Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 36 (2010) 187–191

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

An aqueous gel-casting process for γ-$LiAlO_2$ ceramics

Xiaogang Xu, Zhaoyin Wen*, Jiu Lin, Ning Li, Xiangwei Wu

CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences,
1295 DingXi Road, Shanghai 200050, P.R. China

Received 2 January 2009; received in revised form 12 June 2009; accepted 10 July 2009
Available online 11 August 2009

Abstract

Methyl cellulose (MC) was used as the gelation agent in the gel-casting of γ-$LiAlO_2$ because it could form strong gels during heating. The thermal gelation behavior of the MC solution was studied based on the measurement of its apparent viscosity as a function of temperature. The effects of MC solution concentration and solid loading on the rheological properties of the γ-$LiAlO_2$ slurries were studied systematically. It was found that all the slurries exhibited a shear-thinning behavior, which was considered to be favorable for the casting process. The compressive strength and relative density of the dried γ-$LiAlO_2$ green bodies were measured, and the microstructure of the green and sintered bodies was investigated.

Keywords: Gel-casting; Methyl cellulose; γ-$LiAlO_2$; Forming

1. Introduction

Gel-casting is an attractive ceramic forming process, which can produce high quality complex-shaped ceramic green bodies [1,2]. In such a process, a high solid loading slurry consisting of ceramic powder, solvent and organic binder is first required. After the slurry is cast into a mold, the organic binder creates a macromolecular network to hold the ceramic particles together. Homogeneous ceramic green bodies with excellent mechanical properties are therefore obtained. In the past few years, a considerable amount of research has been done on the development of aqueous gel-casting technique [3–5]. However, industry has been unwilling to make use of it because the most frequently used monomer, i.e. acrylamide, is a neurotoxin. Alternative low toxicity or nontoxic gelation agents have been studied in order to overcome the shortcomings. Thermogelling polysaccharides were used by Millan and Santacruz [6,7], Prabhakaran and Pavithran reported gel-casting of alumina with urea–formaldehyde [8], and so on.

Methyl cellulose (MC), usually prepared by the reaction of methyl chloride and cellulose, is a common commercial product with broad applications [9,10]. It can be dissolved in water and the MC solution is able to produce very strong gels when heated. The gelation behavior of the MC solution is completely reversible. Gel is formed on heating and return to the original state on cooling. This kind of thermal gelation characteristic makes it one of the promising gelation agents for gel-casting.

γ-$LiAlO_2$ has drawn great attentions in recent years for its potential use as a tritium-breeding blanket in nuclear fusion reactors [11,12]. It exhibits good thermophysical, chemical, mechanical stability as well as favorable irradiation behavior, and can also be used as the ceramic matrix in molten carbonate fuel cells. For such applications, γ-$LiAlO_2$ ceramics of various shapes need to be prepared through different ceramic forming processes. As known, γ-$LiAlO_2$ displays strong basic characteristics in an aqueous system, which makes it difficult to find an appropriate binder for its wet forming processes. In this study, we first present the gel-casting process with MC for the forming of γ-$LiAlO_2$ ceramics.

2. Experimental

γ-$LiAlO_2$ powder was prepared via a solid state reaction method using γ-alumina (γ-Al_2O_3) and lithium hydroxide ($LiOH·H_2O$) as raw materials. The γ-alumina powder (99.9% purity) with a mean particle size of 2.09 μm and a specific surface area of 1.17 m^2/g was provided by Shanghai Fenghe

---

* Corresponding author. Tel.: +86 21 52411704; fax: +86 21 52413903.
E-mail address: zywen@mail.sic.ac.cn (Z. Wen).

0272-8842/$36.00 © 2009 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2009.07.017

