THERMO-MECHANICAL PROCESSING AND MECHANICAL PROPERTIES OF $Ca_2AlWO_{5,5}$ CERAMICS FOR THE FABRICATION OF CERAMIC COMPONENTS FOR PETROLEUM INDUSTRIES

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Abstract. *Complex perovskites oxide ceramics based on tungsten are highly inert to hostile environmental conditions For this reason, these types of ceramics have great potential for use in the petroleum industry where the corrosive environment is a constant problem for the manufacture of parts and components. We are working on the fabrication of temperature sensors encapsulated in ceramics for the petroleum industry. In this context, we produced* $Ca_2AlWO_{5,5}$ *ceramic by thermo-mechanical process using high energy ball mill and aluminum balls.* $Ca_2AlWO_{5,5}$ *ceramic components were manufactured through normal sintering of ceramic compacts. Sintering was carried out in a temperature range of 1200 to 1350°C during 24 hours in air atmosphere. Fabricated through thermo-mechanical process, the ceramic compacts showed high homogeneity in terms of size and distribution of the particles and presented desired mechanical properties required for ceramic encapsulation for the conservation of metallic parts in highly hostile crude petroleum environment.*

Keywords*:* $Ca_2AlWO_{5,5}$ *, thermo-mechanical processing, mechanical properties, petroleum industries*

1. INTRODUCTION

There is increasing requirement for materials and reliable systems for operation in hostile environments such as high temperature or chemically aggressive environments such as the oil petroleum industry. Ceramics are a broad class of materials whose main features, that make them interesting materials for various purposes, are high thermal capacity, resistance to corrosion, the fact that they may be, insulating, conducting or superconducting, magnetic properties or absence of magnetism and to be hard and resistant, but fragile. Thus, many of the new technology incorporate ceramic components due to their extremely versatile and promising structural, chemical, electrical, mechanical, and thermal properties.(Schwartz 1985, Tejuca and Fierro 1993)

We are working on search of new ceramic materials to resist hostile environment of petroleum industry, (Lapa et al 2005, Leonardo et al 2005, Yadava and Sanguinetti Ferreira 2008) in this work were produced a new complex cubic perovskite ceramic, $Ca_2AlWO_{5,5}$ to fabricate ceramic components for encapsulation of metallic temperature sensing devices, used in the petroleum extraction. $Ca_2AlWO_{5,5}$ ceramics were produced by thermo-mechanical processing using high energy ball mill and then sintered through normal solid state sintering route. Their properties were studied by X-ray diffraction, scanning electron microscopy and microanalysis and Vickers micro-hardness tests. After this sintered ceramic components were submerged in crude petroleum during 45 days with periodical observation divided in periods of 15 days. To observe possible changes in microstructural features of ceramics subjected to crude was analyzed by optical microcopy. This article reports these results and discusses its implications on application viability of $Ca_2AlWO_{5,5}$ as ceramic components for the fabrication of ceramic encapsulated temperature sensing devices to be used in petroleum extraction industry.

2 EXPERIMENTAL PROCEDURE

The $Ca_2AlWO_{5,5}$ ceramic powder has been prepared by conventional solid-state reaction route. High purity (99.99%) constituent oxides CaO, Al_2O_3 and WO_3 were mixed in stoichiometric ratios, compacted at 400MPa and calcined at 1200ºC for 24h. After calcinations, materials were furnace cooled to room temperature and were examined by X- ray powder diffractometry (XRD) using a Shimadzu X-ray diffractometer, equipped with Cu - Kα radiation (λ = 1.5406 Å) to determine the structural characteristics and phase identification.

For the study of sintering behavior, $Ca_2AlWO_{5,5}$ ceramic powders were produced in a typical batch size of 100 grams. These ceramic powders were thoroughly milled in a ball mill model MA-50, Marconi Equipments, São Paulo, Brazil, equipped with an stainless steel milling chamber and alumina balls, for a period of 24 h.

Thoroughly milled and homogenized $Ca_2AlWO_{5,5}$ powders were uniaxially compacted in a metallic mould fabricated from abrasion resistant AISI A2 steel (HRC 58) to form circular discs with 30 mm of diameter and 5 mm thickness. A pressing load of 1000MPa has been applied for powder compaction, using a hydraulic press. For every compaction process pressure was applied for 5 minutes to stabilize the pressure distribution in the pressed compact.

