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Ceramics International 35 (2009) 1429–1434

CERAMICS INTERNATIONAL

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Preparation of γ-$LiAlO_2$ green bodies through the gel-casting process

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Received 26 November 2007; received in revised form 20 May 2008; accepted 18 July 2008

Abstract

An aqueous gel-casting process using methacrylamide (MAM) as monomer and *N*,*N*′-methylenebisacrylamide (MBAM) as crosslinker was developed for γ-$LiAlO_2$ ceramics. The precursor γ-$LiAlO_2$ powder with mean particle size of 3.4 μm was synthesized via solid-state reaction process. The zeta potential of the γ-$LiAlO_2$ powders in deionized water and viscosity of the slurries with different solid loadings were measured. It was found that the solid loading of the γ-$LiAlO_2$ slurry that met the requirement of gel-casting could reach 56 vol.%. The effects of pH values and the kind of initiator on the copolymerization of MAM/MBAM were investigated. The green bodies with the binder content of 5.3 wt% exhibited a compressive strength of 12.6 MPa and a yield point as high as 6.4 MPa. SEM results revealed homogeneous and compact morphology of the green bodies. In addition, the compressive strength of the sintered γ-$LiAlO_2$ bodies were studied simultaneously.

Keywords: A. Shaping; B. γ-$LiAlO_2$; C. Strength; Gel-casting

1. Introduction

Lithium aluminate presents three kinds of crystalline phases, i.e. α-, β-, and γ-$LiAlO_2$, with hexagonal, monoclinic and tetragonal structure, respectively [1]. Among the three phases, the γ-$LiAlO_2$ is the most stable one and α- or β-$LiAlO_2$ can transform to γ-$LiAlO_2$ at an elevated temperature [2]. Due to its good thermophysical, chemical, mechanical stability as well as favorable irradiation behavior, γ-$LiAlO_2$ has been recognized as a potential candidate for tritium-breeding materials in nuclear fusion reactors [3,4]. For this kind of application, specifically shaped γ-$LiAlO_2$ ceramics need to be prepared through ceramic forming processes. Up to now, dry pressing has been generally used in forming the green bodies of γ-$LiAlO_2$ parts. However, density gradient occurred in such green bodies and their strengths were relatively low.

Gel-casting technique is an attractive new ceramic forming process, which was first introduced by Omatete et al. [5–7]. In such a process, ceramic powders are dispersed into a pre-mixed organic monomer solution to form a stable and high solid loading slurry [8]. After the addition of an initiator and a catalyst, the slurry is poured into a mould. The monomer polymerizes in situ and green bodies with excellent mechanical property are therefore obtained [9]. Then, just like other ceramic forming processes, binder removal and sintering take place. Compared to conventional forming process such as dry pressing, slip-casting and injection molding, gel-casting has several distinctive advantages: (1) the process is a near-net-shape forming process; (2) it can produce a homogeneous wet cast body with uniform chemistry and density; (3) the strength of a dried green body is so high that it can be machined [5–7,10,11]. In this paper, we will first present the gel-casting process to the forming of γ-$LiAlO_2$ green bodies with high mechanical strength and uniform microstructure.

2. Experimental

2.1. Raw materials

Lithium hydroxide ($LiOH\cdot H_2O$) and γ-alumina (γ-Al_2O_3) were used as the starting materials to prepare γ-$LiAlO_2$ powders. For the gel-casting process of γ-$LiAlO_2$, monofunctional methacrylamide (MAM), $CH_2{=}C(CH_3)CONH_2$ was used as a monomer. Difunctional *N*,*N*′-methylenebisacrylamide (MBAM), $(CH_2{=}CHCONH)_2CH_2$ was used as a cross-linker, Ammonium persulfate (APS), $(NH_4)_2S_2O_8$ as an initiator, a polyelectrolyte, ammonium polyacrylate (PAA, 40 wt% solution) as a dispersant. Lactic acid was applied to adjust the pH value. All the reagents used were chemically pure.

