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Feature article

Photoemission during flash sintering: An interpretation based on thermal radiation

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ABSTRACT

Optical emission spectra were recorded in the range 180–1700 nm during flash sintering of alumina and magnesia silicate glass-containing alumina. The collected spectra, corrected for taking care of instrumental effects, are consistent with thermal radiation effect. A partial exception is represented by the lower density samples treated with low current density, whose spectrum shows very small deviation from the expected thermal radiation at ~680 nm although the corresponding physical phenomenon remains unclear. In any case, the overall photoemission upon flash sintering can be substantially associated with Joule heating, in all tested conditions, with no effect of any other previously reported mechanism like electroluminescence.

1. Introduction

The reduction of fossil fuels consumption and CO_2 emission is one of the main concerns for the research activity of the present century. Many projects are therefore focused on the development of green and environmental-friendly processing technologies. In particular, in the ceramics field, electrical field assisted sintering techniques have been recently proposed, they allowing significant reduction of sintering time and temperature. Among them, particular interest has been risen in the last few years by Flash Sintering (FS), such powder consolidation technology enabling to reduce the temperature needed for densification by several hundred degrees with respect to conventional processes [1,2]. In addition, densification occurs in just few seconds [2] while typical sintering usually requires some hours. Another important issue regards the possibility of using flash sintering on materials with very different electrical behavior, from semiconductors [3] to insulators [4–6] or protonic [7,8], ionic [1,2,9–14] and electronic conductors [15,16] or even to composites[17].

For these reasons, the scientific interest on FS has rapidly increased and a certain number of works starts to try understanding the physical bases of the process. Recently, Todd[18], Zhang [19] and co-workers proposed a model for explaining the incubation of FS as a result of thermal runaway. Nevertheless, such works do not explain which mechanism is leading to densification [18]. As for this point, different hypotheses have been advanced, involving Joule heating [11], formation of Frenkel pairs [4], local overheating at the grain boundaries [4] or interaction between electrical field and space charge region [4].

Usually, FS phenomenon can be divided into three main stages. The first is the process incubation, during which the system works under voltage control and the current slowly increases. The second stage is characterized by an abrupt drop in material resistivity and the current density increases in an uncontrolled way. At this point a power peak is reached and the system is typically turned from voltage to current control in order to avoid the damage of the electric set-up and of the sample. The reasons behind such uncontrolled electrical conductivity increase are not completely clear, yet. Some works in the scientific literature show a good agreement between the measured conductivity and the conductivity evolution expected from temperature/density measurement [11]; other authors pointed out that during the flash the conduction cannot be explained by the typical mechanisms associated with the electrical properties of materials [5,20,21]. The third and final FS stage (also known as steady stage) starts when the electric field is stabilized. During such stage the applied current is equal to the current limit of the system. The material densification occurs during the second and the third stage of the process. Densification and resistivity decrease

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are accompanied by other peculiar phenomena and, in particular, by bright emission of visible light [22–24]. The concomitant presence of these three phenomena allows to define the flash sintering process. Therefore, light emission represents an intrinsic footprint of FS.

Photoemission has always appeared quite unusual and interesting, and it has been studied in order to achieve further indications about the mechanisms involved during the whole process and, especially, on those promoting densification. Emission spectra have been recorded on YSZ by Lebrun [22] and Terauds et al. [23] in the visible and IR range. Also Naik et al. have performed similar measurements during potassium niobate and strontium titanate FS experiments [24], reporting a correlation between light emission intensity and sintering rates. All these authors concluded that the measured spectra show features far different from the black body radiation and explained the observed photoemission in terms of electroluminescence, as a result of the recombination between electrons and holes in the ceramic lattice [22]. Such phenomenona were tentatively attributed to a secondary effect of Frenkel pairs nucleation during the flash process [23]: it was suggested that vacancies and interstitials ionize in neutral defects promoting the formation of free electrons and holes, whose recombination causes electroluminescence. In the meantime, uncharged vacancy/interstitial pairs move under the effect of sintering potential, this generating rapid densification[25].

In 2015, McLaren et al. reproduced the flash event in bulk alkali silicate glasses. In such materials the flash event is associated to an unexpected drop in glass viscosity and, for this reason, it was named Electric Field Induced Softening (EFIS) [26]. Also in this case a strong bright light emission takes place during the process although it shows effects partially different with respect to crystalline ceramics. Such differences are mainly associated to the fact that photoemission in glasses is characterized by very sharp peaks in the visible region. Yu et al., in a recent review on FS, argued that such peaks could be related to the oxidation-ionization of alkali metals (Li and Na), which causes photoemission peaks [27].