The green compacted $Ca_2AlWO_{5,5}$ ceramic bodies were subjected to the sintering process at a temperature of 1300ºC, for 24h. Sintering process of the samples was carried out in ambient atmosphere in high purity alumina crucibles, using a high temperature muffle furnace (Jung 0614).

Microstructures of the sintered ceramics were studied by a scanning electron microscope and microanalysis (JEOL 6460). To observe the microstructure the samples covered with thin carbon coating. The mechanical behavior of the sintered $Ca_2AlWO_{5,5}$ ceramics was studied by measuring micro-hardness using Vickers hardness indentor model HVS-5 No. 0021. For the measurement of Vicker´s microhardness, samples were polished with #220, #400, #600, #1200, #1500 grade sand papers and diamond paste with 1 μm granularity.

After the mechanical characterization, four samples were submerged in crude petroleum, two samples in crude petroleum extracted from the ocean petroleum wells and the other two in crude petroleum extracted from the earth petroleum wells. The samples stayed there for 45 days were monitored by optical microscopy analyses after each 15 days.

3. RESULTS AND DISCUSSION

3.1. Strucrural characterization

X ray Powder diffraction studies were carried out on the sintered ceramic sample. The samples presented a well-defined $A_2BB'O_6$ type complex cubic perovskite structure for $Ca_2AlWO_{5,5}$ ceramics. The XRD spectrum of a typical $Ca_2AlWO_{5,5}$ ceramic, sintered at 1300°C for 24h, is shown in Fig. 1. XRD spectrum of $Ca_2AlWO_{5,5}$ consists of strong peaks characteristics of primitive cubic perovskite structure plus few weak reflection lines arising from the super-lattices. No evidence for a distortion from the cubic symmetry is observed in the XRD spectrum. Due to the ordering of B and B' on octahedral site of the ABO_3 unit cell there is a doubling in the lattice parameter of the basic cubic perovskite unit cell. Thus, the whole XRD pattern of $Ca_2AlWO_{5,5}$ can be indexed in a $A_2BB'O_6$ cubic cell with the cell edge $a = 2a_p$ where a_p is the cell lattice of the cubic perovskite. The XRD spectrum of Ca_2AlNbO_6 is similar to other $A_2BB'O_6$ type complex cubic perovskite oxides e.g. YBa_2NbO_6, $ErBa_2SbO_6$, $DyBa_2NbO_6$ etc reported in JCPDS files.

The basic perovskite composition is ABO_3, where A is a large ion suitable to the 12-coordinated cube-octahedral sites and B is a smaller ion suitable to the 6-coordinated octahedral site. Complex perovskite with mixed species on a site (particularly the B site) may be represented by multiples of this formula unit and a larger unit cell, e.g. $A_2BB'O_6$, $A_3B_2B'O_9$ etc. Presence of the superstructure reflection lines (111), and (311) in the XRD spectrum of $Ca_2AlWO_{5,5}$ is the signature of an ordered complex cubic perovskite structure. (Glasso et al 1961)

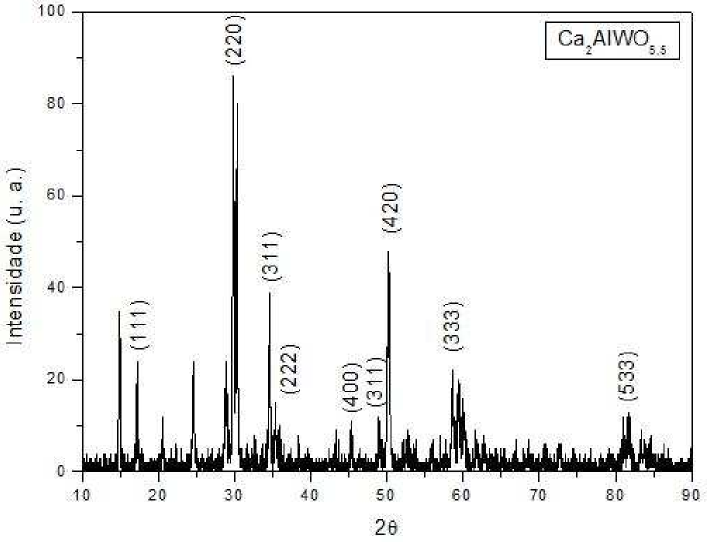

Figure 1. X-rays diffraction spectrum of $Ca_2AlWO_{5,5}$

In a substitutional solid solution BB', there is a random arrangement of B and B' on equivalent lattice positions in the crystal structure. Upon suitable heat treatment, the random solid solution rearranges into a structure in which B and B' occupy the same set of positions but in a regular way, such a structure is described as superstructure. In the superstructure, the positions occupied by B and B’ are no longer equivalent and this feature is exhibited in the XRD spectrum of the material by the presence of superstructure reflection lines. (wells 1989)

