ANALYSIS OF Al$_2$O$_3$ CERAMIC CONFORMED BY COMMERCIAL STARCH CONSOLIDATION UNDER LOW PRESSURE

E. Campos[1*]; F.P. Santos[1]; F.C.L. Melo[3]; R.Y. Honda[2]; R.P. Mota[2]

[1] Escola de Especialistas de Aeronáutica – Guaratinguetá
Laboratório de Materiais Cerâmicos (LabCera) - Departamento de Materiais e Tecnologia
[2] Departamento de Física e Química - UNESP – campus de Guaratinguetá
Av. Ariberto Pereira da Cunha, 333 – CEP 12.516. 410
[3] Instituto de Aeronáutica e Espaço – Centro Técnico Aeroespacial – S. José dos Campos

ABSTRACT

The production of ceramic by commercial starch consolidation process spread swiftly in the scientific circles due to the possibility of production of complex geometry pieces with good mechanical strength and low impact to the environment. However, air or gas bubbles appear during the preparation of the slip and they can cause the appearance of undesirable pores, reducing the ceramic mechanical strength. In this work it was tried to find out a method in order to reduce the bubble number in the colloidal dispersion. The use of vacuum mechanical pump becomes possible the discharge of air or other gases from this dispersion and consequently decrease the number of pores in the ceramic. Under these considerations, Al$_2$O$_3$ samples were made by means of corn commercial starch consolidation that can be or not exposed to the vacuum. After sintering, the samples were analyzed according to their porosity level, mechanical strength, roughness and apparent density, showing that the use of low pressure improved these features.

1. INTRODUCTION

The process used to obtain porous or dense ceramic, conformed by commercial starch consolidation, is an efficient and economical method, taking account of its low environmental impact as well as its great technological potential. The number of works about this issue has been growing continually [1,2,3,4,5]. It is based, fundamentally, on the starch properties and its capacity to form gel in aqueous environment [1]. Ceramic powder, water and starch are mixed together in either an agitator or in a ball mill so as the colloid can reach a reasonable homogeneity. Later on, the slip is poured in an impermeable mold that can be made of plastic, rubber, Teflon, etc. The slip is put into an oven at 55ºC/80ºC during 2 hours. This range is considered as gelling temperature [6]. Thus, the starch absorbs water from the ambient and begins to dilate until the moment in which it becomes gel, providing a connection between the particles and, consequently, the conformation of the ceramic body.

In the following stage, the mold is put into the oven and it is heated at 120ºC during 2 hours in order to dry and to allow extracting of the formed piece. The next stage is the pre-

sintering - the starch burns at a temperature around 300 to 500ºC [4]. Due to the discharge of gas during the burn, the heating rate must be low. After that, the piece sintering is made, obtaining the maximum ceramic densification.

The main goal of this work is the analysis of the ceramic features with vacuum system inclusion after the mixture stage. It is noticed a considerable number of bubbles when the dispersion is removed from the agitator or the ball mill. It is possible the use of ethyl alcohol to eliminate the bubbles because this substance reduces the superficial tension of the colloid. However, the use of components like that could influence on the material composition and generate some modification to the final product. Low pressure should be used to reduce excessive influence on the material composition [7]. In this way, it is expected to get denser, less porous and more homogeneous material with reduction in the presence of the defects improving the mechanical strength.

2. MATERIALS AND METHODS

2.1. Composition

Samples were produced using A-1000 alumina (Al$_2$O$_3$), supplied by ALCOA SA, with density equal to 3.98 g/cm^3, obtained from helium picnometry [4] and corn commercial starch supplied by Refinações de Milho Brasil, with density equal to 1.54 g/cm^3, obtained from the same method. The slip was prepared with 50 vol.% solids and stabilized using 0.50 wt% Disperlam LA.

2.2. Processing

The making of the ceramic samples followed these steps: the powders, initially dry (starches at 30ºC), were sieved in order to reduce the agglomerate and afterward it was mixed together with distilled water and defloculant in a mechanical agitator for 30 minutes.

After that, the slip was put in a ball mill for obtaining a better homogenization of the colloidal dispersion. With the purpose of avoiding accentuated rupture of the starch particles, the time stipulated for grinding was only 30 minutes. Only half volume of this slip was exposed to the vacuum, at 50-55 Torr, and the other part was remained without being exposed.

