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PRODUCTION, CHARACTERIZATION AND STABILITY STUDY OF CERAMIC COMPOSITES Al_2O_3 - CeO_2 - TiO_2 IN PETROLEUM FOR COATINGS OF METALLIC PARTS OF THE PETROLEUM INDUSTRY

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Abstract. *The Petroleum and its derivatives are extremely important to a modern society [1]; however, the peculiar characteristics of petroleum, such as corrosive and chemically reactive character, give rise to hostile environments. With this comes the need to find materials that are able to resist severe environments. One way of solving the problem of surface degradation is the use of ceramic materials based on alumina as an inert coating to hostile environments by the hypersonic thermal spray coating (HVOF) process. With the coating application, it is possible to avoid the process of corrosion and wear of transport and storage tanks of petroleum. In the present work were produced ceramic composites based on Al_2O_3 - TiO_2 reinforced with CeO_2 in proportions of 10-20% by weight of TiO_2 and, 5% and 7% by weight of CeO_2 and studied as structural, microstructural and mechanical properties. We produced these composites by a thermomechanical process, sintered at $1350^\circ C$, analysed by scanning electron microscopy and Vickers microhardness. The results of this study are analysed, discussed in this paper.*

Keywords: *ceramics composites, Alumina-Titania, reinforcement of CeO_2 , inert coatings, stability in crude petroleum.*

1. INTRODUCTION

Discovery of Brazilian pre-salt petroleum reservoir has created an intense demand for new materials capable of withstanding direct contact with the crude petroleum (Thomas, 2001; Becher, 1991). Crude petroleum is a highly corrosive product, a fact that makes it very difficult transport and storage and ceramic materials are the most suitable for this purpose, especially ceramics based on alumina

Ceramic materials are the most suitable for this purpose, especially ceramics based on alumina. To increase the resistance of the alumina ceramic is used additives and the most used are the constituents of TiO_2 , TiN , etc. (Holleck, 1990). Rare earth oxides are used as reinforcements in ceramics based on alumina for increasing the toughness of ceramics.

In the present work, we produced new ceramic composites (Al_2O_3 - CeO_2 - TiO_2) and studied the characterization of these composites through X-Ray Diffraction, Scanning Electron Microscopy (SEM) and Vickers Microhardness. With the analysis, it was possible to observe that the composites have very good properties to be utilized in petroleum industry.

2. EXPERIMENTAL DETAILS

This section describes the methodology used in the fabrication and characterization of ceramic composites based on alumina-titania reinforced with rare earth (ceria). The characterization of these ceramics was performed prior to immersion in crude oil and followed the flowchart shown in Figure 1.