For double cubic perovskite of the formula $A_2BB'O_6$ the intensity, in particular of the (111) and/or (311) superstructure reflection, is proportional to the difference in scattering power of the B and B’ atoms, when all the atoms are situated in the ideal position. A disordered arrangement of B and B’ should result in zero intensity. Therefore Al^{3+} and W^{6+} cations ordering in $Ca_2AlWO_{5,5}$ in B and B’ positions is clearly distinguished by the presence of the significant intensity of (111) and (311) superstructural reflection lines. Based on above discussion we have now indexed the XRD peaks of $Ca_2AlWO_{5,5}$ as an ordered complex cubic perovskite with $A_2BB'O_6$ crystal structure. The lattice parameter of $Ca_2AlWO_{5,5}$, calculated from the experimental XRD data Tab.1 is a_{exp} = 8.1209 Å. This value is in good agreement with theoretical lattice parameter value a=7.2092 Å of $Ca_2AlWO_{5,5}$.

Table 1. XRD data of $Ca_2WNbO_{5,5}$

2θ	d(Å)	I/I_0	hkl
17.2	5.1513	24	111
29.86	2.9898	86	220
34.6	2.5903	39	311
35.42	2.5322	15	222
45.38	1.9969	11	400
48.92	1.8604	12	311
50.2	1.8159	48	420
58.6	1.5740	22	333
81.68	1.1779	13	533

3.2. Microstrucrural characterization

Production and functional ability of polycrystalline ceramic products are highly dependent on their microstructural features, which in turn are highly influenced by sintering kinetics. (Reed 1988, Richardson 1982) Microstructural features define the final product quality of the ceramic products and their mechanical strength. In the present case we were able to sinter $Ca_2AlWO_{5,5}$ ceramics by normal solid state sintering process at the temperature we used.

To examine the microstructure of complex cubic perovskite $Ca_2AlWO_{5,5}$ sintered ceramics we used the technique of scanning electron microscopy, using secondary electrons. This characterization was to assess the order in relation to the microstructure homogeneity, size and distribution of grains, porosity and the presence of phases in ceramics. A typical SEM micrograph of $Ca_2AlWO_{5,5}$ sintered polished ceramic is shown in fig.2. As we can verify from this micrograph, ceramic presents a highly homogeneous microstructure and particle size distribution.

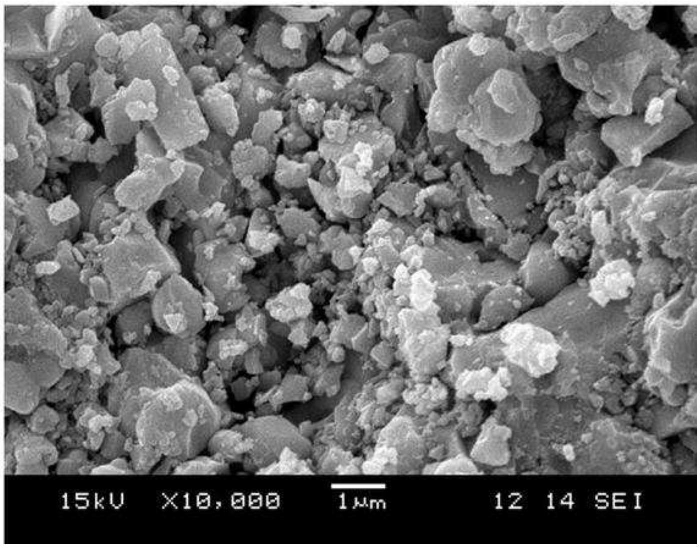

Figure 2. Scanning Electron Micrograph of $Ca_2WO_{5,5}$ sintered ceramic

3.3. Vickers micro-hardness tests

To study mechanical properties of the $Ca_2AlWO_{5,5}$ sintered ceramics we carried out Vickers microhardness (MHV) tests and we applied a load of 200 gf for 15 seconds for these tests.

