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Green approach in the sol–gel synthesis of defect free unsupported mesoporous alumina films

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ABSTRACT

Sol–gel synthesis of defect free alumina films by the hydrolysis of metal alkoxide precursors require proper drying and calcination procedures. In the present paper an attempt has been made to gain control over the difficult process of sol–gel synthesis of plain, porous, defect free alumina films through proper design and selection of parameters like contact angle (120°), viscosity (1–2 Pa s), drying and calcination temperature. SANS, AFM, TEM probes were used to investigate porous alumina film (α alumina) made up of parallel channels with cylindrical shape. Nitrogen adsorption studies (BET method) were carried out to determine porosity and surface area of the film. The SEM and X-ray diffraction studies were done to characterize the alumina film. The kind of technique used during synthesis of alumina film is not only cost affective but has an added advantage of controlling the shape and geometry of alumina film. The novel technique of disc furnace introduced here has overcome the difficulties of cracking and deformation in the sol–gel synthesis of alumina film during calcination. It has been shown that various sizes of porous, plain unsupported alumina films with a diameter of 30–50 mm and thickness of 0.5–5 mm were prepared by using sol–gel method.

1. Introduction

There is a need to divert the attention towards the non silaceous material to make periodically organised and well ordered material [1,2]. In 1950s and 1960s it was Roy who first brought sol–gel science to broad attention of ceramic industry [3]. In late 1980s all sol–gel research was carried out in the area of thin film coating, however production of monolithic structure was neglected [4]. The global production of the alumina is four million tonnes per year, and is used in various industries. Commercially porous alumina films are used in pharmaceutical, wine and beer clarification industry [5]. It can even be used in highly corrosive environment [6]. A wide range of applications are possible as the structural and textural properties of the resultant aluminas and can be controlled by using sol–gel process [7]. It has been observed that the sol–gel synthesis of porous alumina films is still not widely commercialized due to the inherent problems faced during the course of synthesis. Fabrication of dense alumina monoliths is difficult because either sol is not seeded properly or dried boehmite gel becomes brittle and briable [8]. Cracking remains the bone of contention for decades and membranes with thickness more than 5 μm [9] are difficult to process. It is very tough to prepare ceramic from gels as drying of gel without cracking is difficult [10]. To prepare crack free ceramic films it is necessary to monitor the drying, calcination temperature and number of coatings applied on the films [11]. In order to prevent the cracking of ceramic film, a thorough study of various heating schedules, stresses and gel uniformity is essential [12]. The other limitation is deformation of the gel film which tends to lift it upwards in the direction of evaporation and then curve in opposite direction as the drying proceeds in the final stage [13]. These limitations have restricted a more widespread use of sol–gel process for production of films and monoliths [14]. Thus it is essential to accept challenges for clear understanding of the processes, events and mechanism to conduct the experiments so as to fabricate the desired product [15].

Sol–gel synthesis of alumina film requires pairing between chemical and processing conditions resulting in harmonizing ex situ measurements with in situ characterization methods, which happen in synchronized manner from formation of metal alkoxides solution to the finishing stage monolithic film [16,17]. The whole process starts with introduction of organometallic precursor to water and its peptization for the formation of aqueous sol [18]. It includes proper selection of the peptizing agent, keeping in mind

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pH of the resultant solution [11]. The temperature of sol formation is also important, which in the present case is maintained at 90 °C to prevent the bayrite [19] formation. The duration of clear and stable sol formation based on observation is 12–18 h. The drying and firing are two major events occurs in the course of desired product formation. In between these two events there are many permutations and combinations of physical and chemical processes occurs which leave the mark eventually on the final calcined product. The physical processes which are important in the final consolidation of product are surface properties, contact angle, gel viscosity, evaporation, surface tension of the gel and crystallization during firing. The answer for crackfree plain dried alumina film by sol–gel method lies in the fact that proper selection of surface on the basis of contact angle measurement is necessary. The next parameter which has marked effect on the cracking of the film is viscosity [20]. Varying precursor concentration in the sol by evaporation of the solvent, an optimal rheological state where structural evolution from dilute sol to development of three dimensional gel network can be achieved for the gel casted on the mould.

In the present work, we have best dealt with sol–gel synthesis of alumina film by hydrolysis of aluminium alkoxide precursor by employing controlled environment. Without addition of any binder, this approach has resulted in to formation of porous, wrap free, and crack free alumina monoliths. Herein we report a simple, ecofriendly, aqueous and economical method of minimizing cracking and deformation problems present in the synthesis of ceramic films by sol–gel method. The characterization of the film has been done by using probes such as SEM, TEM, AFM, BET, XRD and SANS. Collectively these techniques show insight into the internal porous structure and topography of the film.

