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Viscous flow activation energy adaptation by isothermal spark plasma sintering applied with different current mode

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ABSTRACT

Theoretical understanding in the innate function of electric current on the spark plasma sintering of amorphous powder is very limited. We proposed an improved isothermal model considering particle size evolution in this work to study the effect of current mode on shrinkage of amorphous $Fe_{41}Co_7Cr_{15}Mo_{14}Y_2C_{15}B_6$ powder. It revealed a reduction in the activation energy from 71.1 ± 1.6 kJ·mol^{-1} under direct current to 55 ± 2.0 kJ·mol^{-1} under pulse current, representing a resultant acceleration of densification by adjusting current mode. The enhancement of consolidation is attributed to increase of electric density induced by pulse current.

The development of Fe-based bulk metallic glass (BMG) materials has progressed in short order during the last few decades and a large number of compositions can now be manufactured [1–3]. The absence of grain boundaries, usually considered to be weakness in crystalline materials, leads to better mechanical properties, which enables probable application of BMG in industry products such as sports equipment and medical devices. Spark plasma sintering (SPS) is an advanced pressure and electric current assisted sintering technique to consolidate a variety of materials with excellent [4,5] performance including full dense Fe-based amorphous alloys [6,7]. Unlike hot pressing (HP) and hot isostatic pressing (HIP), in SPS, a current is directly applied in graphite die and pass through the powder bed companied with axial pressure. Thus, the heat is generated through the Joule effect. Owing to its unique heating source and assisted current filed, SPS has advantages such as high heating rate, low sintering temperature and quick powder consolidation. Considerable research has been undertaken on the SPS of recently developed Fe based amorphous alloy powders [8–11] in order to utilize their excellent mechanical and electrochemical properties [12]. However, most of the reported investigations are focus on the effect of different additives, heating rate and loaded pressure. The inherent role of pulse current in densification is not established. The present study seeks to analyze the effect of pulse current on the densification characteristics of the amorphous alloy.

$Fe_{41}Co_7Cr_{15}Mo_{14}Y_2C_{15}B_6$ amorphous powder with sphere morphology was used in the study. The glass transition temperature and the crystallization temperature of the powder are $T_g = 565$ °C and $T_C = 603$ °C respectively. A fixed axial pressure of 40 MPa and heating rate of 100 K·min^{-1} were chosen during the sintering process. To investigate the effect of pulse current on the densification process, two current modes with on/off circle of 8: 2 ms, and without pause were applied.

A viscous sintering theoretical framework is utilized in the study to investigate the densification process. The isothermal shrinkage of a sample by viscous flow can be expressed as [13]:

$$\frac{\Delta L}{L_0} = \frac{3\gamma}{4D\eta}t \tag{1}$$

where L_0 (mm) is the initial height, ΔL (mm) the shrinkage, $\Delta L/L_0$ the shrinkage ratio of the powder, γ (J·m^{-2}) the surface energy, D (m) the average diameter of powder particle, η (Pa·s) the coefficient of viscosity and t the time (s). In most amorphous powder shrinkage studies, displacement data were recorded in constant heating experiment without soak period and isochronal model was adopted which was regarded as more accurately representing the brisk shrinkages [14,15]. However, due to the high heating rate of SPS, viscous flow between T_g and T_c is extremely rapid (e.g. less than 30 S under heating rate of 100 °C min^{-1}) leading to limited data observation. As a consequence, inaccurate data caused by the experimental errors will be easily induced and introduced into the subsequent calculation leading to wrong results. Thus, for the purpose to ensure the study accuracy, temperature of 570 °C, 580 °C, 590 °C and 600 °C with soak time fixed as 10 min and isothermal model framework were adopted in the study. All the samples obtained are cylindrical with diameter of 20 mm. At temperature range from 570 °C to 600 °C, the relative densities of the samples sintered under direct current are 78.4%, 80.0%, 85.8%, and 89.4% while under pulse current are 80.9%, 81.4%, 84.9% and 88.9%.

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Within a small temperature range, the viscosity coefficient of an amorphous material follows an Arrhenius equation [16]:

$$\eta = \eta_0 \exp\left(\frac{-Q}{RT}\right) \tag{2}$$

where η_0 (Pa·s) is the frequency factor, Q (J·mol^{-1}) the activation energy for viscous flow, and R (8.314 J·K^{-1}·mol^{-1}) the universal constant. Thus, the shrinkage rate in isothermal conditions can be obtained by differentiating Eq. (1) with respect to time and applying Eq. (2) as:

$$\frac{d\left(\frac{\Delta L}{L_0}\right)}{dt} = \frac{3\gamma}{4D\eta_0} \exp\left(\frac{-Q}{RT}\right) \tag{3}$$

The shrinkage curves of Fe-based amorphous powders under different soak temperatures and corresponding XRD spectra of final sintered samples are shown in Fig. 1. The diffraction patterns show obvious diffused halos (Fig. 1(b) and (d)) characteristic of fully amorphous materials, indicating the inexistence of crystallization process regardless of direct current or pulse current applied in sintering. Thus, all the samples obtained remained their amorphous state and all the data collected from soak period followed Eq. (3). If γ, D, η_0, and Q are assumed to be constant as reported in many published articles [14–16], slopes of the shrinkage with respect to soak time will be constant too. However, the shrinkage curves in Fig. 1(a) and (c) show variational slopes which indicate parameters in Eq. (3) varied along with the shrinkage. Considering the actual sintering process, powder particles grow up through the inter-particle neck. As a consequence, average diameter of powder particle D increase, and in contrast, the surface energy γ decrease along with the powder densification. Thus, according to Eq. (3), the shrinkage tendency will slow down with the increase of time t, which is in accordance with the shrinkage curves in Fig. 1(a) and (c).

