Regular article

Direct current-enhanced densification kinetics during spark plasma sintering of tungsten powder

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A B S T R A C T

Rapid densification associated with spark plasma sintering has been well documented; however theoretical understanding is still very limited. In this work we proposed a densification creep model to explicitly elucidate the effect of current density on densification kinetics, by taking electromigration into account. This new model was then validated experimentally. It is found that an increased current density decreases densification activation energy (energy barrier), thus accelerating powder densification. In essence, the rapid densification is caused by direct current that accelerates mass transport and increases dislocation mobility.

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Spark plasma sintering (SPS), a well-known rapid densification technique, has garnered widespread popularity due to its versatility to sinter a variety of materials [1–8]. Nevertheless, this electric current-assisted sintering technology involves multi-field coupling of temperature, stress and electric, which makes its densification mechanisms difficult to be understood. The traditional model framework based on hot deformation of powdery materials is not suitable for describing current-assisted sintering. Thus far only few modeling attempts have been undertaken to address the densification mechanisms of SPS [9]. An explicit model that considers synergetic effects of multiple fields (electric, temperature and stress) is therefore critically needed to enable the understanding of densification mechanisms and kinetics of SPS.

Although many reports proved that direct current (DC) contributes to rapid sintering [10–12], an understanding of its role in densification processes is still ambiguous. In the past, Joule heating was considered to be the main contribution of DC on densification [9]. However, some recent studies have shown that effects associated with DC other than Joule heating also play a significant contribution on rapid densification. These effects include electric current-enhanced mass transfer [13–15]. Frei et al. [16] observed that the electrical current remarkably enhanced the neck growth during sintering and attributed it to electromigration. Therefore, it is critical to consider the non-thermal contributions of DC

during current-assisted sintering. Unfortunately, the majority of analytical models [10,17–22] of densification kinetics in the literature overlooked the contribution of electromigration, thus the intrinsic contribution of direct current to the densification kinetics remains unclear. Olevsky et al. [9,23] established a comprehensive densification kinetics model, suggesting that electromigration-related material flux was a significant contributor of the rapid densification. In their model, two mechanisms (power-law creep and grain boundary diffusion) were considered. However, in a creep process involving a high stress level, dislocation plays a dominant role on densification [24,25]. The Bernard-Granger creep model, has been used to study the densification mechanisms at different sintering stages. Despite of successful applications of this model to metals [24,25] and ceramics [26,27], the Bernard-Granger model does not consider the contribution of electromigration. In this paper, we developed a densification model to elucidate the densification kinetics of SPS, by incorporating electromigration into the Bernard-Granger creep model.

In the creep model, the densification kinetics equation can be written as [28]:

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{1}{\rho}\frac{d\rho}{dt} = \frac{BD\mu_{\text{eff}}b}{kT}\left(\frac{b}{G}\right)^p\left(\frac{\sigma_{\text{eff}}}{\mu_{\text{eff}}}\right)^n \tag{1}$$

where $\dot{\varepsilon}$ is the creep rate, ρ the relative density, t the time, B is a constant, D the diffusion coefficient, b the Burgers vector, k the Boltzmann constant, T the temperature, G the grain size, μ_{eff} the instantaneous shear

modulus, σ_{eff} the instantaneous effective stress acting on the powder bed, p the grain size exponent and n the stress exponent.

Electromigration is a forced atomic diffusion process with the driving force arising from an electric field and associated electric current in metals. The DC can provide an additional driving force for atomic diffusion by electromigration [29,30]. Obviously, there is a corresponding potential energy, Q_e, for electromigration driven by the current density j. According to Tu et al. [31], the value of Q_e for vacancy diffusion due to electromigration, is given by:

$$Q_e = A|Z^*|e\rho' j \qquad (2)$$

where A is a constant, Z^* the effective valence, e the charge of an electron (the product Z^*e is called "the effective charge"), ρ' the resistivity and j the current density. Eq. (2) is also applicable to self-diffusion of pure metal. Diffusion is known as a thermally activated process and the diffusion coefficient D follows an Arrhenius equation:

$$D = D_0 \exp\left(-\frac{Q}{kT}\right) \qquad (3)$$

where D_0 is the frequency factor, Q the activation energy. When electromigration is taken into account, the effective diffusion coefficient, D_{eff}, can be expressed as [31,32]:

$$\begin{aligned} D_{eff} &= D_0 \exp\left(-\frac{Q - Q_e}{kT}\right) = D_0 \exp\left(-\frac{Q - Q_e}{RT} N_A\right) \\ &= D_0 \exp\left(-\frac{Q'}{RT} + \frac{A_1|Z^*|e\rho' j}{RT}\right) \end{aligned} \qquad (4)$$

where R the gas constant, N_A the Avogadro constant, Q' the activation energy for a mole of atoms, A_1 the constant. Substituting Eq. (4) in Eq. (1) leads to a kinetics equation:

$$\frac{1}{\mu_{eff}}\frac{1}{\rho}\frac{d\rho}{dt} = \frac{BbD_0}{RT} e^{-\frac{Q_d}{RT} + \frac{A_1|Z^*|e\rho' j}{RT}} \left(\frac{b}{G}\right)^p \left(\frac{\sigma_{eff}}{\mu_{eff}}\right)^n \qquad (5)$$

where Q_d is the apparent activation energy of the mechanism controlling densification. The above Eq. (5) incorporates the contributions of heat, external load and electromigration to densification.

