THERMOGRAVIMETRIC CHARACTERIZATION OF GELCAST ALUMINA COMPOSITES

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Abstract

Gelcasting is a new method for forming advanced ceramics based on obtaining intermediary gels promoted by polimerization "in situ" within the ceramic slurry. Gelcast composites of an ALCOA A-1000 alumina and the copolymer obtained using acrylamide and N,N′-metylenebisacrylamide as monomers were characterized by thermogravimetrv. Polymer distribution was determined by thermogravimetric analysis of small size specimens that were taken from different parts of the alumina composites formed in different shapes. Derivative thermogravimetry was used to identify the resulting polymerization stage within the gelcast body, as well as to study the influence of mold materials and operating conditions. All the composites show an even distribution of the polymer in the bulk, which enables machining in the green state and obtaining high density alumina bodies after sintering.

Keywords: alumina, composites, material characterization, thermogravimetry

Introduction

Gelcasting is a new method for forming advanced ceramics developed at Oakridge Laboratories [1, 2]. This method is based on the knowledge of polymer chemistry and conventional ceramic forming such as slip casting [3, 6]. Forming is promoted by the gelling effect that occurs due to polymerization "in situ" within a ceramic slurry. After a drying step, near-shaped composites are formed with only 4% of polymer, which may be machined in the green state. For ceramic processing, the following binder burnout step can be performed without taking special care to avoid slumping and/or deformation.

Thermogravimetry and derivative thermogravimetry have been used for quantitative and qualitative analysis of polymers in composites [7] and organic binders in ceramic compositions [8]. The purpose of this paper is to show how thermogravimetric curves (TG) and their derivatives (DTG) can be used to characterize the gelcast composites, in terms of the polymer formation stage and its distribution

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within the composite body, and to choose the best operating conditions for gelcasting, drying and burnout steps.

Experimental procedure

An ALCOA A-1000 alumina, having a mean grain size of 1.2 μm was used as the raw material. Two water soluble monomers were used with a slurry of alumina. The monomers were: acrylamide (AM) and N,N-methylenebisacrylamide (MBAM). The alumina was dispersed in a solution of both monomers, containing 15% AM and 0.2% MBAM using DARVAN C as dispersant. Using a mechanical shaker the slurry was mixed for four hours and aged at room temperature for twentyfour hours. The slurry contained about 50% vol alumina, calculated on the base of alumina and water only. The amount of monomer was such that in the composite its content related to alumina was about 4%. After mixing, the slurry was deareted, and then the catalyst (N,N,N',N'- tetramethylenediamine) and the initiator (ammonium persulfate) solution were added. Immediately after this addition, the slurry was poured into molds, and kept in a nitrogen atmosphere. Aluminum, glass and plastics were used as mold materials. After polymerization, gelcast bodies were dried in a controlled humidity chamber, and afterwards in an oven up to 110°C.

Thermogravimetric analyses of small size specimens of about 15 mg, taken from different parts of the alumina composites formed in different shapes, were performed using a Perkin Elmer TG7 Thermogravimetric Analyzer. The air flow was 25 cm^3 min^{-1} and the heating rate was 20°C min^{-1}.

Results and discussion

Reference curves

Figure 1a shows typical TG and DTG curves of a dried alumina slip containing only the dispersant. There is a total loss of 0.74 wt%. In the DTG curve, there are two main peaks, the first due to the loss of adsorbed water, and the second, which is broader, due to the Darvan-C dispersant decomposition. The continuous mass loss is due to the simultaneous structural water loss from the alumina substrate. Figure 1b shows typical TG and DTG curves of a dried AM+MBAM copolymer sample. As can be seen up to about 200°C, there is a 1.15% mass loss of residual water. At 230°C, a three-stage polymer burnout begins. The first stage, with many little DTG peaks up to 385°C, the second with a sharp peak at 405°C, and the last one with a broader peak between 500 and 670°C, due to the carbonaceous residue burnout, which ended at this temperature, with total mass loss.

