ISSN 2176-5480

22nd International Congress of Mechanical Engineering (COBEM 2013)
November 3-7, 2013, Ribeirão Preto, SP, Brazil

PRODUCTION AND STUDY OF STABILITY OF Y2O3 REINFORCED AL_2O_3-ZrO_2 CERAMICS IN CRUDE PETROLEUM ENVIRONMENT FOR INERT COATING APPLICATIONS

Yogendra Prasad Yadava
Departamento de Engenharia Mecânica, Universidade Federal de Pernambuco50, CEP 50740-550, Recife –PE, Brasil
yadava@ufpe.br

Bruna de Souza Constantino
Departamento de Engenharia Mecânica, Universidade Federal de Pernambuco50, CEP 50740-550, Recife –PE, Brasil
brunna_souza_@hotmail.com

Marília de Barros Lima Barbosa
Departamento de Engenharia Mecânica, Universidade Federal de Pernambuco50, CEP 50740-550, Recife –PE, Brasil
mariliablb@gmail.com

Juliana Carvalho da Silva
Departamento de Engenharia Mecânica, Universidade Federal de Pernambuco50, CEP 50740-550, Recife –PE, Brasil
julianacarvalhodasilva@gmail.com

Ricardo Artur Sanguinetti Ferreira
Departamento de Engenharia Mecânica, Universidade Federal de Pernambuco50, CEP 50740-550, Recife –PE, Brasil
ras@ufpe.br

Abstract. *Discovery of Brazilian pre-salt petroleum reservoir has created a intense demand for new materials capable of withstanding direct contact with the crude petroleum. Petroleum drilling equipments, storage tanks and transportation systems suffer from constant physical stress caused by chemical attack of crude petroleum on its structure. Ceramics are materials with high chemical stability in hostile environment and therefore can be used as an inert coating material as an alternative to resolve such problems. However, ceramics are highly fragile in nature. because they are mostly formed by ionic bonds and / or covalent bonds, which provide a limited number of independent slip systems necessary to achieve a homogeneous plastic deformation.. To date, ceramics based on alumina are most widely used in practice where there is demand for high strength and high toughness and its intrinsic fragility is still a fatal factor. To reduce vulnerability and increase strength and toughness usually the ceramics are reinforced with incorporation of one or more ceramic additives Mechanical properties of alumina based ceramics improved considerably with the addition of TiO_2, TiN, ZrO_2 etc. as reinforcement additives). In the present work we have produced rare-earth oxide (Y_2O_3) reinforced Al_2O_3-ZrO_2 ceramic composites (AZY) in proportions of 5-20 wt% ZrO_2 and 2% wt% Y2O3with high mechanical strength, through thermo-mechanical processing and sintering techniques To evaluate the quality of materials developed and the possibility of using them as inert protective coatings or ceramic components for crude petroleum extraction, storage and transportation systems, we have studied the physic-chemical and mechanical stability of these materials in crude petroleum originated from earthen and offshore petroleum wells of Sergipe region of Brazil. AZY ceramics were produced through thermo-mechanical processing and sintering techniques. Structural, microstructural and mechanical tests showed that AZY ceramics with 15-20wt% ZrO_2 ceramics with 2 wt% of Y_2O_3 additives presented better results in terms of mechanical hardness and microstructural characteristics). The study of stability of AZY ceramics in petroleum extraction environment showed that ceramics did not present any additional phase except the constituent phases. Result of microscopy and Vickers hardness tests also showed that there is no visible change in these characteristics of ceramics after even 60 days of submersion in crude petroleum. Thus we conclude that AZY ceramics could be potential materials for inert coating in crude petroleum environment.*

***Keywords:** Al_2O_3-ZrO_2, Y_2O_3 additives, ceramic composites, stability in crude petroleum*

1. INTRODUCTION

Recent findings of Brazilian pre-salt petroleum reservoir have attracted attention from around the world because it is the largest known pre-salt petroleum reservoir on the earth. This discovery has created an intense demand for new materials capable of withstanding direct contact with the crude petroleum as it is a highly corrosive and chemically reactive fluid. Petroleum drilling equipments, storage tanks and transportation systems suffer from constant physical stress caused by chemical attack of crude petroleum on its structure. Ceramics are materials with high chemical stability and therefore can be

ISSN 2176-5480

used as an alternative to solve the problem of wear, however, on its fragile structure which are mostly formed by ionic bonds and / or covalent bonds, which provide a limited number of independent slip systems necessary to achieve a homogeneous plastic deformation commonly observed in metallic materials makes these materials need improvement in their mechanical properties.

