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CHARACTERIZATION AND STUDY OF STABILITY IN CRUDE OIL OF THE CERAMIC COMPOSITE ALUMINA-ZIRCONIA-LANTANIA PRODUCED BY SOLID STATE SINTERING AT DIFFERENT TEMPERATURES

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Abstract. *Several problems affect oil and gas producing companies as a result of the corrosion process. The crude oil composition and production conditions lead to corrosive attacks of its equipment for storage and transport, which represents a large portion of the total costs of this sector. Thus, ceramic tiles applied through spraying hypersonic heat are being studied, aimed at applications such as protection against corrosion in metallic arrays of the oil industry and that must be chemically stable and resistant to corrosion and high temperatures. This work studied ceramics produced from ceramic oxides Al_2O_3, ZrO_2 e La_2O_3, where were fixed 2% (by mass) of Lantania and added 10%, 15% and 20% of a Zirconia in an Alumina matrix. Ceramic powders were produced by mixing in ball mill, compressed in uniaxial press and sintered in one of the three different thermal cycles – 1350 ºC, 1500 ºC e 1650 ºC, obtaining 09 different samples. The samples had their stability analysed after 90 days of continues immersion on crude oil from source wells of sea and land of the Sergipe. For characterization, Optical Microscopy (OM), Vickers micro Hardness and X-Ray Diffraction (XRD) techniques were used. Studies of the stability of the ceramic indicate that all the samples showed good response after soaking in crude oil, but the best mechanical properties belong to the ceramics sintered at 1650 ºC.*

Keywords: *Alumina-Zirconia-Lantania, Composites, Corrosion, Crude Oil, Ceramic coatings*

1. INTRODUCTION

Advanced ceramics have excellent characteristics in terms of resistance to high temperatures and to corrosive chemical environments (Carter and Norton, 2007). Other characteristics intrinsic to these materials, such as fracture toughness, have been studied and improved from the incorporation of rare earth oxides (Souza, 2013; Rêgo, 2012).

Recent researches seek the development, production and characterization of the addition of small amounts of nano-scale inclusions, such as the presence of Zirconia in an Alumina matrix, can inhibit grain growth during sintering, increasing the final properties of the ceramic (Rodrigues et. al., 2012).

Crude oil storage tanks are intensely exposed to corrosion: at the top of the tanks gases evaporate from the stored product, such as sulfur compounds, which have dissolved in the water; while in the bottom of the tanks, the accumulation of sediments, water and other impurities promote the corrosive attack. (Vieira, 2013).

In general, corrosion can have direct and indirect consequences, as replacement of damaged equipment and equipment failures. One way to control it is to use preventive methods - paint, addition of corrosion inhibitors, coatings, etc., and over-sizing projects (Gentil, 2012).

Alumina-Zirconia-type composites stabilized with rare earth oxides for ceramic coating purposes with good mechanical properties and chemically inert to the aggressive environment of crude oil (Araújo, 2015).

In this context, this work presents the production and characterization of the ceramic composite Alumina-Zirconia-Lantania for use as a ceramic coating that aims to protect metal matrix in the petroleum industry.

2. EXPERIMENTAL PROCEDURE

The ceramics Alumina-Zirconia reinforced with lanthanum oxide were produced by a thermo mechanical process and characterized using Vickers Micro hardness test, Optical Microscopy and X-Ray Diffraction technique. The flowchart in Fig. 1 summarizes the experimental procedure utilized.