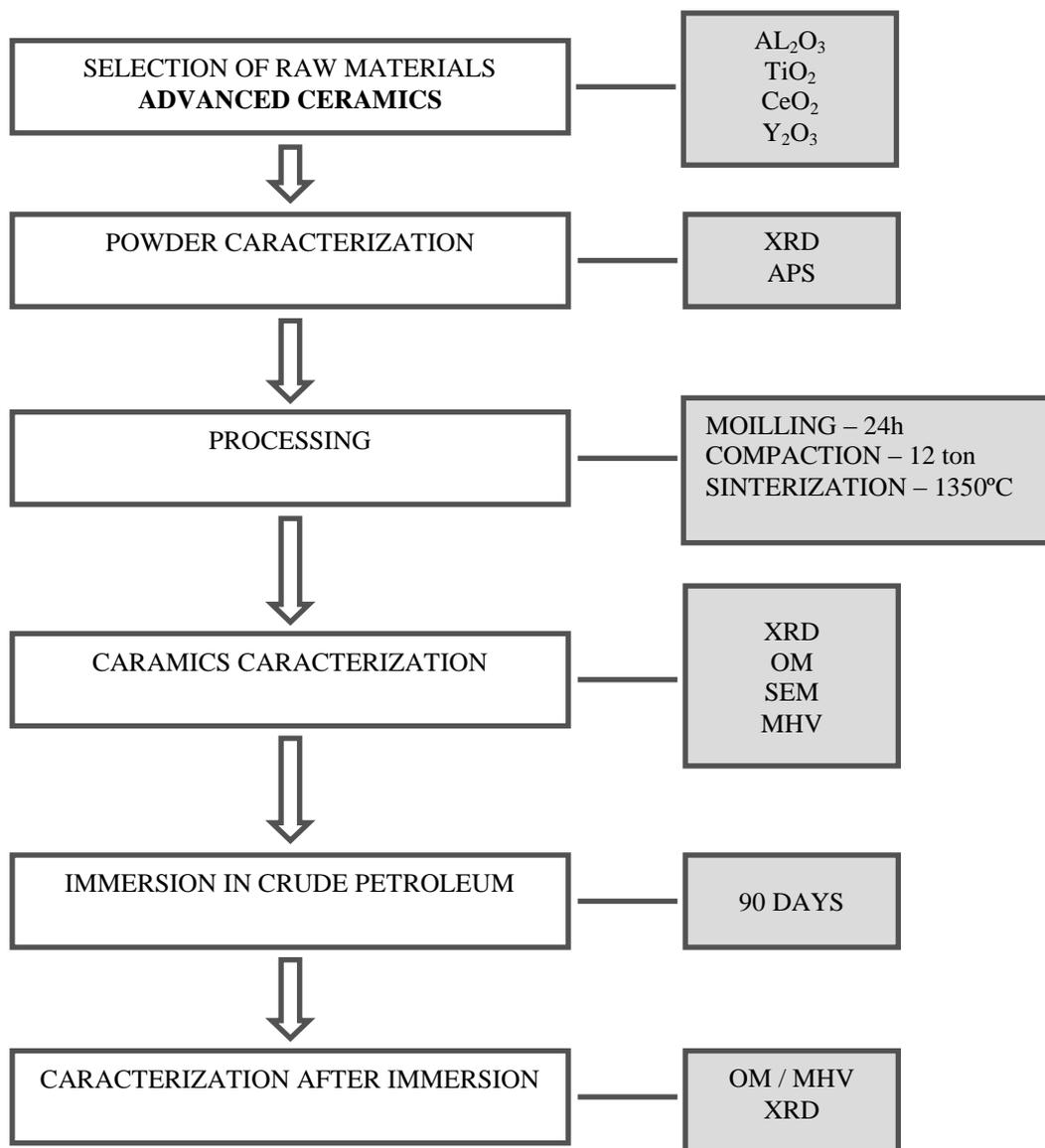


Figura 1 - Flowchart of the experimental procedure.

The quality of ceramic depends, among other factors, the physical and chemical characteristics of the materials used in its composition. In this work was used oxides: Al₂O₃, TiO₂, CeO₂, with high purity for the preparation of ceramic composites. The characterization of the constituents was carried out by X-ray diffraction that was used X-ray diffractometer (Bruker, model D8 Advanced Davinci) with Cu-Kα radiation ($\lambda = 1.5406 \text{ \AA}$). The powders of the oxides were weighed on an analytical balance and were divided into 6 groups of ceramic mixes as showed in Table 1.

Table 1 – Percentage of oxides to composition of ceramics composites samples.

Composition	Al ₂ O ₃	TiO ₂	CeO ₂	Total em %
1	85%	10%	5 %	100%
2	80%	15%	5 %	100%
3	75%	20%	5 %	100%
4	83%	10%	7 %	100%
5	78%	15%	7 %	100%
6	73%	20%	7 %	100%

Particle size distribution analysis of constituent powders (Al_2O_3 ; TiO_2) was carried out using a LAZER particle size analyzer Microtrac, model S3500, through wet process to assess the effect of grinding on the size of the ceramic powder before and after 24 hours of milling.

The constituent powders of each sample type were mixed in an agate mortar for 20 minutes to homogenize the composites. After this, the samples were compacted by uniaxial pressing in a manual hydraulic press (SCHIWING SIWA, ART6500089) which was applied a load of 12 ton/cm² by using a mold 15 mm in diameter to obtain the composite ceramic discs.

The compacted discs were subjected to a sintering process at a temperature of 1350° for 24 hours, using a high temperature muffle furnace (furnace Jung model 0614). After sintering, samples were separated for to be subjected the analysis of X-ray diffraction, Vickers hardness and scanning electron microscopy. The ceramics composites were polished to be a "mirror-like shine" and are therefore ready for analysis.

