceramics.

The images shown in Figs. 9-11 were obtained by dispersive energy spectroscopy (DES) coupled to the scanning electron microscopy (SEM). The DES technique allows the observation of chemical microanalysis of the composites. The DES was performed in three different regions for each ceramic sample in order to verify the chemical elements present in each of the three distinct phases of the composite formed by the three constituent oxides. In this way, the DES analysis was performed to verify if there was contamination during the processing of the composite and to identify the three phases present in the material.

In the analysis by DES, illustrated in Figs. 9-11, the constituent elements of the composites can be observed: oxygen (O), zirconia (Zr), aluminum (Al), and lanthanum (La_2O_3). The percentage of each element varies according to the analyzed region of the composite, showing the distribution of the particles. There were no unexpected elements in the ESD analysis, indicating that there was no contamination during the processing of samples.

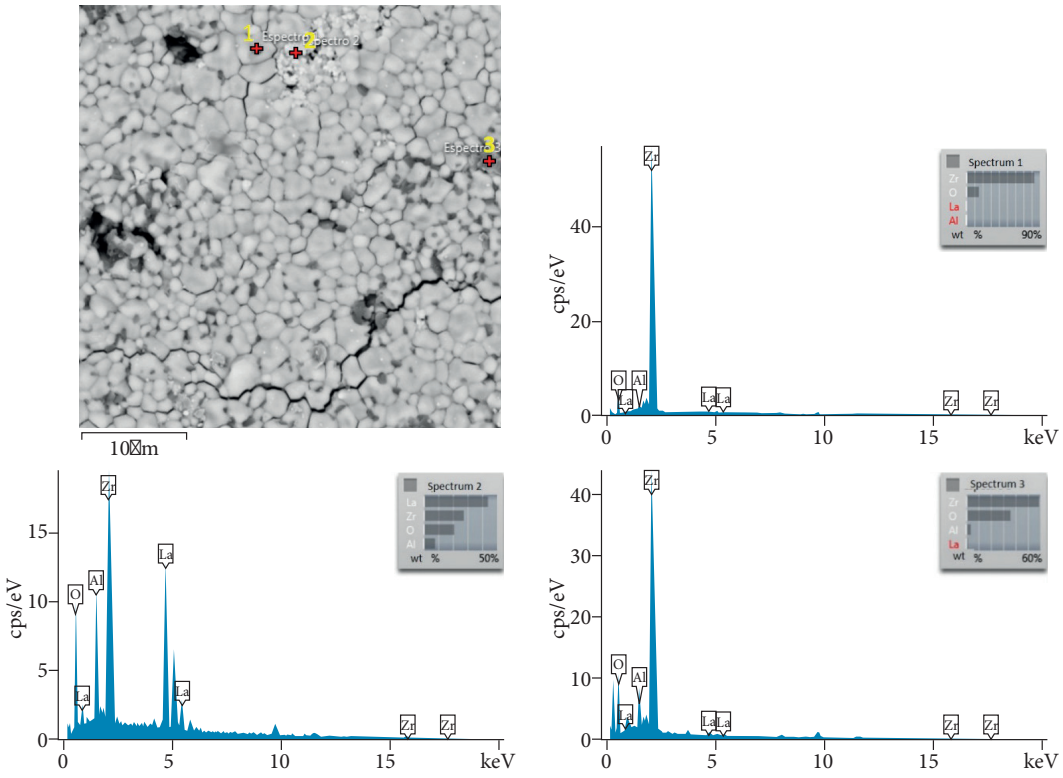

Fig 9. DES analysis of the sample with 5 wt% La_2O_3.

