PRODUCTION AND CHARACTERIZATION OF OF HIGH BRITTLE TOUGHNESS La_2O_3 REINFORCED ALUMINA – TITANIA CERAMIC COMPOSITE COATINGS FOR CRUDE OIL STORAGE TANKS.

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Abstract. *The increasing development of the petroleum industry has required new technologies in the production of materials that resist the corrosive environments such as storage and transportation of crude oil. Accordingly, the ceramic materials that are highly resistant to hostile environments have great potential for such applications. As ceramic materials are fragile, in this work we have produced and characterized La_2O_3 reinforced alumina – titania ceramic composite with high brittle toughness and high mechanical strength. Alumina - titania ceramic composites added with 1-3% La_2O_3 were produced through thermo-mechanical processing and normal sintering techniques.structural, microstructural characterizations and mechanical tests were carried out to evaluate the use of these composites in the manufacture of crude petroleum oil storage tanks made of metallic matrix coated with the composites ceramics developed in this work. The results will be presented and discussed in this paper.*

Keywords*: La_2O_3 reinforced alumina – titania, ceramic composite coatings, crude petroleum oil*

1. INTRODUCTION

Due to the recent growth of the Brazilian oil industry, it has become necessary to improve conditions for crude oil transportation and storage. As crude oil is a highly corrosive substance it is required that for safer transportation and storage, the tanks should be inert to the attack of crude petroleum. For this reason, studies of inert coatings for the protection of these tanks are needed. Ceramic materials present several special properties: high heat capacity, corrosion resistance, the fact that they can be insulators, conductors or superconductors, magnetic properties presence or absence of magnetism and being hard and tough, and thus could be potential coating materials for such applications. However, ceramic materials are fragile it is necessary to increase their brittle toughness by other ceramic reinforcements. In this work we have studied the potential of using La_2O_3 reinforced alumina-titania ceramics for their use as inert coating materials. . These La_2O_3 reinforced alumina-titania ceramics were produced by thermo-mechanical processing using high energy ball milling and sintering in a muffle furnace at a temperature of 1350°C for 36 hours. Sintering behavior, microstructure and mechanical properties of these ceramics were studied by X-ray diffraction, scanning electron microscopy (SEM) and Vickers hardness (HV)) tests

2. MATERIALS AND METHODS

For the production of Al_2O_3-TiO_2 composites, TiO_2 ceramics were added in Al_2O_3 in 5% to 20 wt% ratios and 1 wt% La_2O_2 was added in the respective compositions. Final weight of each composition was fixed in batches of 100gms. Table 1 presents the experimental compositions of ceramic powders. 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%.

Table 1. Experimental compositions of ceramic powder

COMPOSITION	MIXTURE 5%	MIXTURE 10%	MIXTURE 15%	MIXTURE 20 %
Al_2O_3	94	89	84	79
TiO_2	5	10	15	20
La_2O_3	1	1	1	1

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 1350°C during 36 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. Figure 1 presents a typical picture of ceramic pellet after sintering process.

Figure 1. The pellets after the sintering process.

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).

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 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:

$$HV = \frac{(1854,4P)}{d^2} \text{ , Kgf/mm}^2 \quad (1)$$

where P is the load and d is the average diagonal of the square identation produced by the pyramidal indentor in the sample (Iost and Bigot 1996).

The microstructure of the sintered composite ceramics was 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).

3. RESULTS AND DISCUSSION

3.1. Vickers Microhardness Tests

Vickers microhardness tests of La_2O_3 reinforced alumina-titania ceramics showed the following results, displayed in Tab. 2. Alumina is considered a ceramic material with high mechanical hardness, addition of small amounts of titania and La_2O_3 reinforcement have a cause a complex effect on the hardness values.

Table 2. Vickers microhardness tests of 1 wt%La_2O_3 reinforced alumina-titania ceramics

Mixture	**5 wt% TiO2**	**10 wt% TiO2**	**15 wt% TiO2**	**20 wt% TiO_2**
Microhardness (kgf/mm²)	192.77	291.28	120.23	116.45

Vickers microhardness tests of La_2O_3 reinforced alumina-titania ceramics up to 10 wt% addition of TiO_2 but after that it decreases drastically. La_2O_3 reinforced alumina-titania ceramics with 10 wt% of TiO_2 298.28 kf/mm^2.