The microstructure analysis of ceramic composites were carried out by scanning electron microscopy (HITACHI, model TM3000). For the surface observation the samples were covered with a thin layer of graphite in a carbon coating unit (Cressington, model 108carbon / A). Mechanical properties of the sintered ceramics were studied through Vickers microhardness testing using a microhardness tester indenter model HVS-5 No. 0021, application a load of 50 kgf for a period of 15 seconds. Nine readings were taken and the two most discrepant were removed. The microhardness was obtained by the arithmetic mean of the remaining 7 readings.

3. RESULTS AND DISCUSSION

3.1 Particle Size Analyse

The study of particle size analysis was carried out to analyze the grain size distribution, considering that it is a fundamental factor for the sintering, microstructure and mechanical properties of the final product. The particle size distribution curves of the powders constituents (Al_2O_3 ; TiO_2) are shown in Figure 2. From this curve, the parameter D50 was obtained which is related to the median of the distribution corresponding to the mean particle diameter (D_m).

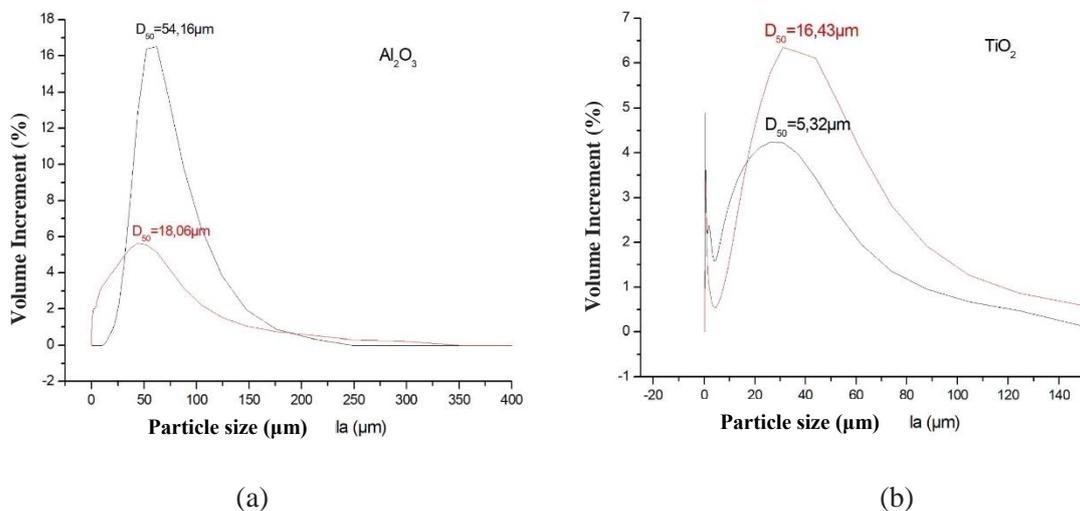


Figure 2: Granulometric distribution after and before milling (a) Al_2O_3 , (b) TiO_2

Through the result of the particle size analysis before and after grinding, it is possible to verify if the alumina had a significant reduction from 54.16 μm to 18.06 μm and the Titania reduced from 16.43 μm to 5.32 μm. However, for a better sintering of the composites, it is necessary to guarantee the homogeneity in the particle size of the constituent ceramics. For the continuation of this project, was used alumina milled for 24 hours and the Titania supplied by the manufacturer.

3.2 X-Ray Diffraction

Ceramics composites sintered were analyzed by X-ray diffraction to analyze the structure. Observing the X-ray diffraction of Figure 3, it was possible verified that even after heat treatment; do not have formation of new phases, in the other words, the composite preserved individual characteristics and phases of the constituent powders.