To date, ceramics based on alumina are most widely used in practice where there is demand for high strength and high toughness. The intrinsic fragility of the ceramics is still a fatal factor for use of these materials in structures and mechanical industrial applications. To reduce vulnerability and increase strength and toughness usually the ceramics are reinforced with incorporation of one or more ceramic additives (Evans, 1990; Becher, 1991).

Mechanical properties of alumina based ceramics improved considerably with the addition of TiO_2, TiN, ZrO_2 etc. as reinforcement additives (Fu, 2001). When a ceramic is used as lining for storage tanks and transportation, high fracture toughness is a primary factor. Nucleation and propagation of cracks is a major problem for these applications. Initial studies show that addition of small percentages of rare earth oxides in alumina ceramics reinforced with titania (Al_2O_3-ZrO_2) can increase the toughness of these ceramics (Xu, 1999).

For this purpose, in this work, we have produced rare-earth oxide (Y_2O_3) reinforced Al_2O_3-ZrO_2 ceramic composites in proportions of 5-20 wt% titanium oxide with high mechanical strength, through thermo-mechanical processing and sintering techniques. To assess the quality of materials developed and the possibility of using them as protective coatings of crude petroleum storage and transportation systems we have studied the physic-chemical and mechanical stability of these materials in crude petroleum originated from earthen and offshore petroleum wells of Sergipe region of Brazil. Results of these studies have been presented and discussed in this article.

2. EXPERIMENTAL DETAILS

For the production of Y_2O_3 reinforced Al_2O_3-ZrO_2 (AZY) ceramics, ZrO_2 ceramics were added in Al_2O_3 in 5% to 20 wt% ratios and 2 wt% Y_2O_3 was added in the respective compositions. Table 1 below presents the phase composition of the ATC ceramics.

Table1Chemical composition of AZY ceramics

Ceramics	Al_2O_3 (wt%)	ZrO_2 (wt%)	Y_2O_3 (wt%)
AZY1	93	5	2
AZY2	88	10	2
AZY3	83	15	2
AZY4	78	20	2

Final weight of each composition was fixed in batches of 100gms. Each batch of ceramic mixtures was thoroughly mixed and homogenized separately in a high energy ball mill (Equipments Marconi MA-50, São Paulo, Brazil), having stainless steel milling chamber and high purity alumina balls, for a period of 24 h. In this type of ball milling process, the number of balls required for milling under general conditions is 50-55% of the net capacity of the milling chamber. However, occupation of this volume is not effective, given the gaps between the balls, so the actual volume occupied is approximately 60%. Particle size and particle size distribution of ceramics before and after grinding were determined by LASER particle size analyzer model MASTERSIZE 2000, Malvern Instruments.

For the composite formation by normal solid state sintering, finely ground and homogenized ceramic mixtures were uni-axially compacted in a metallic mould fabricated from abrasion resistant AISI A2 steel (HRC 58) to form circular discs with 30 mm of diameter and 2 mm thickness. A pressing load of 12 ton/cm² was applied for powder compaction, using a hydraulic press (SCHIWING Siwa, model ART6500089). For every compaction process pressure was applied for 10 minutes to stabilize the pressure load distribution in the pressed compact. Compacted ceramic mixtures were subjected to the normal solid state sintering process at in the temperature range 1200 to 1400°C during 24 hours at ambient atmosphere. Sintering was carried out at ambient atmosphere in high purity alumina crucibles, using a high temperature muffle furnace muffler (Jung 0614) followed by furnace cooling till the ambient temperature.

Structural characteristics and identification of phases were investigated by X-ray powder diffractometry (XRD) using Shimadzu X-ray Difratometer, equipped with Cu - Kα radiation (λ = 1.5406 Å). After composite formation confirmed through X-ray diffractometry, we studied the bulk density, mechanical properties and microstructural features of the sintered AZY ceramics, in order to evaluate their potential as toughened ceramic coatings for crude petroleum storage tanks.

Sintered densities of composites were determined by Archimedes method using distilled water. The mechanical behavior of the sintered ceramic composites was studied by measuring Vickers micro-hardness using Vickers hardness indenter model HVS-5 No. 0021. For the hardness tests, sintered composites were polished with # 200, # 400, # 600, # 100, # 1200, # 1500 grade sand papers successively and finally mechanical polishing with diamond paste having 1

ISSN 2176-5480

micron granularity. For this testing a Vicker's hardness indentor model HVS-5 No 0021 was used. The Vickers micro – hardness (H_v) is given by equation (Iost, 1996):

$$MHV = 1.8544P/d^2$$

where *P* is the load and *d* is the average diagonal of the square identation produced by the pyramidal indenter in the sample.

