COMMERCIAL STARCH CONSOLIDATION TECHNIQUE FOR SHAPING SILICON CARBIDE (SiC) CERAMICS

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Abstract. Silicon carbide (SiC) is a versatile material due to its abrasive and refractory properties, besides high hardness and resistance to large temperature gradients. In order to wide the range of applications of these ceramics, this work made experiments to obtain SiC bodies of complex geometry and controlled porosity using the forming method of commercial starch consolidation. This technique, a "direct-consolidation" method, is based on the fundamental properties of the starch. Among these properties are the ability of its granules to absorb water in temperatures between 55°C and 80°C, which is its driving consolidation mechanism. The ceramics were prepared using commercially available silicon carbide powder and corn starch, without physical or chemical modification. Besides the original work in obtaining SiC ceramics using the forming method of starch consolidation, it was necessary to include an extra step in the overall processing technique. This step consisted on use of the mechanical shaker associated with a controlled vibration mode during the colloidal dispersion homogenizing phase. The ceramic pieces were sintered at 2050°C of temperature. It has been concluded that the present technique of starch consolidation for shaping SiC is highly viable, yielding ceramic pieces with acceptable mechanical strength, good homogeneity and reasonable densification, besides offering a low cost production.

Keywords: ceramics, silicon carbide, starch consolidation

1. Introduction

The techniques of "direct-consolidation", in which the molds are impermeable, allow to obtain a good homogeneity of the material and a better contraction control and of the final dimensions during the sintering phase. The ceramic slips are consolidate in a mould, for example, by polymerisation reaction (gel casting), destabilisation (direct coagulation consolidation, DCC), polycondensation reactions (hidrolysis assisted solidification, HAS) and freezing (Quick Set®) (Lyckfeldt and Ferreira, 1998).

In this work, ceramics were prepared by a recent technique. This technique belongs to the family of "direct-consolidation" methods, based on the fundamental properties of the starch and in its capacity of gel formation in water. This enables its use as binder and pore element former.

Recent works about this technique show that it has a large potential for application in several areas of science and technology (Lyckfeldt and Ferreira, 1998; Alves et al., 1998; Lemos and Ferreira, 2000; Campos, 2001; Campos et al., 2001a; Campos et al., 2001b; Campos, 2001c).

The gelling, adhering and forming film capacities are important for starch properties which become it widely used (Menezes, 1996). Such properties can be modified by chemical or physical handling or even for action of certain enzymes for obtaining of new characteristics for specific applications.

In the starch consolidation method, the aqueous suspensions of ceramic powders and starch are poured in molds and heated up to temperatures between 55°C and 80°C, where growth of the starch particles take place by the water absorption of the slip, promoting the ceramic particle aglomeration and, consequently, the formation of a solid body. Besides, these particles upon dilating act as binder, allowing the solid body extraction of the mold once drying takes place (Lyckfeldt and Ferreira, 1998).

After burn-out and sintering of the ceramic piece, the material obtained has porosity corresponding to the size, form of the starch particles.

In this work, this technique was used to obtain ceramic from SiC and corn commercial starch. The objetive was to show the capacity as well as to look for new technological applications.

2. Materials and methods

2.1 Starch and defloculant

The corn commercial starch used in this work was manufactured by Refinações de Milho Brasil Ltda. This starch had not any physical or chemical modification. It was chosen mainly due to its low cost and easy reproducibility. According Campos (2001a), this starch has density equal to 1.52 g/cm^3.

Commercial powders of SiC has a surface typically similar to others oxides due to the reaction of surface oxidation of the particles during the production process, with formation of silica (SiO_2) according to Pandolfelli et al. (2000). Since the SiO_2 superficial layer, the main groups on the surface of the SiC particles are the silanol groups (Si - OH). The development of surface loads on SiC particles depends on the suspension pH as well as with Al_2O_3 particles.

The stabilization of the SiC suspensions is also affected by the degree of particle's superficial oxidation. Since the SiO_2 level increases on the surface, it is observed that, for a fixed pH, the wettability becomes more negative, suggesting an electric charge increasing on the surface that is responsible for the efficient stabilization of the suspensions.

Since Al_2O_3 suspensions, SiC suspensions also present maxima values of viscosity and slip tension in the region with pH close to the isoelectric point. On the other hand, smaller values are obtained in high pH region due to the repulsion among the particles caused by the increasing of surface charges.

