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### PRODUCTION AND CHARACTERIZATION OF ZIRCONIA-ALUMINA CERAMIC COMPOSITES, REINFORCED WITH RARE EARTH OXIDES ( $Y_2O_3$ AND $La_2O_3$ ), FOR APPLICATION AS TBC IN THE EXHAUST NOZZLES OF GAS TURBINES

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**Abstract.** *Industrialization has driven research towards maximizing the efficiency of processes and equipment, and ceramics have been widely used in the industry to meet this demand. The aerospace sector, which deals with high pressure, temperature, and friction, has greatly benefited from the application of ceramics. One of the devices that suffers from the harsh conditions this sector imposes are the exhaust nozzles of gas turbines. Previous studies have shown that ceramic composites with a metallic matrix, such as zirconia, have improved mechanical properties that can be optimized by adding oxides such as alumina. To improve their mechanical strength and fracture toughness and reduce their inherent fragility, additives such as rare earth oxides, can be incorporated. The present work aims to determine the mechanical properties and suitability of zirconia-alumina ceramic composites reinforced with lanthania and yttria, both rare earth oxides, to evaluate their potential for application as a thermal barrier coating in the aerospace industry. The composites were produced by thermomechanical processing and sintered at 1350 °C for 12 hours. Structural and microstructural characterization was carried out using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), and mechanical properties were evaluated using Vickers microhardness (HV).*

**Keywords:** *aerospace sector, exhaust nozzles, thermal barrier coating,  $ZrO_2-Al_2O_3-Y_2O_3$ ,  $ZrO_2-Al_2O_3-La_2O_3$*

#### 1. INTRODUCTION

Gas turbines have been the driving force behind the development of the Brazilian aerospace sector, as they are in charge of generating the propulsion of airplanes and aircrafts. The power generated by these equipment is much greater than that of machines with the same weight, and therefore more efficiently (Pereira and Benegra, 2011).

Nozzles play a crucial role in producing the force required for rocket propulsion, as they convert the thermal energy of gases into kinetic energy. In this process, hot gases flow inside the equipment with high velocity and temperatures often exceeding 3000 K. Through convection and radiation, heat transfer occurs between the hot gases and the nozzle, elevating the temperature of the equipment up to 2000 K. Operating under such high temperatures presents a significant challenge when it comes to ensuring the safety and reliability of the nozzle. (Zhang, 2011)

Evidence has shown that by optimizing the tolerance of the nozzle's wall, made of nickel and cobalt superalloys, to especially high temperatures, the efficiency of rocket engines can be greatly enhanced. An attainable method to accomplish this improvement is the application of a plasma-sprayed ceramic coating to the surface of the wall. This is justifiable because the ceramic coating acts as an artificial thermal barrier, effectively impeding the heat transfer from the turbulent combustion gases to the metallic substrate (Alhama and Campo, 2013).

Over the years, several research endeavors have been dedicated to the development and manufacturing of ceramic thermal barrier coatings (TBCs) for turbine components. TBCs consist of complex structures composed of multiple layers and materials designed to endure severe conditions such as harsh temperatures, environmental factors, thermal cycling, and stress conditions throughout numerous aircraft takeoffs and landings (Gleeson, 2006).

TBCs are deposited on various critical parts of gas turbines, including transition pieces, combustion lines, first-stage blades and vanes and other high-temperature components of gas turbines, serving a twofold purpose: to

increase the inlet temperature, thereby improving efficiency, or to reduce the cooling system requirements (Cao et al, 2004).

Numerous studies from various fields have consistently demonstrated and established that ZrO<sub>2</sub> has exceptional properties, such as high strength, hardness, wear resistance, corrosion resistance, elastic modulus and thermal expansion coefficient similar to that of steel and iron, as well as high fracture toughness and chemical properties (Lin et al, 2021). With a compression strength of 2000 MPa, ZrO<sub>2</sub> can withstand diverse mechanical environments. Moreover, when subjected to stress on the surface of ZrO<sub>2</sub>, a crystalline modification impedes the crack propagation (Gautam et al, 2016).

Nevertheless, ceramic materials are inherently brittle, a factor that has limited the use of aforementioned materials in aerospace applications. Many efforts have been made to improve the properties of ceramic materials, and a viable solution to the challenge imposed by the intrinsic fragility of ceramics is the development of hybrid ceramic/metal materials (Camerini, 2013).