Ceramic Co., Ltd. The LiOH·H_2O (AR, 95.0% purity) was supplied by Sinopharm Chemical Reagent Co., Ltd. Stoichiometric amounts of LiOH·H_2O and γ-Al_2O_3 were mixed by ball-milling for 4 h with ethanol as the milling medium, and the weight ratio of powder/ethanol was 1/4. The resulting slurry was dried in oven box and then calcined at 1000 °C for 2 h. The γ-$LiAlO_2$ powder with a mean particle size of 8.8 μm and a specific surface area of 0.4 m^2/g was therefore obtained. 0.50–2.04 g MC was dissolved into 100 g deionized water to prepare the precursor solutions of concentrations ranging from 0.5 to 2 wt%. γ-$LiAlO_2$ powder was slowly added to the MC solutions under mechanical stirring to prepare slurries of solids fraction between 0.3 and 0.5. Afterwards, the resulting slurries were degassed for 15 min and cast into a stainless steel mould. After gelling at 60 °C for 2 h, the wet γ-$LiAlO_2$ green bodies (8 mm × 8 mm × 40 mm) were removed from the mould and dried naturally under the laboratory environment. The MC content referred to the dry green parts varies between 0.35 and 1.75 wt%. Binder burnout was carried out at 300 °C in air for 2 h, with a heating rate of 1 °C/min and a natural cooling. Sintering was carried out at 1200–1500 °C for 4 h.

The apparent viscosity as a function of temperature for the precursor MC solutions with concentrations of 1, 1.5 and 2 wt% was measured by a rotary rheometer (Brookfield RVDVIII+, USA) to determine their gelation temperature. The shear rate was kept at 2 s^{-1} and the heating rate was 5 °C/min. Rheological properties of the γ-$LiAlO_2$ slurries were evaluated systematically. The influences of MC solution concentration and solid loading on the shear viscosity and shear stress versus shear rate of the γ-$LiAlO_2$ slurries were investigated using the rotary rheometer. The measuring shear rate range was 0–400 s^{-1} and the temperature was kept at 5 °C using a circulating bath (Brookfield TC502P, USA) to avoid evaporation. The compressive strengths of the green bodies were examined with bars of 5 mm × 5 mm × 12.5 mm by the universal testing machine (Instron-5566, USA), and the compression rate was 0.2 mm/min. The relative green density was measured based on the Archimedes' principle. TG/DSC analysis (NETZSCH STA409PC, Germany) was used to study the pyrolysis process of the MC polymer network in γ-$LiAlO_2$ green parts. The microscopic morphology of the green and sintered bodies was observed by scanning electron microscopy (SEM, FEI Quanta 200 FEG).

3. Results and discussion

3.1. Gelation of the MC solution

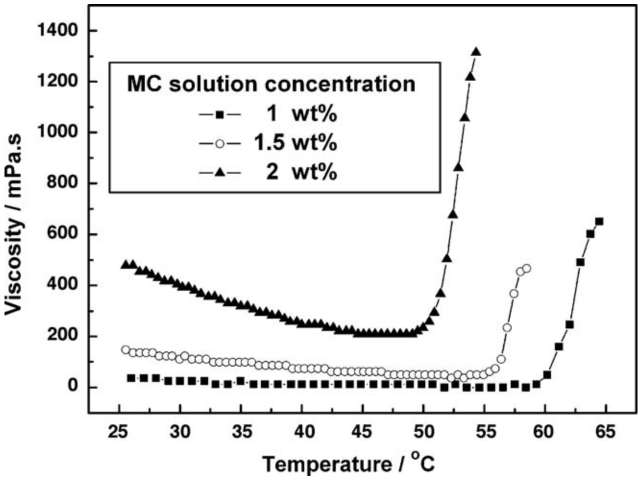

Fig. 1. The apparent viscosity versus temperature for MC solution with different concentrations.

Fig. 1 shows the apparent viscosity versus temperature for MC solution with different concentrations. It was observed that the viscosity of the MC solution reduced slowly before an abrupt rise with the increasing temperature. When the MC was dissolved in water, the molecules were hydrated in the solution and there was little polymer–polymer interaction other than chain entanglement. When the temperature increased, these molecules lost their hydration waters, which led to the gradual decrease of the viscosity. After the dehydration of the MC molecules, a polymer–polymer association took place and the molecules formed an infinite three-dimensional network, a sharp increase of the apparent viscosity occurred. The concentration of the MC solution displayed an effect on its gelation temperature. While it varied from 1 to 2 %, the gelation temperature of the MC solution decreased from 60 to about 50 °C.