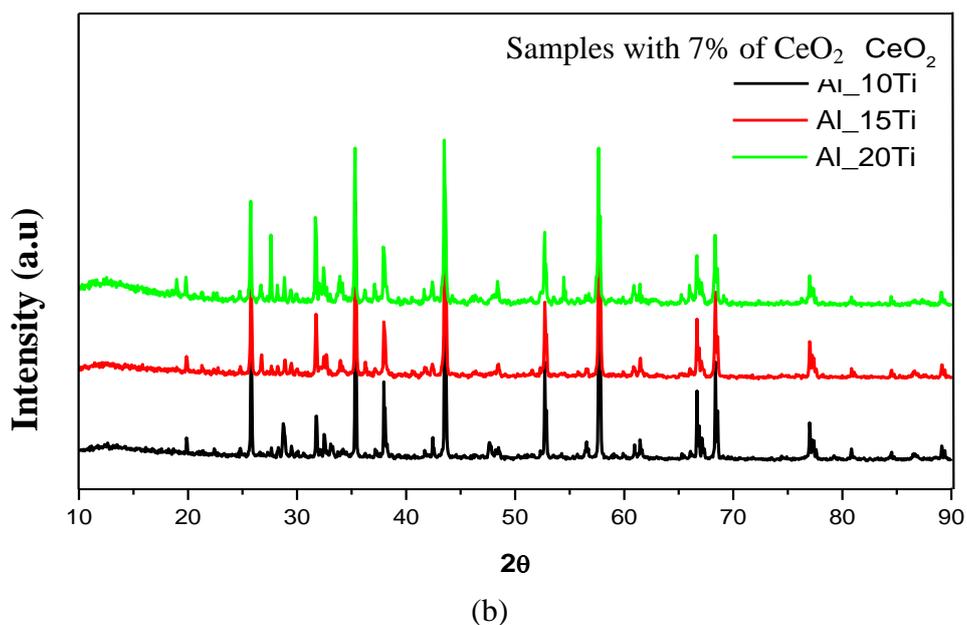
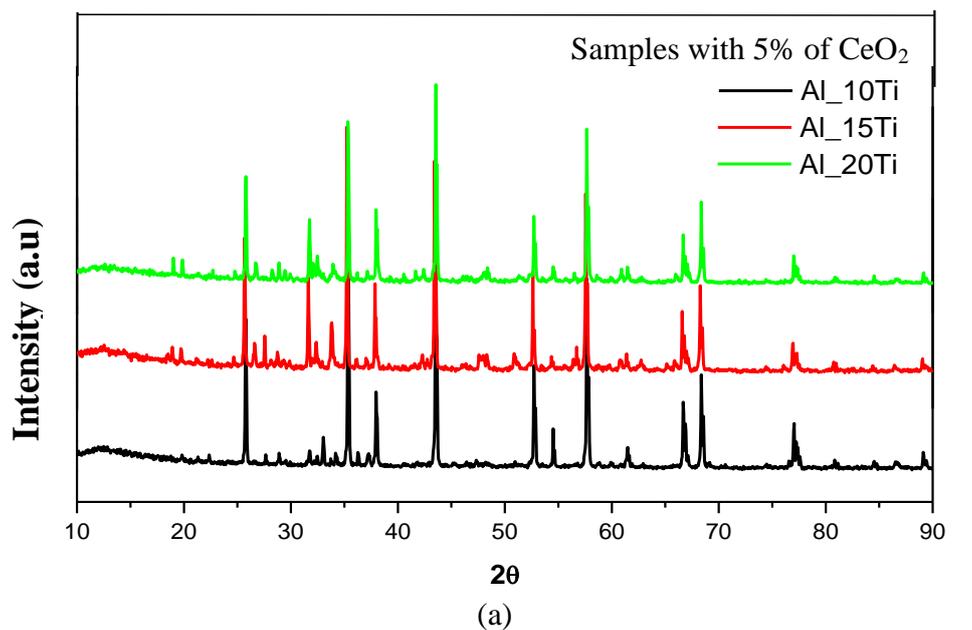


Figure 3 - DRX of samples sintered at 1350°C for 24 hours, (a) Samples with 5% of CeO_2 , (b) Samples with 7% of CeO_2

The diffractograms indicate that after the heat treatment no new phases were formed, and that all peaks indexed are characteristic peaks of one of their constituents, that is, the composite preserved the characteristic and individual phases of each of the powders starting.

3.3 Scanning Electron Microscopy (SEM)

The analysis of the microstructure of the composite was performed using SEM (Fig. 4). It is possible to observe that with increasing percentage of TiO_2 did not have visible difference though images, but with increasing percentage of CeO_2 is better distribution of the grains and an improved densification of the composite.

