

Al₂TiO₅ -BASED CERAMICS OBTAINED BY HYDROTHERMAL PROCESS

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Aluminum titanate is a very interesting compound due to some special properties as: high refractivity, low thermal conductivity and low thermal expansion coefficient, that confers to the aluminum titanate based ceramics high resistance to the thermal shock. Eutectoid decomposition in the initial oxides and low mechanical strength limit the well-known properties of aluminum titanate desired in several applications. In order to minimize these limitations new synthesis routes and additives were studied. In the present work the phase formation and sintering behavior of aluminum titanate powders obtained by hydrothermal method is studied using DTA/TG, XRD, IR and ceramic properties determination (density, absorption, porosity) as investigation methods.

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1. Introduction

Aluminum titanate ceramics were heretofore known as an important high-temperature employable product, as articles for high-temperature portions of an automotive engine, parts for high-temperature portions in electric and electronic devices, parts in nuclear reactors such as shielding materials for use in nuclear fusion reactors, tools for a melting furnace of non-ferrous alloys and ferroalloys or articles for measuring the temperature of molten metal or glass in a furnace [1].

Aluminum titanate, named also tialite, is used in a variety of high-temperature branches for its properties. The thermal expansion coefficient with values ranging between $0.2-1 \times 10^{-6} \text{ K}^{-1}$ [2] is comparable with the fused silica expansion coefficient (10 times higher), but the monocrystals present an extreme anisotropy, with values ranging between $(+3) \rightarrow (-19) \times 10^{-7} \text{ K}^{-1}$ [3], causing the occurrence of microcracking phenomena at the grain boundary. Tialite have also an excellent thermal shock resistance, low Young modulus, high refractivity temperature (melting point $\sim 1850 \text{ }^\circ\text{C}$) [4] and is non-wetted and does not react with many molten non-ferrous metals and alloys.

The common use of this material for high temperature applications is limited by the low fracture strength, caused by the microcracking phenomena and the thermodynamic decomposition over a given range of temperature. The phase equilibrium diagram shows that $1200 \text{ }^\circ\text{C}$ is the temperature below tialite becomes thermodynamically unstable [5].

As the correlation between the grain size and microcracking is proved a grain size distribution and a small size of particles are desirable for a good sintering behavior and a limited development of the microcracks [5].

There are many studies for the improvement of overall properties, starting from different synthesis methods to the introduction of additives and obtaining of aluminum titanate based ceramic

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composites. Powder preparation was accomplished by different techniques like sol-gel method [3,4,6,7,8], oxidation in high-frequency plasma flame [9], infiltration techniques [10], etc.

Thermal stability of aluminum titanate is improved in case of MgO, SiO₂ and Fe₂O₃ addition, which forms germs of crystallization or solid solution [3,11,12], while Al₂O₃, ZrO₂, ZrSiO₄ form with aluminum titanate ceramic composites [10, 13].

So far, no hydrothermal methods were used for tialite powder preparation. Byrappa and Yoshimura [14] have defined hydrothermal reaction as "any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above room temperature and at pressure greater than 1 atm in a closed system". For the individual oxides, as TiO₂ [15] and Al₂O₃ or aluminum hydroxides [16] there are literature information, but not for the aluminum titanate powders.

In the present work the precursor powders of tialite were prepared by a combination of conventional sol-gel hydrolysis and hydrothermal processing and the aluminum titanate phase formation sintering was studied.

2. Experimental procedure

2.1. Powder preparation

Reagent grade aluminum and titanium isopropoxides were used as Al₂O₃ and TiO₂ sources. The required amount of aluminum isopropoxide was dissolved in propyl alcohol by ultrasonication, and then heated at 70 °C, by refluxing under N₂ atmosphere. Titanium isopropoxide was homogenized in propyl alcohol then added drop-wise in the hot solution. The atomic ratio Al : Ti was kept 2 : 1. The final solution was aged for 2 hours at 70°C, by refluxing under N₂ atmosphere.

Hydrolysis of aluminum and titanium alkoxides was carried out mixing the solution with distilled water, added drop-wise. The composition for the starting solution and the experimental conditions used for the powder preparation are listed in Table 1.

Table 1. The composition for the starting solution and the experimental conditions.

Sample	Metal precursors	Molar ratio		pH of the mixture	Conditions of reaction	
		$\frac{C_3H_7OH}{\sum \text{alkoxides}}$	$\frac{H_2O}{\sum \text{alkoxides}}$		Temperature [°C]	Time [h]
1	Al(O-iC ₃ H ₇) + Ti(O-iC ₃ H ₇)	75	7.4	5.5	70	2, N ₂

A definite amount of solution was transferred into a Teflon-lined pressure vessel, which was sealed and heated. The rest of the solution was dried for the removal of the volatile compounds and water and subjected subsequently to hydrothermal treatment after adding the correspondent amount of water at the required pH. The hydrothermal powder was recovered by filtration, then dried at 110 °C for 12 hours. The hydrothermal conditions for the different samples are presented in Table 2.

Table 2. The hydrothermal conditions of the treatment.