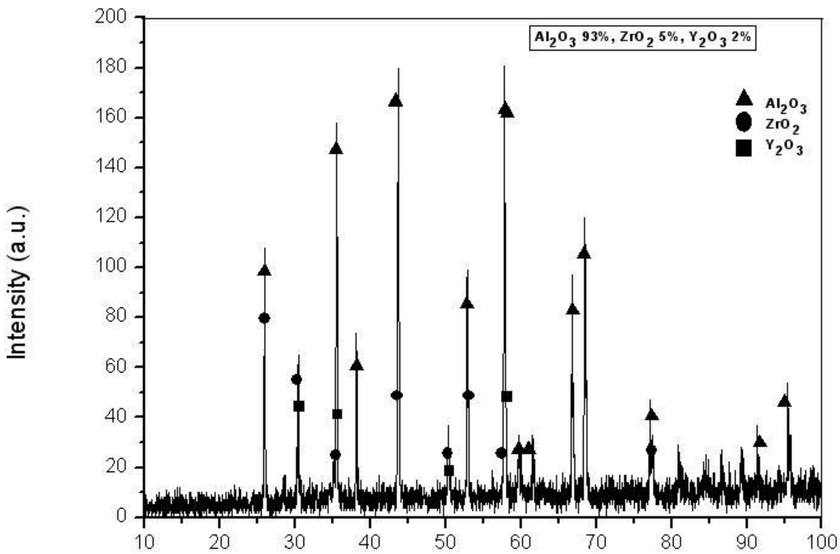
The microstructure of the sintered composite ceramics were studied by scanning electron microscope (JEOL JSM-5900), using secondary electrons. As these composites are electrically non-conducting, to observe the microstructure, samples were covered with thin gold coating using a sputtering unit (Coater BAL-TEC SCD050).

For the study of stability of AZY ceramics in petroleum extraction environment, sintered ceramics were submerged in crude petroleum for 60days. Crude petroleum for this study, extracted from the earthen and offshore petroleum wells of the North-east region of Brazil, was provided by PETROBRAS, Brazil. Al_2O_3-ZrO_2 ceramic composites were periodically taken out from the petroleum reservoir every 15 days and subjectd to X-ray diffractometry, Microscopy and mechanical testing to observe if there are any changes in their structural and microstructural characteristics due to crude petroleum environment.