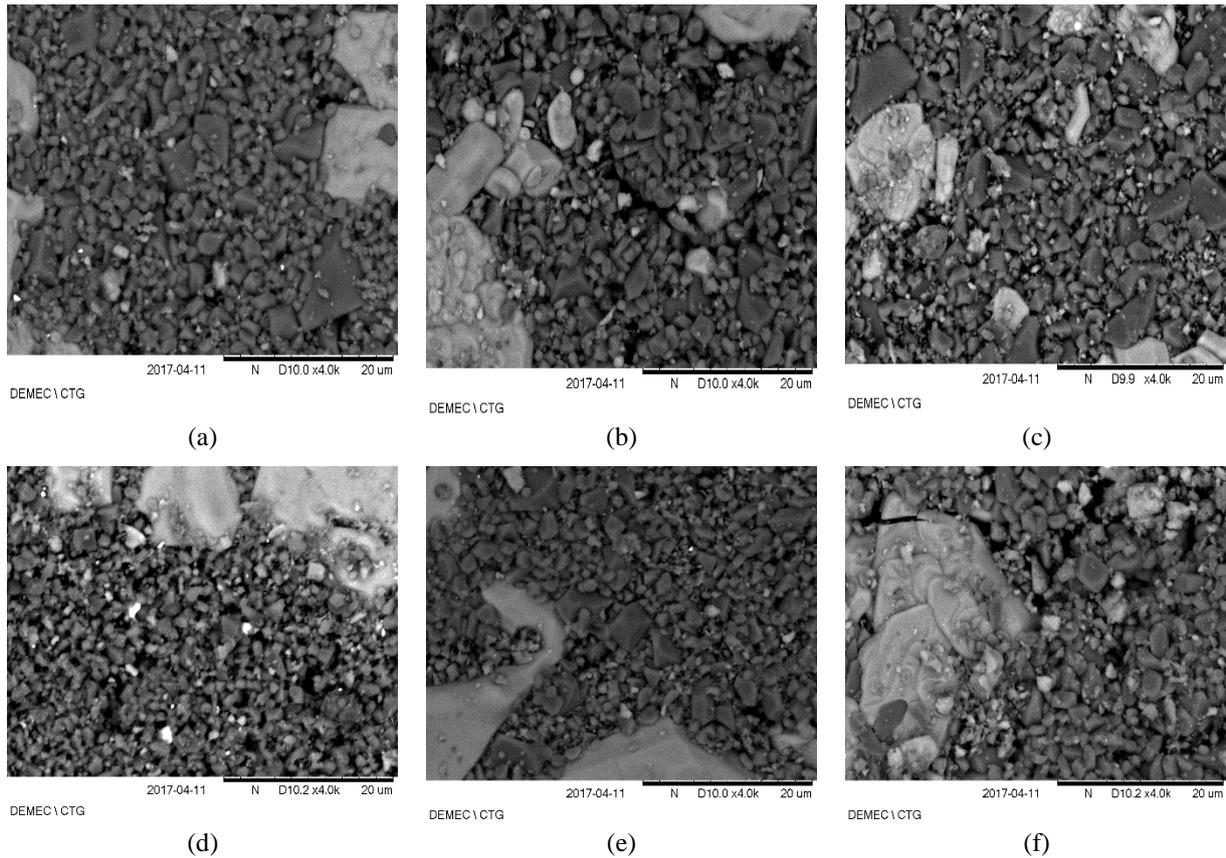
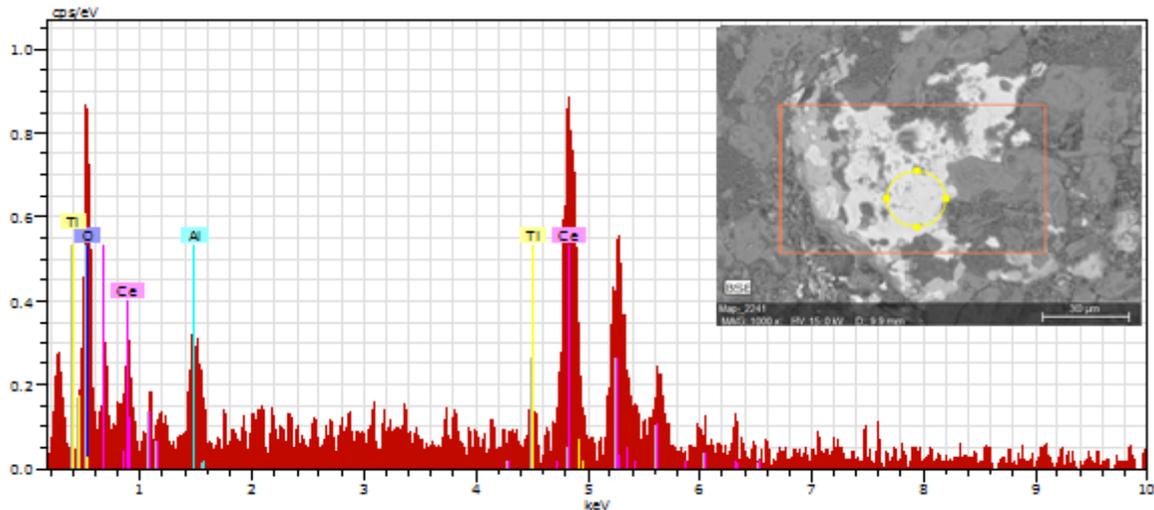