According to Pandolfelli et al. (2000), the dispersing agents more frequently used to promote the stabilization of SiC aqueous surfaces are polielectrolytes. Besides, it does not exist a single condition of stabilization for each material. In order to obtain better dispersion conditions, considering each group material/pH/dispersing for different behaviors, it can be observed functions of these arrangements. The stabilization of the SiC suspensions can also be influenced by other factors, such as the concentration of solids, the molecular weight and the formation of the polielectrolyte. In this work, it has been decided to use a polielectrolyte, the Dolapix CE64, of ammonium polimetacrilate (Tarì , 1999).

2.2 Silicon carbide

In this work it was used SiC F-1000 supplied by the Alcoa-Emas in which the following analyses were performed:
a) determination of the particle size (by X-rays attenuation) using the sedimentation of the material in water, based on the law of Stokes and using the Quantachrome Microscan II equipment;
b) crystalline structures (by X-rays diffractometry) using a Siemens Kristalloflex equipment that utilizes copper atom emission at angles between 4º to 70º (2θ). This technique allows to verify the crystalline phases and, mainly, in the case of crystalline materials, to identify their chemical compositions;
c) density of the powder by the helium picnometry using a Micromeritics picnometer model 1305. This technique allows the determination of the density by the expansion of helium in a cell with the sample, in relation to a calibrated cell;
d) analysis of the powder specific area, that is, the total area superficial of the solid by unit mass. Among the several methods used, the BET method was, developed in 1938 by Brumauer, Emmett and Teller. Starting from the equation of the isotherm, the needed number of molecules to form a N_2 monolayer on the surface can be evaluated and, as area occupied by the molecule is known, can calculate the material specific superficial area.

2.3 Processing of the ceramic pieces

SiC samples were produced by the starch consolidation forming method. A slip was produced with 50% (in volume) of distilled water and a maximum 0,5% (in mass) approximately of defloculant, 50% (in volume) of dried matter (powder): 90% SiC and 10% corn starch.

Initially, following the mixing of all components, the slip was put into the ball mill for a better homogenization. It was noticed that the viscosity suspension increased a large agglutination took place, interrupting the homogenization process after a few minutes. For this reason, the process was changed, introducing frequency controlled oscillations on the colloid during the mixture stage. This was shown to be quite efficient, sparing the use of the ball mill equipment at that stage.

After the slip was put into no porous molds. Molds of different shapes and materials were made to demonstrate the process flexibility. After the molds were filled, these were put on the electric mortar equipment for air bubbles

releasing. This process was shown to be practical and offered a better result than others that uses vacuum, mentioned elsewhere (Campos et al., 2001a, 2001b, 2001c).

In the gelling stage, the molds with slip were put in a oven and kept at 75°C for two hours.

Drying occurred when the molds were opened, heated up 120°C and keep at that temperature for two hours. After the drying stage, the pieces acquire enough mechanical strength so that they can be removed and handled. In this point of the process it can already noticed the occurrence of some defects such as cracks due to forming tensions and bubbles caused either by excess lubricant or lack of binder. These pieces are then discarded, not needing through the whole process.

Samples were burned out at temperature of 1000°C for one hour and after were sintered, at temperature of 2050°C and holding, for thirty minutes at same temperature.

2.4 Characterization of the ceramic

Three parameters were chosen in this work for the surface roughness analysis: Ra (medium roughness), Rt (total roughness) and R_3z (medium roughness of the third peak and depression).

Quantachrome model Autoscan-33 mercury porosimeter was used for the determination of the porosity. This equipment uses a maximum pressure of 33,000 psi, allowing measurements of pore diameters between 10 μm to 100Å.

Three-points flexural test, was made, with speed test of 0.5 mm/min, performed in an EMIC essay machine connected to a 1000 kgf loading cell.

Apparent density was determined by method based on the ASTM C20-87 norm and Archimedes' principle. This technique is used to evaluate and to compare products that are not attacked by water. Besides apparent density parameter, apparent porosity also was obtained by this method.

