

24th COBEM - 2017



24th ABCM International Congress of Mechanical Engineering
December 3-8, 2017, Curitiba, PR, Brazil

COBEM-2017-2599

**PRODUCTION AND STUDY OF STABILITY IN CRUDE OIL OF
Al₂O₃-ZrO₂ COMPOSITE CERAMIC REINFORCED WITH RARE EARTH
OXIDE (CeO₂) FOR USE AS METAL MATRICES COATING**

Yadava, Yogendra P.

yadava@ufpe.br

Constantino, Bruna S.

Brunaconstantino8@gmail.com

Ferreira, Ricardo A. S.

ras@ufpe.br

Padilha, Manuella B.

manuella.bp@hotmail.com

Cordeiro, Raquel B.

Federal University of Pernambuco, Department of Mechanical Engineering, Recife, PE, Brazil

rbcordeiro@hotmail.com

Abstract. *Considering world's major power still becomes from oil, investments in materials that improve its transport and oil storage is extremely essential. The crude oil is highly corrosive, so your transport and storage in metallic systems cause a considerable loss of material. Thus, an alternative to resolve this problem is the internal coating of an inert material to crude oil that has high fracture tenacity and mechanical strength. Ceramic are a potential material due to your good compatibility with the desired. With the combination of Al₂O₃-ZrO₂-CeO₂ is expected high sintered density, high mechanical strength and highly inert to chemical attack crude oil. Ceramic discs were manufactured with ZrO₂ percentages ranging from 5 to 20% by weight of the total mixture from homogenizing the components in a ball mill, material compacting and sintering at high temperature. Once formed the discs, they are being subjected to various tests and analysis as the Vickers hardness, optical microscopy, XRD, SEM and study of stability in crude oil from wells of Sergipe. Until the given moment, all results are as expected so that once reached the goal of this project it will be of great significance and technological value for the oil industry.*

Keywords: *Al₂O₃-ZrO₂-CeO₂, Ceramic Composite, Crude Petroleum, Stability*

1. INTRODUCTION

Crude oil is a highly corrosive product, so the surface degradation tanks for storage and transportation of crude oil, which are made of metallic materials, is a serious problem in the petroleum industry. One way to prevent the corrosion of these matrices is by using inert coating.

Ceramics are being studied to this end. So, to reduce the ceramic's brittleness and increase strength and toughness, they can be reinforced by incorporation of one or more ceramic additives (Evans, 1990; Ai et. al., 1995 and Becher, 1991).

Mechanical properties and toughness of ceramics based on alumina improves considerably with the incorporation of TiO₂, TiN, ZrO₂, etc. as additives reinforcements (Fu et. al., 2001; Gong et. al., 2001; Rak, 1998; Fu et. al., 1994).

This study is targeting a Al₂O₃-ZrO₂-CeO₂ ceramic composite produced by thermo mechanical process. And its characterization made by Vickers hardness, optical microscopy, XRD, SEM and study of the stability in crude oil.

2. EXPERIMENTAL PROCEDURE

Initially there was a mixture of the Alumina compound (Al_2O_3), Zirconia (ZrO_2), and oxide of cerium (CeO_2). Were added at 5%, 10%, 15% and 20% of Zirconia (weight) to Alumina and 3 (%wt) CeO_2 . Four different compositions, as shown in Table 1, were produced by a thermo mechanical process and then characterized.

Table 1. Compositions of the $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2$ samples.

SAMPLE	COMPOSITION		
	Al_2O_3	CeO_2	CeO_2
1	92	5	3
2	87	10	3
3	82	15	3
4	77	20	3

The ceramics were initially prepared by mixing the powders during 24 hours in a ball mill, to ensure homogeneity of the resultant powder. After that, using a metallic matrix and hydraulic press, the samples were compacted in the form of circular discs, by uniaxial pressing process (using a SCHIWING SIWA press, ART6500089 model) under a load of 12 tons for 5 minutes without the use of binder. Then the samples were sintering in a high temperature furnace, at 1350°C during 24 hours.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD)

It was used the powder method to do the XRD test in the sintered samples. This method provides the structural information, such as the determination step, particle size measurement and shows the presence of disorder in the structure. This constitutes a X-ray diffraction beam on the sample, so that there is a relationship between the distance between the planes that reflect the beams and the angle of diffraction. XRD diagrams are shown in Fig. 1.

