Rheological behavior of yttria aqueous suspensions for impregnation method

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ABSTRACT

Preparing ceramic suspensions is an important step in ceramic processing. In order to apply a near net shape technique as impregnation method, high-solids suspension being enable to cover the total surface of organic matrix with good adhesion is necessary. The aim of this work is to adequate yttrium oxide suspensions through a rheological study in order to produce Y_2O_3 porous bodies with fine characteristics for incandescence applications such as gas burners. This work concerns at studying the effects of some variables such as dispersant content, solid loads, pH and additives concentration on the rheological behavior of yttrium oxide aqueous suspensions to succeed fine Y_2O_3 porous bodies. Flow curves with shearing rate interval from 0 to 1000s^{-1} showed that 1 wt.% of dispersant was enough to gain the lowest viscosity value for 30 vol.% yttrium oxide suspensions.
The porous ceramics were careful and thermally treated seeing that burning off the organic structure could induce sensible residual stresses and disrupting the ceramic network. Sintering at 1450 ºC showed ceramics with good structural stability and high porosity.

Keywords: yttrium oxide, rheology, porous ceramics, ceramic foams, ceramic processing.

1 . Introduction

In traditional ceramic processing, porous structures have been avoided in ceramic components inasmuch as of their inherently brittle nature, but in the last years, an increasing number of applications that require porous ceramics have appeared. Such applications include gas burners[1], radiant burners[2], filters of molten metals, high-temperature thermal insulation, support for catalytic reactions, etc.

There are many different methods to manufactured ceramic foams, such as replica[3], sacrificial template and gel casting[4]. The first one is considered the easiest and the cheapest method for producing porous structures. The great

flexibility of this method is the fact that it is applicable to any ceramic material that can be appropriately dispersed into a colloidal suspension [5,6,7]. Therefore the knowledge about colloidal processing is also important. This process results in a more uniformed particle packing, better microestrutural control while firing and high mechanical strength of ceramic.

Yttrium oxide (Y_2O_3) is one of the most important rare earth oxides, being applied in a variety of technologies areas as luminescence materials[8] and biomaterials[9]. Some of the its main proprieties are: high melting point (2400ºC), high refraction index (≅1,9), low expansion coefficient and high corrosion resistance[10,11].

This work extends to adequate yttrium oxide suspensions in base on rheological studies in order to produce Y_2O_3 porous ceramics by impregnation method.

2. Experimental

2.1 Raw material

The material for this study was commercial yttria (Aldrich, Gmb), with the following characteristics: mean particle size of 6.51 μm, specific surface area of 8.52 $m^2.g^{-1}$ and density of 5.83 $g.cm^{-3}$. The yttria powders (Y_2O_3) were prepared by optimized conditions according to our in prior studies[12] using attritor milling at 1600rpm for 3h (zirconia balls, $\phi_{balls} = 2\text{mm}$) in ethanol media.

2.2 Stability of the Y_2O_3 powders in aqueous media

The stability of Y_2O_3 powders in aqueous media was based on measuring the electrophoretic mobility of the particles in a pH range from 2 to 12, using a light phase scatter analyzer (ZetaPALS, Brookhaven Instruments Corporation, USA). Aqueous suspensions were prepared with 0.5 g L^{-1} solid concentration and NaCl (10^{-2}M) as indifferent electrolyte. The dispersant ammonium polyelectrolyte, PAA (Duramax D- 3005, Rohm and Haas Company, USA), was used. KOH and HCl solutions to adjust the pH from 2 to 12 were used. Before measuring, the suspensions were homogenized using ultrasonic device (Hielscher 400US, Germany) for 2 min.

2.3 Processing of the suspensions and conformation

Y_2O_3 aqueous suspensions were prepared varying solids concentration from 15 vol.% to 30 vol.%. In order to stabilize the suspensions an ammonium polyacrylate (PAA) was used as polyelectrolyte/dispersant (Duramax D-3005, Rohm and Haas, USA) with concentrations ranging from 0wt.% to 2 wt.% (referred to dry solids). Basicity of the medium was provided by adding tetramethylammonium hydroxide (TMAH), supplied by Aldrich-Chemie (Germany). Carboxymethyl-cellulose (CMC) were added to the suspension (based on suspension weight) for enhance the adhesion of the ceramic suspension on the support material surface. Therefore its effectiveness on the rheological behavior was also evaluated.