The evaluation of the sample surfaces was made by computational routines that consider the level differences of brightness due to the positions or elevations of each point of the images of this surface (Russ, 1992). In order to determine such elevations, a plug-in based in depth from focus method was used. This plug-in uses as data input a group of images, denominated stack, and extracted with successive displacements of the graduate ring that controls the focus of the microscope. After the stack is obtained, a matrix of odd-numbered dimensions travels the images and, for the same coordinates, two outputs are determined: an image in which all the regions in focus are present and another image in which the brightness gradients correspond to the elevations of the surface. The images were obtained in a Nikon model Epiphot 200 microscope with a lens of 50X, and an final magnification of 500X. Diagnostic Instruments model Spot Insigt Color QE digital camera was connected to this microscope.

Sweeping Electronic Microscopy is a technique that presents a good condition for qualitative analysis of the samples. In this work this technique was used to observe the fracture surface, after three-points flexural test. The images were obtained in the Sweeping Electronic Microscope model LEO 435 VPI, using secondary electron process and 15 kV in voltage.

3. Results and discussions

3.1 Analysis of the ceramic powder

In the Tab. (1) real density, the mean diameter and the specific area of silicon carbide are showed suggesting that this material has low speficic area.

Table 1 Density, medium diameter and specific area of SiC.

Density	Medium diameter	Specific area
3,4 g/cm^3	7,0 μm	2,6 m^2/g

Figure (1) shows the SiC powders X rays diffractogram referring to a hexagonal structure, without the significant presence of pollutants.
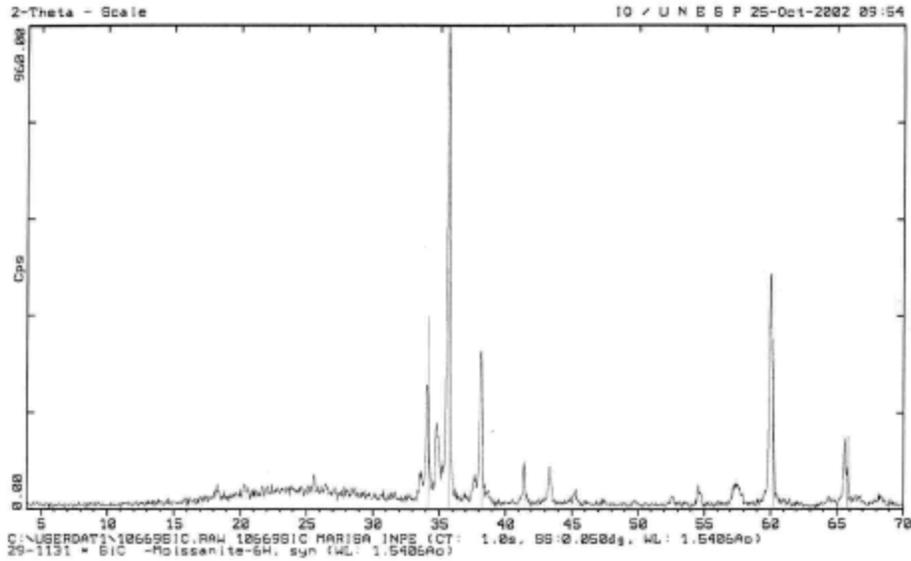
Figure 1 - SiC powder X ray diffractogram.

3.2 Ceramic analysis

The starch forming technique was shown effective in the manufacturing of silicon carbide ceramic pieces for several different shapes, using molds of different materials, as shown in Fig. (2-a). Figure (2-b) displays both sinterized (2050°C) and bur-out (1000°C) pieces.
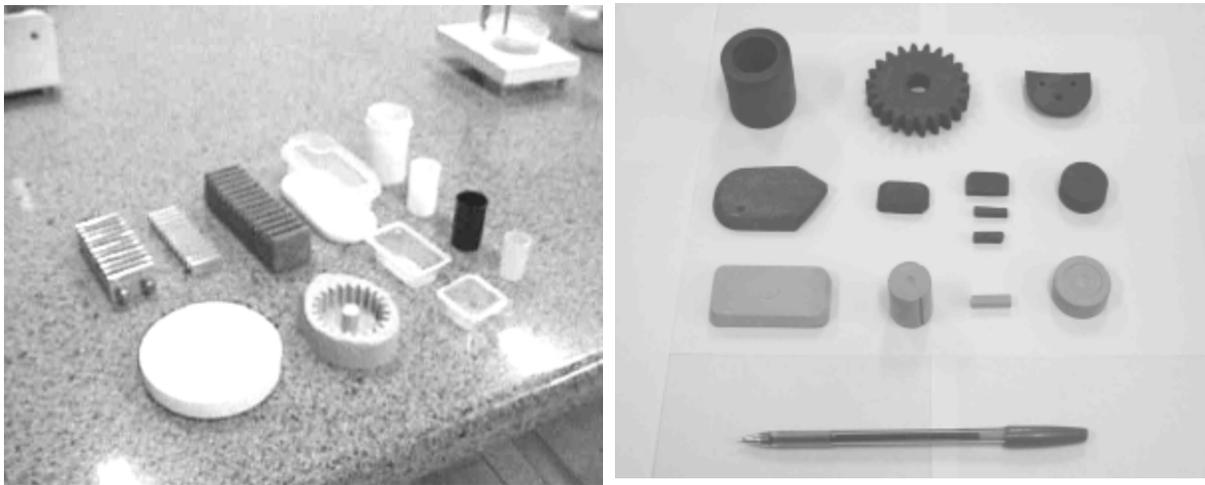
a) Used molds