The stability of ZrO<sub>2</sub> is strongly influenced by the type and quantity of the oxide used to lower the temperature of the t-m transformation. Previous research (Kuranaga, 1997) substantiated the role of rare earth oxides as stabilizing agents to ZrO<sub>2</sub> under ambient temperature, leading to cost-effective processes while preserving the desired mechanical properties (Kuranaga, 2005).

In the present study, zirconia-alumina ceramic composites (ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) reinforced with rare earth oxides, namely yttria (Y<sub>2</sub>O<sub>3</sub>) and lanthania (La<sub>2</sub>O<sub>3</sub>), were produced through thermomechanical processing. These composites were subsequently characterized using X-ray Diffraction, Scanning Electron Microscopy, and Vickers microhardness. This work aims to determine the mechanical properties and suitability of these ceramic composites to evaluate their potential for application as a thermal barrier coating in exhaust nozzles.

## 2. MATERIALS AND METHODS

For the development of the composites, both with a zirconia-alumina ceramic matrix, but each reinforced with a different rare earth oxide, the proportions of zirconia, alumina and rare earth oxides were the same. Al<sub>2</sub>O<sub>3</sub> was added in ZrO<sub>2</sub> in 10wt% ratios and the rare earth oxides were added at a 5wt%. Table 1 presents the phase compositions of the composites.

Table 1. Ceramic components compositions, in percentage per weight

Ceramics	ZrO <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	La <sub>2</sub> O <sub>3</sub> (wt%)	Y <sub>2</sub> O <sub>3</sub> (wt%)
C.La	85	10	5	-
C.Y	85	10	-	5

The weight of each sample was fixed at 50g. Using a ball mill (Equipments Marconi MA-50), each batch was mixed for a period of 6 hours, in a stainless-steel milling chamber with 35 alumina balls. Equation 1 is used to determine the number of balls according to the size of the chamber:

$$P = 0,6pVd_b, \quad (1)$$

where  $P$  is the total volume of the balls, in g,  $V$  is the chamber's effective volume, in cm<sup>3</sup>,  $p$  is the balls' occupation ratio (between 0,5 and 0,55) and  $d_b$  is the density of each ball, in g/cm<sup>3</sup>. The milling process allows the ceramic mixtures to be mixed and homogenized, while still reducing particle size, which increases the reaction rate of the components and improves the mechanical properties of the ceramics.

Subsequently, the ground and homogenized samples were compressed into disc by a uniaxial press (Schiwing SIWA, modelo ART6500089), using a metallic mold, fabricated from abrasion resistant AISI A2 steel (HRC 58). The ceramic powder was subjected to a load of 5, 7 and 12 ton/cm<sup>3</sup> for, respectively, 1, 1 and 3 minutes, totalling 5 minutes, to ensure the stability of the pressure load distribution in the pressed compact. Each disc weighed 3g and had a 15 mm diameter and an average 3 mm thickness.

The compacted discs later underwent the normal solid state sintering process, at 1350 °C for 12 hours. Sintering was carried out from ambient temperature in high purity alumina crucibles, using a high temperature muffle furnace (Jung 0614), followed by furnace cooling until the samples returned to the initial temperature. The sintering process is important because of the many changes it inflicts on the ceramic, like porosity reduction and the thickening of grains. The sintered discs were subjected to metallographic processing, with sandpaper granulometry varying from 200 to 1200, and polished with an electric rotary sander (Arotec, Aropol 2V) until the surface acquired a mirror-like appearance.

The structural characteristics and identification of phases were analyzed by X-ray diffractometry (XRD) using a Shimadzu X-ray Diffractometer, equipped with Cu-Kα radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Once the analysis confirms the

composite formation, mechanical properties and microstructural features of the sintered ceramics are studied, in order to assess their potential as ceramic coatings for the nozzles of gas turbines.

The mechanical properties of the sintered ceramic composites were studied using a Vickers hardness indenter, model HVS-5, N° 0021. To obtain the Vickers micro-hardness, 12 indentations were made and the two most disparate values were excluded from the calculation of the arithmetic average and standard deviation. The results from this process express the resistance imposed by the surface of the ceramic composites to the penetration of a pyramidal diamond. The microstructure of the sintered ceramic composites was studied by Scanning Electron Microscopy (SEM), using a scanning electron microscope (Oxford, X-act) and Energy Dispersive Spectroscopy (EDS), using a unit attached to the microscope (Tescan, Mira 3). Because the composites are not electrical conductors, the samples were covered by a thin layer of gold, using a sputtering coater (Quorum, SC7620).