Rheological behavior of suspensions was performed with a rheometer (Haake RS600, Thermo Scientific, Germany). The sensor system consisted on a double cone rotor and a stationary plate (DC60/1º). Characterizing the suspensions stability the flow curves were determined in a control rate mode (CR). Measurements were performed by increasing the shear rate from 0 to 1000 s^{-1} in 5 min, maintaining at 1000 s^{-1} for 2 min and returning to 0 in 5 min. Temperature was maintained constant at 25ºC during these experiments. For each CR cycle 200 points were measured. In order to decrease the agglomerates size, the suspensions were stirred for 3 min at high shear rate (Quimis, Q-252-K18). After that, they were subject to mechanical mixing for 30 min to promote suspensions homogeneity (HeidolpH, mod. RZR1).

Polyurethane foams (PUF) of 10 ppi, (Crest Foam Industries - USA) with dimensions (40x35mm) were submerged in the suspension while they were compressed to fill all the pores. The samples were dried at room temperature for 24 h. The impregnated foams were subjected to a heat treatment (at 1ºC min^{-1} to 800) in the electric furnace (EDG, EDG 1800), to extract the support material and others additives. Finally the samples were sintered in air atmosphere, at 1450ºC/1h with 1ºC min^{-1} as heating rate. Fig. 1 shows a diagram of the impregnation process developed in this work.

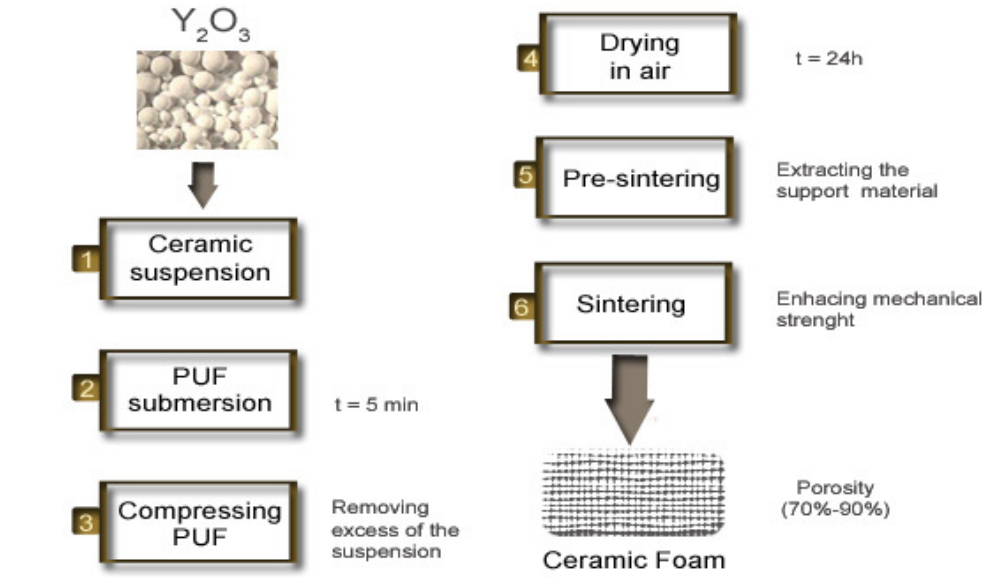


Fig. 1 – Diagram of impregnation process

3. Results and discussion

3.1 Powders characterization

TABLE 1 shows the comparative values of mean particle size and specific surface area of the Y_2O_3 powders before and after attrition milling. It can be seen that the milling was effective on reduction of the particles aggregates size (from 6.52 to 1.31 µm) and the increase on the specific surface area was also observed.

TABLE 1 – Values of mean particle size and specific surface area of Y_2O_3 powders

Time of milling (h)	**Specific surface area ($m^2.g^{-1}$)**	**Mean particle size (d_{50}-µm)**	
		Cilas	**Calculated by BET**
0	8.52	6.52	
3	13.59	1.31	

Powders morphologies of Y_2O_3 as received and after milling during 3 hours were observed by SEM (Fig. 2), where can be verified that before milling the Y_2O_3 powders consisted of the aggregates platelet particles (Fig.2a). In Fig.2b the milling effectiveness (around from 5µm to 2 µm) on reduction of the particles aggregates size is observed.