Figure 4 - Results obtained of SEM micrograph with magnification of 3000x (a) Sample 1 - with 10% of TiO_2 -5% CeO_2 , (b) Sample 2 - with 15% of TiO_2 -5% CeO_2 , (c) Sample 3 - with 20% of TiO_2 -5% CeO_2 , (d) Sample 4 - with 10% of TiO_2 -7% CeO_2 , (b) Sample 5 - with 15% of TiO_2 -7% CeO_2 , (c) Sample 6 - with 20% of TiO_2 -7% CeO_2 .

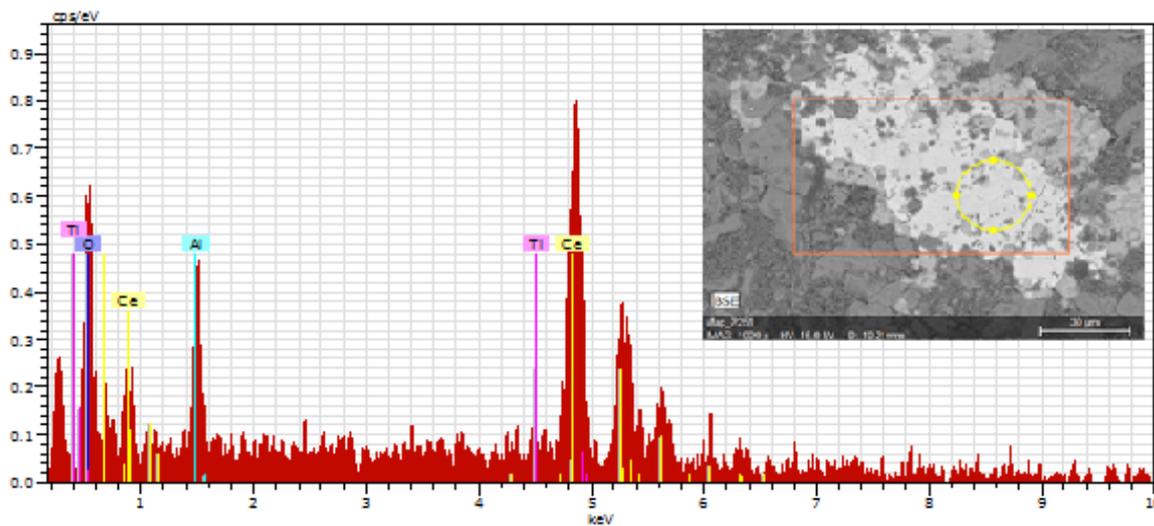
As a result, we have composites with a uniform surface morphology, grain homogeneity and particle size distribution.