The values of μ_{eff} and σ_{eff} can be calculated by empirical equations [28]:

$$\mu_{eff} = \frac{E_{th}}{2(1+\nu_{eff})}\frac{\rho - \rho_0}{1 - \rho_0} \qquad (6)$$

$$\sigma_{eff} = \frac{1 - \rho_0}{\rho^2(\rho - \rho_0)}\sigma_{mac} \qquad (7)$$

where E_{th} is the Young's modulus, ν_{eff} the Poisson's ratio, ρ_0 the initial green density of the powder compact and σ_{mac} the macroscopic compaction pressure.

In the following, the above theoretical outline is applied to reveal the effect of DC on densification kinetics during SPS. The experiments described in this section have been designed for the purpose of the verification, mostly quantitative, of the impact of current density on the densification kinetics based on the proposed model. In brief, pure tungsten powder (purity >99.9%) with an average particle size of 1 μm was used and graphite dies with various diameters of 20, 40 and 60 mm were employed to vary current densities. The sintering was performed in an SPS apparatus (HP D25, FCT Systeme GmbH, Rauenstein, Germany) with a vacuum chamber. The temperature range investigated was 1200–1250 °C. The heating rate 100 °C min⁻¹, dwell time 6 min and pressure 40 MPa were fixed as constants respectively for all the experiments. As a result, the electric current has minor fluctuation in the soaking stage, as shown in Fig. 1. On this account, we assumed that the current was constant in the isothermal stage of SPS.
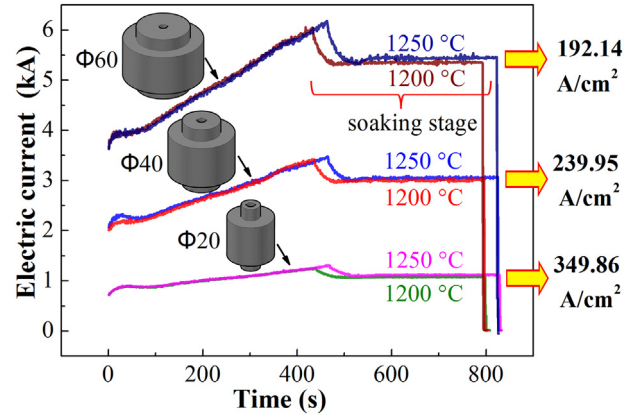

Fig. 1. Electric current vs. time, showing that various current densities (349.86, 239.95 and 192.14 A/cm²) were obtained when different size dies were used (20, 40, 60 mm) during SPS.

To estimate current density j at the soaking stage, all the electric current is assumed to pass through the punches and powder bed directly and no current flows through the die sleeve, because the current density of die sleeve was much less than that of punches and sample [33]. Hence, dividing average current by the cross-sectional area of punch, the current densities at different die sizes (other conditions were constant) during the soaking stage can be obtained. Fig. 1 shows that a small diameter of the punch resulted in a higher current density under the same conditions during SPS. In this way, different current densities can be obtained by controlling die diameter.

Fig. 2 shows the curves of densification rate $(\frac{1}{\rho}\frac{d\rho}{dt})$ vs. dwelling time at different current densities. In general, an increased current density increases densification rate. Such an effect is more prominent at the initial sintering stage (stage 1 in Fig. 2). For instance, the densification rate at 349.86 A/cm² is almost 40% higher than that at 192.14 A/cm² at the beginning of the soaking process. To explain this phenomenon, the densification kinetics analysis based on the new model was carried out as follows.

To determine the stress exponent n, Eq. (5) is rewritten as a logarithmic form:

$$\ln\left(\frac{1}{\mu_{eff}}\frac{1}{\rho}\frac{d\rho}{dt}\right) = n \cdot \ln\left(\frac{\sigma_{eff}}{\mu_{eff}}\right) + K + \frac{A_1|Z^*|e\rho' j}{RT} \qquad (8)$$

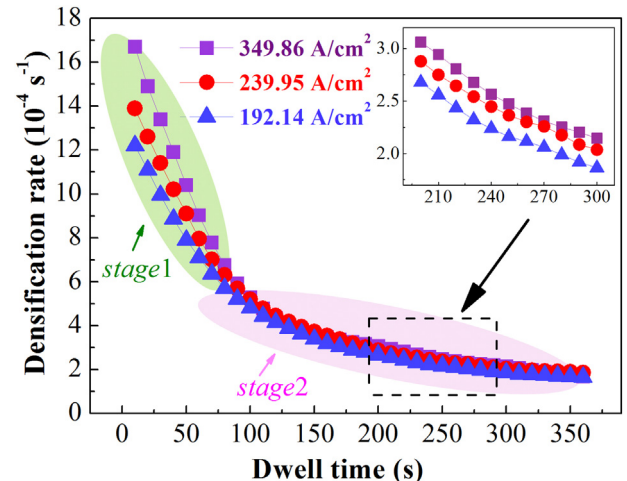Fig. 2. Densification rate at different current densities at the soaking stage at 1200 °C.