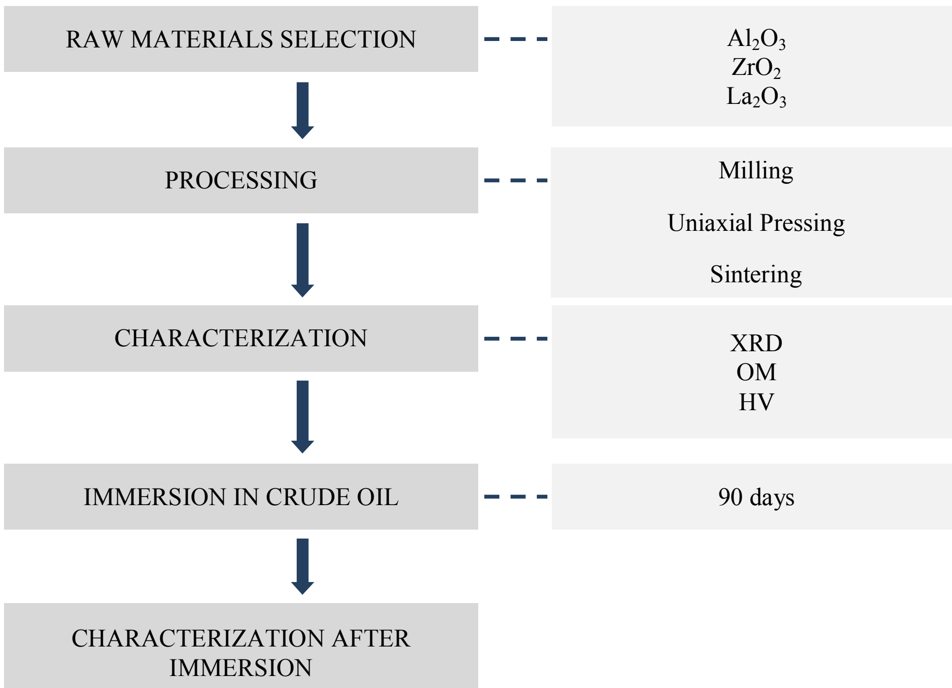

Figure 1. Flowchart summarizing the experimental procedure used to produce the ceramics

First, the ceramic oxides were selected and weighed. Aluminum oxide (Al_2O_3, Elizabeth, 99% purity), zirconium oxide (ZrO_2, Acros, 99% purity) and lanthanum oxide (La_2O_3, Vetec, 99.9% purity) were used to produce 03 different compositions that were added from 10-20% of Zirconia (by mass) to Alumina and 2% of Lantania. Then the compositions were mixed and milled in a ball mill (Marconi, model MA-500) during 12 hours.

After that, the mixed powder were pressed using a hydraulic press machine (SCHWING SIWA, ART6500089) producing discs of 30 mm in diameter. Every composition was sintered in a muffle furnace using one of the 03 different thermal cycles, with sintering temperatures of 1350 ºC, 1500 ºC or 1650 ºC. Finally were providing 09 different patterns, as shown in Table 1.

Table 1. Composition and sintering parameters of the patterns produced.

PATTERN	COMPOSITION (% wt)	SINTERING PARAMETERS	
		Temperature (ºC)	Time (h)
01	$Al_2O_3 – 20ZrO_2– 2La_2O_3$		
02	$Al_2O_3 – 15ZrO_2– 2La_2O_3$	1350	24
03	$Al_2O_3 – 10ZrO_2– 2La_2O_3$		
04	$Al_2O_3 – 20ZrO_2– 2La_2O_3$		
05	$Al_2O_3 – 15ZrO_2– 2La_2O_3$	1500	2
06	$Al_2O_3 – 10ZrO_2– 2La_2O_3$		
07	$Al_2O_3 – 20ZrO_2– 2La_2O_3$		
08	$Al_2O_3 – 15ZrO_2– 2La_2O_3$	1650	2
09	$Al_2O_3 – 10ZrO_2– 2La_2O_3$		

The samples undergo metallographic preparation and were characterized by the techniques described above. They were also immersed in crude petroleum of wells from sea and land during 90 days. After that they were characterized again.

3. RESULTS AND DISCUSSION

3.1 Vickers Microhardness

Vickers micro Hardness test was performed in the samples just after sintering and also after immersion of the samples for 90 days in crude petroleum. For the Vickers micro hardness test was used a hardness tester (Importecnica, HVS-5) and 08 indentations were performed in each case. The averages results of the indentations are shown in Fig. 2.