3. RESULTS AN DISCUSSION

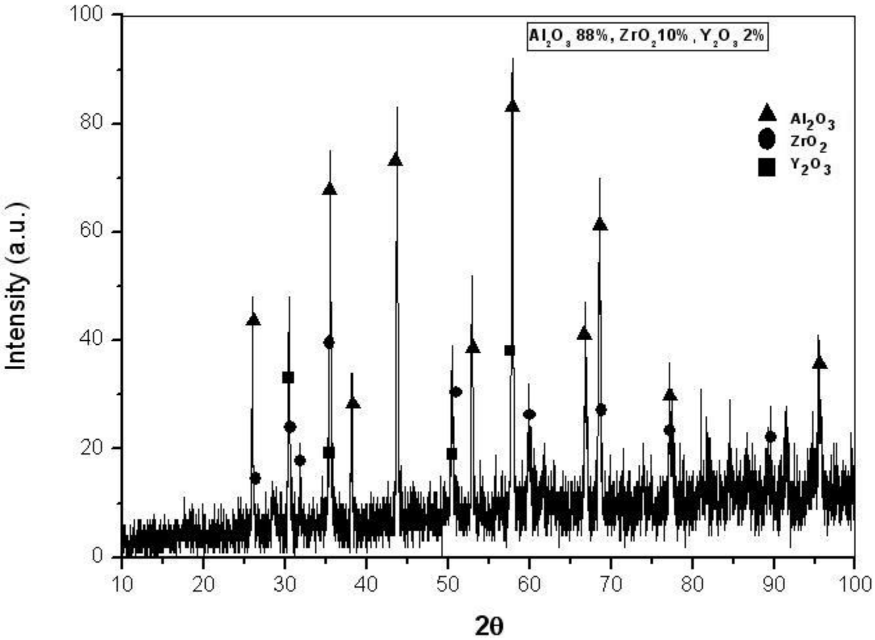
3.1 Phase composition

Structural characterization and phase composition identification of AZY ceramics were investigated through X-ray diffractometry. Typical XRD patterns of AZY ceramics are presented in Fig. 1. As seen from the XRD patterns, the AZY ceramics did not present any additional phase except the constituent phases, i.e. Al_2O_3, ZrO_2, Y_2O_3 as expected. Also the presence of the Y_2O_2 phase is very rarely observed in the XRD patterns due to their very small quantity in the composites. As seen from the XRD patterns, ATC ceramics did not present any additional phase except the constituent phases, i.e. Al_2O_3, ZrO_2, Y_2O_2 as expected. Also the presence of the Y_2O_2 phase is very rarely observed in the XRD patterns due to their very small quantity in the composites.

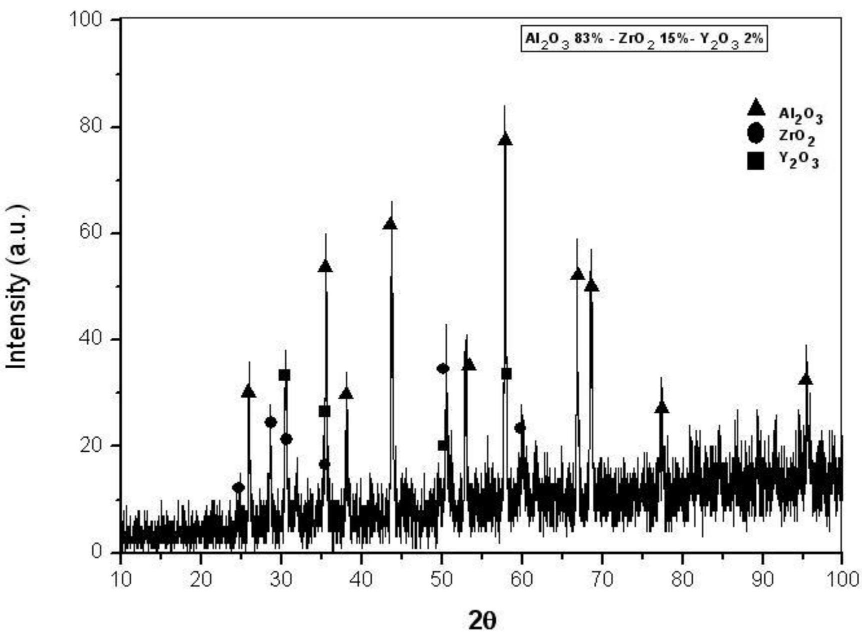


(a)

ISSN 2176-5480

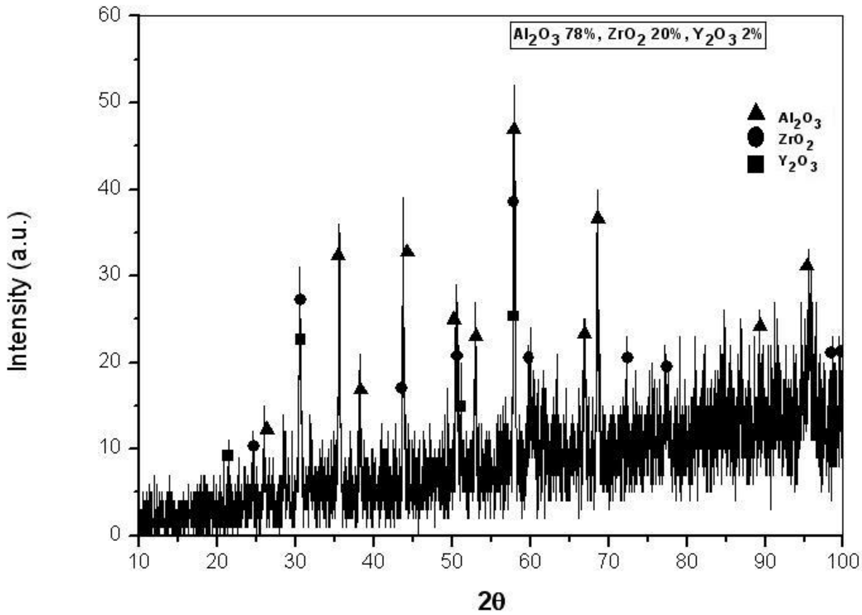


(b)



(c)

ISSN 2176-5480



(d)

Figure 1. X-ray Diffraction spectrum of AZY ceramics (a) Al_2O_3-ZrO_2, 5wt% ZrO_2, (b) 10wt% ZrO_2, (c) 15wt% ZrO_2, (d) 20wt% ZrO_2 and 2wt% of Y_2O_2 additives