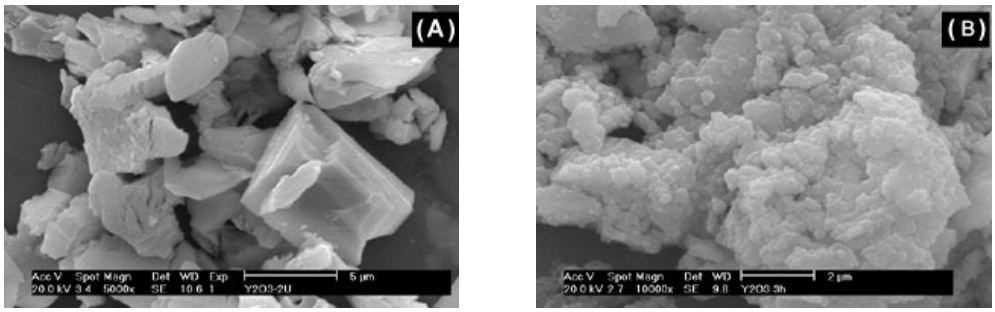


Fig. 2 - Powders micrographies of Y_2O_3: (A) as received (B) after milling for 3h.

3.2 Zeta potential (ζ) as function of pH and dispersant concentration

The zeta potential of Y_2O_3 as function of the dispersant (PAA) from 0.0 to 2.0wt% additions and pH media is indicated in Fig. 3. According to literature[13] the stability of the particles occurs around the ζ = 20mV. The Y_2O_3 without dispersant (0.0wt % of PAA) shows ζ indicative values of stability for pH below 6.5 and over 9.5 and the isoeletric point (IEP) is for pH= 8.5. As increasing the PAA concentration, changes are observed on Y_2O_3 stability. For all PAA concentrations the IEP shifts from pH 8.5 to around pH 6.5. For the 0.5wt.% of PAA the system stability condition begins at pH 8. For the PAA additions of 1.0 and 2.0wt.% the stability conditions become around at pH 7. This change on the behavior is due to the adsorption of dispersant molecules on particles surfaces. The highest zeta potential value (the highest degree of stability) takes place at pH 10 (≅ 56 mV). Based on this data, adding 1 wt.% of dispersant was enough to form stable suspensions from pH 8.0 on.

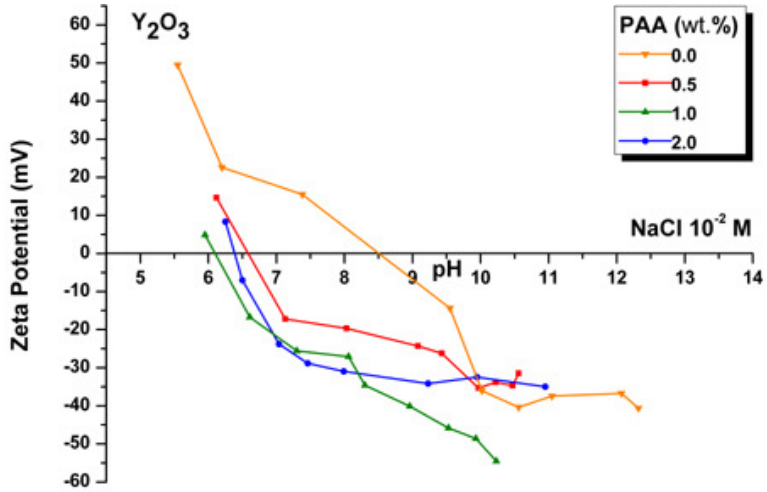


Fig. 3 - Zeta potential variation as function of pH and PAA concentration.

3.3 Effectiveness of the dispersant concentration and pH on suspensions viscosity

The viscosity variations as function of the PAA additions are illustrated in Fig. 4, where Y_2O_3 aqueous suspensions were prepared with 25vol% and at a shear rate of 500 s^{-1}. A great decrease of viscosity with addition of 0.5 wt.% PAA (from 70 mPa.s to 25 mPa.s) is observed. This fact may be associated to the dispersion mechanism supplied by PAA via electrosteric repulsion[15]. Adding 1wt.% of PAA, the suspension presented the lowest viscosity value. From this concentration on is not observed betterment on flow behavior.

A variação da viscosidade em decorrência da concentração de dispernsante (PAA) é mostrada na Fig. x. Para este estudo preparou –se suspensões aquosas de Y_2O_3 com 25vol% de sólidos (≅ 63%p), as quais foram submetidas a uma taxa de cisalhamento de 500s^{-1}. Sem adição de dispersante (0,0%p de PAA) a suspensão apresentou maior resistência ao fluxo (viscosidade ≅ 70mPa.s). Ao adicionar-se 0,5%p de PAA, nota-se uma diminuição significativa na viscosidade de ≅ 70mPa.s para ≅ 25mPa.s. Este fato pode estar associado ao mecanismo de dispersão eletroestérico do dispersante. Com 1%p de PAA, a suspensão apresentou o menor valor de viscosidade (≅ 10mPa.s), comprovando o comportamento observado no gráfico de potencial zeta (Fig.x). A partir desta concentração não se observa diminuição na viscosidade.