3.2. Rheological properties of the γ-$LiAlO_2$ slurries

The effects of the precursor MC solution concentration on the rheological properties of the γ-$LiAlO_2$ slurries are shown in Fig. 2. It was found that all the γ-$LiAlO_2$ slurries exhibited a shear-thinning behavior over the measuring shear rate range. At low shear rates, the structure of the slurry was close to equilibrium and the rheological behavior of the slurry was dominated by the thermal motion. With the shear rate increased, the ceramic particles in the slurry were arranged to form a two-dimensional layered structure. The resistance to flow, primarily caused by the particle and solvent movement between different layers, became lower under the influence of shear. Therefore, a decrease of the shear viscosity versus shear rate was observed. In addition, both the apparent viscosity and

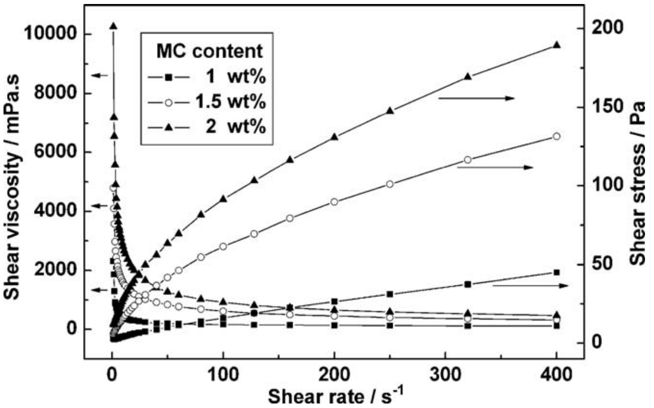

Fig. 2. Effects of the precursor MC solution concentration on the rheological properties of the γ-$LiAlO_2$ slurries.

the shear stress of the slurries increased while the MC content rose from 1 to 2 wt%. At the shear rate of 100 s^{-1}, the slurry prepared from the precursor solution containing 1 wt% MC exhibited a shear viscosity of 158 mPa s, while the slurries with 1.5 and 2 wt% MC displayed viscosities as high as 615 and 913 mPa s, respectively. Therefore, MC solution with lower concentration was believed to be more suitable for the slurry preparation, and 1 wt% was chosen as the optimum concentration for the precursor MC solution.

For the gel-casting process, the solid loading of a slurry has a direct influence on the density of the green parts. On the other hand, a low viscosity of the slurry is beneficial to both milling and casting processes. Therefore, it is important to achieve a solid loading as high as possible while maintaining a proper fluidity of the slurry. Fig. 3 shows the rheological curves of the γ-$LiAlO_2$ slurries with solid loadings of 40, 46 and 50 vol.%, respectively. As expected, the apparent viscosity and shear stress of the slurries displayed a remarkable increase tendency with the rise of the solid loading content. The slurry with a solid loading of 50 vol.% possessed a shear viscosity of 1200 mPa s at the shear rate of 100 s^{-1}, which was barely enough to satisfy the requirement of casting. Furthermore, the shear stress versus shear rate depicted in Figs. 2 and 3 had also been analyzed using the Herschel–Buckley model [13]:

$$\tau = \tau_0 + k\gamma^n$$

where τ is the shear stress, τ_0 the yield stress, k a consistency coefficient, γ the shear rate and n the flow behavior index. The values of the flow behavior index (n), determined by the software provided with the equipment, were all smaller than unity, which was a typical characteristic of a pseudoplastic fluid.

3.3. Green strength and microstructure

Fig. 4 shows the influences of precursor MC solution concentration and solid loading on the relative density and compressive strength of the dried γ-$LiAlO_2$ green bodies. The solid loading of the suspensions in Fig. 4(a) was 40 vol.%, and the concentration of MC solution in Fig. 4(b) was 1 wt%. It could be seen in Fig. 4(a) that both the relative green density and the compressive strength increase with the concentration of the precursor solution. when the concentration of the precursor solution varied from 0.5 to 1.5 wt%, both the MC content in the dry green parts and the crosslinkage of the polymer network increased. And the higher the crosslinkage value, the more the drying shrinkage of the green parts. Therefore, the relative density displayed an increase tendency with the MC solution concentration. And as shown in Fig. 4(b), the impacts of the solid loading were similar to that of the concentration of the

