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ScienceDirect
Ceramics International 38 (2012) 867–870
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Gelcasting of Al_2O_3/Ag nanocomposite using water-soluble solid-salt precursor

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Received 6 June 2011; received in revised form 18 June 2011; accepted 23 June 2011
Available online 6th July 2011

Abstract

In the present work, Al_2O_3/5 wt.% Ag nanocomposite was prepared by gelcasting process. Silver nitrate was used as the source of silver nanoparticles in the alumina matrix. Dolapix ET85 was found as the most effective dispersant agent to neutralize of unwelcome influence of silver ions on the behavior of slurry. The results indicated that the rheological properties and sedimentation behavior of the prepared slurries were significantly modified using 1.5 wt.% dolapix ET85, which also acts as a chelating agent. The FTIR investigations showed the preventative effect of dolapix on the damaging of rheological properties in the presence of silver ions. The average particle size of silver nanoparticles was measured to be about 50 nm using TEM microscopy.

Keywords: B. Nanocomposite; Gelcasting; Slurry; FTIR

1. Introduction

Gelcasting method uses the slurries of ceramic powders with a high solid content and an aqueous solution of monomers [1]. By in situ polymerization of the dissolved monomers, a 3-dimension network is created that binds ceramic particles together [2]. In order to prepare the ceramic parts at controlled conditions, the specimens are dried and sintered [3]. Up to now, there are few reports on fabrication of nanocomposites by the gelcasting method. Niihara et al. reported the fabrication of Al_2O_3/Ni nanocomposite [4]. In another research, Ananthakumar et al. fabricated Al_2O_3/SiC nanocmposite by the gelcasting method [5]. In the mentioned works, the second phase of nanocomposites was introduced as the particles and no water-soluble precursors. It was observed that metal ions had detrimental effects on the performance of dispersant agent and slurry viscosity.

In this work, gelcasting process by solid-salt precursor, water-soluble one, was used for the fabrication of Al_2O_3/Ag nanocomposite, which would illustrate a better distribution of nanoparticles in matrix. This composite has a potential for antibacterial applications. A chelating agent was utilized to form a complex component with silver ions, which prevents the undesirable effects of metal ions on slurry properties.

2. Materials and methods

Alumina powder (mean particle size, 0.7 μm; specific surface area, 15 m^2/g) and $Ag(NO_3)$ were purchased from Martinswerk and Merck Companies, respectively. For gelcasting process, methacrylamide (MAM) was used as the monomer, N,N′-methylenebisacrylamide (MBAM) as a coupling agent, N,N,N′,N′-tetramethylethylenediamine (TEMED) as a catalyst, and ammonium persulphate as an initiator. All of these materials were purchased from Merck Co. and were chemical pure. Dolapix ET85 was used as a dispersant agent (Zschimmer & Schwars Co.).

The premix solutions contained distilled water, monomer and cross-linker. The weight ratio of monomer to cross-linker was 5:1, and the total weight percentage of monomer and cross-linker in distilled water was 15. An appropriate amount of dolapix ET85 was added to above solutions. The silver nitrate

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doi:10.1016/j.ceramint.2011.06.062

was added to the prepared solution to obtain a final solution containing 5 wt.% Ag. Final slurries were prepared by the addition of 50 vol.% alumina powder. The prepared slurry was mixed for 24 h by a ball mill. In the next step, 2 wt.% aqueous solution prepared from the mixture of initiator (APS) and catalyst (TEMED) and was added to the slurry. Finally the prepared slurry was cast into a rectangular mold. The gelation occurred at 50 °C. After 1.5 h, the green sample was demolded and then transmitted to a chamber of 95% relative humidity at 30 °C. The dried samples were finally sintered at 1300 °C by microwave. The used supplements for microwave sintering have been presented in Ref. [6].

The sedimentation test was done in test tubes with a capacity of 10 ml. The rheological properties of the slurries were measured by a rotary rheometer (MCR-300). The debinding condition in air was determined by thermogravimetric and differential thermal analysis (TG–DTA) up to 600 °C (STA-PL1640). The FTIR spectra of the compounds were recorded using a Bruker Vector-33-FTIR spectrometer in the region 400–4000 cm^{-1} by KBr Pellet method. Transmission electron microscope (TEM, Philips EM208S) was applied to observe the silver nanoparticles dispersed within the alumina matrix.

3. Results and discussion

The sedimentation tests were performed by using slurries containing 10 wt.% alumina powder and 5 wt.% Ag. Fig. 1 shows the effect of dispersant amount on the sedimentation height. It can be observed that the sedimentation height increases with increasing the dispersant amount from 1 to 1.5 wt.%. However, the further addition of dispersant over 1.5 wt.% led to a lower sedimentation height (higher sediment height). From the data presented in Fig. 1, it is clearly determined that the optimal concentration of dispersant is 1.5 wt.%.

