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DEVELOPMENT AND CHARACTERIZATION OF ALUMINA-TITANIA CERAMICS COMPOSITES REINFORCED WITH HO_2O_3 FOR FABRICATION OF INERT COATING IN METALLIC TANKS OF PETROLEUM INDUSTRY

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Abstract. *Due to the importance of petroleum and its derivatives for modern society, it is necessary to develop technologies that improve processes and transports of petroleum. The crude oil creates hostile environments and in the process of transport and storage of petroleum are used metallic materials, which corrode becoming a critical problem in this industry. One way of solving this problem is the use of ceramics based on alumina as inert coating on hostile environments. In this work was studied a structure, microstructure and mechanical properties of ceramic composite based on* Al_2O_3*-*TiO_2 *reinforced* Ho_2O_3*. The composites were produced by a thermomechanical process, sintered at 1350°C, were analyzed by x-ray diffraction, optical microscopy, scanning electron microscopy, and microhardness. Analyses were performed before and after immersion in earth and offshore crude petroleum to study stability of the developed composites and concluded that the ceramic composites immersed in petroleum show stable in hostile environments.*

Keywords*: ceramics composites, Alumina-Titania, reinforcement of* Ho_2O_3*, inert coatings, stability in crude petroleum*

1. INTRODUCTION

Nowadays, the petroleum is the most important source of energy and its derivatives are essential to society (HOLLECK, 1990). Crude oil consists not only hydrocarbons but also by other organic compounds, the most common being the sulfur, nitrogen, and on oxygen and some metals. These constituents make it a chemically aggressive and highly corrosive product, thus affecting the transport and storage industry. The surface degradation of metallic materials transport tanks is an obstacle that the oil industry has been facing.

An alternative to solve the problem of surface degradation of metallic materials of the storage tanks and transportation is the use of coatings which are resistant and inert to chemical and corrosion attack caused by crude petroleum. Ceramic materials, by having properties such as high corrosion and mechanical strength, 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, ZrO_2, Cr_2O_3, NiO, etc. (FU, Y.; GU, Y.W.; DU, H, 2001; FU, C.T.; WU, J. M.; LI, A. K, 1994). Rare earth oxides are used as reinforcements in ceramics based on alumina for increasing the toughness of ceramics.

In the present work, it was produced ceramic composites based on Alumina-Titania (TiO_2-Al_2O_3) reinforced with Holmia (Ho_2O_3) and studied the stability of this composites when immersed in earth and offshore crude petroleum, and were made comparisons of optical microscopy, X-ray diffraction and hardness of the samples before and after immersion in crude petroleum by a total of 60 days. With the analysis, it was possible to observe that the composites suffered no major mechanical, structural and microstructural changes shown to be stable in the petroleum environment.

2. EXPERIMENTAL DETAILS

A major concern in the application of ceramic materials is related to its manufacturing method, because they influence directly in their final properties. Figure 1 following the processing flow of the ceramic powders.