b) SiC ceramic pieces conformed by starch consolidation

Figure 2 - Used molds and SiC ceramic pieces conformed by starch consolidation.

Table (2) shows the results of the surface roughness measurements. The roughness can be considered relatively high. This possibly occurred due to the SiO_2 content on the samples outer surface.

Figure (3) displays Weibull' diagrams for the samples, presenting the curves ln(ln (1/1-P)), vs. $\ln \sigma$ and the rupture probability (P) vs. the rupture strength (σ) in MPa.

The reference rupture strength (σ_0), the mean strength parameter (σ_{50}) and Weibull module (m) are presented in Tab. (4) for all samples sintered at 2050°C of temperature. It can be observed that ceramic have a good homogeneity due its high weibull module in spite of its strength has not a high value as we desired. Thus, this process may be convenient for some uses of ceramic pieces principally if a regularity on the piece form and feature is needed (Chiang et al., 1997).

Table 2 – Roughness parameters of the silicon carbide ceramic: Ra (medium roughness), Rt (total roughness) and R_3z (medium roughness of the third peak and depression).

Parameter	Statistic	Value [μm]
Ra	Media	3,14
	Median	3,07
	Standard deviation	0,26
R_3z	Media	12,14
	Median	12,30
	Standard deviation	0,95
Rt	Media	24,05
	Median	23,20
	Standard deviation	3,61
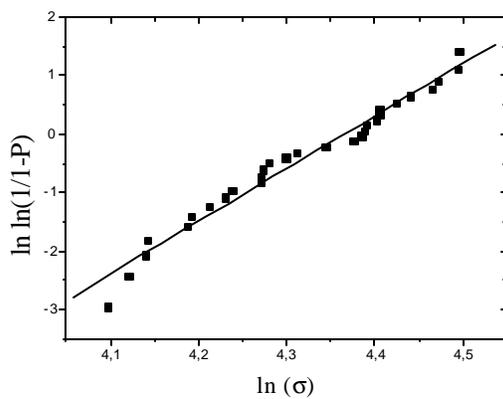
(a)
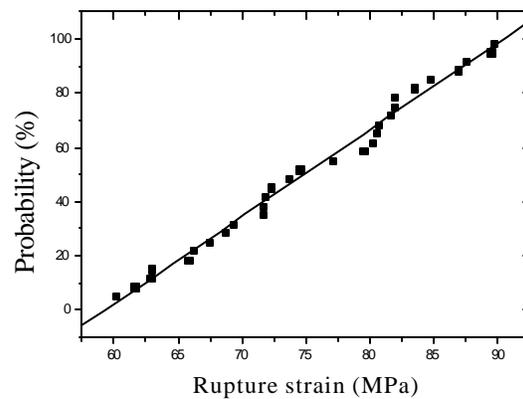
(b)

Figure 3 – Weibull´s diagrams – (a) lnln (1/1-P) vs lnσ and (b) probability vs rupture strength. P is the rupture probability and σ is the rupture strength in MPa.

Tabel 4 – Results of three-points flexural test after analysis by Weibull statistical method.

m	σ_{50} (MPa)	σ_0 (MPa)
10,3	75,4	79,1

Table (4) shows the pore diameter, the apparent density, the apparent porosity and relative density related to measured density shown in Tab. (1). The results indicate that pieces obtained are porous and these pores are locate in macroporous region (Campos, 2001).

