PRODUCTION OF HIGH BRITTLE TOUGHNESS ALUMINA-TITANIA CERAMIC COMPOSITE COATINGS FOR CRUDE PETROLEUM 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 alumina-titania based ceramic composites having high brittle toughness and high mechanical strength. Alumina-titania ceramic composites added with 1-3% ceria 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*: alumina-titania, brittle toughness, crude petroleum, storage tanks*

1. INTRODUCTION

The crude petroleum is a highly corrosive material so there is considerable degradation of surface of the tanks for storage and transportation of crude oil, which is made of metallic materials, is a serious problem in the petroleum extraction industry. Thus, an alternative to solve this problem is to use a type of coating inert to such corrosion. Ceramics usually have this characteristic and may be a choice of material for this coating. In the high technology industries ceramic materials appear as tools for many applications, especially for use in high temperature and hostile environment.

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 and Becher, 1991)

Mechanical properties of alumina based ceramics improved considerably with the addition of TiO_2, TiN, ZrO_2 etc. as reinforcement additives (Fu et al. 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-TiO_2) can increase the toughness of these ceramics (Xu, 1997). In this work we have produced Al_2O_3-TiO_2 composite ceramics with reinforcement of CeO_2 to evaluate their potential as a surface coating to protect surface degradation of the tanks for storage and transportation of crude petroleum. Preliminary results of this study are reported and discussed in this article.

2. MATERIALS AND METHODOLOGY

For the production of Al_2O_3-TiO_2 composites, TiO_2 ceramics were added in Al_2O_3 in 5% to 20 wt% ratio and 1wt% CeO_2 was added in all the compositions. Final weight each composition was prepared in batches of 100gms. Each batch of ceramic mixtures was thoroughly mixed and homogenized separately in a high energy ball mill having stainless steel milling chamber and high purity alumina balls, (Equipments Marconi MA-50, São Paulo, Brazil) 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%. For this calculation following formula can be used:

$$P = V \times d_b \times p \times 0.6 \tag{1}$$

Where, P = amount of balls (Kg); d_b = specific weight of the balls (Kg / L), V = net volume of the milling chamber (L), p = apparent occupancy rate of the balls (0.50 to 0.55). For the mill, the theoretical density of alumina is 3.98 g / cm ³, $V = \pi r^2 h$ = 3.14 x 6.5 x 14.8 cm³ = 1963.442 cm^3 = 1.963 L, and considering also that the rate of ideal occupation is in the range of 20% - 25% of the net volume of the mill, it appears that $V_{25\%}$ = 490.86 cm ³ = 0.49086 L . Thus, P = 490.86 x3, 98x0.50x0. 60 = 586.09 g. Since the mass of a alumina ball is 19.1198 g, the total number of balls in the mill that optimizes the process is 30.81 (total mass / mass unit = amount of balls, or 586.09 / 19.1198 = 30.81). So, Accordingly, the ideal number of balls is approximately 31 units. The speed of rotation of the ball mills is calculated according to the critical angular velocity (*CAV*), which is the speed at which the components of centrifugal forces and the weight of the material is equal (resulting void the action of milling), and is related to the internal diameter of the mill (D) by the following equation:

$$CAV = \frac{43.2}{\sqrt{D}} \tag{2}$$

The ideal speed of rotation is around 75% of the critical speed, applicable to mills with grinders bodies of low density, it is recommended values below, the order of 60%, when using high-density bodies grinders. Fig. 1 illustrates four different situations, in terms of speed of rotation of the mill, determining different milling yields. In (a) the centrifugal acceleration (a_c) is much lower than the acceleration of gravity (g), which creates an angle formed by the balls (β) less than 45° and, consequently, a low degree of milling.