### 3. RESULTS AND DISCUSSIONS

#### 3.1 X-ray diffraction (XRD)

The diffractogram peaks were identified through qualitative analysis, utilizing well-established diffractometry parameters available in databases such as the International Centre for Diffraction Data (ICDD), the Inorganic Crystal Structure Database (ICSD), and the American Mineralogist Crystal Structure Database (AMCSD).

The structural characteristics and identification phases analyzed by XRD exhibited the typical behavior of  $ZrO_2$ - $Al_2O_3$  reinforced with their respective rare earth oxides ( $La_2O_3$  and  $Y_2O_3$ ). The ceramic composites did not display additional stages, only the constituent phases,  $ZrO_2$ ,  $Al_2O_3$  and either  $La_2O_3$  or  $Y_2O_3$ , indicating no reaction between the constituent materials, resulting in composite formation. The presence of rare earth oxide phases can be subtly observed in the XRD patterns due to their low percentage in the compound.

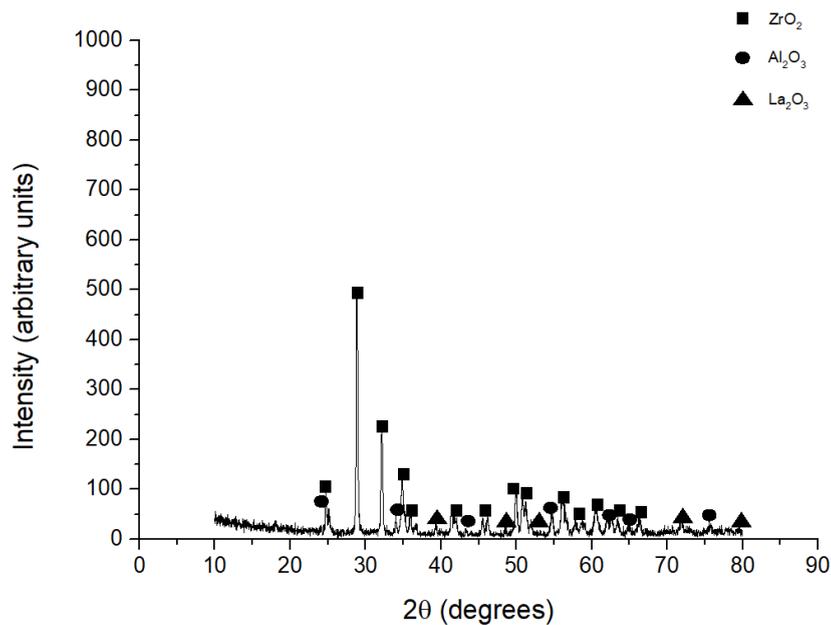


Figure 1. Diffractogram of the lanthania sample.

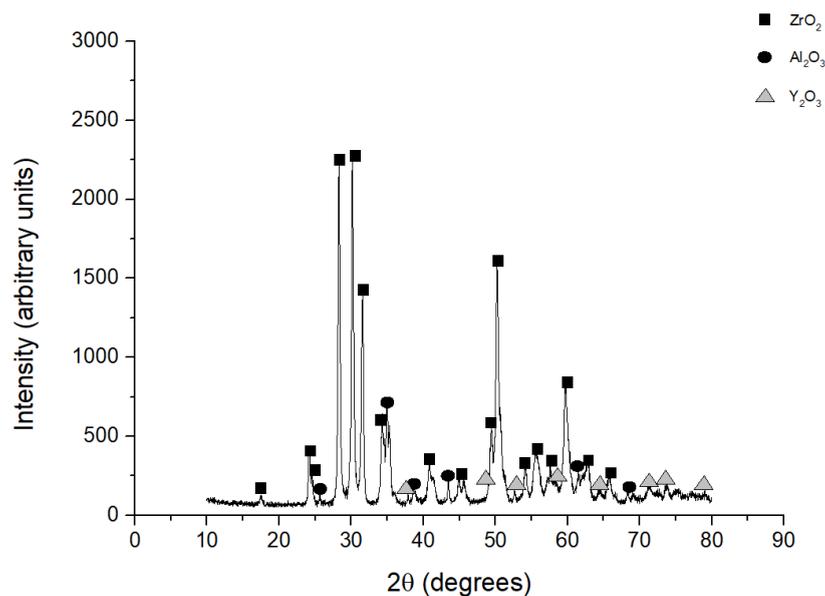


Figure 2. Diffractogram of the yttria sample.

