11th International Conference
on Advanced Materials

Rio de Janeiro Brazil
September 20 - 25

ICAM2009

Gelcasting of alumina and aluminum hydroxide using Chitosan as a binder agent

J. Brandi(1), J. Ximenes(1), Mariselma Ferreira(1), Rafael Salomão(1)*

(1) PPGNM, Universidade Federal do ABC, e-mail: rafael.salomao@ufabc.edu.br

Abstract – This work presents novel consolidation method for alumina based porous ceramics through the use of a natural polymer as binding agent (chitosan). A suspension of alumina was prepared and mixed with chitosan solution in acid pH. After extrusion in an alkaline solution, solid fiber-like bodies or beads can be formed. These products were characterized by X-Ray diffraction (XRD), scanning electronic microscopy (SEM), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR).

The binding agents present key role in the development of alumina based porous ceramics, specially concerning their use in high temperatures (above 1000ºC) for long periods. Their main function is to promote suitable mechanical strength to the green parts before sintering. However, depending on their composition, low melting point compounds can be formed, reducing the porosity and refractoriness. Due to this, several binding agents based on organic polymers instead of inorganic compounds (such as sodium silicate and phosphate or calcium aluminate cements), have been developed over the last two decades and have received the general denomination of gelcasting. In this process, a certain polymeric material is dissolved in the ceramic suspension, after proper particles packing and dispersion. By means of pH and temperature changes, polymerization agents or foreign ions release, the organic chains are linked, restraining particles mobility. After this point, the ceramic part is dried at low temperatures, in order to prevent polymer degradation or water vapor pressurization, and sintered. An important technological advantage of this method lies on its versatility, allowing several combinations of ceramic and polymeric systems.

A novel gelcasting method for producing Al_2O_3-$Al(OH)_3$ porous ceramics, using small contents of chitosan as biding agent is presented in this work. Chitosan is a linear polysaccharide obtained by the deacetylation of chitin, which is a natural polymer found in structural components in the exoskeleton of arthropods or in the cell wall of some fungi. Chitosan contains residues of D-glucosamine and some N-acetyl-D-glucosamine groups distributed randomly. As a natural polymer, chitosan comes from a renewable inexpensive source, unlike other polymeric systems, employed in the same purpose such as unsaturated polyesters.

Initially, Al_2O_3-$Al(OH)_3$ aqueous suspensions were prepared in a paddler mixing, using acetic acid as dispersing agent. Following, a diluted chitosan acetic acid solution was dropped into the suspension (generating a chitosan content at about 1 wt% after drying). This system extruded through a 300 µm diameter needle into an 8% NaOH solution, kept at 25ºC. These fiber-like parts were kept in the solution for 20 min, washed with distilled water, dried at 60ºC during 24h and then sintered at 1500ºC (5h, 2ºC/ min). Green and fired products were characterized by XRD, FTIR, DSC, TGA and SEM.

Alumina and aluminium hydroxide particles exhibit positive zeta potential in a wide range of acid pH, what means that its surface presents a charge density predominantly positive. Chitosan is soluble in pH < 6.0 due to the protonation of $–NH_2$ groups linked to the glucosamine residues, converting the polysaccharide into a positively charged polyelectrolyte. Due to these effects, alumina and aluminum hydroxide dispersed in acetic acid and chitosan can be easily mixed. When this mixture is extruded in a solution of NaOH (pH~ 9.0), alumina and aluminum hydroxide become negatively charged, reacting with the amino groups in chitosan, restraining and consolidating particles as a rigid body.

SEM images of green and sintered alumina, aluminium hydroxide and chitosan are presented. The all-alumina green bodies present uniform microstructure, with no macroporosity and high densification as an indication of good dispersion and mixing processes. The images of the sintered bodies show that there are no residues of alginate, high sintering and densification, low porosity and possibly suitable mechanical properties. The sintered all $Al(OH)_3$ sample presents high sintering, low densification, high surface area and porosity. Finally, an intermediate state can be seen for a sample of 50/50 Al_2O_3/ $Al(OH)_3$. No significant traces of the binder were detected in the green or sintered samples. TGA analysis for green bodies of alumina and/or aluminum hydroxide showed no significant mass loss related to chitosan decomposition. For green bodies containing $Al(OH)_3$, a mass loss coherent with the stoichiometry of the dehydration reaction was observed (approximately 58 %wt). DSC analysis for chitosan presents a drying peak, below 100ºC, thermal decomposition between 290 and 320ºC, and finally, a third exothermic peak corresponding to the beginning (below 400ºC) of chitosan total decomposition. Alumina sample did not show any significant reactions. Samples containing $Al(OH)_3$ presented a dehydration endothermic peak between 250 and 350ºC. Any of the samples analyzed showed significant effect related to the presence of chitosan. XRD and FTIR analysis were performed to confirm the presence of chitosan in the ceramic bodies, but again it could not be detected because its poor crystallinity and to the small amount of the polymer added to the composition.