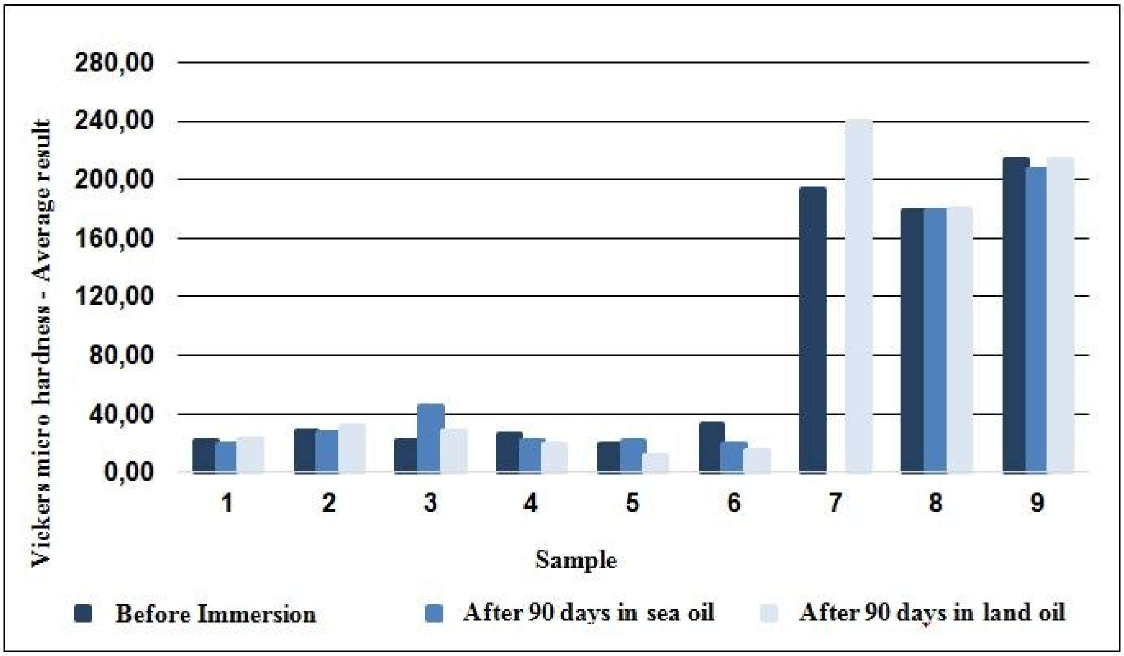

Figure 2. Comparative study of the average Vickers micro hardness of the samples before immersion and after 90 days immersed in crude oil from sea and land wells

An analysis of the average values of the micro hardness, kgf/mm², concludes that the sintered samples at 1350 ºC did not present satisfactory results. However, as the sintering temperature increases to 1650 ° C there is a considerable improvement in this characteristic.

Sample 09, $10ZrO_2$ (%wt) sintered at 1650 ºC, present the higher Vickers micro hardness result and it remains almost in the same value even after immersed in crude petroleum.

3.2 X-Ray Diffraction

After sintering, the samples were analysed by XRD. The XRD patterns confirmed that a ceramic composite has been formed. These results were also useful to compare with the XRD results of those samples after immersion in crude petroleum. Figures 3-5 show the XRD results of samples sintered at 1650 ºC after immersion.