3.2 Sintered Densities

The sintered density was measured by Archimedes method for the four composite compositions. Variation of the sintered density of AZY ceramics is presented in Fig. 2. It can be seen from this figure that sintered density decreases slightly from 5 to 10wt% ZrO_2 addition and then it increases slightly for for composites having 15wt% and 20 wt% ZrO_2. Decrease of sintered density due to addition of small wt% of ZrO_2 is consistent with the results of similar studies (Muccillo , 2004; Su et al, 2006) on ZrO_2-Al2O_3 system. With further increase of ZrO_2 content (20wt%), increase in sintered density may explained by the reduction of grain boundary of Al_2O_3 matrix because of the decrease of diffusion path length due to presence of Y_2O_3 additive resulting in better sinterability of the composite. High sintered density generally contributes to high mechanical strength and toughness.

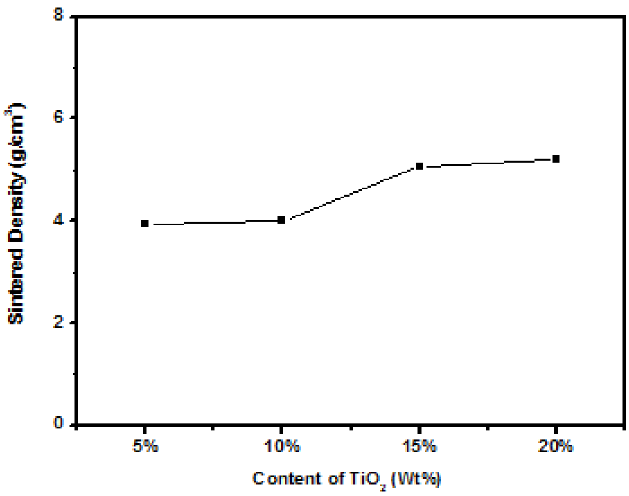


Figure 2 Sintered density of AZY ceramics

3.3 Mechanical Properties

Mechanical properties of the AZY ceramics were studied through Vickers microhardness (MHV) tests and variation of MHV with ZrO_2 content is presented in figure 3. AZY ceramics presented an increasing trend of MHV in

ISSN 2176-5480

all cases. The increase in MHV may be associated with the modifications in particle size distribution and homogeneity of the grain sizes which generally increase the hardness of sintered ceramics. In the present case it seems that presence of 2wt% Y_2O_2 additives enhanced the sinterability by way of liquid phase sintering process and its contribution has been more effective with higher ZrO_2 contents.

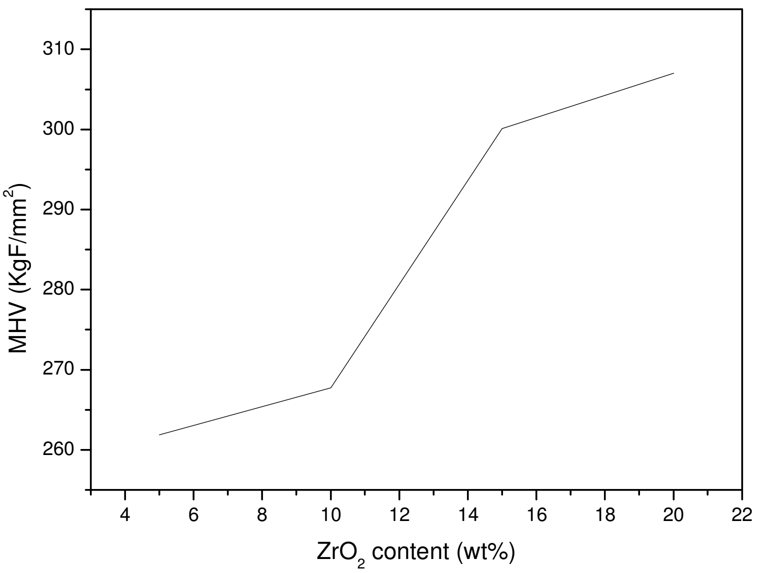
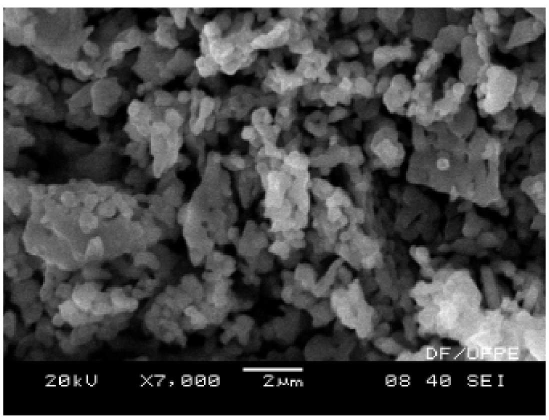