Polymer quantitative and qualitative analysis by TG and DTG

In Fig. 2a are typical TG curves of samples taken from five different parts of a 80 mm diameter and 8 mm thick round plate gelcast composite: from three different top levels, from bulk and from the bottom surface. As can be seen, up to 250°C, the adsorbed water (W_s) is lost, corresponding to 0.41, 0.41 , 0.96, 0.96 and 1.11 wt% losses. The total respective final mass losses (T_1) are respectively, 1.35, 1.85,
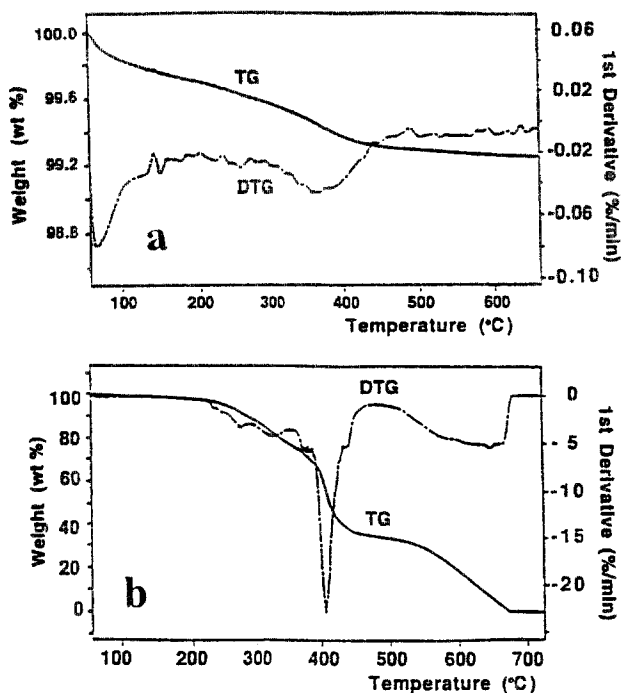
Fig. 1 Reference TG and DTG curves. a) Dried A-1000 alumina slip containing Darvan-C;
    b) AM+MBAM dried copolymer. Air flow=25 cm³ min⁻¹, heating rate=20°C min⁻¹

4.25, 5.20 and 5.30 wt%. From Fig. 1a, the total mass percent loss of the A-1000
plus Darvan-C sample is 0.74% and the adsorbed water loss represents 0.20% of
the initial weight. The polymer content (P_c) of the samples of Fig. 2 can be esti-
mated by $P_c=[(T_1-W_s)-(0.74-0.20)]$, and their values are respectively 0.40, 0.90,
2.75, 3.70 and 3.65 wt%.

The corresponding DTG curves are in Fig. 2b. The polymer decomposition can
be identified by the three burnout stages between 250 and 550°C, except for the two
first upper surface samples which show a totally different DTG curve behavior,
what probably indicates that the polymerization at the upper surface was inhibited.
These two composite samples show a thermal behavior similar to that of the sample
of alumina plus the organic dispersant Darvan C in Fig. 1a, but with a slightly
higher and increasing total mass loss, due probably to their AM and MBAM mono-
mer content and/or to some partial copolymerization.

Effect of operating conditions

By TG and DTG curves, effects of gelcast operating conditions on the polymer
distribution can be observed and optimized. Samples taken from gelcast composite
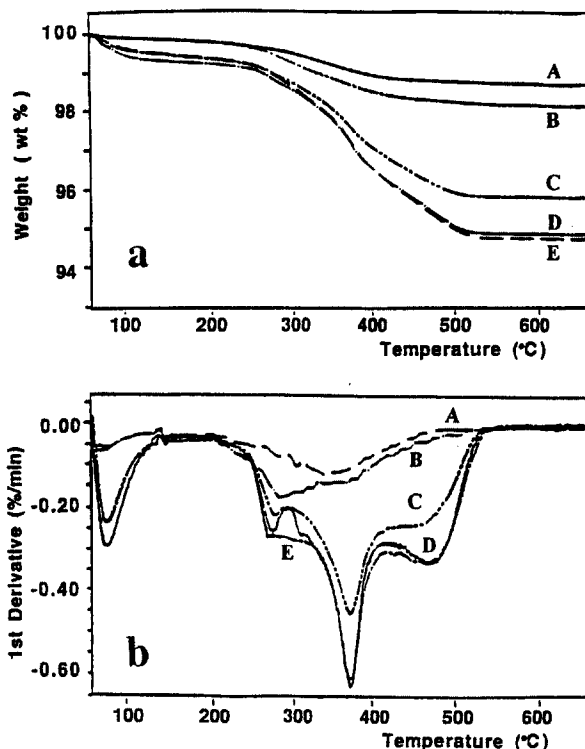plates obtained after faster drying steps show a significant unhomogeneity of poly-