Tabel 4 – Pore mean diameter, density and apparent porosity of SiC ceramics.

Pore diameter [Å]		Apparent porosity [%]	Apparent density [g/cm³]	Relative densification [%]
Media	Median	44,08	1,73	50,73
9692	833			

It was possible to observe, with the depth from focus technique, characteristics of several levels of the material surface. Four different analysis were made in samples shaped by starch consolidation. Figure (4-a) displays an image obtained by light microscopy of the SiC ceramic sample surface, with 500X total magnification and also the areas

where these analysis were performed. Each image is part of the stack of images that was used to elaborate the map of elevations.

Figure (4 -b) shows the map of elevations obtained from a 20 images stack, by a variation of the focal distance.
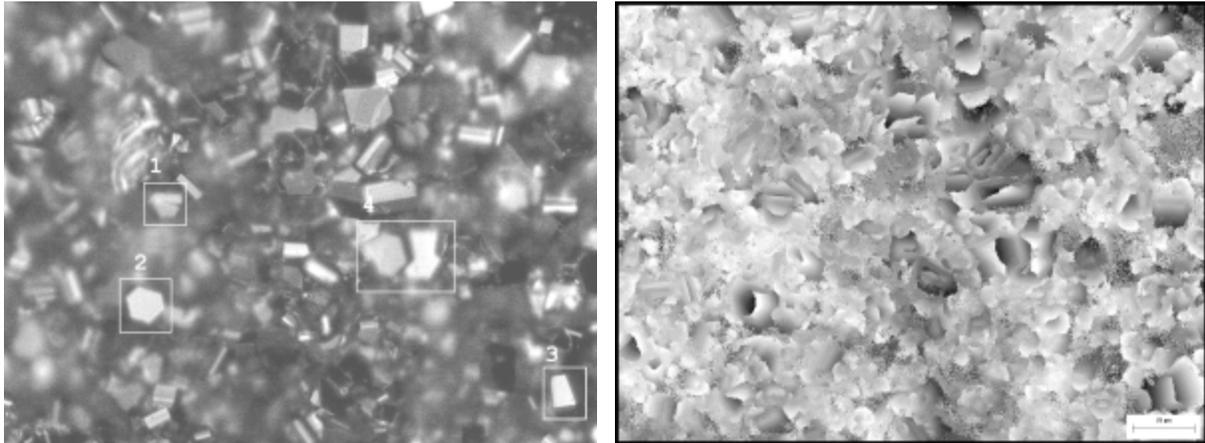
a) Light microscopy image with 500X magnification – SiC produced by starch consolidation.

b) Map of elevations – SiC produced by starch consolidation.

Figure 4 – Ligth microscopy image and map of elevations of the SiC ceramic surface.

In this work SEM images were made with 200X and 500X magnification on fracture surface, as shown in Fig. (5), allowing a qualitative analysis. This reinforces what was observed also in Tab. (4), that is, the porosity is relatively high. It is possible to verify that grains present good homogeneity, a narrow range of size distribution and an isotropic format.
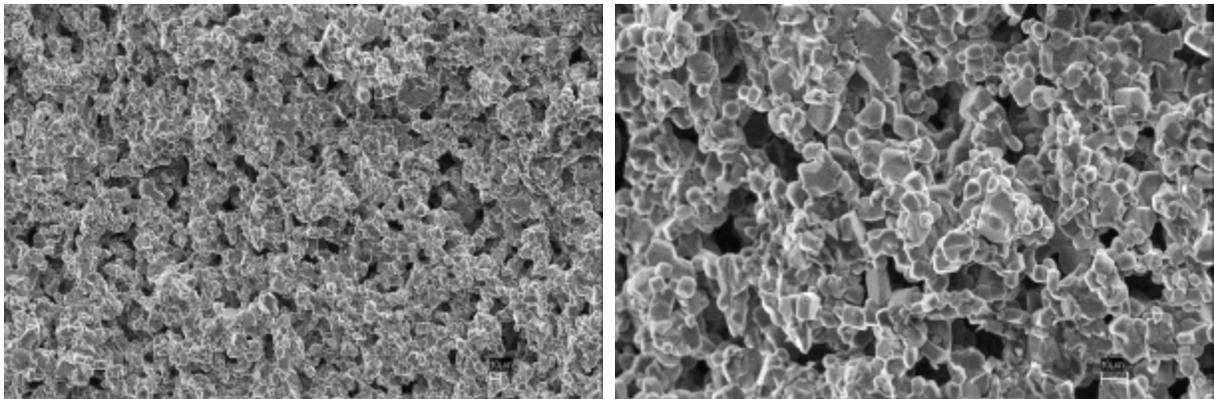
SEM image with 200X magnification – SiC produced by starch consolidation.