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doi:10.1016/j.ceramint.2008.07.012

2.2. γ-$LiAlO_2$ powder preparation and characterization

γ-$LiAlO_2$ powder was prepared by conventional solid-state reaction method. Stoichiometric amounts of $LiOH{\cdot}H_2O$ and γ-Al_2O_3 were mixed by ball-milling for 24 h. The slurry was dried in air, γ-$LiAlO_2$ was then obtained when the powder was calcined in air at 900 °C for 2 h. Finally, the synthesized γ-$LiAlO_2$ powder was ball-milled for another 4 h to gain suitable particle size distribution and proper specific surface area. The mean particle size and particle size distribution of γ-$LiAlO_2$ powder were determined by a JL-1177 laser particle size analyzer.

2.3. Slurry preparation and gel-casting

A 10 wt% premixed solution was first prepared by dissolving the monomer and the crosslinker in deionized water with the weight ratio of monomer to cross-linker of 5:1. γ-$LiAlO_2$ powder was slowly added to the premixed solution under mechanical stirring. An appropriate amount of lactic acid was used to adjust the pH value of the suspension, and the content of dispersant was controlled at 1.5 wt% of the γ-$LiAlO_2$. The temperature was kept at 0 °C in an ice water bath during the whole process. After the addition of APS, the degassed slurry was poured into a mould and gelled at 60 °C for 2 h. Then the wet green body (8 mm × 8 mm × 40 mm) was removed from the mould and dried carefully to avoid cracking. Binder burnout was carried out at 300 °C in air for 2 h, with a heating at the rate of 1 °C/min and a natural cooling. Sintering was carried out at 1500 °C for 4–24 h, with a heating at the rate of 2 °C/min, and a cooling at the rate of 2 °C/min to 800 °C followed by a natural cooling.

2.4. Characterization

Zeta potential of the γ-$LiAlO_2$ at different pH values was measured by a JS94G+ microiontophoresis apparatus. The suspension with 0.02 wt% of γ-$LiAlO_2$ for measurement was adjusted by HCl and NaOH to fix the pH value. The viscosity of the γ-$LiAlO_2$ slurry with different solid loadings was measured by a NDJ-79 viscometer. The conversion ratio of copolymerization of MAM/MBAM at a given pH value was evaluated by determining the content of carbon–carbon double bonds remained in the solution using the oxidation-reduction titration method. The compressive strength and yield point of the dried green bodies as well as the sintered samples were examined with bars of 5 mm × 5 mm × 12.5 mm by the Instron 5566 universal testing machine. The microscopic morphology of the green bodies was observed by scanning electron microscopy (SEM, EMPA-8705Q, HII).

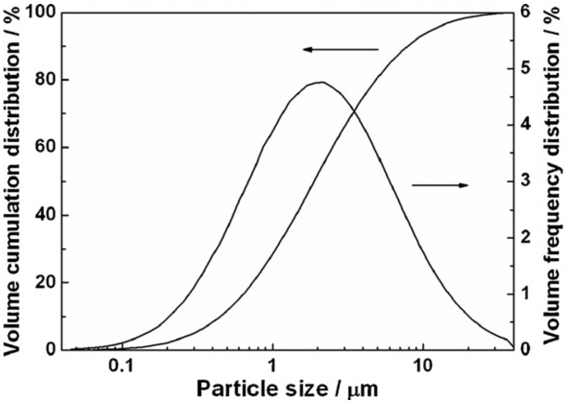

Fig. 1. Particle size distribution of γ-$LiAlO_2$ powder.

3. Results and discussion

3.1. γ-$LiAlO_2$ powder characterization

It has been demonstrated that the particle size distribution and specific surface area of ceramic powders have great influences on the performance of a slurry [12]. Micro or sub-micro ceramic powders are usually considered to be favorable for obtaining a stable suspension with high solid loading. Fig. 1 shows the particle size distribution of the γ-$LiAlO_2$ powder synthesized at 900 °C and followed by a 4 h ball-milling. As shown, the powder has a particle size distribution with the minimum particle size less than 0.1 μm and the maximum larger than 10 μm, over 70% of the powders are within the range from 0.5 to 5 μm. The mean particle size is 3.4 μm, and the specific surface area is 2.11 m^2/g.