Fig. 2 TG curves of different parts of a gelcast alumina composite plate (a); corresponding
DTG curves (b). Air flow=25 cm³ min⁻¹, heating rate=20°C min⁻¹, top samples: A
(up to 50 μm deep); B (up to 200 μm deep); C (up to 500 μm deep); D bulk sample;
E bottom sample (up to 50 μm deep).

mer content, with a higher polymer content at the bottom than at the bulk of the composites.

Gelcast composites obtained with insufficient initiator show significant polymer content gradients either in their upper or lower parts, but the bulk polymer content is practically the same than in case of well gelcast composites.

The effect of mold material was analyzed by lateral surface samples of the composites. While the metal and/or the glass mold do not interfere with the polymerization process, showing at the lateral surface the same polymer content than at bulk, the plastic mold inhibits the polymerization at the slip/plastic interface. It is important to note that even though, the bulk polymerization of plastic molded gelcast bodies is similar to the metal or glass molded ones.

Complementary processing

Different composites were obtained in the form of plates, cylinders and rods and other complex shapes. Polymer content distribution curves can be obtained from TG curve data, as shown in Fig. 3. TG curve results indicated that the pre-heating
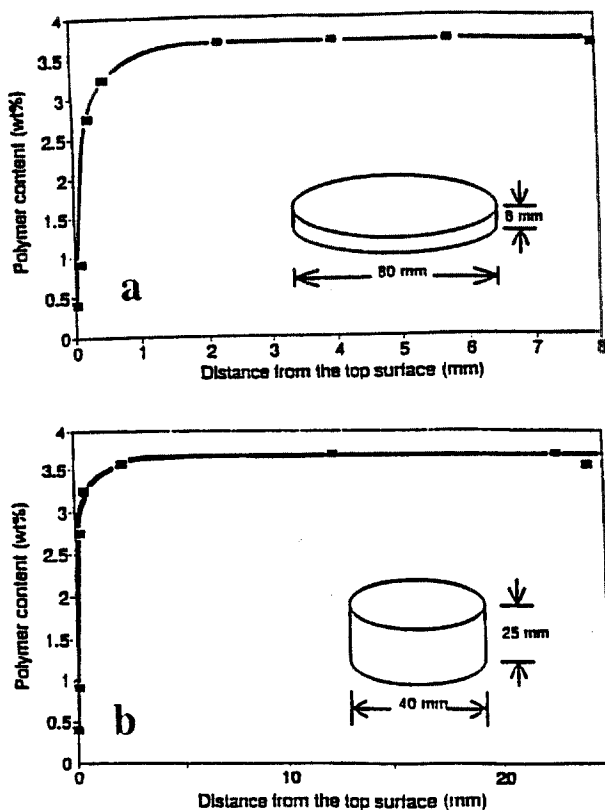
Fig. 3 Polymer content distribution curves of alumina gelcast composites: plate (a), cylinder (b)

step for the burnout of the dispersant and polymer of gelcast green bodies could be performed at 600°C. After sintering at 1600°C, the resulting alumina body densities were from 3.91 to 3.93 g cm^{-3}.

Conclusions

Quantitative analysis of the polymer content in gelcast alumina composites can be done by thermogravimetric analysis, and qualitative analysis by derivative thermogravimetry.

The polymer content of the external surfaces of gelcast composites depends on the material of the mold or on the ambient atmosphere.

All the composites show an even distribution of the polymer in the bulk, which enables machining in the green state and obtaining high density bodies after sintering.

From TG and DTG curve analysis the operating conditions for gelcasting and drying steps can be optimized, as well as for the polymer burnout step for ceramic processing.

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