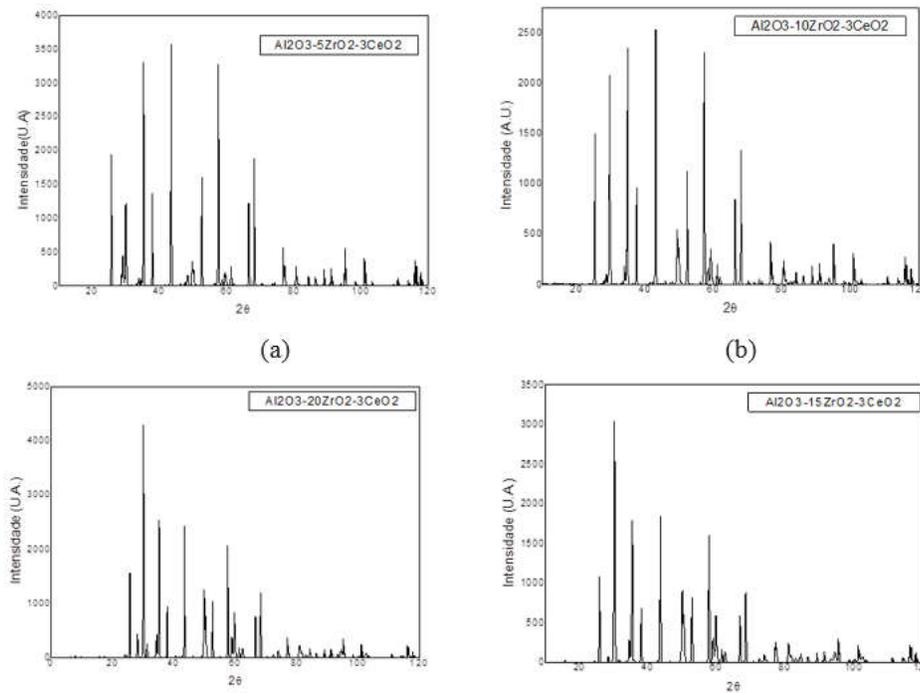


Figure 1. Figure 1: XRD results of the 04 compositions of the $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2$ ceramic composite

The XRD patterns obtained shows none reaction between the constituent materials typical of the development of composite materials.

3.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Detector (EDS)

The SEM images present the surface analysis of the samples. And can be noticed its good homogeneity and size and distribution of grains.

To analyze the microstructures of the tablets after the sintering process used the electron microscopy technique (SEM). This characterization was intended to evaluate the microstructure in relation to homogeneity, size and distribution of grain and porosity. Below are micrographs of samples in Fig. 2.

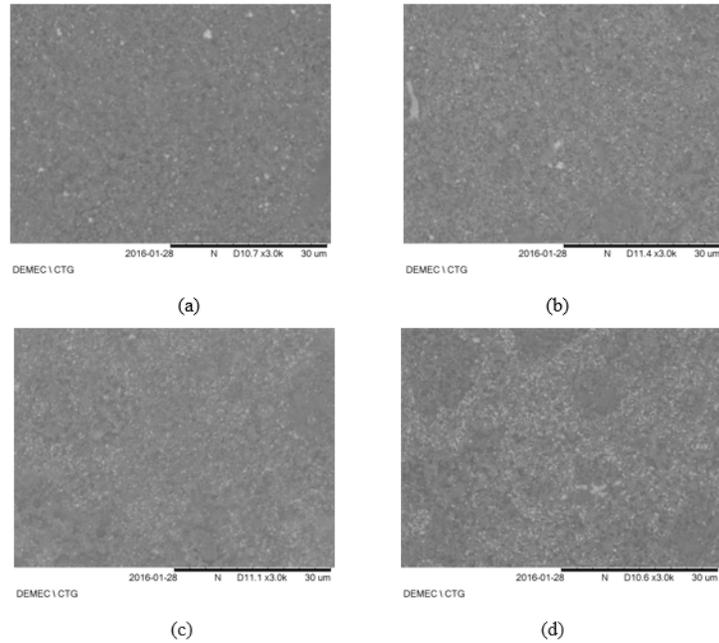
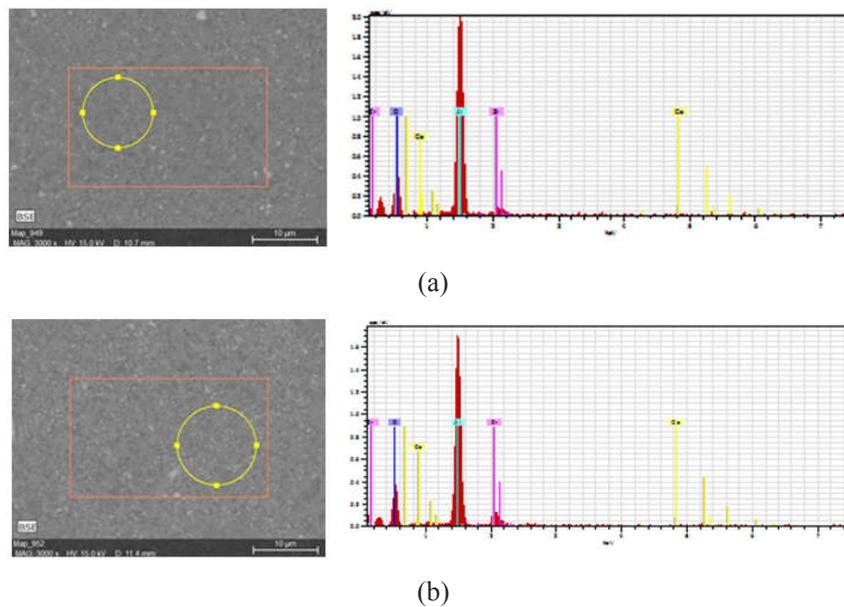