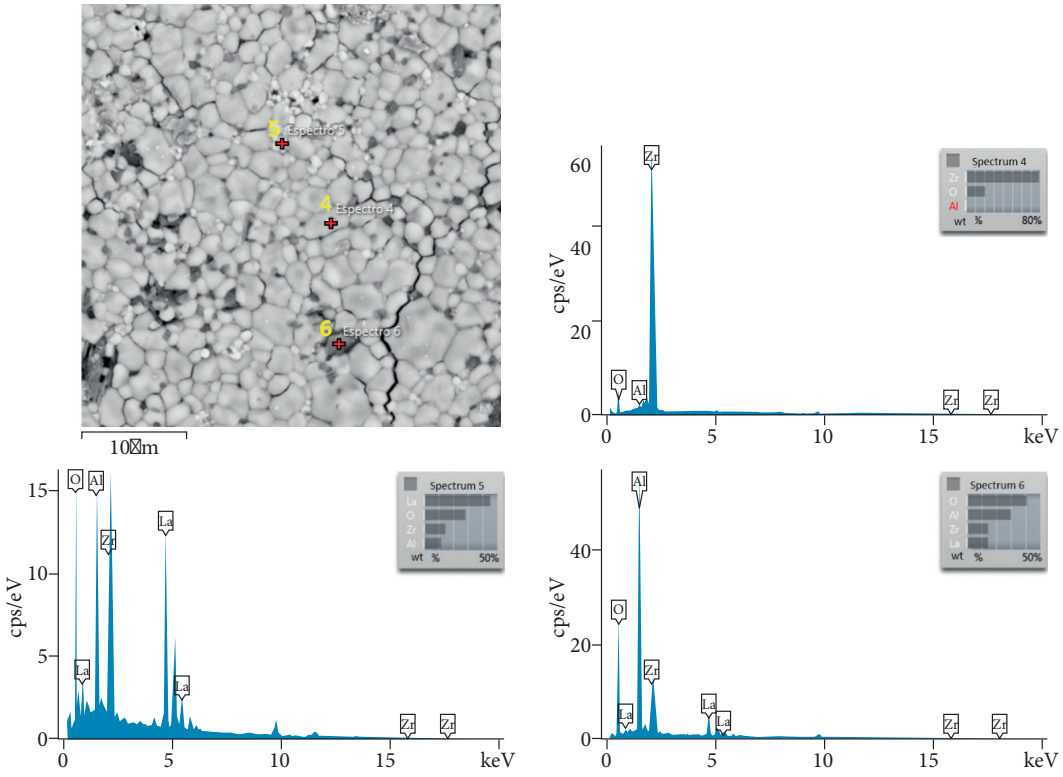

Fig 10. DES analysis of the sample with 7 wt% La_2O_3.