Table 2. Vickers microhardness values of the first $Ca_2AlWO_{5,5}$ ceramic disc sintered at 1300^0C

	1st identation	2nd identation	3rd identation	4th identation	5th identation	**6th** identation	**7th** identation
D1	363.69	35.56	31.33	32.19	28.88	35.75	29.13
D2	29.06	31.94	36.56	31.00	31.00	25.19	33.81
HV 0.2	376.76	325.60	322.06	371.53	413.74	399.47	374.49

The average hardness is MHV 369.09. It can be observed from these results that the ceramics achieved a reasonable degree of hardness structural ceramic applications, in confirmation of a high degree of homogeneity of the grains and grain size distribution as observed scanning electron microscopy results.

3.4. Optical microscopy analysis

After the mechanical characterization, we submerged four samples in crude petroleum. Two of them in ocean petroleum and the other ones in earth petroleum. They stayed there for 30 days and we analyzed it by optical microscopy every 15 days Figs. 3, 4, 5, 6, 7, 8 and 9. This analysis was made to observe the microstructure of samples before and after submersion in crude petroleum and analyze if they suffered any change due to hostile chemical environment of the crude petroleum. . As we can observe following figures the ceramics submerged in both type off petroleum didn’t suffered any microstructiral changes.

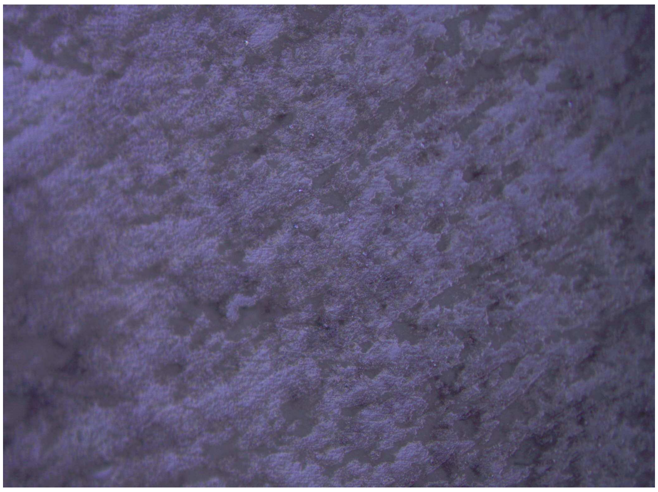

Figure 3. Ceramic before submerged in crude petroleum (Magnificatio 200X)

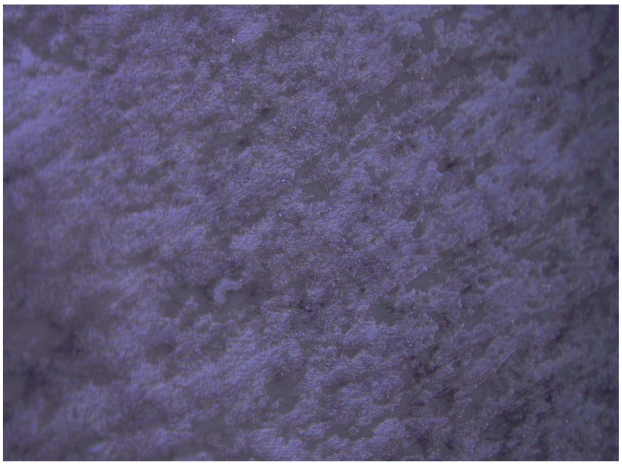

Figure 4. Ceramic submerged in ocean petroleum for 15 days (Magnificatio 200X)

Figure 5. Ceramic submerged in ocean petroleum for 30 days (Magnificatio 200X)

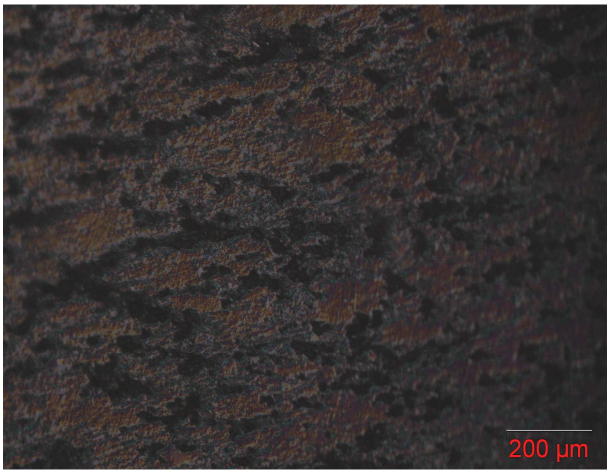

Figure 6. Ceramic submerged in ocean petroleum for 45 days (Magnificatio 200X)