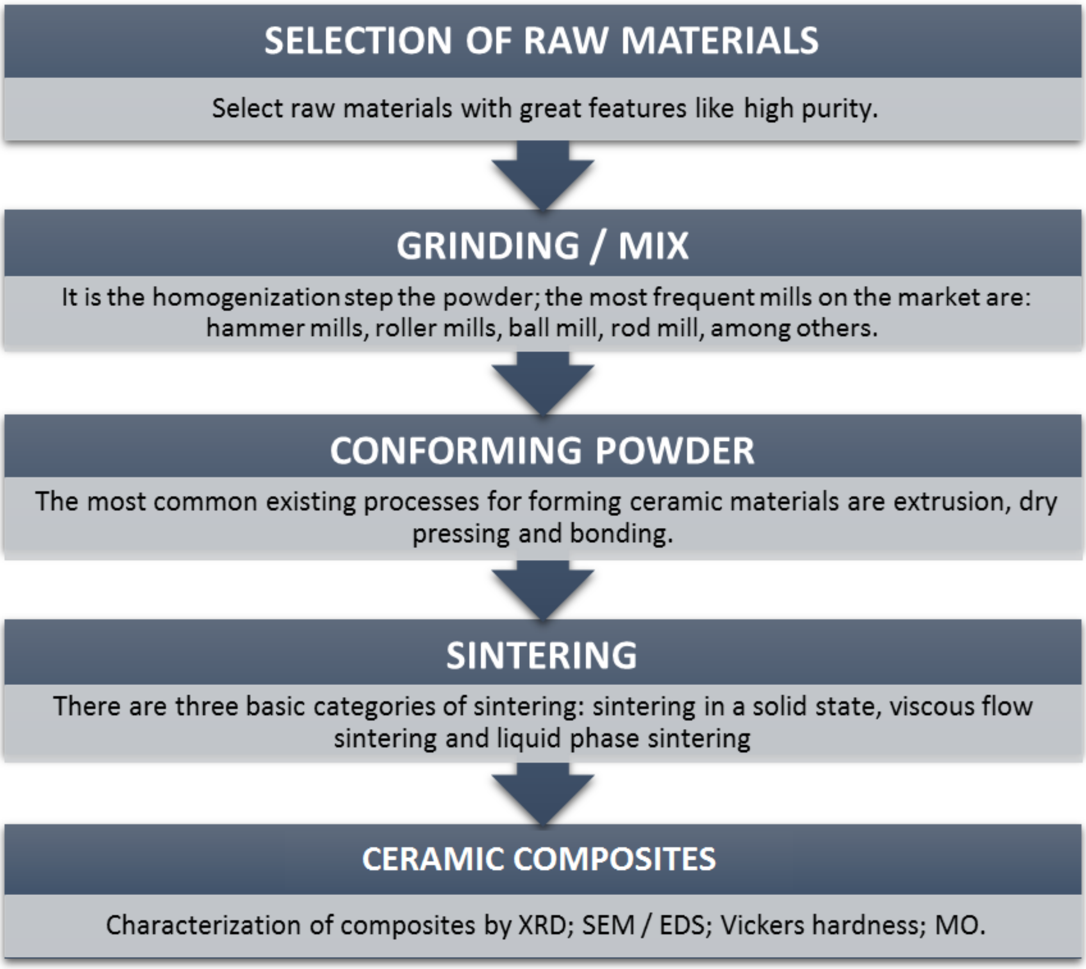


Figure 1 - Flowchart of manufacturing and testing process of the ceramic pellets.

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: Al_2O_3, TiO_2, Ho_2O_3, with high purity for the preparation of ceramic composites. The characterization of the constituents was carried out by X-ray diffraction that was used a Siemens D-5000 diffractometer with Cu-Ka radiation (λ = 1.5406 Å). The powders of the oxides were weighed on an analytical balance and were divided into 4 groups of ceramic mixes (Table 1).

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

Composition	Sample (A)	Sample (B)	Sample (C)	Sample (D)
Al_2O_3	94,0 %	89,0 %	84,0 %	79,0 %
TiO_2	5,0 %	10,0 %	15,0 %	20,0 %
Ho_2O_3	1,0 %	1,0 %	1,0 %	1,0 %
TOTAL (%)	100 %	100 %	100 %	100 %

The constituents of each sample type were mixed for a period of 24 hours in a ball mill using alumina cylinder and alumina balls to obtain a better homogeneity and reduced graininess. Particle size distribution analysis was carried out using a LAZER particle size analyzer Malvem Instruments model MASTERSIZE 2000, though wet process to assess the effect of grinding on the size of the ceramic powder before and after 24 hours of milling. Homogenized mixture, taken out from the ball mill, was 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 30 mm in diameter to obtain the composite ceramic discs.

The compacted discs were subjected to a sintering process at a temperature of 1350º for 24 hours in ambient atmosphere, 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, scanning electron microscopy and optical microscopy. The ceramics composites were polished to be a "mirror-like shine" and are therefore ready for analysis.

Microstructure analysis of ceramic composites were carried out by scanning electron microscopy (model JEOL JSM-5900). Optical microscopy (OM) was used to analyze the surface of the samples before and after immersion in earth and offshore crude petroleum and see if there was chemical attack of the surface. The optical microscope used was an Olympus BX 51, with magnification of 50, 100 and 200 times. Mechanical properties of the sintered ceramics were studied though 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.

For the study of stability of ceramic composites (Al-Ti-Ho) in petroleum extraction environment, sintered ceramics were submerged in crude petroleum for 60 days. The crude petroleum used in this work was extracted from the earth and offshore petroleum wells of the Northeast region of Brazil provided by Petrobrás. Finished this period, ceramics were subjected to X-ray diffraction, optical microscopy and Vickers microhardness testing. They were compared with the original ceramics to observe if there are any changes in their structural, microstructural and mechanical characteristics due to crude petroleum environment.