Fig. 2 shows the viscosity curves versus shear rate for slurry containing 50 vol.% Al_2O_3 and 5 wt.% Ag in various quantities of dispersant. The viscosity decreased with increasing the amount of dispersant up to 1.5 wt.%, which is in agreement with the results of sedimentation test. As Fig. 2 further reveals, the prepared slurries at all amounts of dispersant exhibit shear

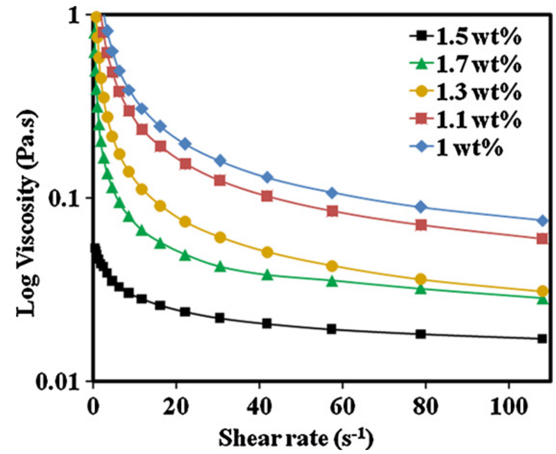

Fig. 2. Influence of dispersant concentration on viscosity of slurries with 50 vol.% of Al_2O_3 and 5 wt.% Ag.

thinning behavior that is a relevant rheological behavior for casting.

Fig. 3 shows the FTIR spectra of pure dolapix ET85 (Fig. 3a) and a combination of $Ag(NO_3)$ and dolapix ET85 with the weight ratio of 1:1 (Fig. 3b). The aim of this test is to display the reaction between silver ions and dolapix ET85. In the present work, dolapix ET85 acts as a chelating agent as well as dispersant agent. Chelating agents are organic compounds containing the functional groups such as carboxylic ($COOH^-$) or amine (NH_x) groups that can trap the metal ions into their structures [7], and as a result, metal ions would not be able to behave like a free one. Based on the above-mentioned argument, it is expected that the undesirable effects of silver ions on the rheological properties can be neutralized by dolapix ET85 as a chelating agent.

In Fig. 3a, the absorption bands at 1410 and 1590 cm^{-1} can be attributed to the ionized carboxylic groups in the solution [8]. The peak observed at 842 cm^{-1} is due to amine groups (N–H). Furthermore, the absorption bands in the range 1000–1400 cm^{-1} were recognized as the ester group [9].

The addition of silver nitrate to dolapix ET85 causes some changes in FTIR spectra (Fig. 3b). As observed, the peak at 842 cm^{-1} has been completely eliminated. It should be noted

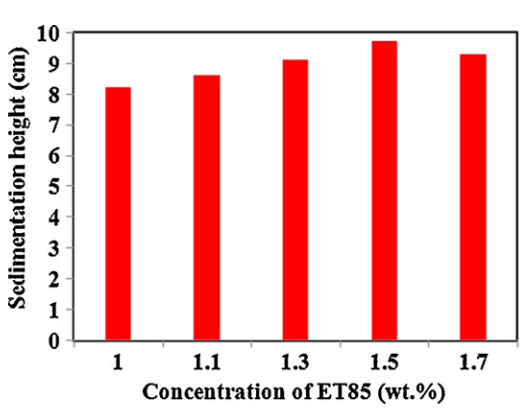

Fig. 1. Sedimentation behavior of slurry in the presence of different concentrations of dispersant.

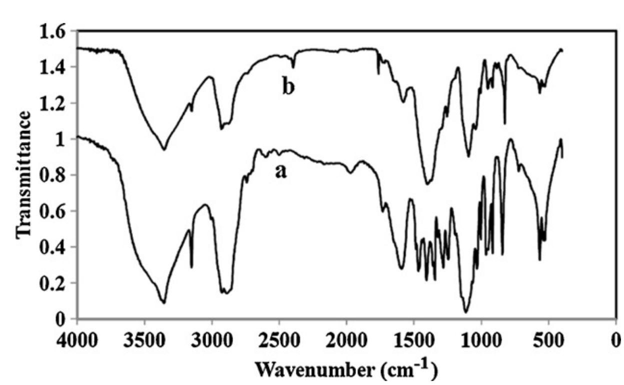

Fig. 3. FTIR spectra: (a) dolapix ET85, and (b) dolapix ET85 reacted with silver nitrate.

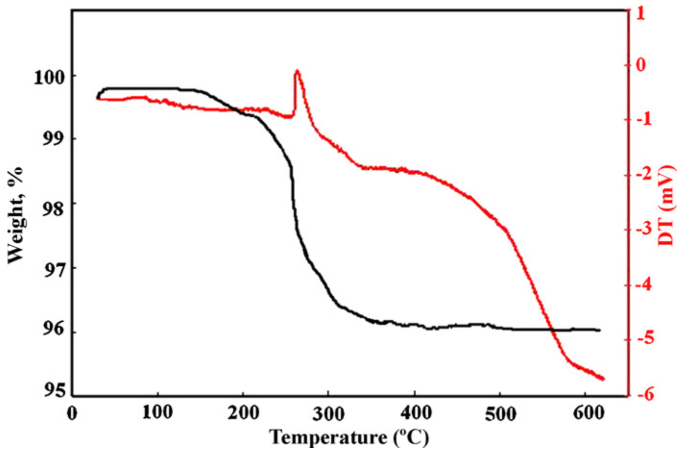

Fig. 4. Pyrolysis of dried Al_2O_3/Ag precursor sample.