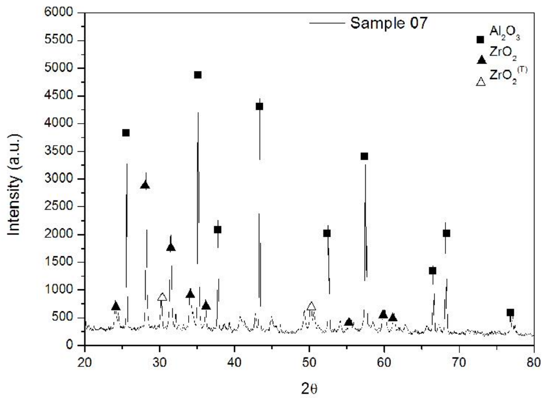

Figure 3. XRD result of the Sample 07

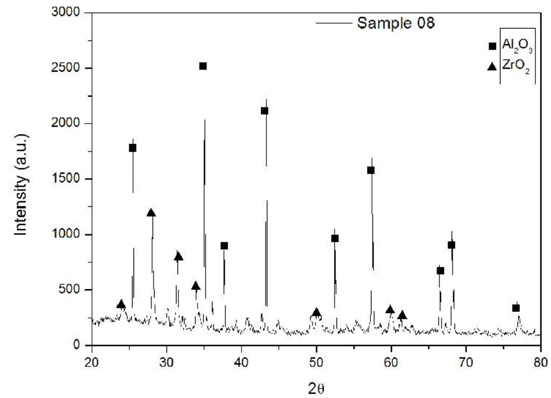

Figure 4. XRD result of the Sample 08

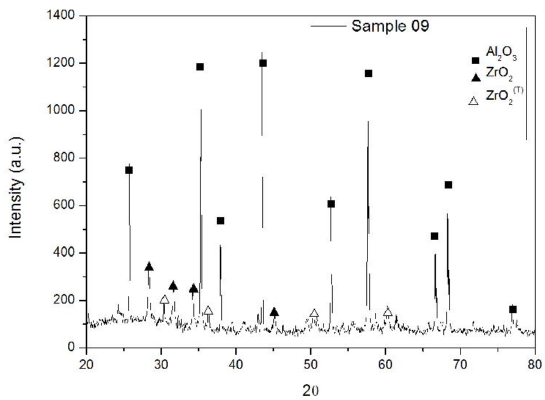

Figure 5. XRD result of the Sample 09

Analysing the XRD images above, can be notice that only the constituent powders peaks are identified.

After immersion in crude oil for 90 days, samples were retested by XRD, in order to assess their stability in that environment. Figures 6-8 show a comparison between the results obtained before and after immersion in crude oil from the wells of land and sea of Sergipe-Brazil of the samples 7, 8 and 9, respectively.

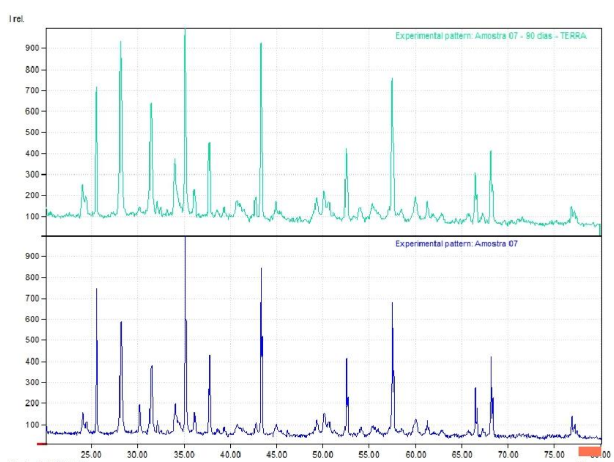

Figure 6. Comparison of XRD results before immersion (blue line) and after 90 days immersed in land petroleum (green line) of the Sample 07

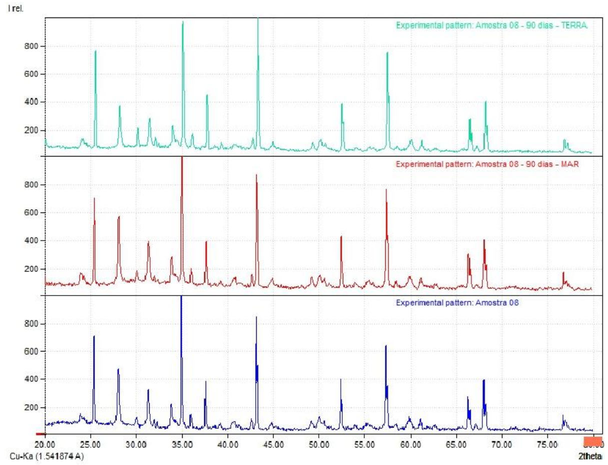

Figure 7. Comparison of XRD results before immersion (blue line), after 90 days immersed in sea petroleum (red line) and after 90 days immersed in land petroleum (green line) of the Sample 08