3. RESULTS AND DISCUSSION

3.1 Characterization of the materials

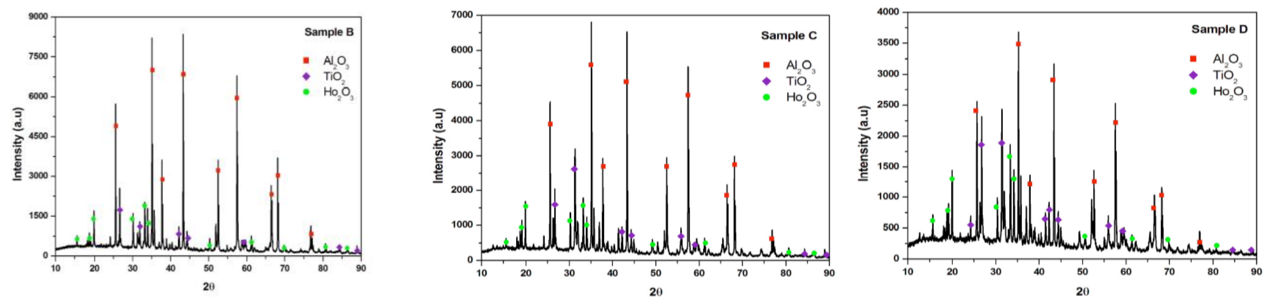
3.1.1 Particle Size Analysis

Through analysis of milling particle size, before and after 24 hours of milling, was observed a decrease of 95.25% for particle medium diameter.

3.1.2 XRD diffraction

Through the analysis of X-Ray diffraction, it was possible to obtain the diffraction related raw materials (Al_2O_3, TiO_2, Ho_2O_3) used in the formation of ceramic composites studied and to observe the characteristic peaks and indexes them based on the standard JCPDS and other research (MORAES, F. A. et al., 2011; SANTOS, R. K. S.; BATISTA, M. S.; ASSAF, E. M., 2005; WANG, Y. et al., 2009).

Composites sintered were analyzed by X-ray diffraction to analyze the structure. Observing the X-ray diffraction of Figure 2, 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.

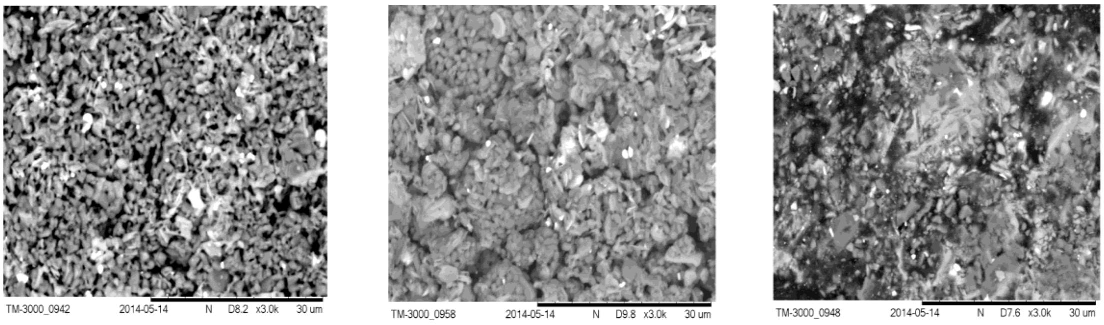


(a) (b) (c)

Figure 2 - DRX of samples sintered at 1350ºC for 24 hours, (a) Sample B - with 10% of TiO_2, (b) Sample C – with 15% of TiO_2, (c) Sample D – with 20% of TiO_2.

3.1.3 Scanning Electron Microscopy (SEM)

The analysis of the microstructure of the composite was performed using SEM (Fig. 3) and it is possible to observe that with increasing content of TiO_2 is better distribution of the grains and an improved densification of the composite. As a result, we have composites with a uniform surface morphology, grain homogeneity and particle size distribution.



(a) (b) (c)