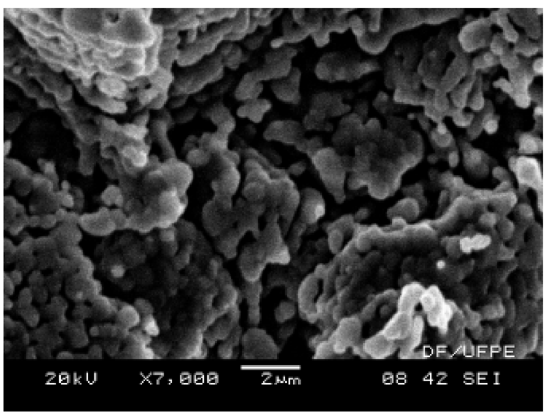
Fig. 3 Vicker's microhardness of AZY ceramics

3.4 Microstructures

Micrstructure of the AZY ceramics has been studied by scanning electron microscopy (SEM), using secondary electrons. Typical SEM micrographs of these composites are presented in following figure 4. From these micrographs it is observed that with increasing percentage of ZrO_2 there is a considerable modification in grain sizes as well as grain size distribution. In microstructures of AZY ceramics with 15 - 20wt% of ZrO_2, we can observe a well defined particle shapes and particle size distribution which may be attributed to $Y2O_2$ additives, which seems to act as liquid phase sintering aids in the presence of higher ZrO_2 contents.The different formats (cuboid, angular, lamellar and spheroidal) of particles / agglomerates of cerium dioxide are fundamentally dependent on the method of synthesis used (Muccillo , 2004). It appears that $Y2O_2$ in this case acts like a grain refining agent, through liquid phase sintering, which results in highly homogenous microstructure with homogenous grain sizes and grain size distribution. In conclusion, AZY ceramics with 15 - 20wt% of ZrO_2 content presented better results in terms of microstructure and mechanical hardness.

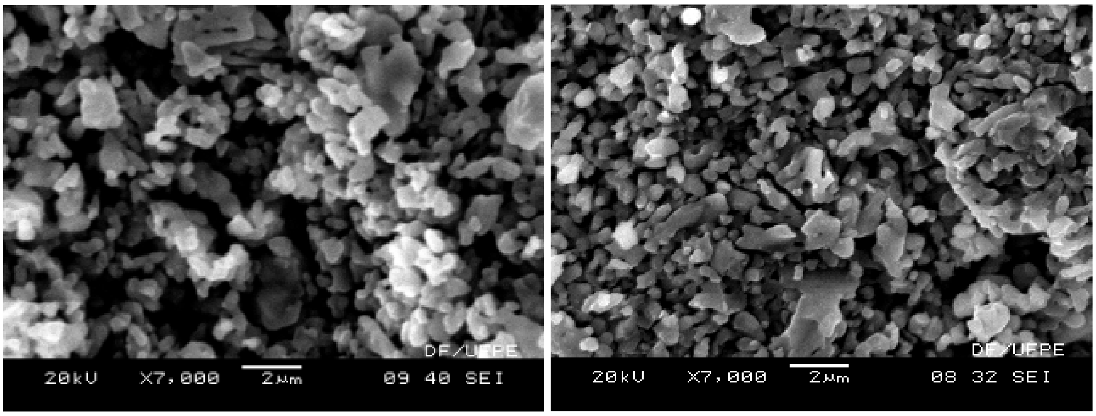


(a)



(b)

ISSN 2176-5480



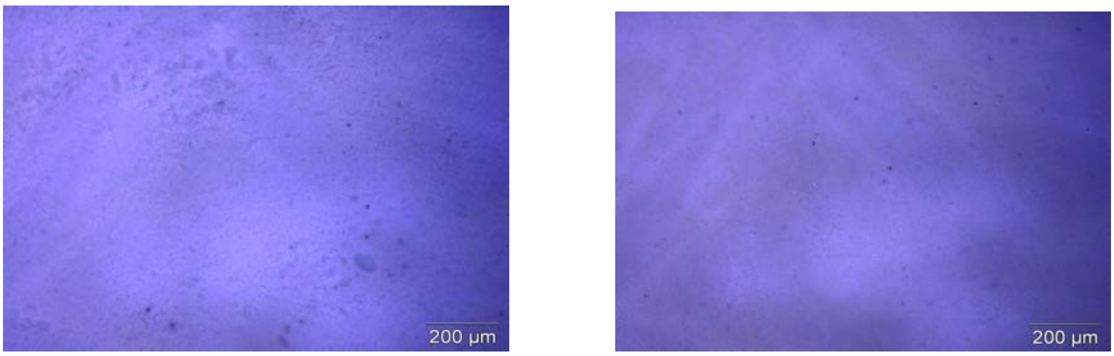
(c) (d)

