Scripta Materialia 150 (2018) 82–86

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular article

Current-induced abnormal and oriented grain growth in corundum upon flash sintering

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ARTICLE INFO

Article history:
Received 17 January 2018
Received in revised form 1 March 2018
Accepted 3 March 2018
Available online xxxx

Keywords:
Flash sintering
Alumina
Grain growth
E-field
F-centers

ABSTRACT

An electrical current upon flash sintering experiments modifies the defect chemistry of corundum and causes the formation of color centers (F-centers), consisting of discharged oxygen vacancies. This phenomenon interacts with the diffusion kinetics in the anodic region and promotes abnormal growth of some grains which reach several hundreds of micrometers in just few minutes, the grains being strongly oriented orthogonally to the current flow.

Flash Sintering (FS) is an innovative consolidation technology which has been successfully applied to different classes of ceramics [1–8].The peculiar characteristic of flash sintering is the presence of the so called "flash event", characterized by rapid densification [9], electrical resistivity drop [2,9] and photoemission [10,11]. During the flash event, the ceramic undergoes to a sort of transition from insulator to semiconductor-like behavior, the power source being switched from voltage to current control to stabilize the system. The process is typically divided into three stages: stage I or incubation (under voltage control), stage II or flash event (transition from voltage to current control) and stage III or steady stage (under current control).

Although the flash event trigger has been proven to reside in a thermal runaway of Joule heating [12,13], it is still not clear whether Joule heating by itself can explain rapid densification, photoemission and electrical resistivity drop. Some authors suggested that such effects are simply related to a rapid heating process [11,14,15] while others proposed that they are related to the nucleation and ionization of Frenkel disorder [10,16]; in other works, the formation of percolative transient liquid film on particles surface has been suggested [17,18].

In any case, it is clear that during stage III the material undergoes to a partial transformation associated to reducing conditions created by the DC current application. Such partial reduction in the flash state was reported by Downs, who pointed out the formation of a blackened region in the cathodic area of YSZ specimens [19]. Kim et al. showed that, when YSZ samples are subjected to an electric current for a relatively long time ($t > 100$ min), the cathodic region is characterized by abnormal grain growth [20], thus suggesting an interaction between mass transport and the partial reduction. More in detail, they observed an activation energy decrease for grain coarsening in the cathodic region and this was attributed to lower migration energy for cations diffusion accounted for by the partial reduction. Such results have been more recently validated by Qui et al. who pointed out that abnormal grains are formed in YSZ during flash experiments although the dwell time in the flash state was lower than 1 min [21]. The correlation between partial reduction and enhanced grain boundary mobility has been also confirmed by grain growth rate measurements on ceramics with fluorite structures, like YSZ and GDC, in reducing atmosphere [22].

The aim of the present work is to investigate whether similar phenomena can be observed also in highly stoichiometric oxide like α-alumina.

Commercially available alumina powder (Almatis, CT3000SG, 99.8% pure) was shaped in dog bone-like specimens by uniaxial pressing at ~120 MPa using ~5 wt% distilled water as binder. Details of the sample geometry is reported in [19]. The green specimens were pre-sintered in air at 1250 °C for 2 h (heating rate = 10 °C/min). Two platinum wires were forced within the holes present on the opposite side of the pre-sintered specimen and were used as electrodes. They were connected to a DC power supply (Glassman EW series 5 kV–120 mA) and to a multimeter (Keithley 2100). Then, the sample was introduced in a pre-heated tubular furnace (Nabertherm P3300) at 1200 °C and kept there for 3 min to homogenize the temperature. The power supply was turned on to apply 1000 V/cm and in few seconds the system switched from voltage to current control. Current limits in the range

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https://doi.org/10.1016/j.scriptamat.2018.03.004
1359-6462/

2–6 mA/mm^2 were used and the current was let to flow through the ceramic for 2–4 min.

Microstructural analysis was carried by SEM (Jeol JSM 5500) and OM (Zeiss). SEM micrographs were taken on the free surfaces of the as-sintered specimens and after careful polishing with SiC papers and thermal etching at 1200 °C for 2 h. The grain size was evaluated by the linear intercept method [23].

The sintered samples were studied by photoluminescence spectroscopy by the Jasco FP6300 (150 W Xe lamp) instrument using an excitation radiation of 300 nm; the light emitted from the sample was recorded in the range 320–500 nm. All spectra were collected with a bandwidth of 5 nm.

Fig. 1 shows the blackening effect in flash sintered alumina specimens: the effect is particularly evident when high current and larger times are used. The phenomenon starts from the positive electrode (+) and grows toward the negative one. This behavior is substantially different from previous results on YSZ, where the blackening develops starting from the cathodic region (−) [19,24]. The origin of the different behavior is not completely clear but it could be associated to the limited mobility of oxygen vacancies in corundum. A strong ionic current is sustained during the FS process in YSZ; positively charged oxygen vacancies ($VO^{\cdot\cdot}$) move toward the cathode (−) where they are consumed according to the reaction

$$VO^{\cdot\cdot} + 1/2\ O_{2(g)} + 2e' \rightarrow O_O^x \quad (1)$$

Alternatively, they can trap electrons provided through the metallic electrode and be discharged:

$$VO^{\cdot\cdot} + 2e' \rightarrow VO^{\cdot} + e' \rightarrow VO^x, \quad (2)$$

thus reducing the oxidation state of the surrounding cations and causing partial reduction and electrochemical blackening. The initial oxygen vacancies population is much smaller in corundum than in YSZ and their mobility is extremely limited, only very few vacancies being able to reach the cathodic region. On the other hand, the anode acts as a sort of oxygen vacancy source [24] forcing the reaction in Eq. (1) toward the left. Such vacancies can trap the electrons moving in the conduction band and be discharged.