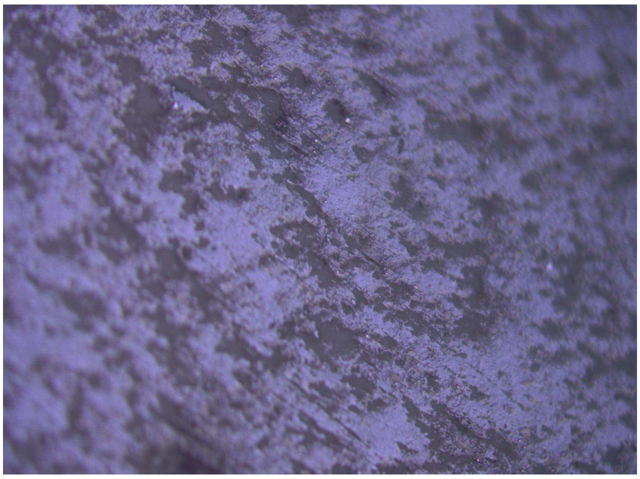

Figure 7. Ceramic submerged in earth petroleum for 15 days (Magnificatio 200X)

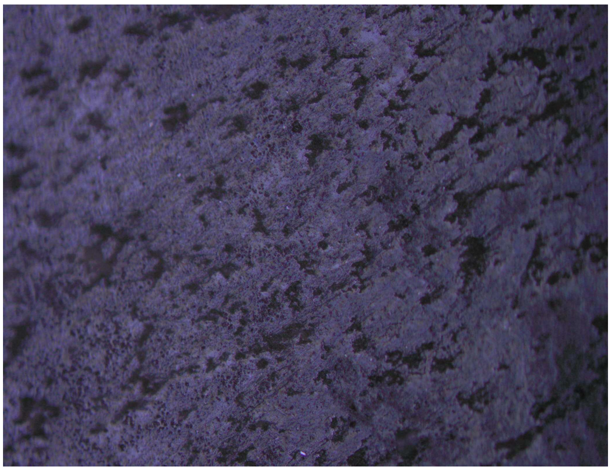

Figure 8. Ceramic submerged in earth petroleum for 30 days (Magnificatio 200X)

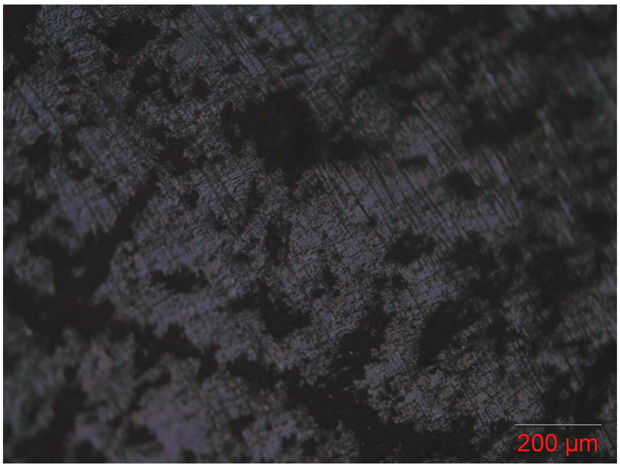

Figure 9. Ceramic submerged in earth petroleum for 45 days (Magnificatio 200X)

4. CONCLUSIONS

In this work, we have produced polycrystalline $Ca_2AlWO_{5,5}$ ceramics using solid-sate reaction process and studied its structural characteristics, in detail, using X-ray powder diffractometry. Presence of superstructural lines in the XRD spectra reveals that $Ca_2AlWO_{5,5}$ have an ordered complex cubic perovskite structure. As our aim of this study is to evaluate potential of these ceramics for ceramic components application for temperature sensors for petroleum industries, where microstructural characteristics and good mechanical strength are of vital importance, ceramic components fabricated through solid state sintering route presented a reasonable degree of these characteristics. It was found through analysis, that the $Ca_2AlWO_{5,5}$ ceramics showed a reasonable value of microhardness and a very homogeneous microstructure for structural ceramic applications. Our studies also showed that these ceramics are stable in crude petroleum originated from earth and ocean petroleum petroleum wells. So, $Ca_2AlWO_{5,5}$ sintered ceramics could be potential candidates for the fabrication of ceramic components for temperature sensors for temperature monitoring in petroleum wells.

5. ACKNOWLEDGEMENTS

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