3.2. Effect of pH on zeta potential of γ-$LiAlO_2$

The zeta potential is an important parameter indicating the stability of ceramic particles dispersed in a liquid medium. The more positive or negative the zeta potential, the higher the repulsive energy and the more stable the slurry will be. Fig. 2 shows the zeta potential of γ-$LiAlO_2$ powder in deionized water with and without dispersant as a function of pH value. It is found that the zeta potential of γ-$LiAlO_2$ changes from -21.9 mV at pH 7.4 to -52.7 mV at pH 11.5 in the absence of a dispersant. With the addition of 1.5 wt% dispersant, it becomes -16.6 to 63.3 mV. In other words, the zeta potential of γ-$LiAlO_2$ becomes more negative at higher pH values, but gets close to the isoelectric point (IEP) under slightly basic pH conditions.

It is well known that the γ-$LiAlO_2$ can hydrolyze intensely and produce a large amount of OH^- anions in an aqueous solution. The pH value of the γ-$LiAlO_2$ suspension of 0.003 mol/L is as high as 10.8. These OH^- anions can reacted with the hydroxyl groups on the surface of γ-$LiAlO_2$ particle, so the zeta potential of γ-$LiAlO_2$ is relatively low at high pH values and increases with a decreasing pH value. When a dispersant is added to the suspension, it can ionized in water to form the negative polyacrylic acid radical (PA^-) and ammonium cations (NH_4^+). The PA^- ions can be absorbed by γ-$LiAlO_2$ particles, while the NH_4^+ ions will react with OH^- to form $NH_3{\cdot}H_2O$. The combined actions lead to the change in zeta potential of the suspension after the addition of the dispersant.

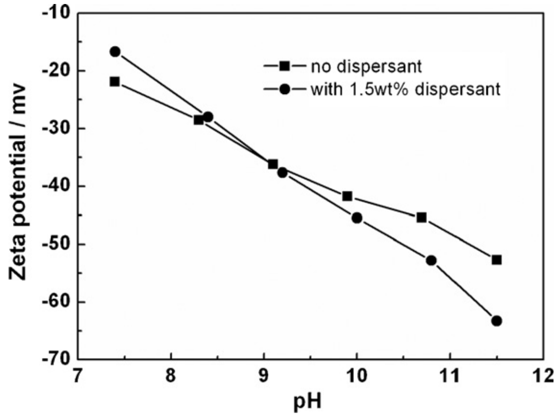

Fig. 2. Zeta potential verse pH value of γ-$LiAlO_2$ in deionized water.

3.3. Copolymerization of MAM/MBAM

Copolymerization of monomer and crosslinker is the kernel of a gel-casting process. The copolymerization can form a strong, cross-linked, there-dimensional polymer network. The conversion ratio of carbon–carbon double bonds during polymerization at different pH values was measured and was given in Fig. 3. Under neutral or near-neutral conditions, over 97% carbon–carbon double bonds took part in the free radical copolymerization process initiated by APS. In the presence of a strong base, the conversion ratio decreased from 96% at pH of 10.8 to 93.4% at pH of 12.3. This small change indicated that high pH value had a negative effect on the copolymerization of MAM/MBAM.

Fig. 3 together shows the relationship between the conversion ratio of carbon–carbon double bonds and the initiator amount at the pH of 10.8. It is observed from the figure that the conversion ratio stayed above 96% when the amount of initiator was above 1 g/l. As is well known, it is usually impossible to achieve a 100% conversion ratio in the free radical polymerization process. The process is normally considered to be finished when more than 95% monomers participate in the reaction. Therefore, 1 g/l was considered to be the appropriate initiator amount for γ-$LiAlO_2$ slurry.

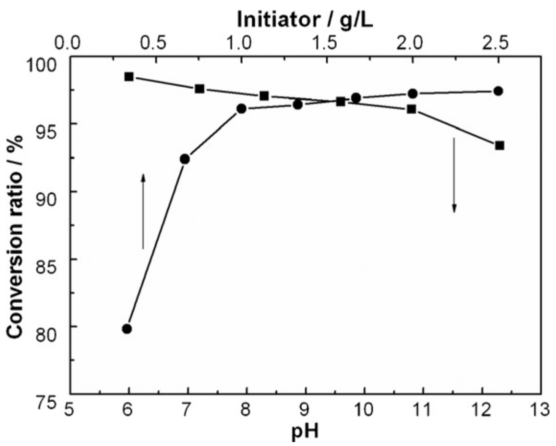

Fig. 3. Effect of pH value and initiator concentration on the conversion ratio of carbon–carbon double bonds.