The formation of discharged oxygen vacancies upon FS is confirmed by the photoluminescence spectra reported in Fig. 2. A broad peak is centered around 410–420 nm and its intensity increases with the applied current. The emission in corundum at such wavelength is associated to the well-known F-centers [25–27] which consist in oxygen vacancies filled with two electrons, i.e. zero-charge defects. Therefore, photoluminescence analysis points out that the current flow upon the flash process changes the material defect chemistry. This can interact with densification, which is based on atomic diffusion, but also with charge transport. In fact, oxygen vacancies acts as electrons donors [28] increasing n-type conductivity. The larger conductivity generated in the blackened regions causes a local current concentration and subsequent blackening propagation.

Remarkably, the blackened regions are characterized by a very singular microstructure. Fig. 3 shows a localized melted path in such areas but, more interestingly, abnormal grain growth takes place, grains much larger than 100 μm being formed in just 4 min. One can also observe that a sharp transition region between abnormal and normal grain growth occurs at the interface between the blackened and the white regions. Such sharp transition is unlikely to be due to local differences in sample temperature, the associated thermal gradient being unreasonable (several hundreds of degrees in few microns). Therefore, this suggests that the defect chemistry local modification due to the current concentration in the blackened regions enhances the diffusion kinetics by athermal effects. It is worth to point out that the abnormal grains growth is not a result of a localized solidification process, their shape being not compatible with dendritic, columnar or equiaxial structures [29].

A detailed observation of the microstructures in Fig. 3 reveals that the abnormally grown grains are oriented orthogonally to the electrochemical blackening propagation direction, i.e. orthogonally to the current flow. Grain size in the range 153–210 μm was measured in the direction orthogonal to the current, it being 41–57 μm in the other (aspect ratio of about ~3.7).

To prove that such grains coarsening cannot be attributed merely to Joule heating, one can estimate the sample temperature needed to justify the observed grain growth in 4 min (holding time in the flash state) in a conventional process by using the coarsening rate relationship in ref. [30] for the alumina powder used here. The results indicate that temperature of about 2600 °C are required for obtaining grains of 210

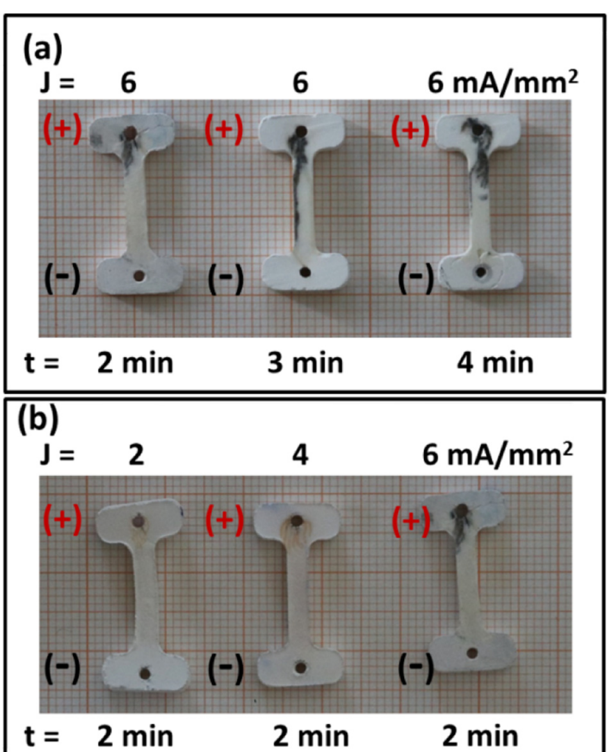

Fig. 1. Electrochemical blackening in corundum subjected to flash process for different dwell times (a) and current limits (b).

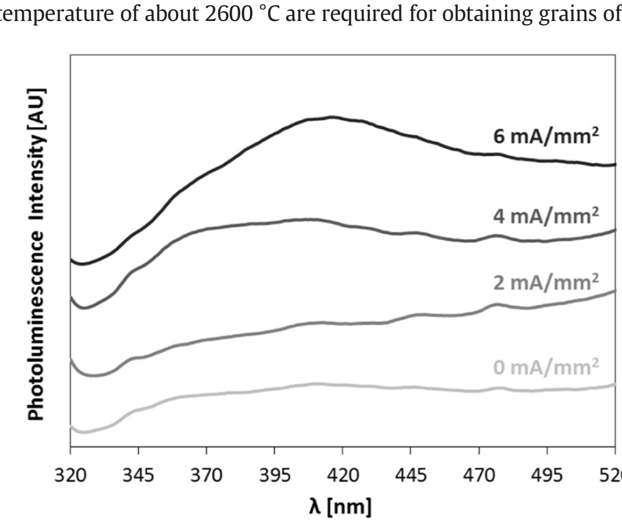

Fig. 2. Photoluminescence emission spectra recorded on flash sintered alumina samples using different current limit and 2 min holding time in the flash state. The sample identified as "0 mA/mm^2" was conventionally sintered at 1550 °C for 2 h. Excitation wavelength = 300 nm.