Figure 2. 3000x magnification's SEM images of the Samples 1 (2a), 2 (2b), 3 (2c) and 4 (2d)

The 15% ZrO_2 and 20% ZrO_2 composites show the best results.

EDS technique was also used to characterize the Samples. Below are the results Fig. 3.



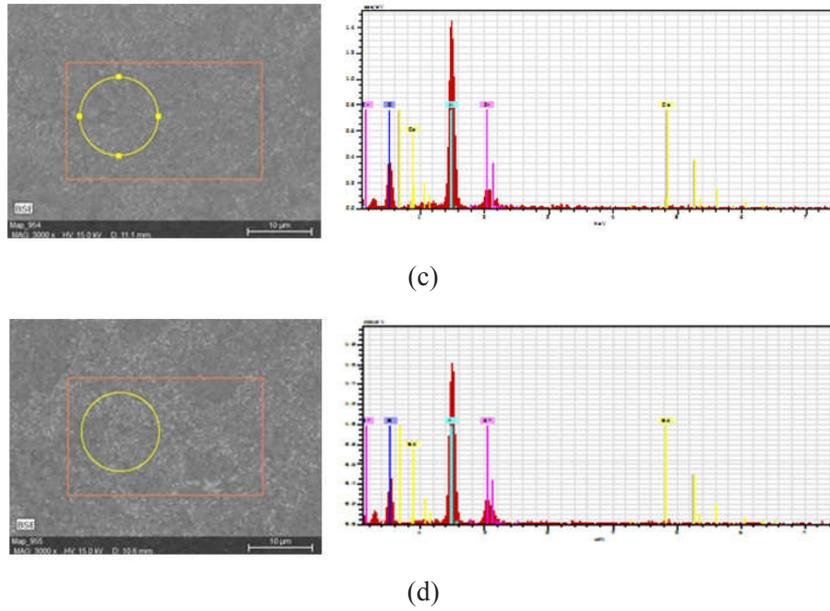


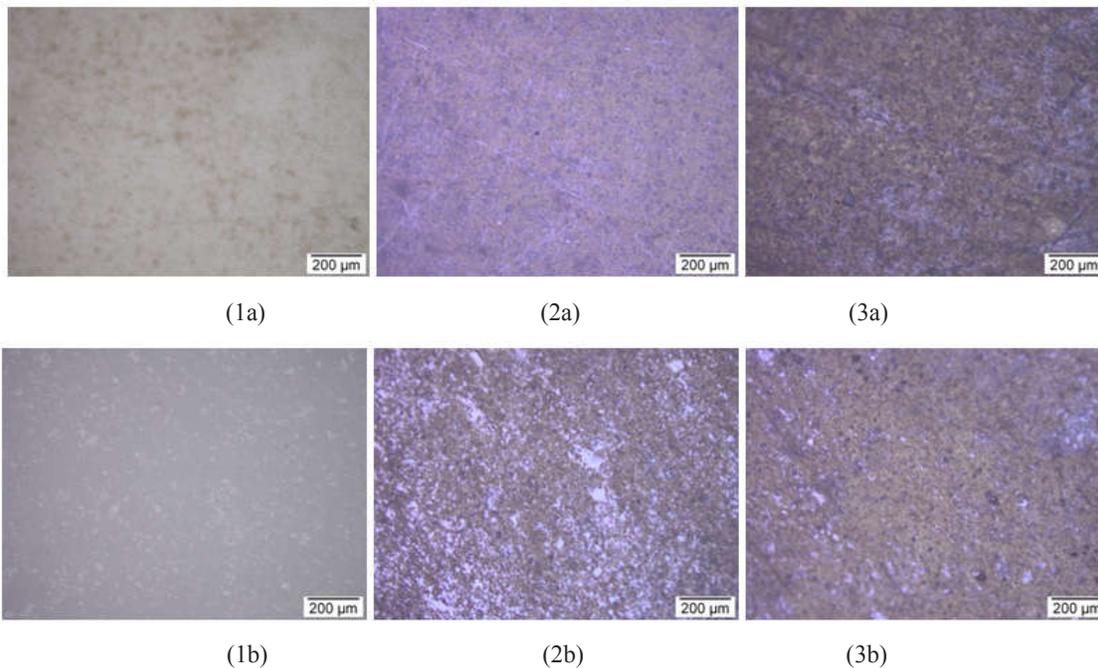
Figure 3. EDS results of the Samples 1 (2a), 2 (2b), 3 (2c) and 4 (2d)

EDS results show only the constituent chemical elements Al, Zr, O, Ce. Meaning that there was no contamination during processing of composites.

3.3 Optical Microscopy (OM)

OM images also showed the good homogeneity of the ceramics sintered, Fig. 4. It was used 100x and 50x magnification to obtain the OM images.