### 3.2 Scanning Electron Microscopy (SEM)

The microstructure of the ceramic composites was analyzed through SEM, a technique where the presence of the phases, also studied through XRD, can be verified and the difference in grain size and distribution is more explicit. The SEM micrographs were taken using backscattering electron mode, and seen in the images below.

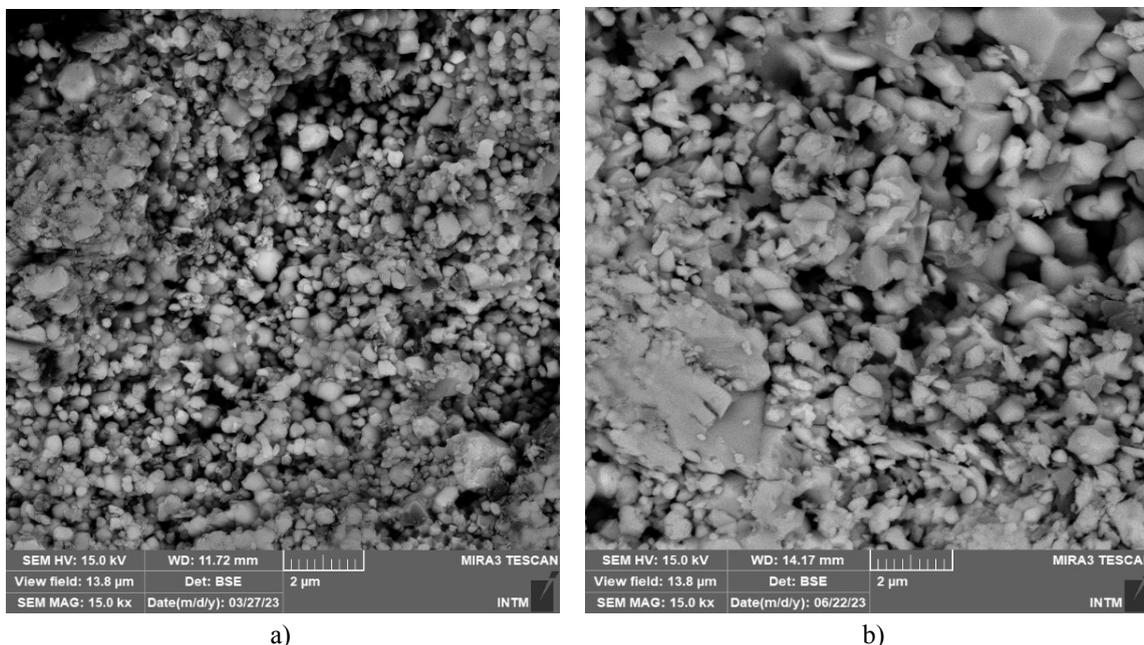


Figure 3. SEM of the samples reinforced with, a) yttria and b) lanthania.

Figures 3a and 3b demonstrate good homogeneity. The rare earth oxides act as grain refinement agents, with yttria having a better outcome than lanthania. The images also confirm the densification of the material, signs of an effective sintering process. The pores seen in the images are expected defects, as they are inherent to the processing of ceramics.

### 3.3 Energy Dispersive Spectroscopy (EDS)

Through this technique, the constituent element of the composites can be visualized, and no signs of contamination were detected throughout the various processes. The presence of each element varies according to the region and the detailed results of the Energy Dispersive Spectroscopy analysis, as element maps, are presented below.