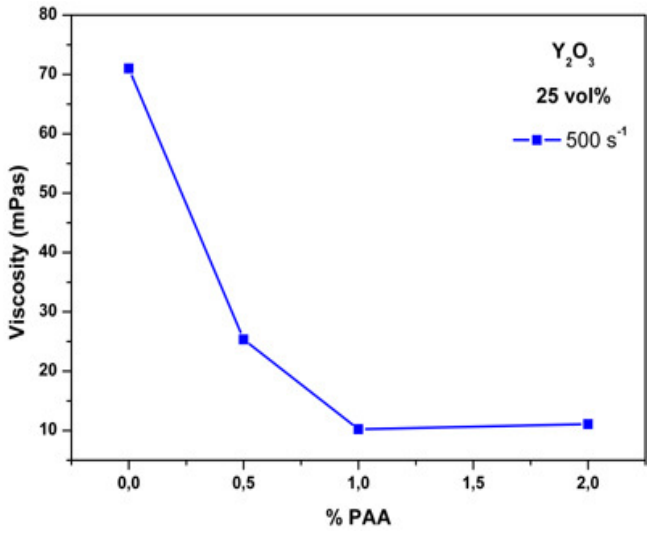


Fig. 4– Viscosity of Y_2O_3 suspensions with 25vol% as function of dispersant concentration (PAA) at a shear rate of $500s^{-1}$.

In agreement with zeta potential curves (Fig. 3), the suspension with pH close to IEP of Y_2O_3 (8.5) showed the highest viscosity value (Fig. 5). At this pH, the particles present low surface charge, near to neutrality. On the other hand, adding TMAH as pH-adjuster, there is an improvement of dispersability by promoting negative charges on surface of the particles. At pH 10, the particles get the highest repulsion potential (high negative surface charge), as DLVO[13**Erro! Indicador não definido.**] theory predicts, supporting dispersion (via electrostatic repulsion) of the particulate system.

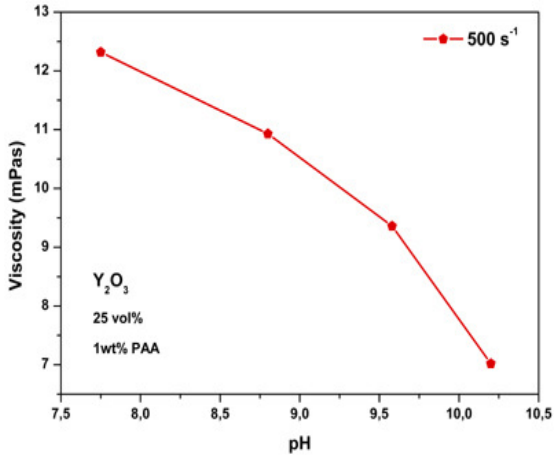


Fig. 5– Viscosity of Y_2O_3 suspensions with 25vol% as function of pH variation at a shear rate of $500s^{-1}$.

3.4 Influence of solids concentration on rheological behavior

The effect of solids concentration on rheological behavior of yttria aqueous suspensions is presented in Fig. 6, that shows the shear stress (Pa) as function of the shear rate from 0 to $1000s^{-1}$. A great increase on flow resistance (viscosity) of suspensions from 15 vol.% to 30 vol.% was observed, due to higher particle concentration and shorter room between particles, which intensifies the interaction degree of particles[14]. The rheological behavior presented by the flow curve of 30 vol.% exhibits higher flow resistance (viscosity) compared to the others flow curves[15].

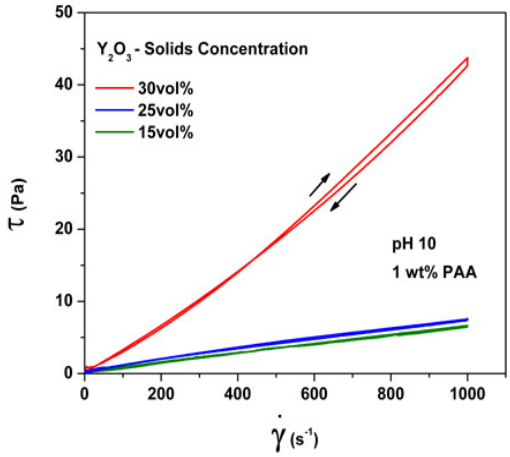


Fig. 6 - Flow curves of Y_2O_3 suspensions as function of solids concentration

3.5 Effectiveness of the binder (CMC) concentration on the rheological behavior

As the binder (CMC) is added in the suspension, it's observed an increase on the viscosity of the system (Tab.1). This effect is associated to larges molecules of CMC that recover the particles flocculating the system. When the amount of CMC is 1 wt.% the suspension shows a greater thixotropy (Fig. 7). It's should be due to the breaking down of agglomerates and rearrangement of the particles during the shear rate. For impregnation method, this rheological behavior is desired, so that the suspension is fluid enough to enter, fill, coat uniformly the sponge surface and under static condition, its viscosity is high to remain on the sponge [16] .