* elson@feg.unesp.br

This pressure was obtained by mechanical pump connected to the processing reactor made of Pyrex glass and measured by Pirani Vacuum Meter at a temperature around 20ºC. It took 1.5 min to reach this pressure. Figure 1 shows the pressure diagram in relation to the temperature [8] for pure water and can be verified from it that significant water vapor must not be present at 20ºC and 50 − 55 Torr, only the normal water percentage expected by the evaporation phenomenon.
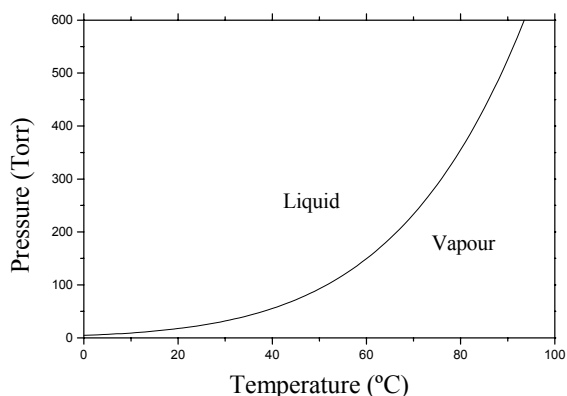

Figure 1 - Phase diagram for pure water [2, 8].

Later, slips were put in plastic impermeable molds with rectangular form so that the gelling starch process was accomplished. The molds were put in an oven at a temperature of 65ºC for 2 hours. The molds were put back in the oven at temperature of 120ºC for 2 hours so as to have the slips dried.

After this step, the samples were extract to the mold and transported to the pre-sintering. In this stage, samples were heated at a temperature of 1000ºC (heating rate of 3ºC/min, in an electric furnace EDG - FA IV). Sintering was made at a temperature of 1650ºC (heating rate of 3ºC/min) and this temperature was kept stable for 1 hour.

2.3. Characterization

Two preliminary tests were made to characterize the sintered pieces: Three-points flexural - according to the ASTM C1161/94 norm [9] and apparent density - according to the ASTM C20/87 norm [10]. The former was made in a test machine EMIC with load of 1000 kgf and advance progress of 0.5 mm/min. The results were analyzed according to the Weibull statistical method. The latter was based on the Archimedes' principle, made with a semi-analytical scale of $\pm$ 0.001g precision, assuming that the density of the distilled water is 1.0 g/cm^3. The last method also allowed obtaining the apparent porosity and the percentage of water absorption. Porosity measures, using a mercury intrusion porosimeter, were also made. Thus, the distribution for diameters of pores was obtained.

Roughness measure was made using a MITUTOYO - SURFTEST 301 rugosimeter, being obtained the following parameters for the analysis: Ra (medium roughness), Rt (total roughness) and R_3z (medium roughness of the third peak and depression).

Specific mass measurements were made by MICROMERITICS helium picnometer. Before this, the samples were heated at 120ºC for 2 hours.

In this work images were also obtained in a scanning electron microscope, LEO 435 VPI model, using secondary electron process and 15 kV in voltage.

3. RESULTS AND DISCUSSION

The test with the mercury porosimeter showed that there was a reduction in volume of approximately 0.010cm^3/g (7.20 %) of the ceramic produced when exposed to the vacuum in relation to the one, which has not been exposed yet. However, in terms of the distribution of pores, the two types of samples had a larger concentration of pores with diameters between 0.01 and 2.00 µm.

The Table I present the values obtained from the Ra, Rt and R_3z parameters, indicating that the ceramic which was under the action of vacuum presented better workmanship. This fact allows supposing that the extraction of gas or air small bubbles held during the mixture process might possibly have re-structured the material making it more resistant.

The results of the mechanical strength parameter (σ_0 − material characteristic rupture strength, σ_{50} - medium rupture strength and *m* - Weibull module) are presented on Table II. In this table, the ceramic obtained without action of vacuum presents lower rupture strength, reinforcing the supposition made in the analysis of the superficial roughness. However, such ceramic presents homogeneity slightly larger, what possibly indicates that there was a larger material displacement during the extraction process of the gas or air. This fact produces a larger amount of defects in the material structure in the subsequent stages of ceramic production.