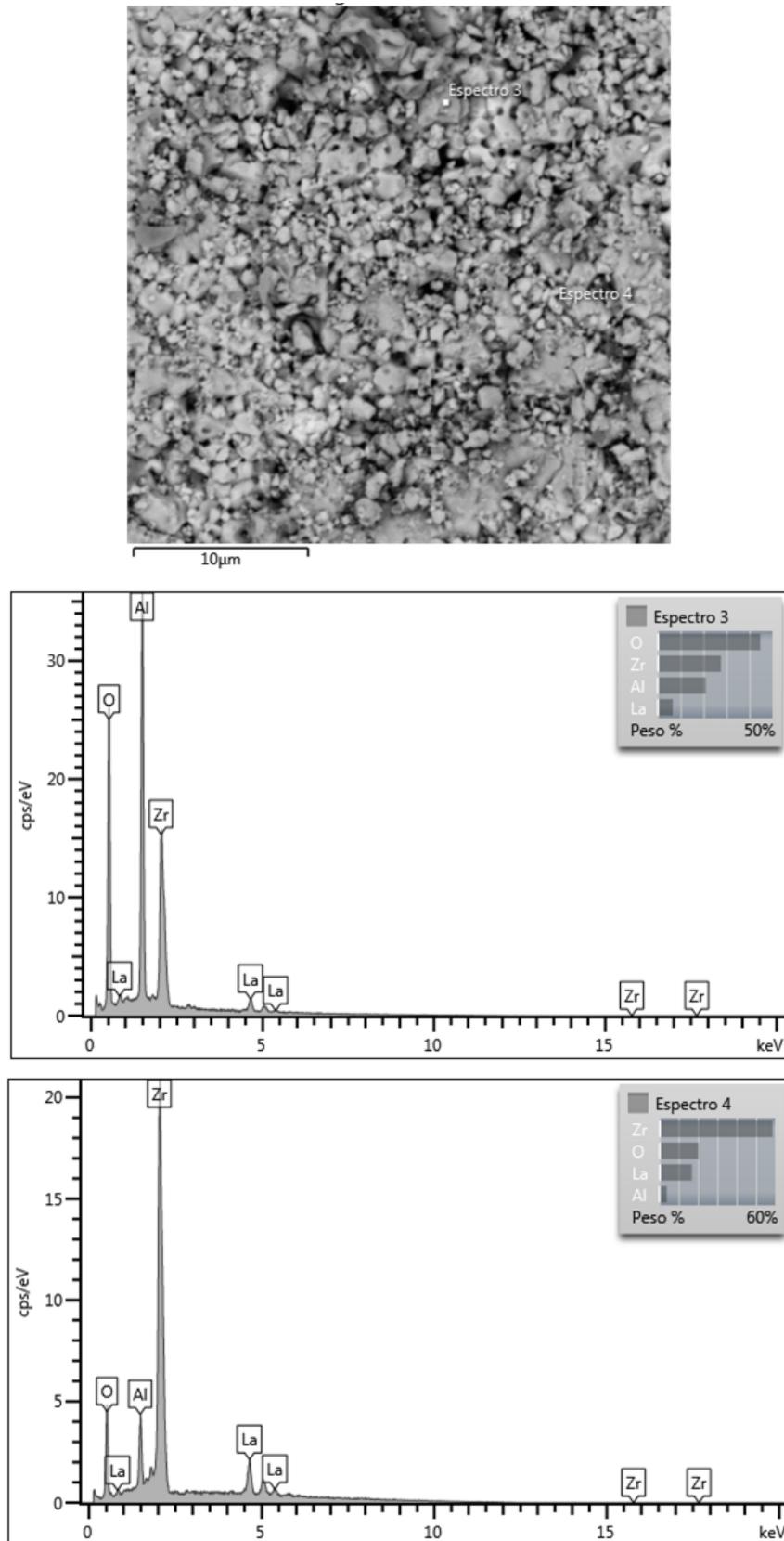


Figure 4. EDS analysis of the lanthania sample.