Sample	Gel Type	Temperature, [°C]	Time, [hours]	pH	Cooling Type
2	Wet	150	24	5.5	Slow
3	Wet	190	48	5.5	Slow
4	Dry	190	48	9.5	Fast

2.2. Ceramics preparation

In order to obtain ceramic bodies, the initial powders were preliminary thermally treated at 450 °C, according to the results of the DTA/TGA, in order to minimize the adsorbed water and organic residues. From the resulted powder pellets were uniaxially pressed then were thermally treated at the temperature of 1300 °C.

2.3. Methods of characterization

All the powders were crunched in an agate mortar and then characterized by IR, DTA/TG, XRD and TEM methods.

The IR spectra were recorded in the 4000-400 cm⁻¹ ranges, with Carl Zeiss Jena Specord M-75 IR spectrometer, in KBr pellets.

The thermal behavior of the powders was studied by DTA/TG up to 1000 °C in air with Al₂O₃ as reference. A MOM OD-102 Derivatograph with a heating rate of 5 °C·min⁻¹ was used.

The X-ray diffraction patterns were recorded with a Shimadzu XRD 3.00 Diffractometer.

The TEM micrographs were obtained by a JEOL 200-CX microscope.

Ceramic properties (apparent density, linear shrinkage, water adsorption and open porosity) were determined for the sintered ceramics.

3. Results

3.1. Powder characterization

IR spectra. The structural evolution can be followed by IR spectroscopy in the region between 400-4000 cm⁻¹. In all the cases the characteristic vibrations due to the molecular water (1550-1650 cm⁻¹) and structural hydroxyl groups (2650-3600 cm⁻¹) are observed. The spectra are presented in the Fig. 1.

The spectra of Samples 1 and 2 are similar, being characteristic for disordered structures. In the Sample 1 (the initial gel), as characteristic bands of the independent components of the gel (AlOOH or Al₂O₃ and TiO₂) are shifted or not present, the formation of Al-O-Ti bonds during the sol-gel process was presumed. In the Sample 2, there are no major differences from Sample 1, except a higher degree of structural ordering.

Samples 3 and 4 are also similar, but are different compared with the IR spectra of samples 1 and 2. They present the characteristic modes of vibration for anatase (732, 765 cm⁻¹) and boehmite (480, 600, 1065 cm⁻¹).

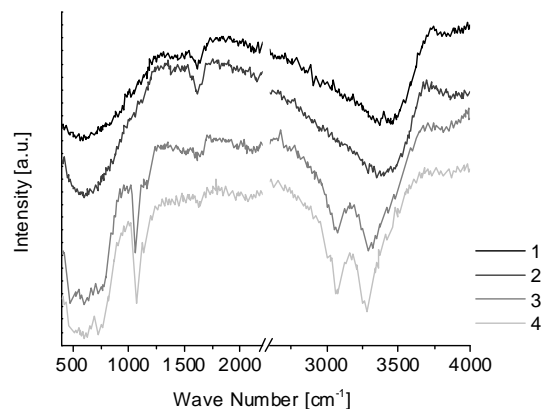


Fig. 1. IR spectra of the samples.

DTA/TG analysis. Both Sample 1 and 2 present the thermal effects of volatile compound and adsorbed water removal (~ 100 °C) and organic residues combustion (~ 275 °C). Lower temperatures are noticed for the hydrothermal treated powder (Sample 2). Samples 3 and 4 have a similar thermal behavior, with the endothermic effect of water and volatile compound removal and the endothermic effect of boehmite dehydration, noticed at ~ 500 °C.

X-ray Diffraction. In the Fig. 2 the diffraction pattern of the samples are shown. The pattern of the Sample 1 presents an amorphous structure for the sol-gel powder. No crystallization for the Sample 2, hydrothermally treated at 150 °C, was noticed.

Increasing of the hydrothermal treatment temperature at 190 °C the crystallization of the boehmite (γ -AlOOH) and anatase (TiO_2) phases was noticed.

The degree of crystallization of anatase is higher in the Sample 3 than in the Sample 4, as shown in Fig. 2. The pseudoboehmite phase (a hydrated phase of boehmite) was noticed in the Sample 3 due to the higher content of water in the wet gel. The Sample 4, starting from the dry gel, presents a better crystallization of boehmite than Sample 3.

The intensities of the lines indicate a well-crystallized structure, both for the anatase and boehmite.

TEM micrographs. The representative micrographs of the samples are presented in the Fig. 3. The Sample 2 presents a homogeneous and amorphous structure with aggregation tendency and nanosize grains (~ 5 nm), as it is shown in the Fig. 3a.

In the Figure 3b the morphology of the Sample 4 is shown, where the crystalline structures of anatase and boehmite, with nanosize grains (below 100 nm), well-defined shapes, degree of crystallization and grain size distribution are noticed.