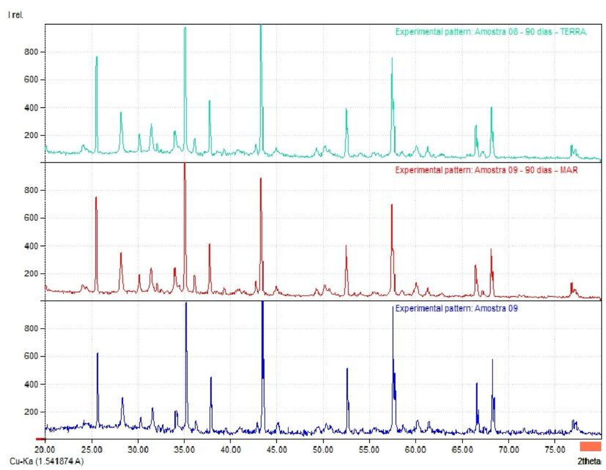

Figure 8. Comparison of XRD results before immersion (blue line), after 90 days immersed in sea petroleum (red line) and after 90 days immersed in land petroleum (green line) of the Sample 09

Since there is no formation of new phases or new material peaks, these results indicate the stability of the composites in crude oil environment under the conditions studied.

3.3 Optical Microscopy

Recently Finšgar and Jackson (2014) shown a review about corrosion inhibitors for steels in the oil and gas industry, where they reinforce that is almost impossible to prevent corrosion, however it is possible to control it and minimize the corrosion damage of well tubular, mixing tanks, coiled tubing, and other metallic surfaces.

For a brief study of the microstructure and the stability of the composites in this environment, studies were performed with optical microscope (Olimpus, BX51M) on the surface of the samples.

First, samples were analyzed just after sintering. After that, the results after 90 days immersed in crude petroleum from sea and land wells were compared with these. The OM images are shown in Fig. 9 and 10.

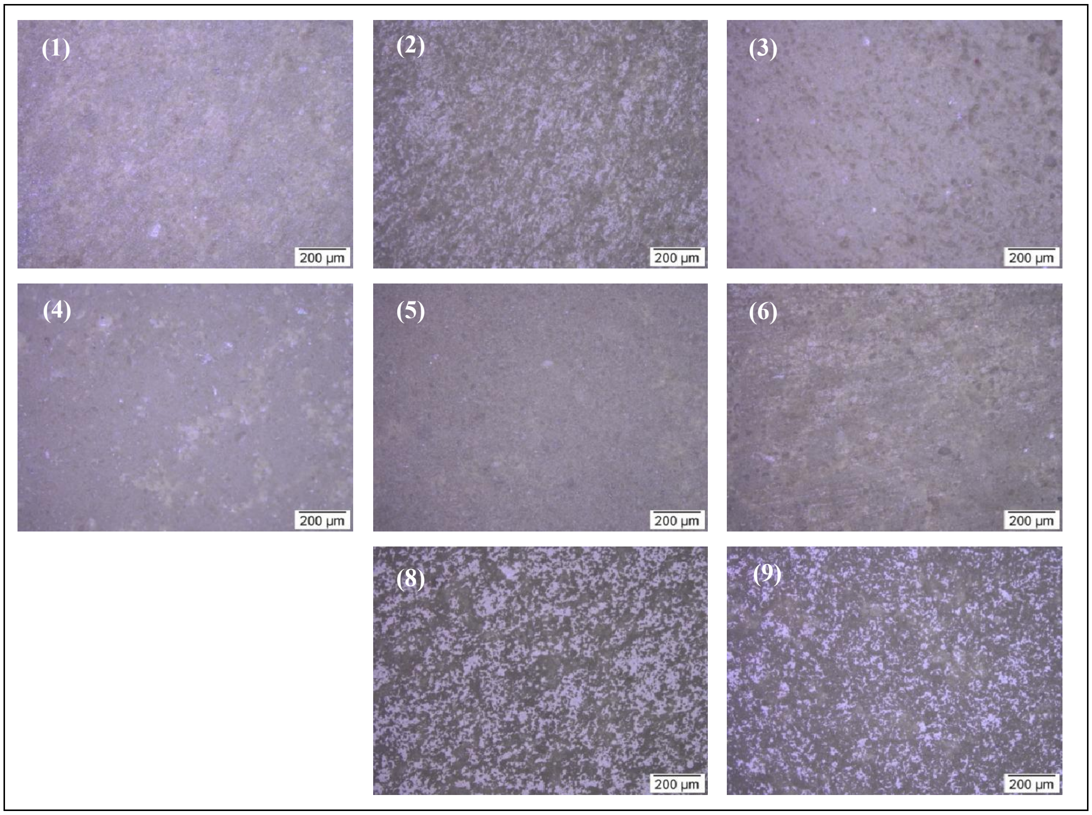

Figure 9. Comparative OM images of the surfaces of samples 01 to 09, respectively, after 90 days of immersion in crude petroleum from sea well