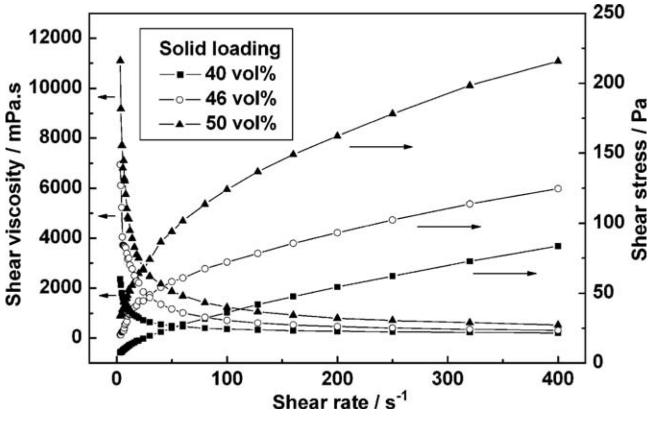

Fig. 3. Effects of the solid loading on the rheological properties of the γ-$LiAlO_2$ slurries.

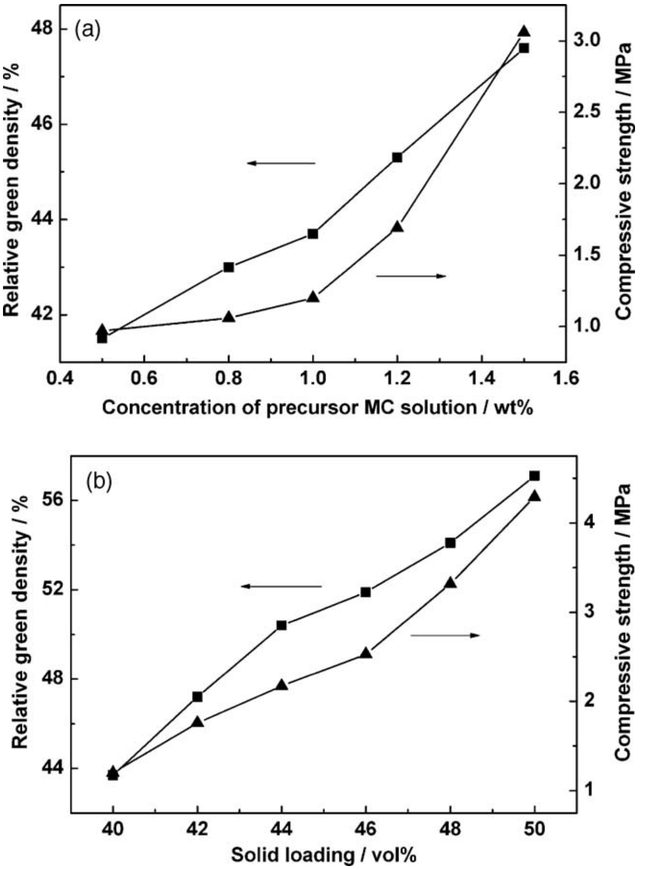

Fig. 4. Influences of (a) the precursor MC solution concentration and (b) solid loading on the relative density and compressive strength for γ-$LiAlO_2$ green bodies.

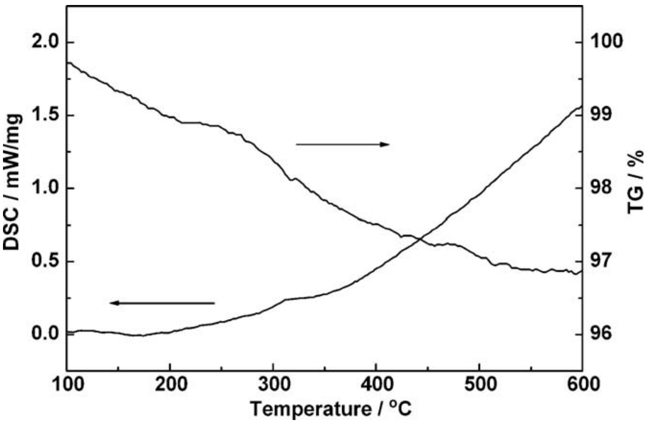

Fig. 5. Pyrolysis process of the MC polymer network in γ-$LiAlO_2$ green bodies.