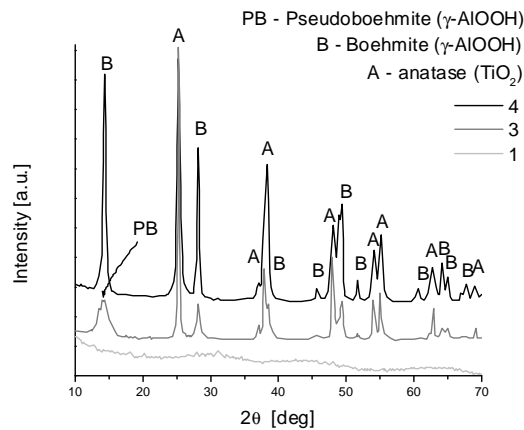


Fig. 2. XRD pattern of the Samples 1, 3, 4.

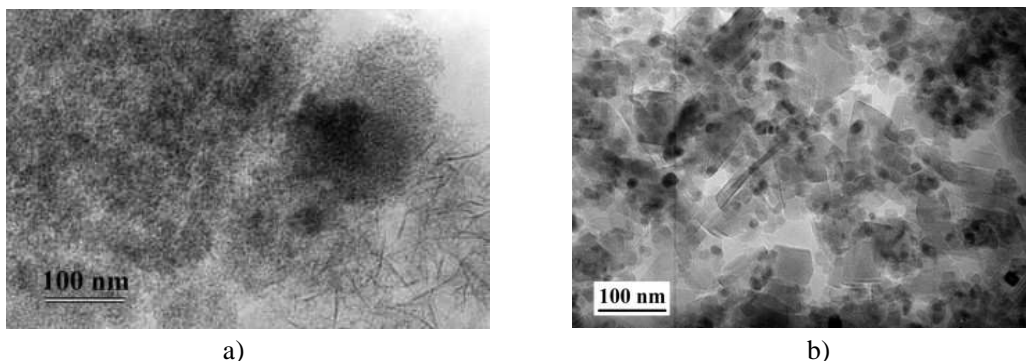


Fig. 3. a) TEM micrograph of the Sample 2; b) TEM micrograph of the Sample 4.

3.2. Sintered bodies characterization

The hydrostatic method and direct measurements of the samples characterized the as obtained ceramic bodies. The values obtained for the ceramic properties are presented in the Table 3.

The values of the linear shrinkage are very high, so the sintering behavior of the powders, as expected, is increased.

Table 3. The ceramic properties of the thermally treated bodies.

Sample	Apparent density, [g/cm ³]	Linear shrinkage, [%]	Absorption, [%]	Open Porosity, [%]
2	3.65	19	3.70	13.57
3	3.00	24	5.13	15.39
4	3.16	13	8.75	27.65

It is well known that the aluminum titanate formation is accompanied with volume increase. In this way, during the thermal treatment, a competition between the phase formation and the densification behavior takes place.

Due to this fact, thought in all cases the apparent densities is high (> 80% from theoretical density of the aluminum titanate) some differences could be noticed depending on the type of powders used.

The Sample 2, which exhibit better ceramic properties (high density, low porosity), is expected to have a lower conversion rate in aluminum titanate.

For the Samples 3 and 4 the apparent densities are lower and the porosity values are higher, due to a higher conversion rate in aluminum titanate that has a lower density as compared with the initial oxides.

In order to improve the overall ceramic properties a pre-sintering treatment at higher temperatures (~ 900 °C) is recommended.

4. Discussion

The structure of the sol-gel sample is amorphous, as the characterization methods proved. The existence of Al-O-Ti bonds, with short distances ordering in the amorphous structure can be assumed, however the powder presents aggregation tendency.

The hydrothermal treatment at 150 °C and relatively low pH value (pH = 5.5) does not modify significantly the physico-chemical characteristics of the initial sol-gel sample.

Increasing of the hydrothermal treatment temperature (190 °C) and pH value (9.5), the crystallization of the individual oxides with crystals of nanosize order can be noticed. The breaking tendency of the Al-O-Ti bonds formed during the sol-gel process was mentioned in the literature [3] but at much higher temperature, leading to TiO₂ anatase crystallization at ~750 °C and α-Al₂O₃ crystallization at ~950 °C. During hydrothermal treatment the pressure lowers tremendously the decomposition temperature of the Al-O-Ti bonds and the crystallization of the individual oxides. This process can be assumed to the negative influence of the pressure over the formation, with increasing in volume, of the aluminum titanate (11%).

Overall, the hydrothermal reaction leads to the obtaining of nanoscale homogeneous mixture of powders with low aggregation tendency and high machinability.

The ceramic properties depend on the precursor powders characteristics.

The high porosity of the ceramic bodies could be explained by high porosity of the precursor powders, by the formation of the transition aluminas during the thermal treatment, as well as by the aluminum titanate formation that has a lower density as the initial oxides.

Further investigations are underway in order to optimize the powder characteristics, aluminum titanate formation and sintering behavior.

5. Conclusions

Considering the sol-gel precursor powder of aluminum titanate as reference, three samples were prepared by hydrothermal treatment in the range of 150-190 °C, for 24 and 48 hours, and pH values between 5.5 and 10.

Analyses of the morphology, structure and thermal behavior were performed on the sol-gel and hydrothermally treated powders.

The phase formation and the densification of the powders in order to obtain ceramic bodies were also approached.

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