3.2. X-Ray Diffraction Analysis

Through the analysis of the the X - ray diffraction patterns of La_2O_3 reinforced alumina-titania ceramics, shown in Fig. 2, we can verify that ceramics with upto 10 wt% TiO_2 addition presented separate identity of constituent oxodes where as ceramics addes with more than 10 wt% TiO_2 presented impurity phases. XRD patterns of 15 and 20 wt% TiO_2 additions presented similar XRD patterns and as such only XRD pattern of 20 wt% TiO_2 has been presented here.

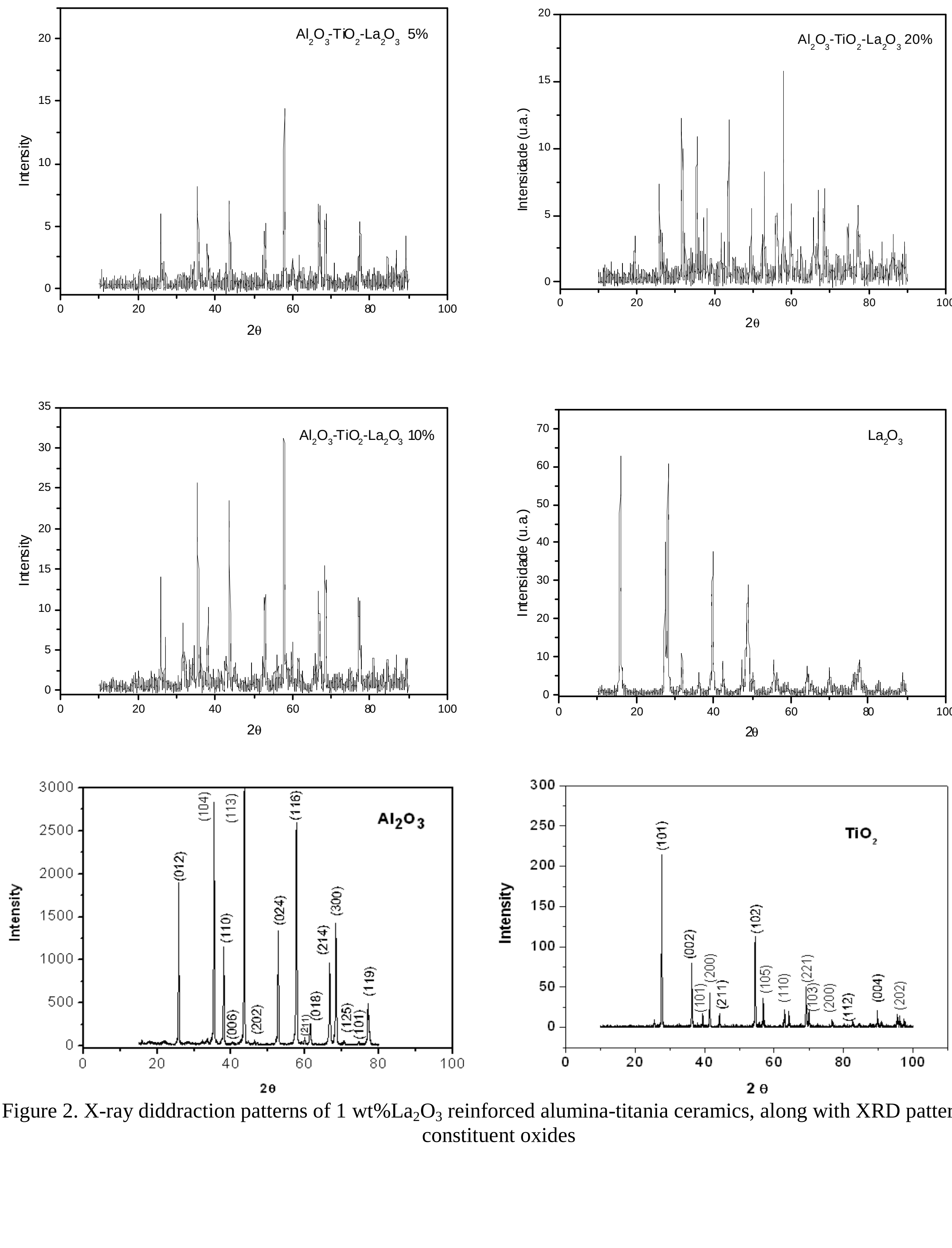

Figure 2. X-ray diddraction patterns of 1 wt%La_2O_3 reinforced alumina-titania ceramics, along with XRD patterns of constituent oxides

3.3. Scanning Electron Microscopy Analysis

According to scanning electron microscopy of La2O3 reinforced alumina-titania ceramics, presented in Figure 3,it is possible to observe there has been gradual modification in microstructure with increase of TiO2 addition. Ceramics with 5wt% and10wt% TiO2 present homogeneity and particle size distribution.