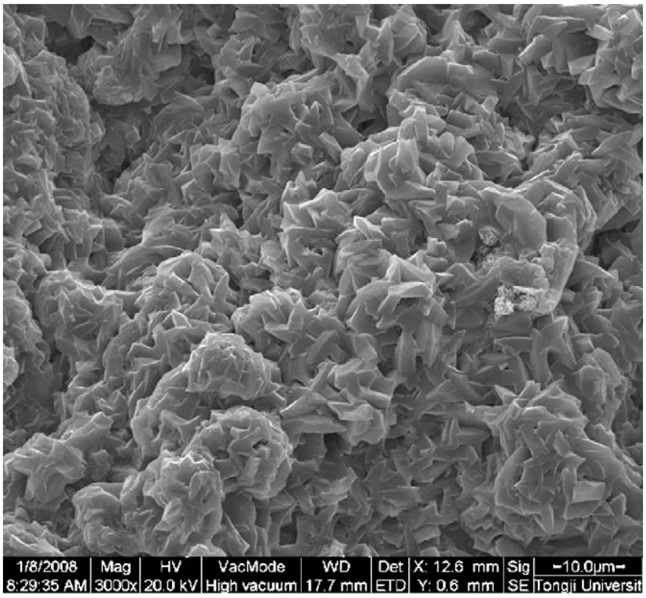

Fig. 6. SEM micrographs of the γ-$LiAlO_2$ green bodies.

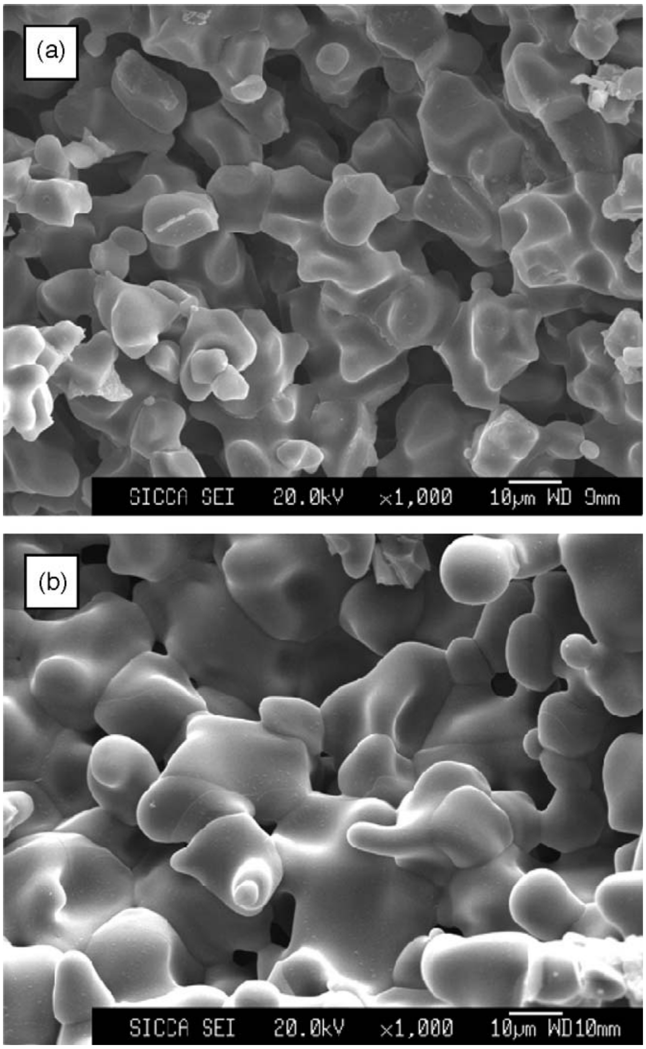

Fig. 7. SEM micrographs of the γ-$LiAlO_2$ ceramics sintered at (a) 1200 °C and (b) 1500 °C.

precursor solution. The γ-$LiAlO_2$ green body prepared from the slurry with 50 vol.% solid loading exhibited a compressive strength of 4.3 mPa and a relative density of 57.1%, respectively, and is strong enough for direct machining.

The pyrolysis process of MC in the dried γ-$LiAlO_2$ green bodies during binder burnout in air was determined via thermal analysis. According to the TG curves shown in Fig. 5, the green samples lost about 3.1% of its weight in the temperature range of 100–600 °C. The DSC curve indicated an exothermic event between 300 and 330 °C, which was attributed to the burnout of the MC polymer network and was accompanied by a weight loss of about 2.1%. And the 1% weight loss before 200 °C was mainly due to the removal of trapped water.