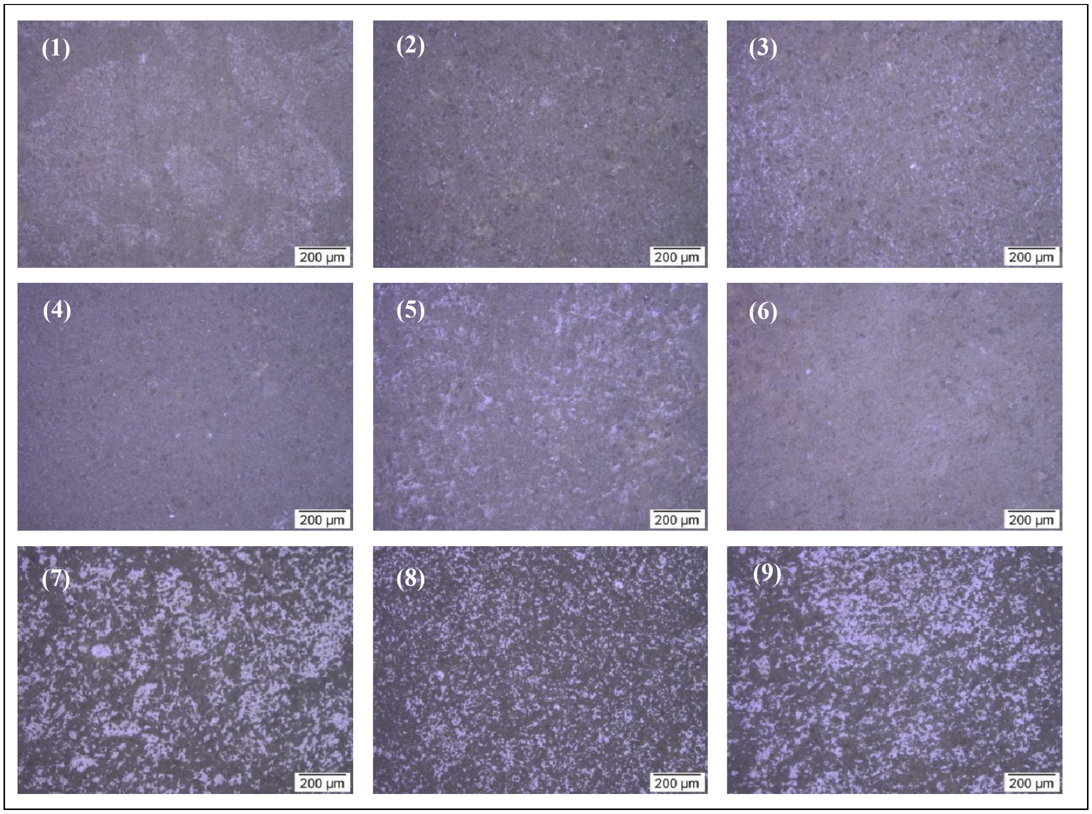

Figure 10. Comparative OM images of the surfaces of samples 01 to 09, respectively, after 90 days of immersion in crude petroleum from land well

Figure 9 there isn't a figure corresponding to sample 07.

OM images indicate that there were no cracks or other forms of surface degradation in the samples, even after a period of 90 days immersed in crude oil of sea and land wells from Sergipe-Brazil.

4. CONCLUSIONS

The best Vickers micro hardness values were obtained in the samples at 1650 °C. Sample 09, shown good stability of this parameters even after immersion.

The XRD results showed the formation of a ceramic composite. These composites were inmmersed in crude petroleum and the results after immersion shown stability while compared with the inital state, since none peak arised.

The composites presented a homogeneous surface with good distribution of grain size. After immersion, there weren't found sign of degradation due to corrosion by crude oil.

Based in the results obtained and in the statements the sintering under 1650ºC parameters was successful and presented the cmposites with the best properties.

5. ACKNOWLEDGEMENTS

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