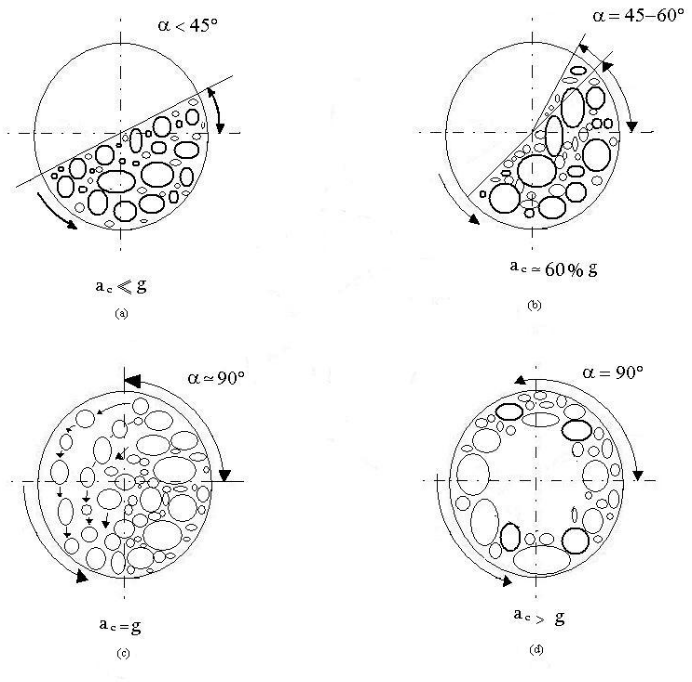


Fig.1. Schematic illustration of interior of a ball mill for four different values of the centrifugal accelerations (a_c), β - angle of cascade

In (c) the angle β is approximately equal to 90°, from which it reaches the critical speed and stops there grinding (β> 90°), situation (d). In (b) the ball shall amount to an angle of 45-60 °, from the horizontal, and roll as a cascade to the bottom promote good degree mill. However, due to the amount of balls, the fall is not free and does not occur for all balls at the same time: most of balls of the internal layer have less centrifugal force and fall before the balls of external layer. Therefore, we should calculate the amount of ideal balls as already mentioned. Of all these movements (drop the ball rolling and most central of rolling on each other) comes the action of shock by grinding, crushing, cutting and friction materials that are mixed with the grinders bodies.

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 has been 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 Al_2O_3-TiO_2 ceramic composites, with 1 wt% of CeO_2 additives, in order to evaluate their potential as toughened ceramic coatings for crude petroleum storage tanks.

Bulk density of composites was 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 micron granularity. 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).

3. RESULTS AND DISCUSSIONS

3.1. Phase composition

Structural characterization and phase composition identification of Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives were investigated through X-ray diffractometry. A typical XRD pattern of Al_2O_3-20wt%TiO_2 ceramic composites with 1 wt% of CeO_2 is presented in Fig. 2. Table 1 below presents the phase composition of the fabricated composites.

Table1: Composition of fabricated Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives

Composite no.	AlTi 1	AlTi 2	AlTi 3	AlT4 1
Al_2O_3	94	89	84	79
TiO_2	5	10	15	20
CeO_2	1	1	1	1

Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives with lower TiO_2 contents (5-15wt%) presented similar XRD patterns and due to this have not been presented here. . Fig.2 also presents XRD patterns of Al_2O_3, TiO_2 and CeO_2 ceramics, used for the fabrication of composites in question, for better comparison of the XRD spectra.

As seen from the XRD patterns, the composites did not present any additional phase except the constituent phases, i.e. Al_2O_3, TiO_2, CeO_2, as expected. Also the presence of the CeO_2 phase is very rarely observed in the XRD patterns due to their very small (1wt%) in the composites. From the XRD studies we can conclude that there is no any chemical reaction within constituent phases of the Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives.