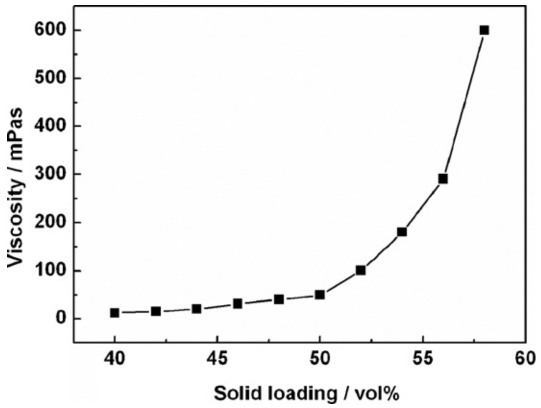

Fig. 4. Viscosity of the γ-$LiAlO_2$ slurry vs. solid loading.

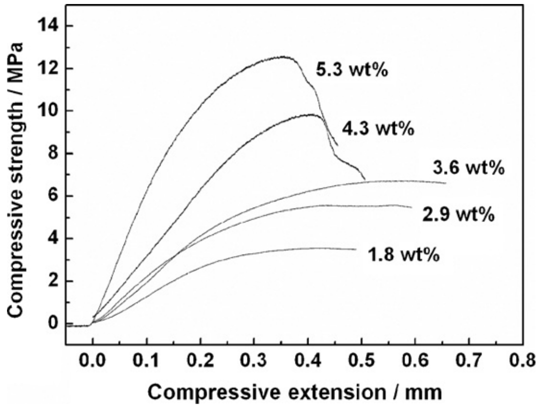

Fig. 5. Compressive strength–extension curves of γ-$LiAlO_2$ green bodies with different binder contents.

3.4. The effect of solid loading on the slurry viscosity

High solid loading and low viscosity of γ-$LiAlO_2$ slurry are beneficial for both mixing and casting during the process. Accordingly, it is important to maintain a proper fluidity of the slurry by optimizing its solid loading. Fig. 4 gives the curves of apparent viscosity for the slurry with different solid loadings. It

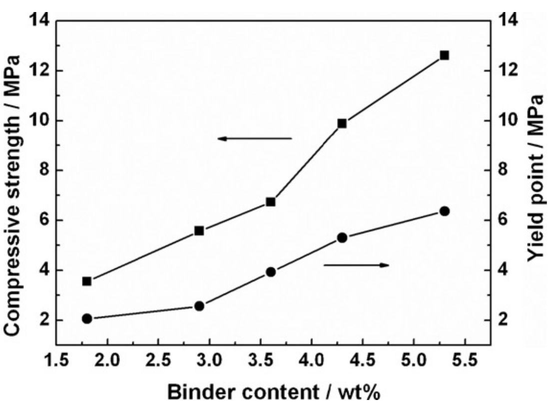

Fig. 6. Influence of binder content on the compressive strength and yield point of the γ-$LiAlO_2$ green bodies.