Owing to this, to calculate the activation energy Q, the parameter D and γ as functions to soak time t need to be determined at first. In this study, the shrinkage data were acquired once per second and Eq. (3) can be expressed as:

$$(\Delta L_{t+1} - \Delta L_t)/(L_0 - \Delta L_t) = \frac{3\gamma_t}{4D_t\eta_0} \exp\left(\frac{-Q}{RT}\right) \tag{4}$$

where ΔL_t and ΔL_{t+1} are the shrinkage at time t and t + 1, $\Delta L_{t+1} - \Delta L_t$ the relative shrinkage within time t and t + 1, $L_0 - \Delta L_t$ the instantaneous height at time t, γ_t and D_t the surface energy and the average diameter of powder particles at time t respectively. In Eq. (4), the parameters γ_t and D_t can be regarded as constant owing to such short time span. However, it should be pointed out that γ_t and D_t continuously varied during shrinkage. Thus, values of γ_t and D_t are needed before applying shrinkage data in Eq. (4). In fact, only D_t affects the subsequent calculation of Q in the model which means the value of γ_t is unnecessary to compute in the study.

In order to study the D_t variation, a hypothesis is proposed as shown in Fig. 2. At the initial stage, the powder re-arrangement under axis pressure results in particles reaching the densest structure within compaction capacity. Assuming spherical particles to be equally diametric and un-deformed, powder stacks into the structure as the left side of Fig. 2. Once the temperature exceeding T_g, viscous flow occurs at the interface of particles leading to transformation of two neighbor layers into one layer, which is shown in the middle part of Fig. 2. Each three particles was assumed to present a shrinkage unit with initial height h and displacement Δd as shown in the red circled zones (Fig. 2). Besides, particle numbers in the units decrease by two thirds in the assumptive structure. To simplify the compute, it is further assumed that viscous flow only occurs between two neighbor layers and Δd is constant in all units, as shown in the right side of Fig. 2. In addition, viscous flow in radial direction such as the blue circled zone (Fig. 2) is neglect, which has no effect in axial shrinkage. Owing to the obtained samples under all sintering parameters being porous, it can be regarded that

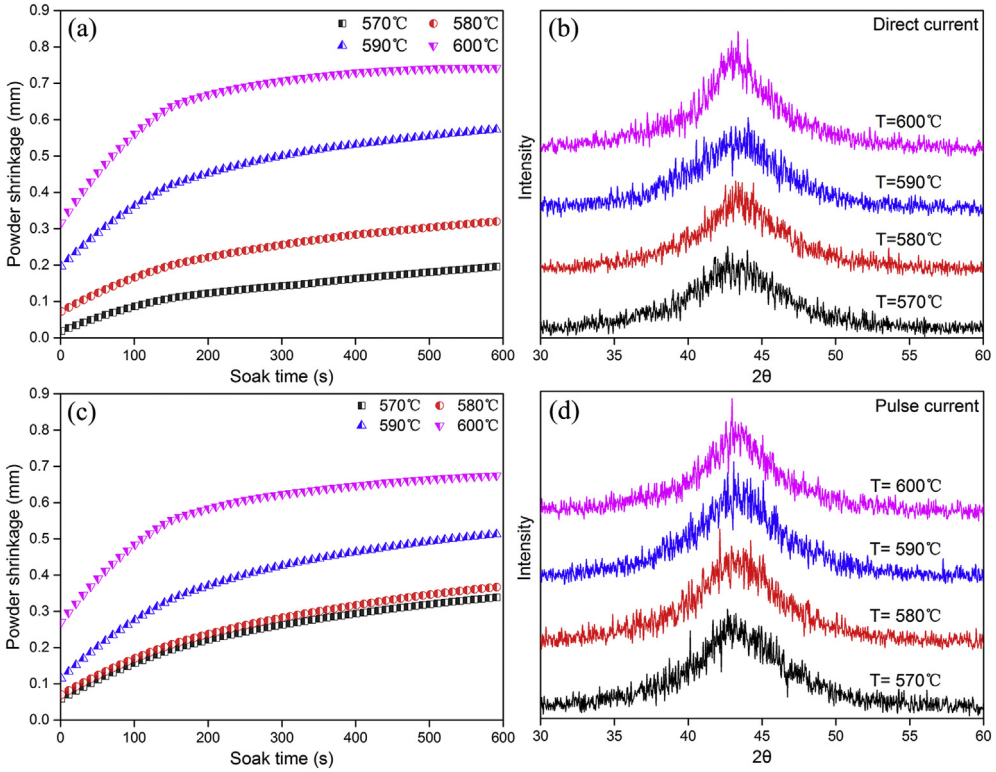

Fig. 1. Shrinkage curves in soak stage under (a) direct current and (c) pulse current and (b), (d) respectively corresponding XRD patterns.