To analyze how the ceramic react with crude petroleum, the discs staid immerse in earth crude petroleum and sea crude petroleum for 30 days, and were compared to samples before being immersed as showed also in Fig. 4.



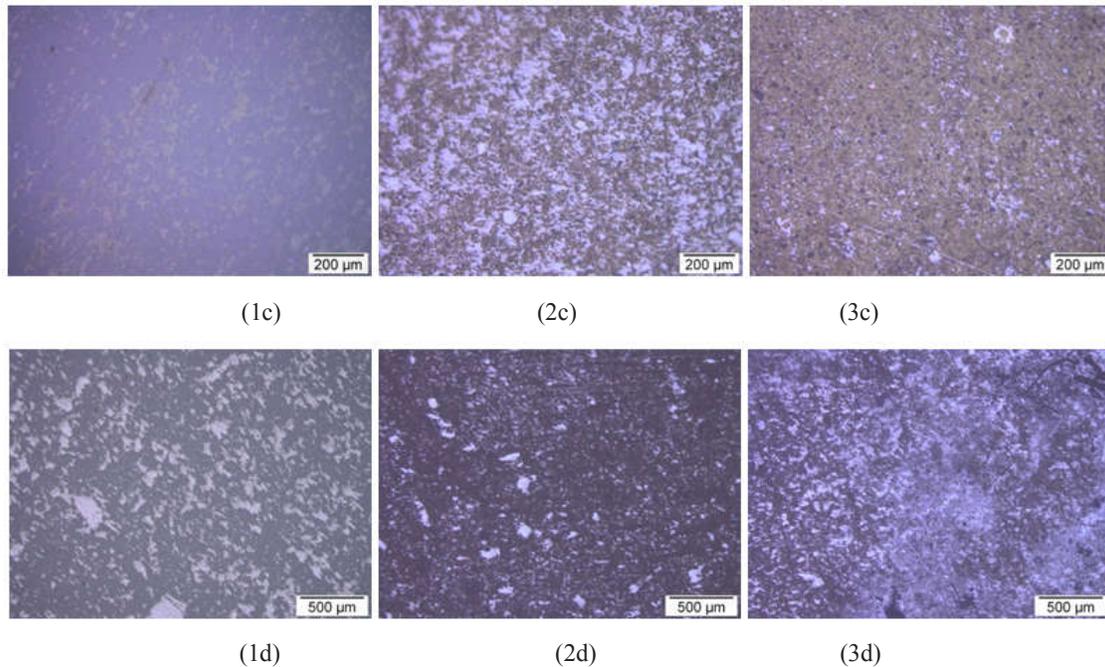


Figure 4. OM images of the samples before and after 30 days immersed in crude petroleum: Sample 1 – (1a - before immersion), (2a – sea), (3a – land); Sample 2 – (1b – before immersion), (2b – sea), (3b – land); Sample 3 – (1c – before immersion), (2c – sea), (3c – land); and Sample 4 – (1d before immersion), (2d – sea), (3d – land).