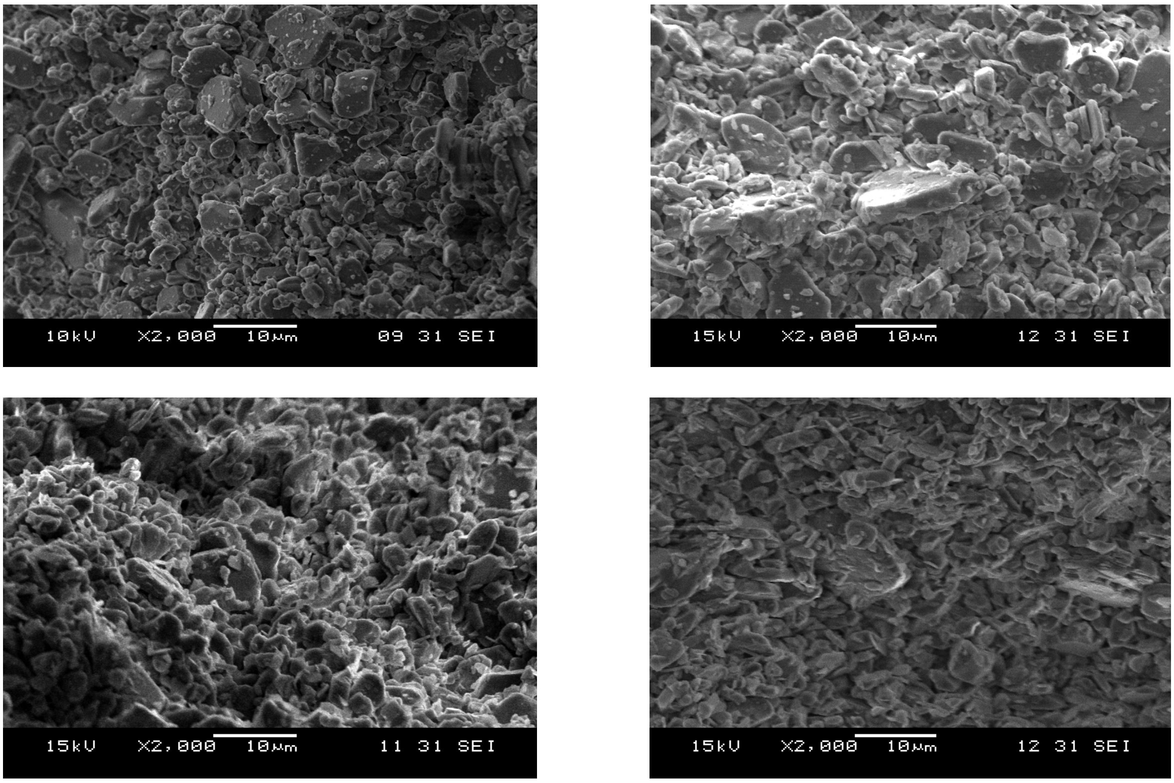

Figure 3. Scanning electron microscopy of C of respectively 5wt%,10wt%,15wt%,20wt% TiO_2 addition.

The composites of 15wt% and 20wt% is observed a different situation, there is a refinement of the grains. La_2O_3 seems that in this case acts as a grain refining agent, through liquid phase sintering process, but at the same time it increases microporosity and sintered bodies.

4. CONCLUSIONS

According to preliminary results of fabrication of ceramic composites of Al_2O_3-TiO_2 with 1wt% La_2O_3, can be concluded that the composites with the content of 5wt% and 10wt% TiO2 presented better results in terms of microstructure, Vickers microhardness, and phase compositions. . Ceramics with 10 wt% TiO_2 presented reasonable mechanical hardnes and can be potential materials for coating purposes.

We are in process of studying fracture toughness and other related mechanical properties along with the study of chemical stability behavior of these composites in extremely hostile crude petroleum environment. These results will be presented in other opportunities in due course.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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