Available online at www.sciencedirect.com

SciVerse ScienceDirect

Scripta Materialia 68 (2013) 785–788

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

Grain growth model for electric field-assisted processing and flash sintering of materials

J. Narayan*

Department of Materials Science and Engineering, North Carolina State University, Centennial Campus, EB-1, Raleigh, NC 27695-7907, USA

Received 30 December 2012; accepted 4 January 2013
Available online 17 January 2013

This paper proposes a model to explain interesting features of grain growth retardation and saturation during electric field-assisted processing and flash sintering of materials. It is argued that electric field-induced defect generation and segregation of these defects at dislocations and grain boundaries can retard the grain growth rate and reduce it to zero as a result of grain boundary melting under flash sintering. Grain growth rates are derived taking into account kinetic and various thermodynamic factors under an applied field and compared with other models.

Keywords: Grain growth model; Electric field-assisted processing of materials; Flash sintering; Field-assisted defect generation; Defect generation and segregation

Electric fields, both DC and AC, have been shown to affect ionic conduction and diffusion transport in ceramics in a significant way [1–4]. In the late 1970s and early 1980s Narayan and co-workers at the Oak Ridge National Laboratory (ORNL) [1–4] studied extensively the characteristics of electrical conductivity in pure (ORNL) and impurity-doped (Norton) MgO single crystals as a function of temperature and applied field, and analyzed the role of defects and impurity clusters in enhancing the electrical conductivity which led to an avalanche and thermal electric breakdown. These studies established the presence of high concentrations of intrinsic (anion and cation vacancies) defects and impurity precipitates in highly conductive regions between the electrodes after cooling. The enhancement of conductivity at high temperatures exhibited an avalanche effect, which, if uncontrolled by limiting the current flow, led to melting and eventually evaporation of materials between the electrodes. These results suggested a predominant role of vacancies and impurities in ionic conduction and diffusion transport.

At lower fields Conrad and co-workers found interesting effects on polycrystalline NaCl, MgO and yttria-stabilized zirconia materials related to grain growth retardation and reduction in flow stress and enhancement in ductility [5–8]. Applied electric (AC and DC) fields have been shown to produce a host of interesting phenomena related to sintering of solid-state materials [9–12]. More recently work by Raj and co-workers [13–15] has shown that the application of DC electric fields in the intermediate range of about 100 V cm^{-1} produced sintering of polycrystalline yttria-stabilized zirconia in mere seconds at furnace temperatures well below 1000 °C, the normal sintering temperature. These sintered samples did not exhibit grain growth. In a recent paper [16], I proposed a unified mechanism to explain the critical elements of field-assisted phenomena ranging from reducing the flow stress to lowering the overall effective sintering temperatures of materials and obtaining dense materials close to the theoretical density. It was argued that intrinsic and extrinsic defect segregation play a critical role and it was shown that while Joule heating cannot explain the anomalously high sintering rates in the solid state [13–15], in the liquid state high diffusivities (10^{-4}–10^{-5} $\mathrm{cm}^2\,\mathrm{s}^{-1}$) can account for the observed sintering rates, densification and clean grain boundaries [11].

This paper focuses on the effect of an electric field on grain growth retardation and presents a grain growth model which takes into account defect segregation as a

---

* Tel.: +1 9195157874; e-mail: J_Narayan@ncsu.edu

1359-6462/$ - see front matter © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.scriptamat.2013.01.008

result of an electric field. The role of space charge, solute segregation, elastic energy and melting associated with grain boundaries is also examined. Based upon the proposed model, an explanation of the grain growth retardation characteristics obtained by Conrad and co-workers [5–8] and the absence of grain growth under flash sintering found by Raj and co-workers [13–15] is proposed.

In a previous paper [16], vacancy concentrations as high as $1.0 \times 10^{19}\ \mathrm{cm}^{-3}$ were observed near dislocations as a result of electric field treatment at high temperatures (>1000 °C), in addition to impurity segregation at grain boundaries in MgO single crystals. In the following, I derive a grain growth model and then examine the effects of an applied electric field, focusing on the presence of high concentrations of defects and selective melting of grain boundaries during the field treatment. The model considers kinetic and thermodynamic components which affect grain growth rate. In the presence of an electric field the supply of vacancies from the grain boundaries is believed to be plentiful. A power law for grain growth is derived, and similarities with the Burke and Turnbull equation [17] in the absence of an electric field are highlighted. In addition, the importance of thermodynamic terms (grain boundary structure and solute segregation) in grain growth kinetics, and the role of diffusion across vs. along the boundary is demonstrated. This model also clarifies the effect of an electric field on grain boundary mobility [18] and retardation of grain growth [5]. High defect concentrations associated with dislocations and grain boundaries can enhance their mobility, but not necessarily the grain growth rate.