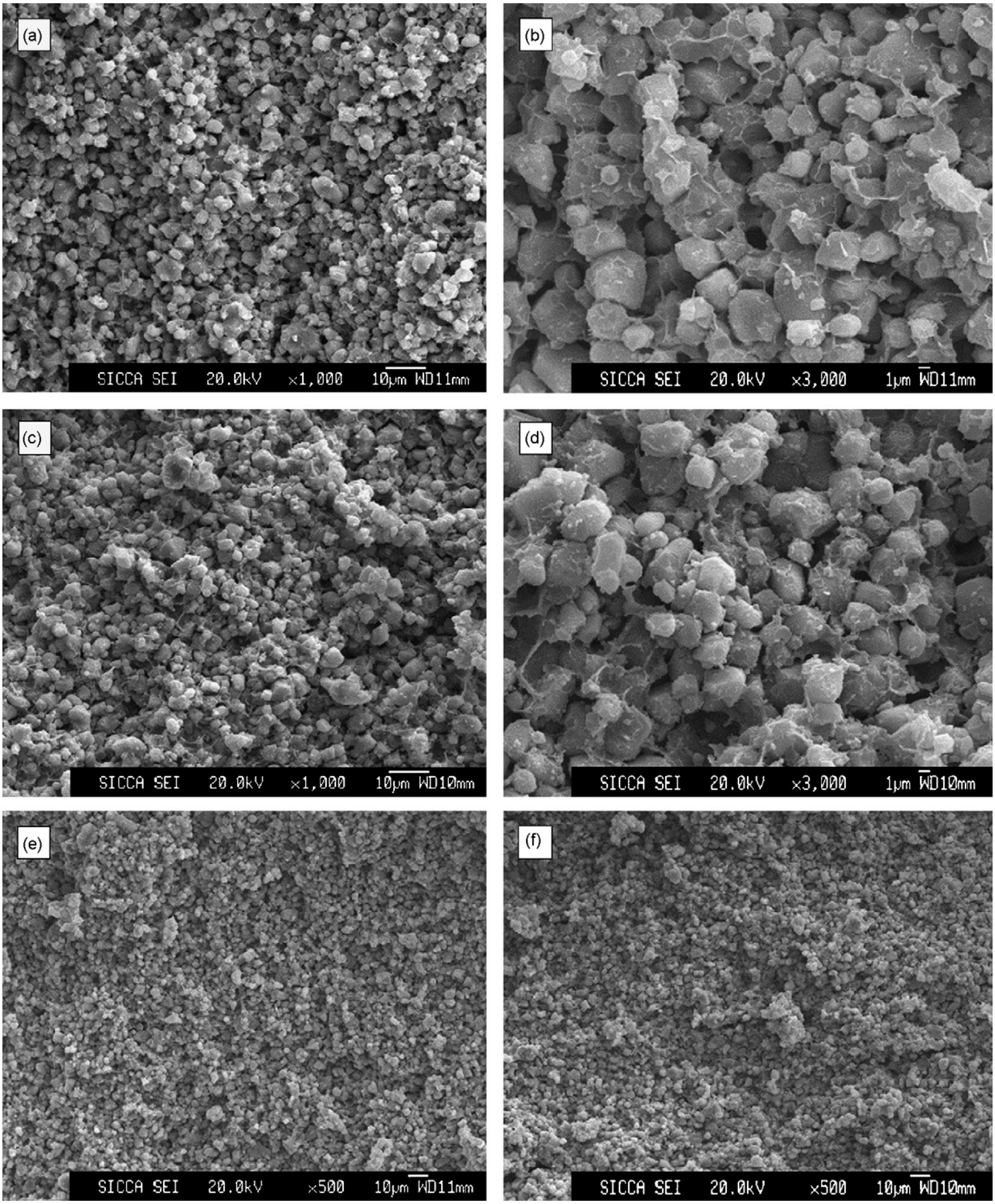

Fig. 7. The microstructure of γ-$LiAlO_2$ green bodies with 3.6 wt% binder content (a, b, e and f) and 5.3 wt% binder content (c and d).

can be seen that viscosities of the γ-$LiAlO_2$ slurry are relatively low and increase slowly while solid loadings are below 50 vol.%. At the shear rate of 175 s^{-1}, the slurry containing 56 vol.% of γ-$LiAlO_2$ possesses a viscosity of 290 mPa s, which can meet the requirement of casting process. When the solid loading continues to increase, the slurry becomes thicker and pastier.

3.5. *Strength and microstructure*

Fig. 5 shows the compressive strength–extension curves of γ-$LiAlO_2$ green bodies with different binder contents. As seen, when loaded by an external force, the γ-$LiAlO_2$ green samples first undergo elastic deformation. During this period, the compressive stress is linearly proportional to the strain, and the

