Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Original Article

Phenomenological understanding of flash sintering in $MnCo_2O_4$

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ARTICLE INFO

Keywords:
Flash sintering
$MnCo_2O_4$
Phase stability
Micro-Raman spectroscopy
Activation mechanism

ABSTRACT

The dual role of electric field in the flash sintering process of conducting $MnCo_2O_4$ is demonstrated. The flash and conventionally sintered $MnCo_2O_4$ samples produced at different temperatures are characterized using energy dispersive X-ray and micro-Raman spectroscopy to elucidate the micro-level spatial distribution of evolved phases. Raman signal mapping over the two ways sintered samples exposes differently grown areas of cobalt oxide based secondary phase. Electrical conductivity of conventionally sintered sample is recorded as a function of temperature and E-field and is utilized to discover the charge carrier activation mechanism during the flash effect. The conductivity before the flash-onset is shown to be comparable to that occurs by Poole-Frenkel effect and Phonon-assisted tunneling i.e. by the mechanism that occurs before the dielectric breakdown of semiconductors and insulators. The observed results, finally, confirm that catalyst like drift action of E-field on cobalt oxide formation is responsible for enhancement in the flash-sintering.

1. Introduction

In the family of electric field assisted sintering techniques, flash sintering method has a unique identity due to the utilization of 'moderate' electric field and current density that sinters the powder compact in a very short time. The essential electric field and electric current for driving the sintering is substantially lower (and thus more practical) compared to those used in the field based electric discharge compaction (EDC) and the current based spark plasma sintering (SPS) respectively which are other electrical effect based fast sintering techniques [1,2]. This new and 'almost' transient process, thus, has become popular in the field of ceramic processing with the name of 'flash' sintering. In this sintering event, the material on a critical combination of electric field and furnace temperature undergoes rapid increase in the conductivity and the specimen temperature which draws the physical shrinkage of the specimen in few seconds [3]. Such conductivity based sintering occurs for the materials having negative coefficient of resistance. The two intermediate processes, the rise of the conductivity and the specimen temperature in this paper will be collectively termed as flash effect.

There are some unique features of this flash sintering effect: in comparison to breakdown field of typical semiconductors, a fairly low value of electric field is applied in the flash effect that leads to electrical and thermal runway kinds of effect. For example, good conducting $MnCo_2O_4$ and (La, Sr)(Co, Fe)O_3 [4,5] can undergo the flash effect under 10–15 V cm^{-1} (100–200 °C), weakly conducting Y_2O_3 stabilized ZrO_2 (YSZ) [6], Gd doped CeO_2 [7] etc and insulating Al_2O_3 [8,9], $BiFeO_3$ [10], $MgAl_2O_4$ [11] etc demand 100–200 V cm^{-1} (700–800 °C) and 1–2 kV cm^{-1} (1100–1200 °C) respectively. These values are very low compared to the electric breakdown fields of tens of kV cm^{-1} for typical semiconductors and dielectrics such as silicon, germanium [12], barium titanate [13]. It is, however, not established that the flash effect is typical electrical breakdown like phenomenon. Recently, Mattia et al has compared the flash effect with the electrical breakdown of alumina and shown that the conductivity of alumina at high temperature shows dependence on electric field described by Poole Frenkel effect (PFE) [9]. This effect describes the conductivity of the insulating materials at high electric fields before the electrical breakdown event [14]. Zafar et al also has shown that a relatively conducting (La, Sr)FeO_3 experiences the non-linear rise in the conductivity following PFE [15]. No literature, however, is available on the electrical breakdown kind of effects on conducting materials. On the other hand, Todd et al has reported that the conduction in 3YSZ under the electric field before (and after) the flash event follow the its usual mechanism that is described by Arrhenius relation of type, $\rho = \rho_0 \exp(Q/kT)$ [16,17]. Dong et al has reported that the flash onset temperature can be predicted solely by considering the Joule heating in the sample. Under the electric field, the developed electrical power dissipation has been decoded as the specimen temperature with the help of heat capacity data [18,19]. Likewise, many groups working in the flash sintering area believe that it is the Joule heating after the breakdown like increase in conductivity that drives the cationic diffusion and the physical shrinkage [7,20]. Further,

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https://doi.org/10.1016/j.jeurceramsoc.2018.06.006
Received 3 March 2018; Received in revised form 31 May 2018; Accepted 3 June 2018

as another distinctive feature, the degree of sintering in the flash process is reported to be enhanced compared to that in the conventional method [4,5]. For the enhanced sintering results, the predictions are extended to electric field drift effects on ionic diffusion [16], additional defects formation [8] etc. Raj et al suggested the formation of lattice defects, such as Frankel pair, during flash sintering of YSZ as the cause of sintering enhancement wherein the electrons will justify for the high conductivity and the ions for the sintering [8]. Narayana observed large number of dislocations and grain boundaries in the transmission electron microscopy study of high electric field treated Ni doped MgO [21]. He suggested that these defects which form additionally under the influence of an electric field play crucial role in the cationic diffusion and sintering. In addition to these, some of the works relies on the belief that the temperature local to the specimen is significantly higher than that is used during conventional process. However, there is no experimental demonstration that confirms the validity of such a higher inner temperature that can lead to sintering in few seconds. Also, formation of a second phase during the sintering process of $MnCo_2O_4$, $SrTiO_3$ [22] and YSZ is also underlined as playing a critical role in the growth of the sintered microstructure. The phenomenological understanding of the flash effect is diverse for different materials and there is a search of unified mechanism that can broadly be accepted for the flash sintering effect. Moreover, the role of the electric field for the sintering process remained explicitly un-discussed.