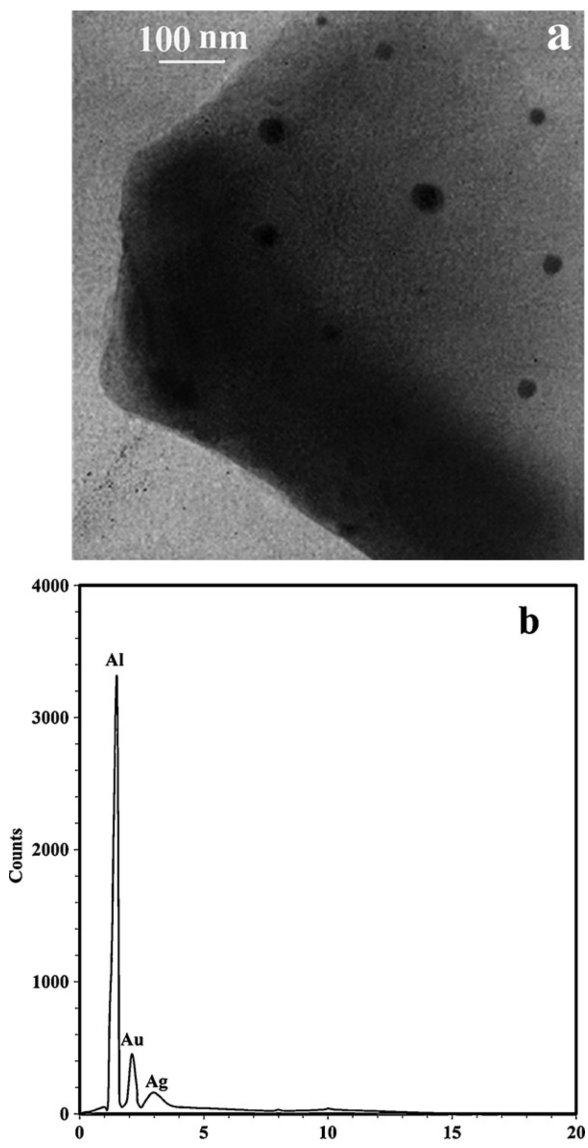

Fig. 5. (a) TEM image of Al_2O_3/Ag nanocomposite, and (b) EDX analysis of composite.

that the peak at 825 cm^{-1} is related to the nitrate ions and it should not be considered as an amine group (at 842 cm^{-1}). Furthermore, the dramatic decrease of transmittance for the peak at 1590 cm^{-1} is attributed to the entrance of silver ions into the structure of dolapix ET85 and reaction with the ionized carboxylic groups. From the above results, it can be concluded that the unfavorable effects of Ag ions on the rheological properties of alumina slurry can be remarkably declined by using dolapix ET85. Moreover, due to the overlapping between the peaks related to nitrate ions (Fig. 3b) and ester groups (Fig. 3a), it was not possible to determine the peaks appeared at the range of 1300–1500 cm^{-1}.

Fig. 4 shows thermal analysis (DTA/TG) of gelcasted specimens in air with the heating rate of 5 °C/min, up to 600 °C. Since the sample was dried before thermal analysis, there was not any important thermal event up to 250 °C. The distinguishable exothermal event at the range of 250–340 °C can be attributed to the combustion reaction of polymers (MAM/MBAM). Although the decomposition reaction of nitrate was observed in DTA spectrum at the temperature range of around 340–580 °C, no significant evident was obtained from the TG spectrum to indicate the effect of the extraction of nitrates which could be attributed to small amount of nitrate. As Fig. 4 further reveals, the weight loss at the temperature range 100–340 °C should be ascribed to the burnout of the cross-link polymer network.

The TEM image of fabricated Al_2O_3/Ag nanocomposite is shown at Fig. 5a. As observed, Ag nanoparticles (<50 nm) appeared as precipitates within the Al_2O_3 matrix. The EDX analysis represents the chemical composition of Al_2O_3/Ag nanocomposite (Fig. 5b). The Au peak is related to Au coating on the surface of sample to do TEM experiment.

4. Conclusions

Al_2O_3/Ag nanocomposite was successfully fabricated by gelcating method using water-soluble solid-salt precursors. Dolapix ET85 (1.5 wt.%) was determined as an excellent dispersant in this system, since it acts as a chelating agent in entrapping of silver ions as well as dispersant. This phenomenon was observed by constituting a complex compound between dolapix ET85 and silver ions by means of FTIR spectra analysis. Furthermore, the presence of carboxylic groups that are responsible to trap silver ions in dolapix ET85 was detected by FTIR. The particle size of silver nanoparticles dispersed in alumina matrix was measured to be less than 50 nm by TEM.

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