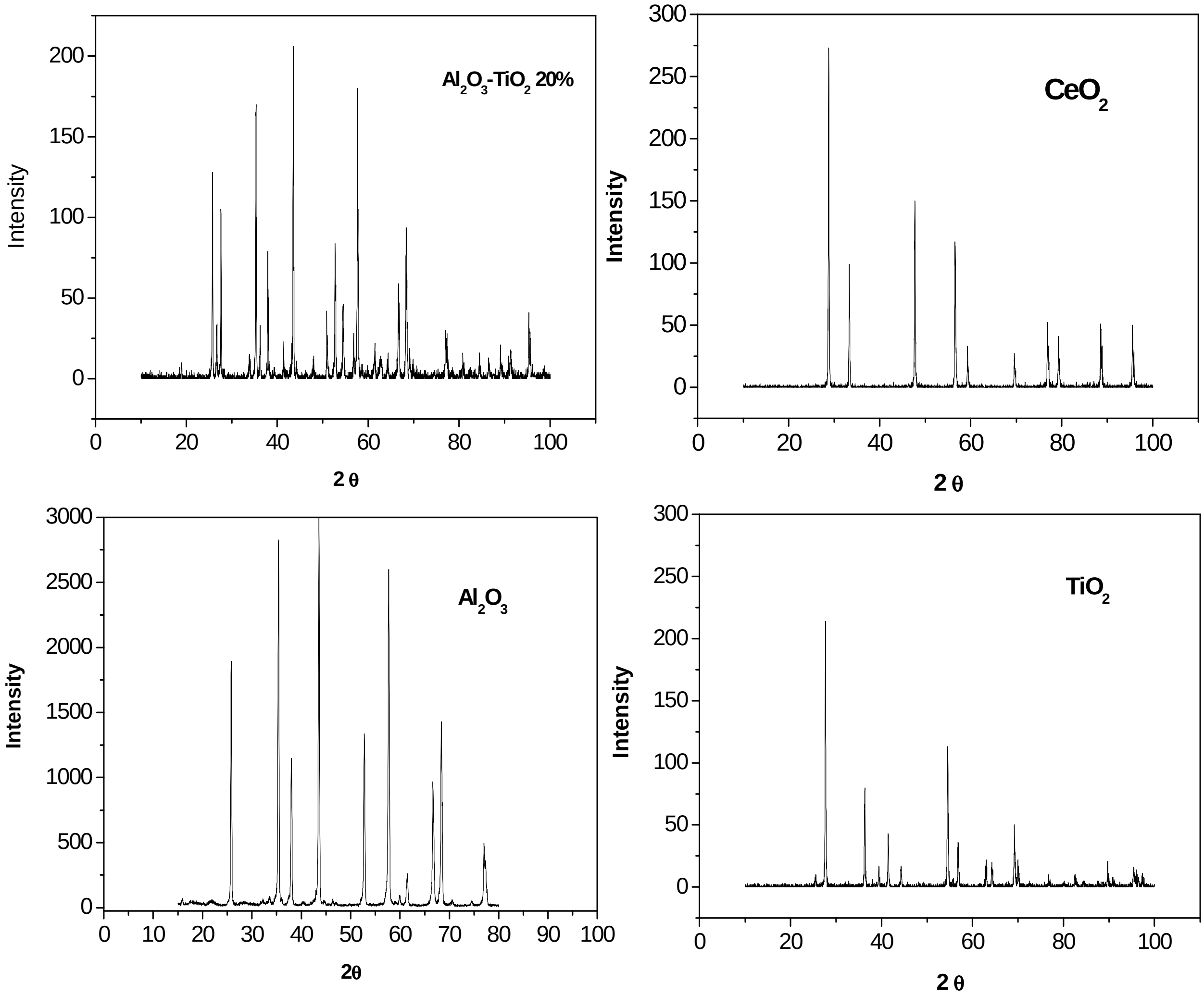


Fig. 2. X-ray Diffraction spectrum of Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives along with the XRD spectra of constituent ceramics TiO2, Al_2O_3, CeO_2 ceramics used for the fabrication of composites for easy comparison

3.2 Sintering Densities

The sintered density was measured by Archimedes method for the four composite compositions. Variation of the sintered density of Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives is presented in Fig. 3. It can be seen from this figure that sintered density decreases slightly from 5 to 10wt% TiO_2 addition and this decrease is more visible for composites having 15wt% TiO_2 and finally sintered density of composites has a considerable increase. Decrease of sintered density due to addition of small wt% of TiO_2 can play a significant role in decreasing the sintered density of the composite. This is consistent with the results of a similar study by Sun et al (2006) in ZrO_2-Al2O_3 system. With further increase of TiO2 content (20$), 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 CeO_2 additive resulting in better sinterability of the composite. High sintered density generally contributes to high mechanical strength and toughness.