When compared in the optical microscopy the surface before and after de immersion, it was found no cracks or fissures, showing no visual evidence of changes in the sample. And even after immersion in crude oil, Optical Microscopy results confirm there were no interaction with the crude oil environment.

3.4 Vickers Micro Hardness

The hardness test is based on their resistance calculations that the material provides the penetration of a square-based pyramid diamond under a given load. The measurement of the hardness of the material is a function of the print mark characteristics and the applied load, which through the diagonals of the measures is calculated by the equation of Vickers hardness.

After sanding and polishing, the specimens were subjected to the test. For samples 5% was used a load of 500g, as for samples 10, 15 and 20% was using a 1000 g load. In each sample were performed 5 indentations to more reliable results as showed in table 2.

Table 2. Vickers Micro Hardness results for $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2$.

5% ZrO_2	26.11 HV	25.02 HV	28.30 HV	24.80 HV	23.68 HV
10% ZrO_2	46.74 HV	38.33 HV	42.48 HV	40.26 HV	44.59 HV
15% ZrO_2	56.96 HV	57.37 HV	62.92 HV	64.40 HV	66.07 HV
20% ZrO_2	62.23 HV	66.59 HV	61.38 HV	59.36 HV	66.24 HV

The arithmetic average of the Vickers harnesses' results were: Sample of 5% ZrO_2 : 25.58 HV, Sample of 10% ZrO_2 : 42.48 HV, Sample of 15% ZrO_2 : 61.54 HV and Sample of 20% ZrO_2 : 63.16 HV.

Analyzing the results is observed that the hardness increased with the increase of the percentage of ZrO_2 .

4. CONCLUSIONS

In this project were analyzed the production of ceramic composite $\text{Al}_2\text{O}_3\text{-ZrO}_2$ with rare earth oxide additive (CeO_2) and some of its mechanical properties and stability in crude petroleum environment.

The results obtained by the X-ray Diffraction of the samples after sintering show there were no formation of other phases and the peaks refer only to the base components. With the scanning electron microscopy was possible to see the homogeneity on its surface and in its microstructure (distribution and grain size).

Optical Microscopy also showed that the surface didn't suffer chemical attack due to contact with petroleum.

The results of EDS demonstrated the purity of the produced material. Finally, the Vickers micro hardness results demonstrate that the hardness of this material increases with larger percentage of ZrO_2 .

5. ACKNOWLEDGEMENTS

The authors are grateful to the CNPq and the Federal University of Pernambuco for supporting the research conducted.

6. REFERENCES

Ai, X., Li, Z.Q. and Deng, J.X, 1995. "Development and perspective of advanced ceramic cutting tool material". *Key Eng. Mater.* p.108–110 98–112.

Becher, P.F., 1991. "Microstructural design of toughened ceramics". *J. Am. Ceram. Soc.*, v.74, p. 255–264.

Evans, A. G., 1990. "Perspective on the development of high toughness ceramics." *Journal Am. Ceram. Soc.*, v. 73 (2), p. 187–192.

Fu, C.T., Wu, J. M. and A. K. Li, 1994. "Microstructure and mechanical, properties of Cr_3C_2 particulate reinforced Al_2O_3 matrix composites". *J. Mater. Sci.*, v. 29, p. 2671–2677.

Fu, Y., Gu, Y.W., Du, H., 2001. "SiC whisker toughened $\text{Al}_2\text{O}_3\text{-(Ti W)C}$ matrix composites". *Scripta Mater.*, v. 44, p. 111–116.

Gong, J., Miao, H., Zhao, Z., 2001. "The influence of TiC-particle-size on the fracture toughness of $\text{Al}_2\text{O}_3\text{-30 wt. TiC}$ composites". *J. Eur. Ceram. Soc.*, v.21, p. 2377–2381.

Rak, Z.S., Czechowski, J., 1998. "Manufacture and properties of $\text{Al}_2\text{O}_3\text{-TiN}$ particulate composites". *J. Eur. Ceram. Soc.*, v. 18, p. 373–380.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.