In the present work, we analyze the flash sintering behavior of two very common ceramics: nearly pure α-alumina and magnesia silicate glass-containing alumina. Such materials have already been successfully densified by FS and corresponding structural evolution has been deeply analyzed as a function of the main process parameters [5,6,28]. Here, we study the photoemission phenomena during FS in the UV/visible and NIR range with the aim to understand the mechanisms responsible for the observed optical phenomena further. The two materials were chosen in order to point out possible luminescent effects occurring in fully crystalline material and in glass-containing ceramic.

2. Experimental procedures

α-alumina (Almatis CT3000SG) and magnesia silicate glass were used to produce dog bone-like samples by uniaxial pressing (maximum pressure = 120 MPa), using distilled water as binder (~5 wt%). The glass was obtained from TEOS and magnesium nitrate as precursor of silica and magnesia, respectively (as described in Ref. [28]). The nominal composition of the glass-containing alumina samples was 90 wt% alumina, 8 wt% silica and 2 wt% magnesia and they were obtained mixing α-alumina and glass (10 wt%) in isopropanol before uniaxial pressing. The gage section of the dog bone samples was 3 mm × 2.5 ± 0.3 mm. Other details regarding the samples geometry are reported in a previous work [29].

Pure alumina green specimens were pre-sintered for 2 h in a muffle furnace (Nabertherm) under static air atmosphere at 1250 and 1450 °C. Glass-containing samples were pre-sintered at 950 °C for 15 min. Heating rate of 10 °C/min and free cooling within the furnace were used in both cases.

The relative density was measured by the Archimedes' method, using an analytical balance (Gibertini, sensitivity ± 0.0001 g). The grain size of pre-sintered sample was determined as an average of 12 measurements, which were carried out on SEM (JEOL, JSM 5500) micrographs using the linear intercept method [30].

After pre-sintering, the specimens were connected to a DC power supply (Glassman, 5 kV–120 mA) and to a multimeter (Keithley, 2100) by two platinum wires, which were forced within the holes realized on the opposite sides of the dog-bone sample. The samples were hung within a tubular furnace (Nabertherm P330) kept at constant temperature of 1200 °C. The temperature was also continuously checked by an S-thermocouple placed close to the sample to guarantee that it was always between 1195 and 1205 °C. Seven minutes after the sample was placed into the furnace, the power supply was switched on to promote the flash sintering of the specimen. For this purpose an electrical field (E-field) in the range 750–1000 V/cm was applied and the current limit was fixed at 4 mA/mm^2. Some specimens were also treated with different current limit (2 and 6 mA/mm^2) for comparison.

The optical emission during FS in the UV/VIS region was measured using the spectrometer USB4000 and the software "Ocean Optic Spectra Suite". The spectrometer was connected to a silica optical fiber, placed near the furnace tube in front of the sample. The background emission of the system (furnace + sample at 1200 °C) was initially recorded and subtracted from the spectra. Some spectra were also collected after the power supply was switched off to analyze the optical emission fading. The integration time was set to 3.8 ms and the mean of 5 collected successive spectra was considered. The optical response of the overall system as a function of wavelength was properly corrected: the spectrum generated by a calibration lamp (Avantes, HD2000) was recorded and the conversion factor was calculated as the ratio between the real emission from the lamp and the light yield measured from the spectrometer. This allowed therefore to calculate the real photoemission as the product of the conversion factor and the measured intensity at each wavelength.

Similar experimental set up and procedures were used for the measurement of photoemission in the NIR. In this case, an Ocean Optics NIR 512 spectrometer was used and the integration time was set to 10 ms. No spectral correction was performed for this spectrometer.

3. Results and discussion

The bulk density of alumina samples pre-sintered at 1250 °C is 2.73 g/cm^3 (relative density = 69%). The estimated average grain size is 0.37 μm. Samples treated at 1450 °C exhibit density of 3.71 g/cm^3 (relative density = 94%) and grain size equal to 0.49 μm. Glass-containing alumina specimens are characterized by bulk density of 1.81 g/cm^3 after the pre-sintering treatment at 950 °C.

The as-recorded optical emission spectra collected in the visible range during the third stage of FS on pure alumina samples pre-sintered at 1250 °C are shown in Fig. 1. The light yield increases with the current limit, although the shape of the spectrum does not change. Quite surprisingly, the spectra obtained here very well compare with those shown in previous works on completely different materials, like YSZ and titanate/niobate, using similar experimental set up [22,24]. In particular, a shoulder around 620 nm and two maxima around 720 and 760 nm appear in all spectra. This first result seems to indicate that the emission in the 180–880 nm range does not depend upon the tested material and its composition.

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