Values obtained from water absorption (WA), apparent porosity (AP), apparent specific mass (ASM) and relative specific mass (RSM) are presented in the Table III. The latter was determined as a function of the specific mass obtained by helium picnometry (3.98 g/cm^3). In fact, all the values presented on Table III emphasize that the ceramic obtained with vacuum exposition is the least porous of all. They absorb smaller percentage of water and, consequently, become denser.

Real specific mass analysis, made by helium picnometry, reinforced the very close results for the two types of ceramic (with vacuum exposition, 3.91 g/cm^3; without vacuum exposition, 3.93 g/cm^3) obtained by the test based on the Archimedes' principle.

Figure 2 shows images obtained by scanning electron microscope (1000X magnification). The these, it can observe that vacuum exposition process produces ceramic with a level of smaller porosity and, consequently, larger value of densification. That is in agreement with the results in the Table III.

4. CONCLUSION

The vacuum system was considered efficient in the sense of producing ceramic with smaller superficial roughness,

smaller porosity and, consequently, larger rupture strength. However, result analysis showed that the vacuum exposition reduces, slightly, the homogeneity degree of the ceramic, observed by Weibull statistical method. This fact is possibly, due to the large material movement as consequence of vacuum application, with different kinetics of bubbles near surfaces and in the bulk of the slip. Producing, in the subsequent stages of ceramic production, larger amount of defects in the materials structure. This fact requires verification and an improvement of the production method in order to minimize such effect on the material.

Table I – Results of superficial roughness: Ra (medium roughness), Rt (total roughness) and R₃z (medium roughness of the third peak and depression) parameters.

	Parameters (with vacuum exposition)			Parameters (without vacuum exposition)		
	Ra (µm)	R₃z (µm)	Rt (µm)	Ra (µm)	R₃z (µm)	Rt (µm)
average	1.43	3.05	13.16	1.50	3.12	13.76
mode	1.22	2.90	11.70	1.42	3.60	16.20
median	1.37	2.90	12.10	1.38	3.25	12.60
high value	2.28	5.00	20.20	2.99	5.50	25.00
low value	0.91	1.80	6.70	0.96	1.50	7.50
standard deviation	0.41	0.72	4.16	0.46	1.02	4.49

Table II – Analysis results by Weibull statistical method (σ_0– material characteristic rupture strength, σ_{50}- medium rupture strength and m - Weibull module)

Conformed ceramics	σ_0 (MPa)	σ_{50} (MPa)	m
with vacuum exposition	130.5	122.6	8.0
without vacuum exposition	122.5	117.6	11.0

Table III - Water absorption (WA), apparent porosity (AP), apparent specific mass (ASM) and relative specific mass (RSM) values obtained by test based on Archimedes' principle.

Conformed ceramics	WA (%)	AP (%)	ASM (g/cm³)	RSM (%)
with vacuum exposition	4.10	12.22	2.98	74.92
without vacuum exposition	4.22	12.47	2.96	74.29
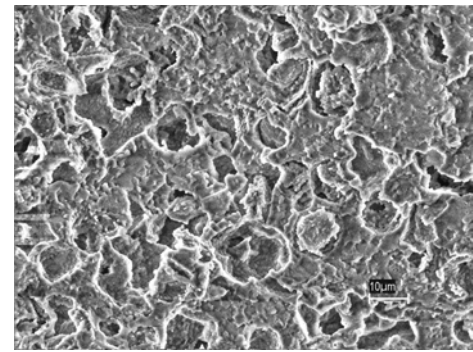
(a)
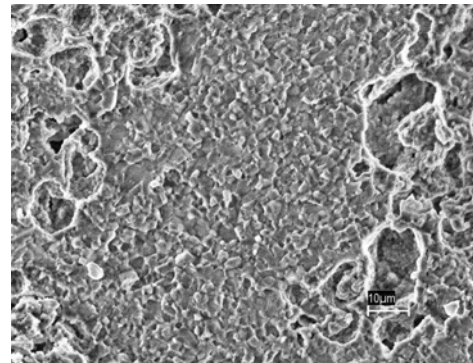
(b)

Figure 2 – Images obtained by scanning electron microscope of Al₂O₃ samples conformed by starch consolidation and sintered at 1650ºC, (a) without vacuum exposition and (b) with vacuum exposition at 50-55 Torr.

5. ACKNOWLEDGMENTS

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