TABLE 1 – Rheological proprieties of yttria suspensions as function of CMC concentration

Solids (vol.%)	**CMC (wt.%)**	**Viscosity at 100 s^{-1} (mPa.s)**	**Thixotropy (Pa s^{-1})**
30	0	31,67	458,20
	0,3	560	6,33 x10^4
	1	2531	1,63x10^5

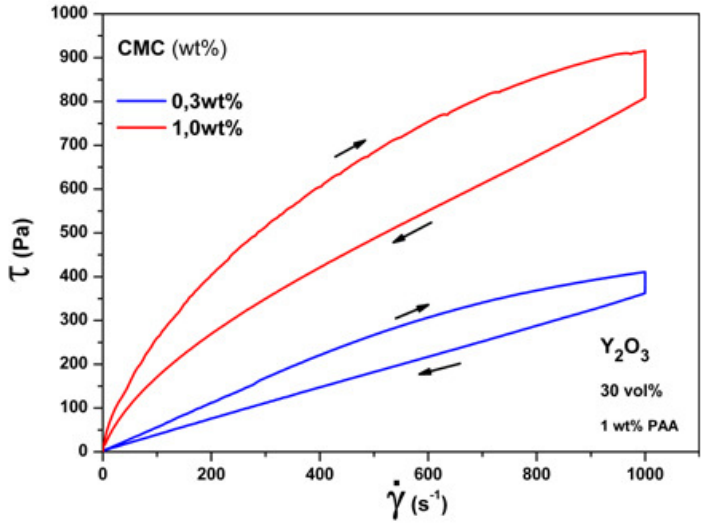
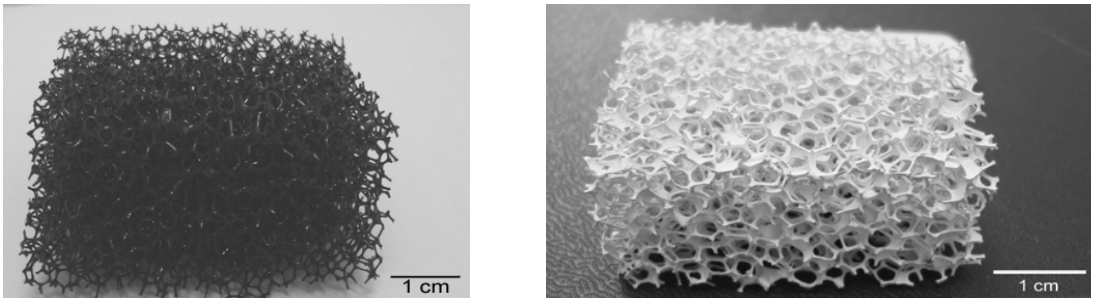


Fig. 7 – Flow curves of Y_2O_3 suspensions as function of CMC concentration

3.6 Ceramic foam

In Fig. 8 is shown the ceramic foam manufactured by impregnation method. The reticulated ceramic maintained the form of the sponge (polimeric perform) Fig.8a, where can be seen cellular structures with thin struts and interconnected open pores.



(a) (b)

Fig 8. – Foam (a) polymeric preform (b) ceramic foam manufactured by impregnation method

4. Conclusions

Ceramic foam of Y_2O_3 was manufactured by impregnation method. Ceramic suspensions with thixotropic behavior showed adequated for this conformation process. This rheological behavior is attributed to CMC concentration. The suspension with 30 vol.% and 1 wt.% of CMC exhibited appropriate rheological characteristics for impregnation. It shows the importance of the prior rheological study, where the stability of the suspensions was evaluated by zeta potential determinations and the flow curves behavior. The

highest stability degree of the yttria suspensions takes place at pH 10 and with 1 wt.% of PAA. The greatest solids load in this study was 30 vol.%, where the stabilization of suspension supplied by 1 wt.% of dispersant at pH 10 (adjusted with HTMA).

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