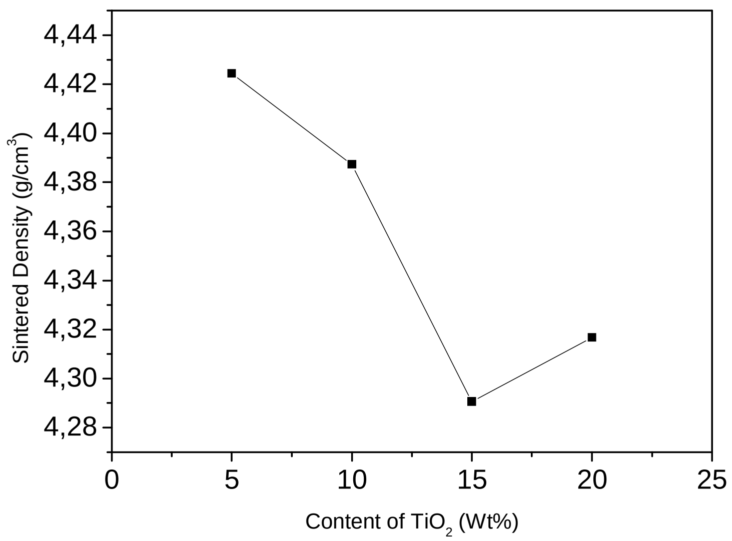


Fig. 3 Sintered density of Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives

3.3 Mechanical Properties

Mechanical properties of the Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives have been studied through the measurements of Vickers microhardness (MHV). In the Vickers microhardness hardness test for each composite sample, five indentations were performend in distinct locations on the polished composite surface to have more secure results. Variation of MHV of the composites with TiO_2 content is presented in Fig.4. Composites presented an increasing trend of MHV at all cases however it became practically constant for composites above 15 wt% TiO_2 content. 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 1wt% CeO2 additives enhanced the sinterability by way of liquid phase sintering process and its contribution has been more effective with lower TiO_2 content.

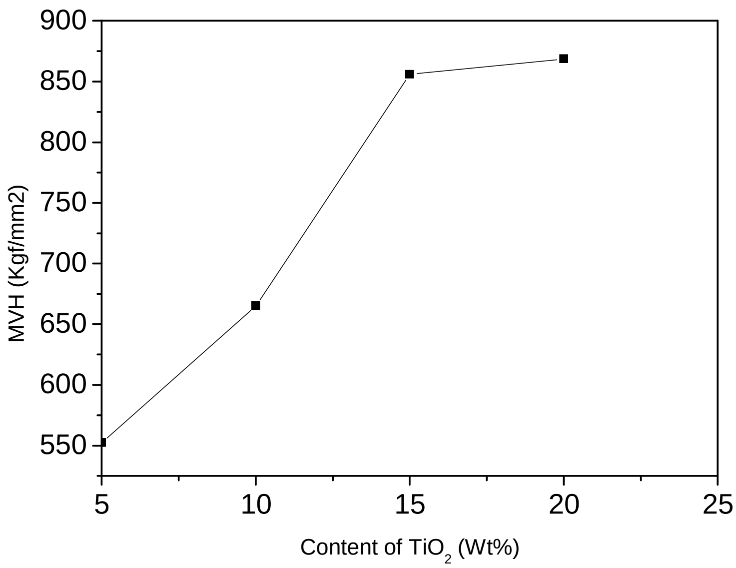
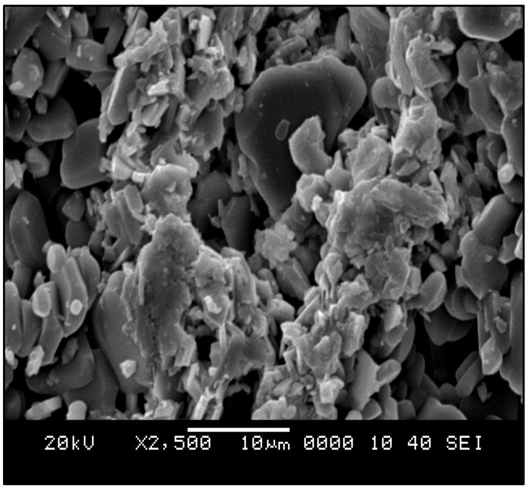