3.4 X-ray dispersive energy spectrometry (ESD)

Elemental analysis of the ceramic composites was carried out by ESD, through the backscattered electrons resulting from the Scanning Electron Microscopy (SEM) test. The analyzes were performed for all 6 ceramics under study, with the percentage of titania (10%, 15% and 20%) and rare earth oxides (5% CeO_2 , 7% CeO_2). Figure 5 shows the ESD results of the samples with 20% TiO_2 ($\text{Al}_{20}\text{Ti}_{5}\text{Ce}$; $\text{Al}_{20}\text{Ti}_{7}\text{Ce}$) and shows that all the composites analyzed have the same elemental base: aluminum (Al), titanium (Ti), cerium (Ce), Yttrium Y) and oxygen (O).



(a)



(b)

Figure 5 - ESD a) $\text{Al}_{20}\text{Ti}_5\text{Ce}$, b) $\text{Al}_{20}\text{Ti}_7\text{Ce}$

3.5 Vickers Microhardness (MHV)

The Vickers microhardness tests performed on the six types of samples were satisfactory, since the values of the microhardness decreased with the increase of TiO_2 percentage. The table 2 and figure 6 show the values of the Vickers microhardness averages and the graph making it possible to compare the mechanical properties between the compositions of the titanium oxide as well as of the cerium oxide.

Table 2 - Results of Vickers Microhardness of sintered composites

TYPE	MHV (Kgf/mm ²)	
	5% CeO_2	7% CeO_2
10% TiO_2	339,20	126,10
15% TiO_2	299,66	81,99
20% TiO_2	105,15	33,07

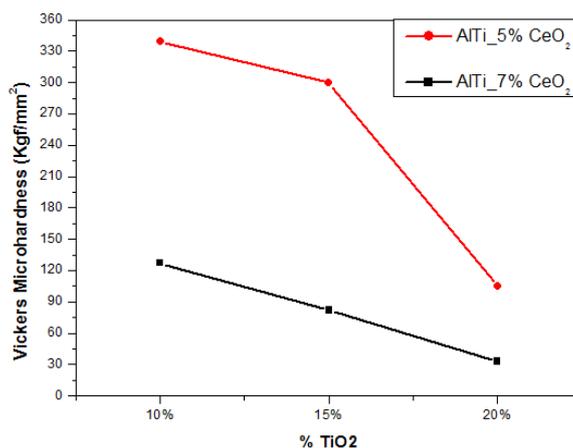


Figure 6 - Result of Vickers Microhardness of sintered composites

For the composites made with ceria (rare earth oxide), it is possible to verify that the best hardness results were obtained in the samples with 10.0% TiO₂, (Al₁₀Ti₅Ce and Al₁₀Ti₇Ce) and the other samples also had satisfactory hardness as shown by Figure 6

It can be observed that the hardness of the samples, regardless of the percentage of the rare earth oxide (CeO₂), decreases with the increase of the percentage of TiO₂. This result was expected because the literature (Fu, Gu, Du, 2001) states that the addition of some oxides such as TiO₂, TiN, ZrO₂, etc., are used to improve the mechanical properties, in this case the toughness fracture of the ceramic.

4. CONCLUSIONS

In this present work, we have developed fabricated and characterized new ceramic composites (alumina-titania-Ceria) for use in the petroleum industry. It was observed that the grinding parameters were satisfied for the alumina, because there was a reduction of 66.65% of the average diameter of the particles, ensuring that the alumina and Titania sizes were close. Structural characteristics were confirmed by X-ray diffraction, which was possible check that no new phase was formed and the composite preserved the characteristic and individual phases of each of the powders starting, indicating the formation of composites. The microstructure was analyzed by scanning electron microscopy, showed high homogeneous and there was a good particle size distribution of the composite and sample with 7% CeO₂ had better results. Mechanical behavior of the composites was studied by Vickers microhardness testing, which the sample with 10% TiO₂ and 5% CeO₂ showed the best result. From these promising results, we conclude that these ceramic composites could be potential candidate ceramic composites for use as a ceramic coating of metallic parts for the petroleum industry. After this, the composites will be immersed in crude petroleum to analysis the stability in hostile environment created by crude petroleum.

5. ACKNOWLEDGEMENTS

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7. RESPONSIBILITY NOTICE

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