Considering n atoms in a grain of radius r with n_V the number density of the atoms, we have the change in number of atoms (dn/dt) with time as:

$$n = \frac{4}{3}\pi r^3 n_v \tag{1}$$

$$\frac{dn}{dt} = 4\pi r^2 n_v \frac{dr}{dt} \tag{2}$$

For this grain of radius r, if we consider atomic jumps across the boundary (Figs. 1 and 2) [19]:

$$\frac{dn}{dt} = f 4\pi r^2 n_s c_v v_D \exp\left(-\frac{\Delta \acute{G}}{kT}\right)\left[1 - \exp\left(+\frac{\Delta G}{kT}\right)\right] \tag{3}$$

where n_S is the surface density of atoms, C_v is the vacancy concentration, v_D is the Debye frequency, f is a geometrical factor for vacancy jumps, $\Delta \acute{G}$ is the activation barrier for vacancy diffusion across the boundary and ΔG is the gain in free energy as shown in Figure 1, which should be negative for the reaction to proceed.

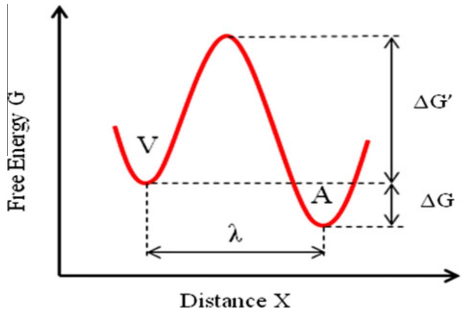

Figure 1. Change in free energy with distance across the grain boundary with jump distance, λ.

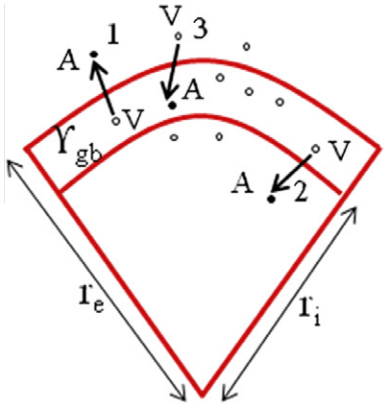

Figure 2. Vacancy jumps (for vacancy–atom exchange) across the interior (radius r_i) and exterior (radius r_e) of a grain boundary.

Since $n_v = n_s/\lambda$, where λ is the jump distance, Eqs. (2) and (3) can be rewritten for grain growth rate as:

$$\frac{dr}{dt} = f\lambda c_v v_D \exp\left(-\frac{\Delta \acute{G}}{kT}\right)\left[1 - \exp\left(+\frac{\Delta G}{kT}\right)\right] \tag{4}$$

The grain growth rate has two terms: $f\lambda c_v v_D \exp\left(-\frac{\Delta \acute{G}}{kT}\right)$ is the kinetic or diffusion term; and $\left[1 - \exp\left(+\frac{\Delta G}{kT}\right)\right]$ is the thermodynamic term, which is associated with phase transformation or gain in energy with the movement of a grain boundary.

Assuming $\Delta G << kT$, we can write grain growth rate as:

$$\frac{dr}{dt} = f\lambda c_v v_D \left(-\frac{\Delta G}{kT}\right) \exp\left(-\frac{\Delta \acute{G}}{kT}\right) \tag{5}$$

As shown in Figure 2, vacancies from grain boundaries jump across the exterior boundary r_e to $r_e + \lambda$ for grain growth. Variations of vacancy concentration c_v and ΔG with r in Eq. (5) determine grain growth function with time.

The net gain in free energy for step (1) is given by:

$$\Delta G = \frac{2\gamma_{gb}\Omega}{r_e + \lambda} - \frac{2\gamma_{gb}\Omega}{r_e} \tag{6}$$

$$\Delta G = -\frac{2\gamma_{gb}\Omega\lambda}{r_e^2} \tag{7}$$

where γ_{gb} is the grain boundary energy and Ω is the atomic volume.

By combining Eqs. (5) and (7), we obtain the grain growth rate as:

$$\frac{dr}{dt_1} = f v_D c_v \lambda \left(\frac{+2\gamma_{gb}\Omega\lambda}{r_e^2 kT}\right) \exp\left(-\frac{\Delta \acute{G}}{kT}\right), \tag{8}$$

which can be rewritten as:

$$\frac{dr}{dt_1} = +\frac{2\gamma_{gb}\Omega D}{r_e^2 kT}, \tag{9}$$

where $D = f\lambda v_D c_v \lambda^2 \exp\left(-\frac{\Delta \acute{G}}{kT}\right)$ is the vacancy diffusion coefficient and f is the geometrical factor.