2. Experimental

2.1. Preparation of alumina hydrogels

Alumina films were synthesized by sol–gel method. The A.R. Grade chemicals were used as received. Initially deionised water was heated in a 15 × 30 cm glass reactor up to the boiling point of water. It helps in escape of dissolved gases present in the water. ATSB (Aluminium tri-sec-butoxide) was added dropwise to this boiling water. The mixture was further stirred upto 10 min. It was then peptised by addition of glyoxylic acid dropwise to the boiling mixture. The mixture was further stirred and boiled for 10 min. The molar ratio of ATSB, water and glyoxylic acid was 1.25:125:0.15 respectively. The solution so obtained was kept under reflux condition for 12–18 h. A clear transparent sol was obtained. The clear sol obtained in above process was further concentrated by evaporating the solvent in the range of 40%–70% before gel casting on the mould.

2.2. Drying of hydrogel to xerogel and further calcinations

The viscous free flowing gel obtained was casted on flat metallic moulds consisting of a coating of ceramic or metal oxide. The thickness of the gel casted was in the range of 1 mm–20 mm. The gel was then kept under visible light source. This step helps in reducing the drying time of gel. Within 5–12 h the film of gel gets hardened and starts peeling off the drying surface. The gel diameter gets reduced upto 30% of the original mould diameter and the thickness of the gel film gets reduced up to 60% of the initial cast volume after drying under visible light source. The resultant film was placed in between two porous transparent glass plates as sandwich. This complete assembly was then kept under visible light source. With overnight drying the solvent content of the aerogel film evaporated and material became hard and flat uniformly. The flat hardened film was then placed between two porous plain specially designed furnace plates for calcination at 1100 °C. The furnace was programmed at temperature ramp rate of 1 °C per minute and maintained at 1100 °C for 3–5 h to obtained the calcined alumina film.

2.3. Process for the synthesis of alumina film

Fig. 1 shows schematic representation of the process of synthesis, drying and sintering of the alumina xerogel film. The first and second step indicates placing and fixing of xerogel film of alumina between two porous transparent flat surfaces. It plays the important role of letting the light rays fall on the gel film, and the porous plate allows the exit of the volatile matter from the film. The plates also help in keeping the film straight. Since surface tension of water plays an important role in the development of cracks in the matrix of the system, a simple light source was used to evaporate the solvent gently from xerogel. This exercise was continued till complete drying of film. The dried film was further subjected to calcination in the specially designed furnace. The reactions may takes place as given below.

$$2Al(OR)_3 + 6H_2O \rightarrow \underset{\text{Where}(OR=OC_4H_g)}{2Al(OH)_3} + 6ROH$$

$$2Al(OH)_3 \xrightarrow[\Delta]{} AL_2O_3 + 6H_2O$$

2.4. Calcination of alumina film by specially designed furnace

Fig. 2 shows the schematic design of the furnace used in the calcination of alumina film. The furnace plates kept the alumina film in its desired position and did not allow it to curve in any direction. The volatile matter in the form of solvent and organic template, evaporated from the alumina film and escaped through the porous plates and vents present in the furnace. The furnace was programmed to heat at the rate of 1 °C per minute up to 1100 °C in order to obtain calcined alumina film. The furnace comprised of two furnace plates which were mounted on right stand by means of

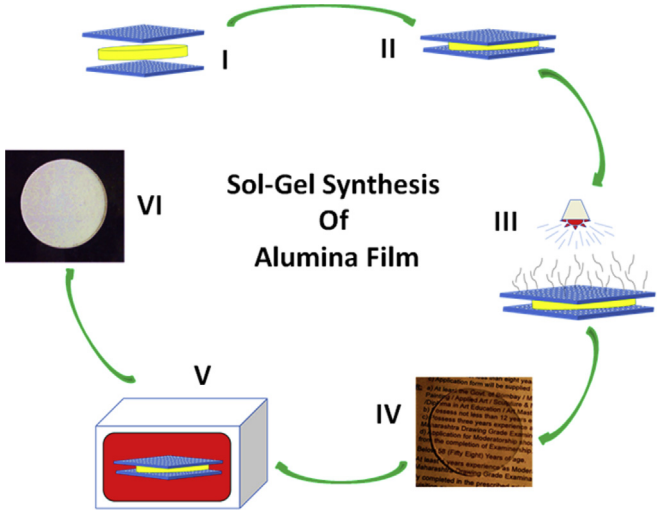

Fig. 1. Schematic presentation of the process of sol–gel synthesis of alumina film, (I) Placing of gel film between porous glass plates, (II) Air drying of gel film, (III) Drying of wet gel film by light source, (IV) Air dried transparent alumina film (V) Calcination of alumina film in furnace, (VI) Calcined alumina film.