In a previous work, the electric field assisted flash sintering of $MnCo_2O_4$ under different electric fields is reported where on the basis of the local temperature a correlation between the microstructure and phase stability characterization results is highlighted [4]. The microstructure was found to be significantly grown after 1080 °C where $MnCo_2O_4$ starts reducing into pure cobalt oxide. The secondary phase formation is considered as having the deriving role in the flash sintering process. However, no direct experimental evidence was pointed out about the role of electric field for controlling the sintering or diffusion process. In the present work, two different roles of the electric field occurring at different stages of the flash sintering effect are discussed. The secondary phase formation analysis is extended to uncover the differences in the area distribution of the phases in the flash and conventionally sintered samples employing energy dispersive x-ray and micro-Raman spectroscopy. Other side, from the current-voltage characteristics and the systematic changes in these with respect to furnace temperature it was suggested that its inherent polarons of $MnCo_2O_4$ which are activated during the rapid conductivity increase by the electric field caused flash effect. The electrical characteristics are utilized in the present work to find out the charge carrier activation mechanism which is shown to rely majorly on the electric field. On these bases, the flash sintering mechanism proposed in Ref [4] is revised in the 'Discussion' section.

2. Materials and method

Commercial $MnCo_2O_4$ powder with average particle size ~1.17 μm and surface area = 4.22 g cm^{-2}) is used in the present work. Flash sintering is performed on dog bon shaped pellets (gauge section: 20 × 3.0 × (1.65 ± 0.05) mm^3) by applying a constant electric field (10.0–17.5 V cm^{-1}) across the sample while being heated with a constant rate (5 °C min^{-1}) in a furnace. Details of the flash sintering experimental set up and sample fabrication/arrangement are mentioned in a previous work [4]. In the electrical circuitry, a fixed maximum current density (1.4–1.6 A mm^{-2}) was set in the power supply in order to avoid excessive heating during electrical runway. At the maximum current point, power supply turns from constant voltage mode to constant current mode. A 60 s hold at the specified maximum currents was considered as the period of flash sintering. Local temperature during the flash sintering event is recorded using pyrometer (Ultimax Infrared Thermometer, UX-20/600–3000 °C), which was calibrated up to 1100 °C prior to the measurement. $MnCo_2O_4$ pellets were also sintered in conventional manner heated with a rate of 5 °Cmin^{-1} up to the similar temperatures and time that were used in the flash process. Morphology and elemental composition of the produced samples is obtained with scanning electron microscopy (Model Jeol JSM 5500 SEM) coupled with energy dispersive x-ray spectroscopy (EDXS) respectively. Micro-Raman spectroscopy (Model Witech alpha 200, Germany made) is employed to investigate the structural information. Raman imaging is also performed with Witech alpha 200 by mapping a specific Raman shift of the phase of interest. In the Raman microscopy/spectroscopy experimental setup a 532 nm Nd-YAG laser is fiber coupled to a microscope, a 100X objective with an approximate spot size of 680 nm is used to focus on to the sample. A maximum laser power of 40 mW is applied for Raman spectroscopy and imaging experiments. Raman signal is collected in back scattering mode and the scattered signal is send to CCD based spectrograph through 600 grooves/mm grating. 100/125 μm optical fiber is used for fiber coupling from microscope to spectrograph. Spectral range of 120 nm equivalent to 3000 cm^{-1} is selected for micro-Raman and Raman imaging experiments. To find out the activation mechanism, current voltage characteristics were recorded on 1300 °C-sintered specimen in a similar to flash sintering experimental set up at furnace temperatures of 200–700 °C in the steps of 100 °C. The electric field was increased with a constant rate of ~ 8 mV cm^{-1} s^{-1} up to approximately 7.0 V cm^{-1}. Different features of recorded current-voltage characteristics are discussed in our previous report [4].

3. Results

3.1. Flash sintering of $MnCo_2O_4$

A typical sharp rise in power dissipation of a specimen as function of furnace temperature is demonstrated in Fig. 1 for $MnCo_2O_4$ subjected to

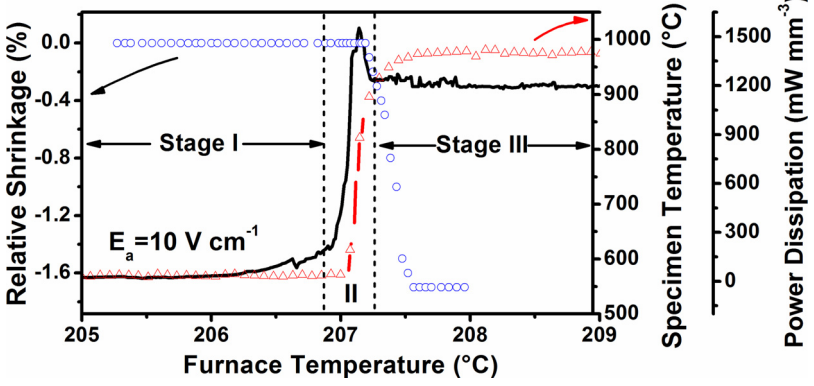

Fig. 1. Power dissipation, specimen temperature and shrinkage of $MnCo_2O_4$ under 10 V cm^{-1} as a function of furnace temperature.