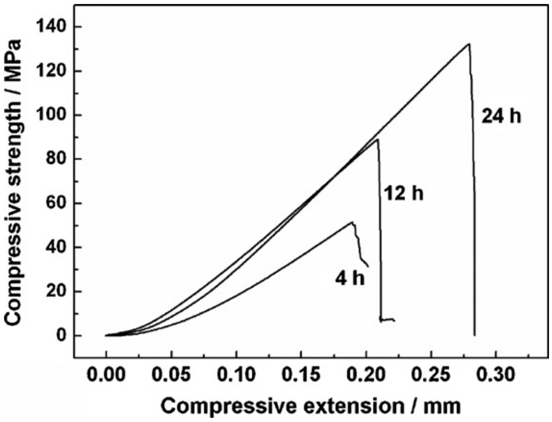

Fig. 8. Compressive strength–extension curves of γ-$LiAlO_2$ ceramics sintered at 1500 °C for different periods.

green sample can return to its original dimensions after the force is no longer applied. Then, plastic deformation occurs when the load exceeds a value corresponding to its yield point. The γ-$LiAlO_2$ green samples are permanently deformed even if the stress is released to zero. At the end of deformation ranges, the gel-casting samples will eventually crack and fracture because of the force accumulation.

Fig. 6 shows the influence of binder content on the compressive strength and yield point of the gel-casting samples derived from the slurry of 50 vol.% γ-$LiAlO_2$. As expected, both the compressive strength and yield point increase with the increasing binder content. At a binder content of 5.3 wt%, the compressive strength and the yield point are 12.6 MPa and 6.4 MPa, respectively, which are strong enough for green machining.

SEM micrographs of the dry bodies with 3.6 and 5.3 wt% binder contents are shown in Fig. 7. It can be seen that the green samples have homogeneous and compact microstructure with few pores. No apparent agglomerates are observed. As figures (b) and (d) shown, the γ-$LiAlO_2$ particles are connected by polymer network formed by the MAM/MBAM copolymer. The network could be considered to be responsible for the favorable strength of green bodies. Fig. 7(e) and (f) are the SEM micrographs for the top and bottom parts of the γ-$LiAlO_2$ green body, respectively. It is well known that the larger and heavier particles tend to settle down during the forming process, which will result in the density gradient of the green bodies. As shown in figures (e) and (f), the particle size distribution of the γ-$LiAlO_2$ powders located near the bottom of the green bodies is similar to that of the top part. Therefore, the segregation of ceramic particles does not occur in the entire gel-casting process. In addition, the result green bodies prepared from the slurry with 55 vol.% γ-$LiAlO_2$ exhibit a green density of 64.6%.

The compressive strength–extension curves of the γ-$LiAlO_2$ ceramics sintered at 1500 °C for different periods are given in Fig. 8. Similar to those of γ-$LiAlO_2$ green bodies, the γ-$LiAlO_2$ ceramics first experience an elastic deformation under an external pressure. But when the load is beyond the elastic limit, the γ-$LiAlO_2$ ceramics break immediately and plastic deformation does not occur, which is different from that of the green bodies. As shown in Fig. 8, the compressive strength of the γ-$LiAlO_2$ ceramics increase with the sintering time. When the time extends to 24 h, the γ-$LiAlO_2$ ceramics exhibit a compressive strength of 132 MPa.

4. Conclusions

Gel-casting process was successfully applied to fabricate γ-$LiAlO_2$ green bodies. The γ-$LiAlO_2$ powder prepared by solid-state reaction with an average particle size of 3.4 μm and a specific surface area of 2.11 m^2/g was performed as a favorable precursor. With 1.5 wt% dispersant, the γ-$LiAlO_2$ slurries were colloidally stable even at high pH values. The copolymerization of MAM/MBAM could be initiated by APS in a wide pH range, and the reaction completed at the initiator concentration higher than 1 g/l. The solid loading played an important role in determining the viscosity of γ-$LiAlO_2$ slurry. After casting, gelling and drying, the γ-$LiAlO_2$ green bodies displayed a satisfactory machinability, with the maximum compressive strength and yield strength of 12.6 and 6.4 MPa, respectively. The compressive strength for the γ-$LiAlO_2$ ceramics sintered at 1500 °C for 24 h reached 132 MPa. In addition, the green bodies demonstrated homogeneous and compact microstructure.

Acknowledgments

This work is financially supported by the “973” Project (2007CB209700) of the Ministry of Science and Technology of China and key project of Natural Science Foundation of China (NSFC, No. 50730001).

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