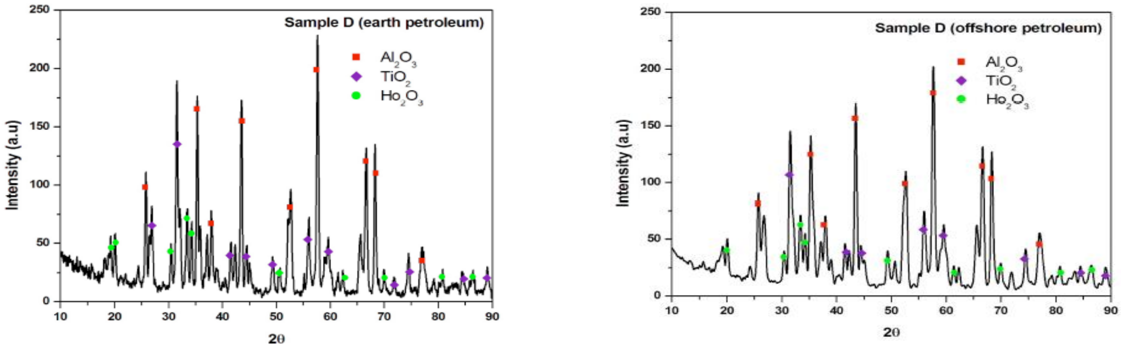
Figure 3 - Results obtained of SEM micrograph with magnification of 3000x (a) Sample B - with 10% of TiO_2, (b) Sample C – with 15% of TiO_2, (c) Sample D – with 20% of TiO_2.

3.2 Study of Stability of Composite Environment of Crude Oil

To access the stability of the ceramic composites developed in the crude petroleum environment, it was compared the results of the analysis of X-ray diffraction, Vickers microhardness and optical microscopy before and after immersion in earth and offshore crude petroleum.

3.2.1 Ray Diffraction (XRD)

Through the diffraction patterns obtained by XRD, displayed in Figure 4 shows that even after direct contact with the crude oil of sea and land, the crystal structures of the composites did not change, showing that there was no change in relation to the structures of composites.



(a) (b)

Figure 4 - X-ray diffraction of composites after immersion in crude petroleum. (a) Sample D immerged in Earth petroleum; (b) Sample D immerged in offshore petroleum.

3.2.2 Optical Microscopy and Vickers microhardness

Optical microscopy was performed to analyze whether or not the surface suffered chemical attack due to direct contact with crude petroleum. By comparing the images before and after immersion in crude petroleum (Fig. 5) it was possible to conclude that were observed no evidence of chemical attack by the petroleum, which indicates a good chemical stability of the composites and sample D with 20% of TiO_2 is what worked best.

Figure 5 – Optical Microscopy (x100) of sample D (with 20% of TiO_2) before and after immersion in earth and offshore crude petroleum.

The mechanical properties of the ceramic composites were analyzed by testing microhardness. Observe in Figure 6 that increasing the percentage of TiO_2 increases the hardness shows that the sample D (with 20% of TiO_2) obtained better results, both before and after immersion in earth and offshore crude petroleum.

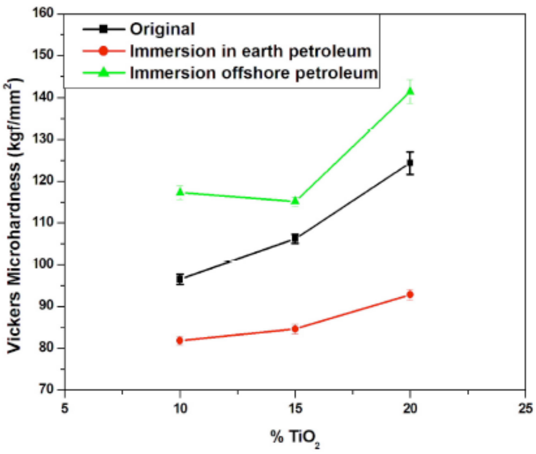


Figure 6 – Vickers microhardness of ceramic composites after immersion in crude petroleum.

4. CONCLUSIONS

In this present work, we have developed, fabricated and characterized ceramic composites (alumina-titania-holmium) for use in the petroleum industry. Structural characteristics were investigated by powder X-ray diffraction, which was possible check that no new phase is formed 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 D (composite Al_2O_3 20% TiO_2 and 1% Ho_2O_3) had better results. Mechanical behavior of the composites was studied by Vickers microhardness testing, which the sample D showed the best result regardless of being immersed in crude petroleum.

After immersion in crude petroleum for 60 days, the ceramic composites were taken out from the petroleum and were analyzed by optical microscopy, X-ray diffraction and Vickers microhardness to analysis the stability in hostile environment. Results attest that its structure, microstructure and mechanical properties have not suffered significant changes at any stage of submersion. From these promising results, we conclude that these ceramic composites are stable in the aggressive crude petroleum environment and thus could be potential candidate ceramic composites for use as a ceramic coating of metallic parts for the petroleum industry.

5. ACKNOWLEDGMENTS

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7. RESPONSIBILITY NOTICE

The authors, Noelle D’Emery, Ricardo Sanguinetti and Yogendra Yadava, are the only responsible for the printed material included in this paper.