SEM image with 500X magnification – SiC produced by starch consolidation.

Figure 5 - SEM images of the SiC ceramic.

4. Conclusions

The conformation technique by starch consolidation is a quite versatile technique and the silicon carbide adapted well to its. This technique produced pieces of complex geometry, with good final finish and homogeneity.

Conformation became viable only after the use of the vibration technique during the homogenization stage, when it transferred to the system a large amount of energy.

Slightly low densification occurred in the pieces made by starch consolidation. This is explained by the fact of performing sintering with solid phase use, that is, only the SiC without any addictive. In this work it was decided not to use addictives to a better know the silicon carbide behavior in the starch consolidation. This was done even knowing that ceramic of SiC can be processed by uniaxial pressing with addictives to achieve liquid phase sintering usually yielding larger densification.

The depth from focus technique demonstrated to be an excellent tool to improve the characterization of the material surface.

References

ALVES, H. M.; TARÌ , G; FONSECA, A. T.; FERREIRA, J. M. F. Processing of porous cordierite bodies by starch consolidation. Research Bulletin. v. 33, issue: 10, p. 1439-1448, 1998.

ANNUAL BOOK OF ASTM STANDARDS. Standard test methods for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick and shapes by boiling water., v. 15.01, C20-87, 1987.

CAMPOS, E. Obtenção e análise de cerâmicas conformadas com amidos comerciais. 2001.Tese (Doutorado em Engenharia Mecânica) – Faculdade de Engenharia de Guaratinguetá, Universidade Estadual Paulista, Guaratinguetá.

CAMPOS, E. et al. Análise comparativa de cerâmicas produzidas por conformação com amidos comerciais, prensagem e colagem. In: CONGRESSO BRASILEIRO DE CERÂMICA, 45, 2001a, Florianópolis. Anais... Florianópolis: ABCERAM, 2001, 1 CD. p. 1502301 – 15023010.

CAMPOS, E. et al. Obtenção e análise de cerâmicas porosas com amidos comerciais. In: CONGRESSO BRASILEIRO DE CERÂMICA, 45, 2001, Florianópolis. Anais.... Florianópolis: ABCERAM, 2001b, 1 CD. p. 1502201 – 15022012.

CAMPOS, E. et al. Conformação de Cerâmicas Porosas com Amidos Comerciais em Moldes de Baixa Molhabilidade. In: ENCONTRO NACIONAL DE FÍSICA DA MATÉRIA CONDENSADA, 24, São Lourenço. Anais... São Lourenço: SBF, 2001c, p. 293-294.

CHIANG, Y.M., BIRNIE III, D.P., KINGERY, W.D. Physical ceramics: principles for ceramic science and engineering. 1ed. New York; John Wiley & Sons / MIT/ 1997.

LEMOS, A. F., FERREIRA, J. M. F. Porous bioactive calcium carbonate implants processed by starch consolidation. Materials Sciende and Engineering: C., v. 11, issue: 1, p. 35-40, 2000.

LYCKFELDT, O. and FERREIRA, J. M. F. Processing of porous ceramics by "Starch Consolidation". Journal of the European Ceramic Society. v. 18, p. 131-140, 1998.

MENEZES, E. W. et al. Starch availability in brassilian food "in vivo" and "in vitro" Assays. Nutrition Research, V.8, p1425-1436, 1996.

PANDOLFELLI, V. C, et. al. Dispersão e empacotamento de partículas: princípios e aplicação em processamento cerâmico. São Paulo. Fazendo Arte Editorial, 2000. p. 19 – 79, 119 – 137.

RUSS, J. C. Computer – Assisted Microscopy – Plenum 1992, New York

TARÌ , G. Advances in colloidal processing of alumina. 1999. Tese (Doutorado em Ciência e Engenharia de Materiais) – Departamento de Engenharia Cerâmica e do Vidro, Universidade de Aveiro, Aveiro,. p. 5-20, 77-87.