Figure 4 SEM micrographs of AZY ceramics: (a – 5wt% ZrO_2, b – 10wt% ZrO_2, c – 15wt% ZrO_2, d – 20wt% ZrO_2., all with 2wt% Y_2O_2

3.5 Stability of AZY ceramics in crude petroleum environment,

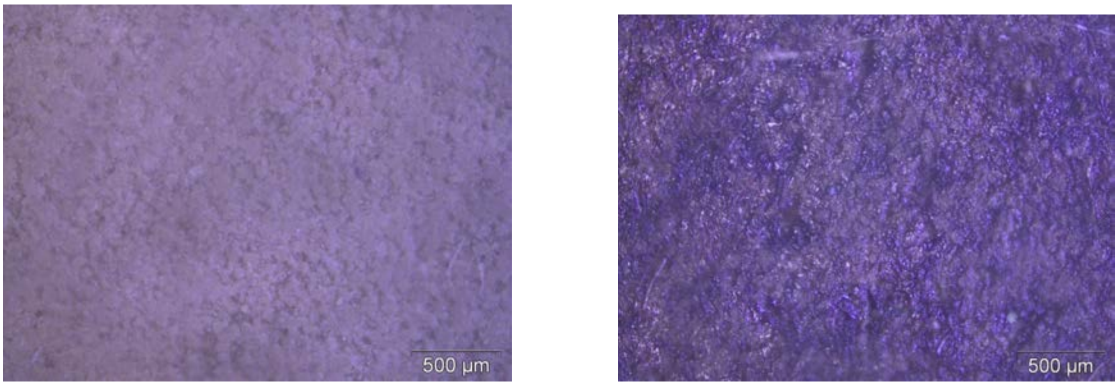
As AZY ceramics with 15 - 20wt% of ZrO2 content presented better results in terms of microstructure and mechanical hardness, we here present results of only these ceramics for the study of stability in crude petroleum environment. AZY ceramic discs were firstly subjected to optical microscopy and partitioned in two equal parts to be submersed each one in the crude petroleum extracted from earthen and offshore petroleum wells, respectively. This was carried out purposely to ensure that ceramics submersed in crude petroleum extracted from earthen and offshore petroleum wells were produced in the same manufacturing conditions. Ceramics were submerged in crude petroleum, extracted from earthen and offshore petroleum wells of Sergipe state of the north-east region of Brazil for 60days. Ceramics were taken out from the petroleum reservoir periodically, every 15 days and tested to observe if there are any changes in their structural, microstructural and mechanical characteristics due to crude petroleum environment. Results of X-ray diffractometry carried out on AZY ceramics after 60 days of submersion in crude petroleum presented identical to the XRD spectrum AZY ceramics before submersion in crude petroleum. They did not present any impurity peaks or other phases. This shows that AZY ceramics did not suffer any structural changes due to crude petroleum environment.

Figure 6 presents the optical micrographs of AZY ceramics before and after submersion in crude petroleum. This microstructural analysis was carried out using optical microscopy because after submersion in crude petroleum it was extremely difficult to use scanning electron microscopy because of vacuum necessities.

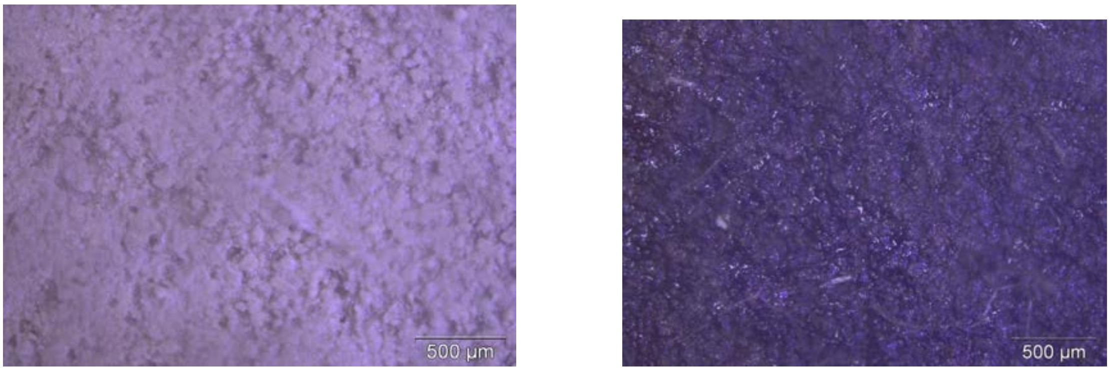


(a) (a´)

