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Short Communication

Flash sintering as a nucleation phenomenon and a model thereof

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Abstract

Isothermal field-assisted sintering of two-phase, 50 vol% 3YSZ-alumina composites exhibit an incubation time for the onset of the flash event. Weaker applied fields and lower temperatures lengthen the incubation period. The effect is highly non-linear. For example at 1300 °C and 150 V cm^{-1} the flash occurs nearly instantaneously (in 10 s), but extends to 2 h at 1275 °C and 65 V cm^{-1}. This behavior is reminiscent of nucleation and growth phenomena in chemically driven experiments involving phase transformations in the solid state. Here, a model for nucleation under electrical driving forces, based upon the growth of embryos of colossal permittivity is presented. Nucleation is the precursor to the onset of a flash. Therefore it occurs at the furnace temperature. Joule heating is a consequence of nucleation not the cause of it.

Keywords: Flash sintering; Incubation time; Nucleation and growth

1. Introduction

Flash sintering is emerging as a distinct mechanism in field assisted sintering of ceramics. The "flash" is initiated above a threshold applied field at a given temperature, while the extent of densification is controlled by the limit on the current density placed at the power supply.[1] The method has been applied to several oxides,[2–8] SOFCs[9,10] as well as to non-oxides.[11] The effect can be induced by both DC as well as AC electric fields.[12] Among the various mechanisms proposed in the literature, Joule heating remains of the greatest interest,[13,14] although the temperatures required for nearly instantaneous sintering are far above what can be reasonably well predicted in this way.

The other suggestion has been to say that a defect avalanche in the form of Frenkel pairs is precipitated which ionize into charge neutral defects and electron–hole pairs. The defects enhance diffusion while the e–h pairs induce high conductivity and photoemission.[15] While, this suggestion does explain why diffusion and conductivity are simultaneously enhanced, a quantitative understanding of how it can happen remains obscure. Some support for the defect induced mechanism is found in residual effects of the flash on defect concentrations in MgO-doped alumina[4] and in yttria stabilized zirconia.[16]

If indeed flash sintering is instigated by the "nucleation" of defects, then it should be accompanied by an incubation time in experiments carried out at isothermal furnace temperatures. Here we report these results, and show that they are related very non-linearly to the applied field. Tentatively, a model for the nucleation of dipole clusters, of abnormally large permittivity, is developed and analyzed to explain these results. Nucleation is a precursor to the onset of the conduction non-linearity, and, therefore, occurs at the furnace temperature. Joule heating is a result of and therefore is subsequent to nucleation.

2. Experiments

The samples were prepared from commercially available tetragonal zirconia (3 mol% yttria stabilized zirconia – 3YSZ) powder (TZ-3YS-E grade; Tosoh Corp., Shunan, Japan) with a particle size of 600 nm. The high purity α-alumina powder (purity >99.99%), was obtained from Taimicron TMDAR, Taimei Chemical Co., Ltd., Tokyo, Japan, and had a particle size of 100 nm. Two phase composites constituted from equal volume fractions (50/50) of 3YSZ and alumina composite was

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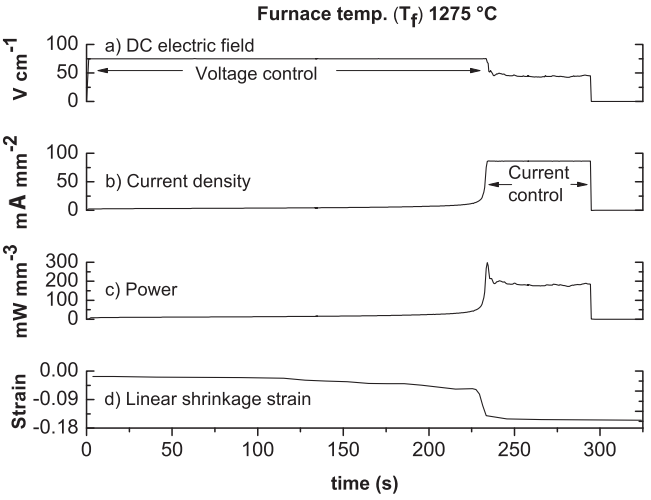

Fig. 1. Isothermal flash sintering verses time curves for (a) DC electric field, (b) current density, (c) power and (d) linear shrinkage strain at 1275 °C for 75 V cm^{-1}.