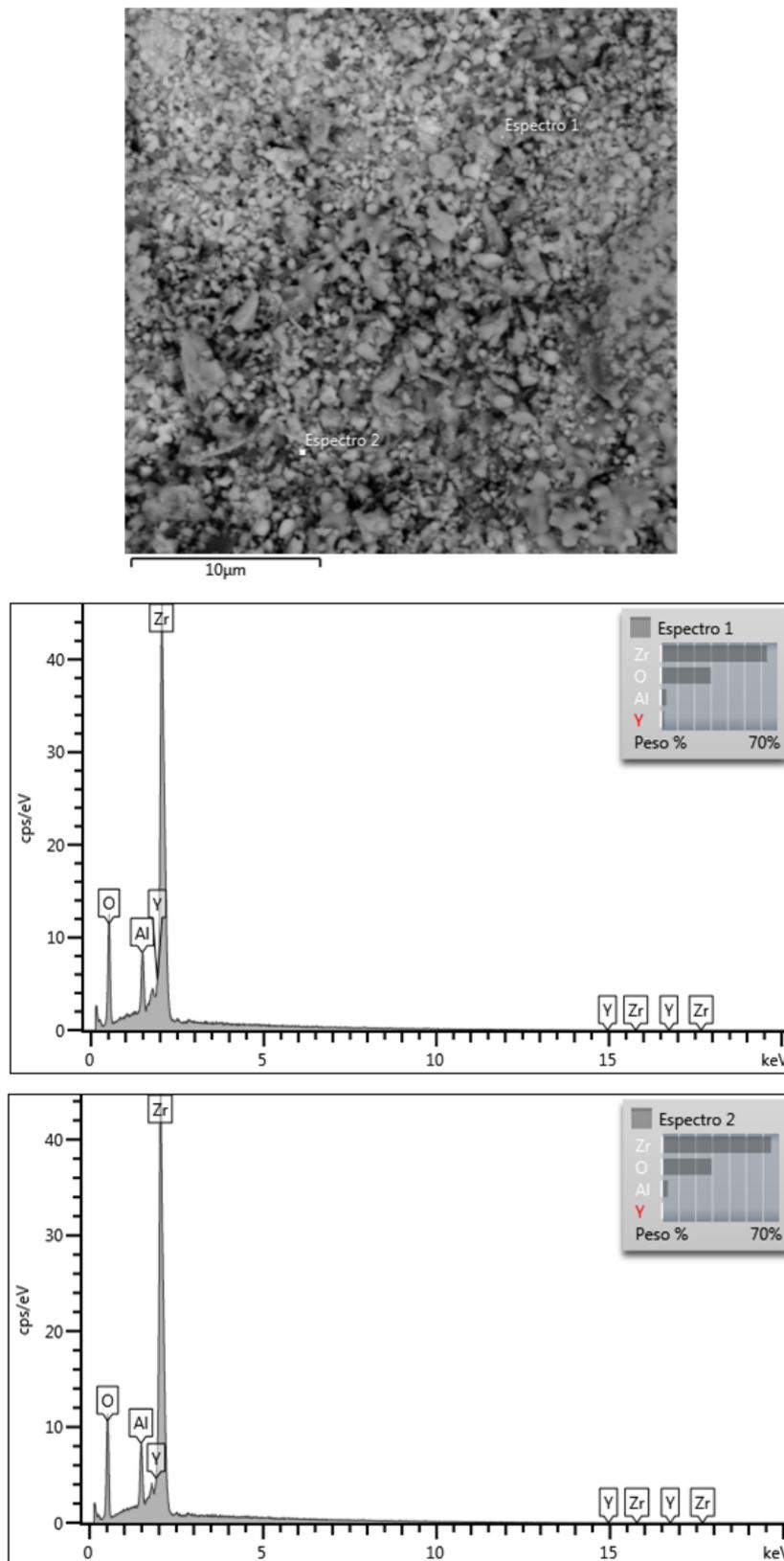


Figure 5. EDS analysis of the yttria sample.

### 3.4 Vickers micro-hardness

The Vickers micro-hardness test allows a connection to be made between the presence of different rare earth oxides in the composites and their microstructure, despite the proportions. Table 2 presents the data collected from this test, as well as the average and standard deviation.

Table 2. Indentation values of the Vickers micro-hardness of each sample and their arithmetic average and standard deviation.

	<b>C.Y</b>	<b>C.La</b>
<b>Vickers micro-hardness (HV)</b>	162.33	158.81
	158.71	155.62
	146.12	151.87
	146.03	146.12
	141.05	141.59
	136.12	139.38
	135.47	133.75
	135.40	127.58
	129.78	122.65
	126.91	120.72
<b>Arithmetic average and standard deviation (HV)</b>	144.092 ± 11.605	139.809 ± 11.824

It is observed in Table 2 that the Vickers micro-hardness of the ceramic reinforced with yttria presents a higher average and smaller standard deviation, indicating that yttria-stabilized zirconia may contribute positively to the increase in fracture toughness, an important property of the ceramic coatings.

## 4. CONCLUSION

The XRD results show that the sintering process was successful and the composites were formed in both cases. The grain size and distribution of the 85%ZrO<sub>2</sub>-10%Al<sub>2</sub>O<sub>3</sub>-5%Y<sub>2</sub>O<sub>3</sub>, as presented in the images generated by SEM, was more efficient than that of the lanthania composite. The yttria composite also has a better Vickers microhardness and standard deviation than the other composite. Therefore, the 85%ZrO<sub>2</sub>-10%Al<sub>2</sub>O<sub>3</sub>-5%Y<sub>2</sub>O<sub>3</sub> composite has mechanical properties and suitability with greater potential for application as TBC in exhaust nozzles of gas turbines in the aerospace sector.

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