ISSN 2176-5480



(b) (b’)



(c) (c’)

Figure 5. Optical micrographs of AZY ceramics in before and after submersion in crude petroleum. (a) and (a´) Before submersion in crude petroleum, (b and b´) after 60 days submersion in crude petroleum extracted from earthen petroleum wells, respectively and (cand c’) after 60 days submersion in crude petroleum extracted from offshore petroleum wells respectively.

As seen from figure 7, microstructural features of AZY ceramics before and after submersion in crude petroleum remain identical and there in any degradation in microstructural features due to crude petroleum environment.

Vickers microhardness tests were also performed on AZY ceramics after 60 days of submersion in crude petroleum extracted from earthen and offshore petroleum wells and results of these tests presented values as that of of AZY ceramics before submersion.

From these promising results we conclude that AZY ceramics are stable in the aggressive crude petroleum environment and thus could be potential candidate ceramic encapsulation in the fabrication of temperature sensors for temperature monitoring in petroleum wells.

4. CONCLUSIONS

In conclusion, we have produced rare-earth oxide (Y_2O_3) reinforced Al_2O_3-ZrO_2 ceramic composites, in proportions of 5-20 wt% ZrO2 and 2wt% Y_2O_2 reinforcement, with high mechanical strength through thermo-mechanical processing and sintering techniques. x-ray diffraction and scanning electron microscopy studies reveal the formation of atc composite ceramics and there is no chemical interaction between constituent (Al_2O_3, ZrO_2, $Y2O_2$ $_2$) oxides. ceo_2 reinforcement is highly effective in microstructural homogenization and in turn increasing the mechanical strength of the atc ceramics with higher (15 - 20wt%) ZrO_2 content.

to assess the quality of materials developed and the possibility of using them as protective coatings of crude petroleum storage and transportation systems we have studied the physic-chemical and mechanical stability of these materials in crude petroleum originated from earthen and offshore petroleum wells of sergipe region of brazil. these studies presented satisfactory results in terms of physic-chemical and mechanical stability of these materials for the use of rare rare-earth oxide (**Y_2O_3**) reinforced Al_2O_3-ZrO_2 ceramic composites with 15 - 20 wt% ZrO_2 and 2wt% of Y_2O_3, for inert coating of metallic parts used in crude petroleum environment of petroleum industry.

5. ACKNOWLEDGEMENTS

Authors acknowledge Brazilian research funding agencies CNPq and FACEPE for the financial support for this study and PETROBRAS for the supply of crude petroleum..

6. REFERENCES

Becher PF, 1991, Microstructural design of toughened ceramics. J Am Ceram Soc. Vol. 74 p.255–264.

Evans AG, 1990,Perspective on the development of high toughness ceramics. J Am Ceram Soc. Vol. 73 p.187–192.

Fu Y, Gu YW, Du H,2001, SiC whisker toughened Al_2O_3–(Ti W)C ceramic matrix composites. Scripta Mater. Vol.44 p.111–116.

Muccillo ENS, Porfírio TC, Tadokoro SK, Rey JFQ, Rocha RA, Steil MC, Muccillo R, 2005, Propriedades físicas do óxido de cério preparado por técnica de solução e a condutividade elétrica em função da pressão parcial de oxigênio em cerâmicas sinterizadas. Cerâmica Vol. 5 p. 159.

Su J, Huang C, Wang J, Liu H, 2006, Mechanical properties and microstructure of ZrO2-TiN-Al2O3 composite ceramics, Mater. Sci. Engg. Vol. A 416 p.104-108.

Xu CH, Ai X, 1997, Applications of rare earth elements in nitride ceramic materials. Mater Rev Vol.11p.46–50.

Iost A, Bigot R, 1996, Identation size Effect: Reality or Artefact? J Mater Sci Vol. 31 p.3573.

7. RESPONSIBILITY NOTICE

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