Fig. 4 Vicker´s microhardness of Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives

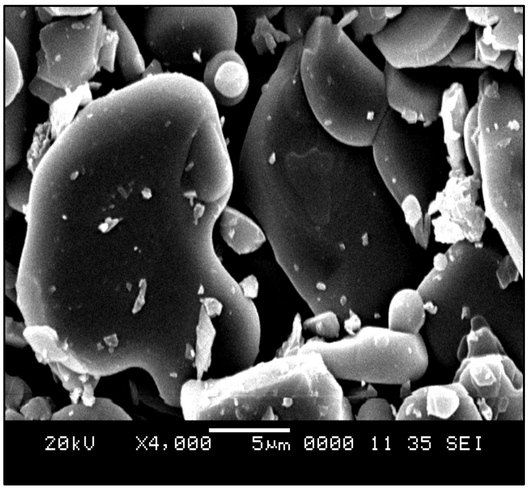
3.4 Microstructure

Micrstructure of the Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives has been studied by scanning electron microscopy (SEM), using secondary electrons. Typical SEM micrographs of these composites are presented in following Fig. 5.

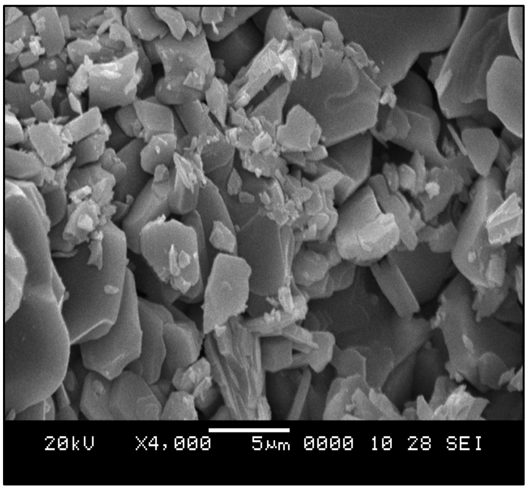
(a)



(b)



(c)



(d)

Fig. 5 SEM micrographs of Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives, (a) 5%wt TiO_2, (a)5%wt TiO_2, (b) 10%wt TiO_2, (c) 15%wt TiO_2, (d) 20%wt TiO_2,

From the micrographs obtained by SEM it is observed that the microstructure of the composites gradually modified with the increase of the TiO_2 content. It was observed that with increasing percentage of TiO_2 there is a considerable modification in grain sizes as well as grain size distribution. In composite with 10wt% TiO_2 though there no considerable change in grain size distribution but there is considerable presence of clusters due to greater content of TiO_2. In composites with 15wt% of TiO_2, we can observe a large grain growth but in all these three composites, effect of CeO_2 additives, which seems practically remains intact, did not present observable effect on the sintering process. The different formats (cuboid, angular, lamellar and spheroidal) of particles / agglomerates of cerium dioxide are fundamentally dependent on the method of synthesis used (Muccillo, 2005). In case of 2owt% TiO_2 composite, we can observe a much different situation. It appears that CeO_2 in this case acts like a grain refining agent, through liquid phase sintering process, which results in highly homogenous microstructure with homogenous grain sizes and grain size distribution. Al_2O_3-20%TiO_2 ceramic composites with 1 wt% of CeO_2 additive presented best results in terms of microstructure and mechanical hardness.

4. CONCLUSIONS

In this work we have presented our preliminary results on the fabrication of Al_2O_3-TiO_2 ceramic composites with 1 wt% of CeO_2 additives for their use as protective4 coatings in crude petroleum storage tanks. From these studies we cn conclude that Al_2O_3-20%TiO_2 ceramic composites with 1 wt% of CeO_2 additive presented best results in terms of microstructure and mechanical hardness, reasonably suitable for aforesaid applications. 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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