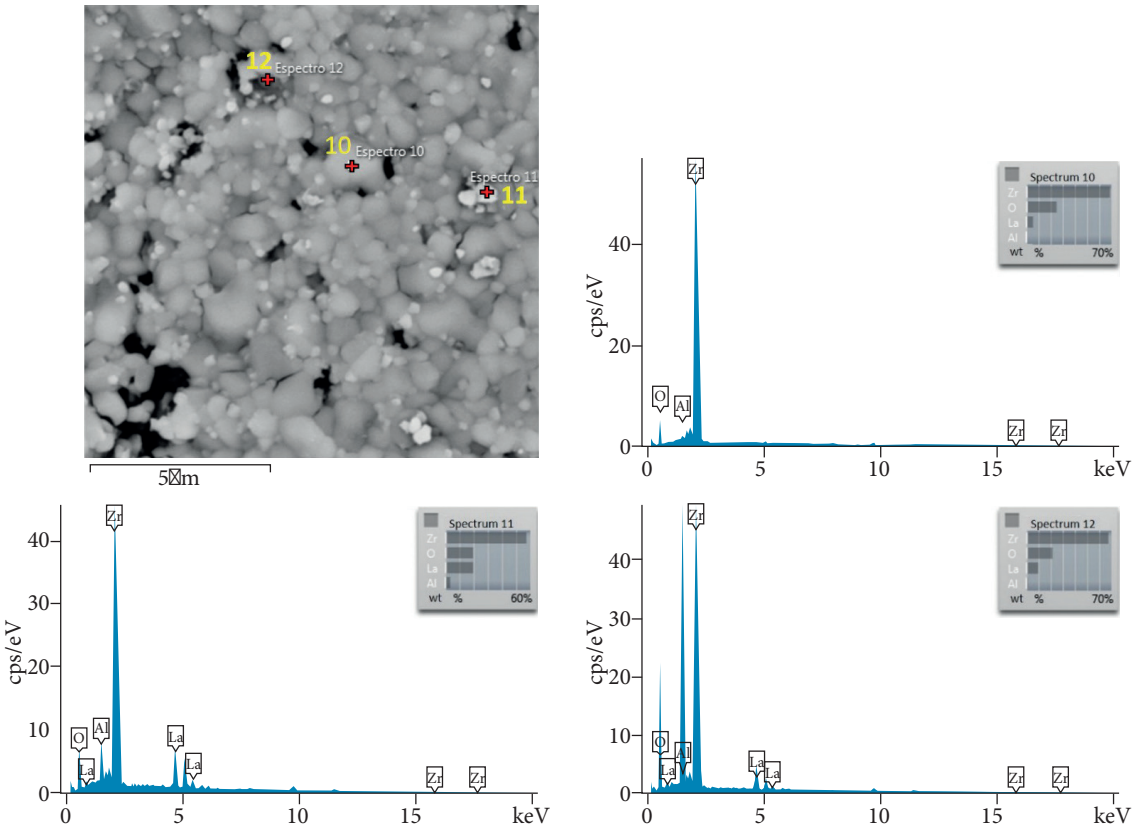

Fig 11. DES analysis of the sample with 10 wt% La_2O_3.

The Vickers microhardness test was used to relate the influence of the variation in the percentage of La_2O_3 in the composites with the obtained microhardness and microstructure already analyzed.

Thirty measurements of Vickers microhardness were performed for each sample, and the two most discrepant values from the others were discarded and the remaining values were used to calculate the mean of the microhardness of each sample. The values and averages for each composite are shown in Table 4.

Table 4. Vickers micro hardness results for the samples

Samples		Vickers microhardness average (HV)	Standard deviation (S_d)
C1	$90ZrO_2$-$5Al_2O_3$-$5La_2O_3$	357.66	33.47
C2	$88ZrO_2$-$5Al_2O_3$-$7La_2O_3$	340.96	48.61
C3	$85ZrO_2$-$5Al_2O_3$-$10La_2O_3$	423.02	72.41

Table 4 shows that the microhardness of the composite with 10 wt% of La_2O_3 presented the higher value. The compositions with 5 and 7 wt% of La_2O_3 exhibited very close values. Sample C3 (10 wt% of La_2O_3) had higher results on the microhardness test, and this may be related to the fact that it is the sample with the highest content of lanthanum. This reveals that the addition of a higher percentage of La_2O_3 may contribute positively to an increase in fracture resistance, which is a very important property for ceramic coatings in the aerospace industry.

CONCLUSIONS

In this work, the effect of the addition of different amounts of La_2O_3 on the physical, mechanical and microstructural properties of ZrO_2-Al_2O_3-La_2O_3 ceramic compounds experimentally developed as possible aerospace coatings was investigated. The percentage of La_2O_3 among the tested composites showed improvements for the zirconia in terms of density, microstructure, and hardness, important properties in the development of ceramic coatings.

The crystalline structure of the composites was characterized by X-ray diffraction, which showed the formation of three phases corresponding to the precursor oxides, proving the formation of the composite. The relative density of the samples corresponded to the mean density values of the constituent oxides, around 4 to 5 g/m³. The electron microscopy of the composites followed by DES revealed a microstructure with a good homogeneity in the distribution of the constituents, with the presence of three distinct phases on X-ray diffraction. The microstructure of the composition C3, with a higher content of La_2O_3, shows the grains are more refined, indicating that La_2O_3 acted as a refinement agent. The average microhardness of the composites varied from 340 to 423 HV, which is considered a good result for this type of material. The composite with a higher content of La_2O_3 (10% by weight), sample C3, exhibited a higher value of microhardness.

The results showed that the addition of 10% of La_2O_3 to the studied composites resulted in improvement of their microstructural and mechanical characteristics, presenting a good perspective for aerospace applications; however, it is still necessary to perform other types of tests, such as fracture resistance, to guarantee that this composite can perform adequately.

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AUTHOR'S CONTRIBUTION

Conceptualization, Gomes NL and Yadava YP; Methodology, Domingues RO, Silva NDG and Lucindo VM; Investigation, Gomes NL and Lucindo VM; Writing – Original Draft, Gomes NL, Domingues RO and Silva NDG; Writing – Review and Editing, Gomes NL; Funding Acquisition, Ferreira RAS and Yadava YP; Resources, Ferreira RAS and Yadava YP; Supervision, Yadava YP.