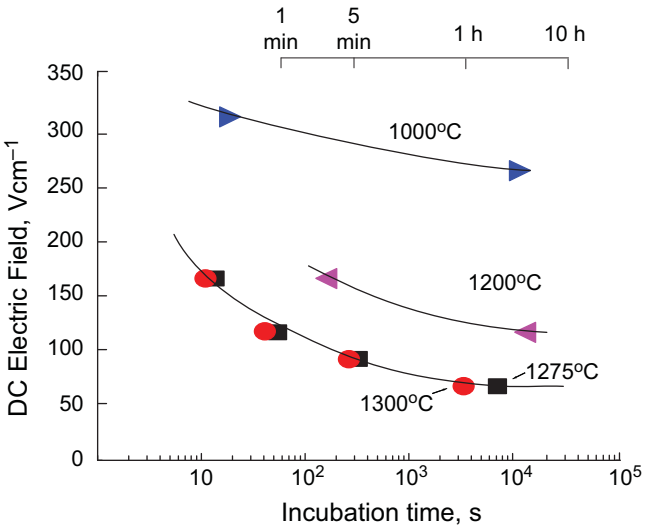

Fig. 2. A semi-log plot of the influence of the electric field on the incubation time at 1000 °C, 1200 °C, 1275 °C and 1300 °C.

prepared by following the procedure reported in Ref. 17. Briefly, the 3YSZ and alumina powders were stirred into distilled water, dried and mixed with 3 wt% binder (B-1000, Duramax, Dow Chemical, USA). The powder was then pressed into dog bone shape pellets with gauge length of 21 mm and cross section of 1.8 mm × 3.3 mm.

The experimental setup for the two-electrode field assisted experiments is described in Ref. 17 The samples were hung into a tubular furnace with two platinum wires, which also served as the electrodes. The furnace was first pre-heated at 600 °C for 60 min to burn-off the binder. Thereafter, the furnace was heated at a rate of 10 °C/min up to the required temperature, and then held at this temperature for isothermal experiments. Experiments were performed at four temperatures, 1000 °C, 1200 °C, 1275 °C and 1300 °C. The DC electric field was applied after holding the specimen at temperature for 30 min. The onset of the flash (after an incubation time) was accompanied by a non-linear increase in conductivity, which was controlled by switching the power supply from voltage to current control.[17] Thereafter, the constant current condition was maintained for 60 s, before the power supply was switched off.

The shrinkage in the specimen was measured from photographs taken with a CCD camera at a rate of once every minute before, and at 1 s intervals after the onset of the flash. The specimen temperature, in the flash state, was estimated from a black body radiation model as discussed in detail in Ref. 17. The model requires values of the emissivity which were assumed to lie in the range 0.72–0.9 drawing upon the work on thermal barrier coatings made from yttria stabilized zirconia.

The specimens were cut along the cross section, polished and thermally etched at 1350 °C for 30 min. The micrographs at five different randomly selected places were taken with a SEM (JSM5500, JEOL). The grain size of alumina and zirconia was determined by linear intercept method, with correction factor of 1.56.[18,19]

A typical specimen response to the applied electric field is given in Fig. 1. In this experiment the furnace temperature was set to 1275 °C, the sample was held at this temperature for 30 min, at which point an electric field of 75 V cm^{-1} was applied. The time shown in Fig. 1 is from the moment of the application of the field. After an incubation time of 234 s specimen shows the abrupt rise in shrinkage and conductivity. The power supply is then switched to current control with the limit set to 85 mA mm^{-2}. The flash condition was maintained for 60 s in current control at which point the field was switched off. The power density, equal to the product of the field and the current density, quickly rises to a peak, and then declines as the conductivity of the specimen continues to increase, eventually settling to a steady state, at a field of 50 V cm^{-1}.

The purpose of these experiments was to measure the change in the incubation time for the onset of the flash as a function of the electric field and the furnace temperature. These results are reported in Fig. 2. At a given temperature the incubation time lengthens non-linearly, even on a logarithmic time scale, as the applied field is decreased, suggesting that the electric field serves as the driving force for the nucleation event. As the temperature is lowered, a higher field is required to instill the flash.

The incubation time is related to the growth of an embryo to the critical size, which grows gradually by diffusion. A smaller electric field increases the critical size which lengthens the incubation time. On the other hand a lower temperature requires more time because diffusion is slower.

The microstructures obtained in these experiments were the same as obtained in constant heating rate experiments as described in Ref. 17. The size of alumina and zirconia grains was measured for experiments carried out at furnace temperature of 1275 °C under different levels of applied field. A typical microstructure taken from 100 V cm^{-1} is shown in Fig. 3. The grain sizes for alumina and zirconia grains at 50 V cm^{-1}, were 693 ± 69 nm, and 684 ± 59 nm. At 73 V cm^{-1} they were 671 ± 62 nm and 612 ± 10 nm respectively. At 100 V cm^{-1}, 758 ± 118 and 645 ± 40 nm, and at 150 V cm^{-1}, 727 ± 151 and 675 ± 68 nm respectively for alumina and zirconia grains. The specimen temperatures estimated from black body