Fig. 6 illustrates the SEM micrograph of the dry green bodies prepared from the 1 wt% precursor MC solution and containing 50 vol.% γ-$LiAlO_2$ powders. It could be seen that the γ-$LiAlO_2$ particles are hold together by an obvious polymer network formed by MC, which was responsible for the favorable strength of the green bodies. Fig. 7 presents the SEM micrographs of the γ-$LiAlO_2$ sintered bodies. The ceramics exhibited uniform microstructure without over growth of the grains. With the sintering temperature rose from 1200 to 1500 °C, the relative density of the γ-$LiAlO_2$ ceramics increased from 65.4 to 80.2%.

3.4. Conclusions

Gel-casting technique with MC as the gelation agent was successfully applied to the forming of γ-$LiAlO_2$ ceramics. The MC solution could gelate at a proper temperature which was related to the concentration of the solution. The higher the concentration, the lower the gelation temperature. During the slurry preparation, the MC solution with a concentration of 1 wt% performed as a favorable precursor, and the slurry with a solid loading of 50 vol.% could maintain a satisfactory fluidity. In addition, all the γ-$LiAlO_2$ slurries exhibited a shear-thinning behavior, which could be attributed to the perturbation within the slurry structure by the shear. After casting and drying, the resultant γ-$LiAlO_2$ green bodies displayed proper compressive strengths and a good machining performance. Homogeneous and compact microstructure was realized in the green and sintered bodies.

Acknowledgements

This work is financially supported by Project No. 2007CB209700 of the Ministry of Science and Technology of China, No. 50730001 of the Natural Science Foundation of China, and No 08DZ2210900 of the Science and Technology Commission of Shanghai Municipality.

References

[1] A.C. Young, O.O. Omatete, M.A. Janney, P.A. Menchhofer, Gelacsting of alumina, J. Am. Ceram. Soc. 74 (1991) 612–618.
[2] O.O. Omatete, M.A. Janney, R.A. Strehlow, Gelcasting—A new ceramic forming process, Ceram. Bull. 70 (1991) 1641–1649.
[3] B. Chen, Z. Zhang, J. Zhang, M. Dong, D. Jiang, Aqueous gel-casting of hydroxyapatite, Mater. Sci. Eng. A 435–436 (2006) 198–203.

[4] S.L. Morissette, J.A. Lewis, Chemorheology of aqueous based alumina-poly(vinyl alcohol) gelcasting suspension, J. Am. Ceram. Soc. 82 (1999) 521–528.

[5] A.A. Babaluo, M. Kokabi, A. Barati, Chemorheology of alumina-aqueous acrylamide gelcasting systems, J. Eur. Ceram. Soc. 24 (2004) 635–644.

[6] A.J. Millan, M.I. Nieto, C. Baudin, R. Moreno, Thermogelling polysaccharides for aqueous gelcasting. Part II. Influence of gelling additives on rheological properties and gelcasting of alumina, J. Eur. Ceram. Soc. 22 (2002) 2217–2222.

[7] I. Santacruz, C. Baudin, M.I. Nieto, R. Moreno, Improved green properties of gelcast alumina through multiple synergistic interaction of polysaccharides, J. Eur. Ceram. Soc. 23 (2003) 1785–1793.

[8] K. Prabhakaran, C. Pavithran, Gelcasting of alumina using urea–formaldehyde. II. Gelation and ceramic forming, Ceram. Int. 26 (2000) 67–71.

[9] J.E. Schuetz, Methylcellulose polymers as binders for extrusion of ceramics, Ceram. Bull. 65 (1986) 1556–1559.

[10] H. Itagaki, I. Takahashi, M. Natsume, T. Kondo, Gelation of cellulose whose hydroxyl groups are specifically substituted by the fluorescent groups, Polym. Bull. 32 (1994) 77–81.

[11] S. Sokolov, A. Stein, Preparation and characterization of macroporous γ-$LiAlO_2$, Mater. Lett. 57 (2003) 3593–3597.

[12] M.A. Valenzuela, L. Tellez, P. Bosch, H. Balmori, Solvent effect on the sol–gel synthesis of lithium aluminate, Mater. Lett. 47 (2001) 252–257.

[13] D.T. Beruto, A. Ferrari, F. Barberis, M. Giordani, Dispersions of micrometric powders of molybdenum and alumina in liquid paraffin: role of interfacial phenomena on bulk rheological properties, J. Eur. Ceram. Soc. 22 (2002) 2155–2164.