REFERENCES

Christian W, Thays, M, Ralf K (2011) Processing of oxide/oxide composites for gas turbine applications based on braiding technique (OXITEX™). Mechanical properties and performance of engineering ceramics and composites VI: Ceramic Engineering and Science Proceedings. 32:23-28. https://doi.org/10.1002/9781118095355.ch3

Denry I, Kelly JR (2008) State of the art of zirconia for dental applications. Dent Mater J. 24(3):299-307. https://doi.org/10.1016/j.dental.2007.05.007

Dichiara AR, Boeing CO, inventors; Ceramic tile, for launch vehicles, comprises oxide ceramic matrix composite comprising ceramic fiber, and cured metal oxide ceramic material impregnating ceramic fiber, where core material has surface(s) covered by ceramic matrix composite. 2005, Patent number US2005084665-A1, US6969546-B2.

Dieese CNM/CUT. Setor aeroespacial. [accessed Jun 27 2018]. http:/www.cnmcut.org.br/conteudo/perfil-do-setor-4

Fahrenholtz WG, Hilmas GE, Talmy IG, Zaykoski JA (2007) Refractory diborides of zirconium and hafnium. J Am. Ceram. Soc. 90(5):1347-1364. https://doi.org/10.1111/j.1551-2916.2007.01583.x

Germer EM (2014) Avaliação do efeito da geometria da seção convergente em tubeiras de motor-foguete (Doctorate Thesis in Mechanical Engineering). Curitiba: Universidade Federal do Paraná. In Portuguese. [accessed Apr 04 2020]. https://acervodigital.ufpr.br/bitstream/handle/1884/36929/R%20-%20T%20-%20EDUARDO%20MATOS%20GERMER.pdf?sequence=1&isAllowed=y

Gleeson B (2006) Thermal barrier coatings for aeroengine applications. J Propul Power. 22(2):376-382, 2006. https://doi.org/10.2514/1.20734

Mecham M. (2012) Out of the lab. AW&ST. 174(13).

Oliveira FS (2013) Study of materials for the manufacture of hybrid propellant rocket nozzle (Master's Dissertation in Mechanical Sciences). Brasília: Universidade de Brasília. In Portuguese. [accessed Jul 20 2018]. https://repositorio.unb.br/bitstream/10482/14083/1/2013_FabioSilvaOliveira.pdf

Opeka MM, Talmy IG, Zaykoski JA (2004 Oxidation-based materials selection for 2000°C + hypersonic aerosurfaces: Theoretical considerations and historical experience. J Mater Sci. 39(19):5887-5904. https://doi.org/10.1023/B:JMSC.0000041686.21788.77

Pereira LX, Benegra M (2011) Revestimentos Alternativos para palheta de turbinas resistentes à oxidação. In: 5º Seminário de Iniciação Científica. 1:359-378.

Rêgo SABC, Ferreira RAS, Yadava YP (2012) Use of aluminum oxides, titanium and cerium in the production of ceramic composites for protective coating of storage tanks and transportation of oil raw. 56 Brazilian congress on ceramics. 46(25):1565-1276.

Santos TWG (2011) Desenvolvimento e estudo das propriedades mecânicas e características microestruturais do compósito cerâmico baseado em Alumina Zircônia aplicado em revestimento e proteção de tanques de petróleo cru (Master's Dissertation in Mechanical Engineering). Recife: Universidade Federal de Pernambuco, Departamento de Engenharia Mecânica. In Portuguese. [accessed Jun 15 2018]. https://repositorio.ufpe.br/handle/123456789/5375

Schloesser J, Fedorova T, Bäker M, Rösler J (2010) Thermal barrier coatings on copper substrates for rocket applications. J Solid Mech Mater Eng. 4(2):189-195. https://doi.org/10.1299/jmmp.4.189

Sutton GP, Biblarz O (2001) Rocket propulsion elements: an introduction to the engineering of rockets. 7th ed. Hoboken: John Wiley & Sons. 2001.

Wu Z-G, Zhao Y-X, Liu D-S (2004) The synthesis and characterization of mesoporous silica–zirconia aerogels. Micropor Mesopor Mat. 68(1-3):127-132. https://doi.org/10.1016/j.micromeso.2003.12.018

Zawada LP, Hay RS, Lee SS, Staehler J (2003) Characterization and high-temperature mechanical behavior of an oxide/oxide composite. J Am Ceram Soc. 86(6):981-990. https://doi.org/10.1111/j.1151-2916.2003.tb03406.x