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Viscous flow activation energy adaptation by isochronal spark plasma sintering

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ABSTRACT

The densification mechanism of amorphous $Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$ alloy powder during isochronal spark plasma sintering was analyzed to determine the innate function of high heating rates. Densification ensued and concluded at gradually lower temperatures while attaining higher maximum rates with increasing heating rates in the first stage. The shrinkage behavior analyzed under the theoretical framework of viscous flow revealed a steady reduction in the activation energy leading to a resultant enhancement of densification rate in the initial stage.

Spark plasma sintering (SPS) is an advanced pressure and electric current assisted sintering technique that has garnered widespread popularity due to its versatility to sinter a variety of materials such as metals, ceramics, and composites [1]. Fully dense compacts can be manufactured by SPS at lower temperatures as compared to other pressure assisted sintering techniques such as hot pressing (HP) and hot isostatic pressing (HIP) [2]. Considerable research has been undertaken on the SPS of recently developed Fe based amorphous alloy powders [3–6] in order to utilize their excellent mechanical and electrochemical properties [7]. Joule heating in the powder caused by the applied direct current results in internal heat generation and allows high heating rates during the process [1,8]. For example, SPS carried out at a heating rate of 100 °C min^{-1} resulted in near full densification within a short cycle time of about 20 min [9]. Although SPS has been utilized to sinter Fe-based amorphous alloys to full density, most of the reported investigations are experimental studies performed using scattered heating rates in the range of 50–100 °C min^{-1} [9–13], and the inherent role of heating rate in the enhancement of densification is not thoroughly established. The present study seeks to analyze the effect of systematic increase in heating rate on the densification characteristics of a recently developed Fe-based amorphous alloy ($Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$) utilizing the theoretical framework on viscous flow sintering.

The process of sintering involves a number of overlapping stages such as formation and growth of necks at the interparticle contacts, pore rounding, and pore closure [14]. Transport of mass during these stages takes place by various mechanisms one of which is usually dominant over the others, and primarily determined by the nature of the material [15]. For example, in amorphous materials, the principal mechanism of mass transport during sintering is viscous flow caused by the driving force of surface tension [16,17]. Studying the densification behavior of amorphous powder compacts during sintering enables identification and analysis of the various aspects of this mechanism. The instantaneous densification rate of the specimen, $\dot{\rho}_n$ (s^{-1}) is estimated according to [18]:

$$\dot{\rho}_n = \frac{d\rho_n}{dt_n} = \frac{\rho_{n+1} - \rho_{n-1}}{t_{n+1} - t_{n-1}} \quad (1)$$

where ρ_n (%) is the instantaneous relative density at time t_n (s). The relative density, ρ (%) is calculated from the instantaneous height L (mm), initial height L_o (mm), and initial relative density ρ_o (%) as [18]:

$$\rho = \frac{L_o}{L}\rho_o \quad (2)$$

The contribution of viscous flow to the isothermal shrinkage of a specimen can be expressed as [19]:

$$\frac{\Delta L}{L_o} = \frac{3\gamma}{4D\eta}t \quad (3)$$

where $\Delta L/L_o$ is the shrinkage of the powder, γ (J m^{-2}) the surface energy, D (m) the average diameter of powder particles, and η (Pa s) the coefficient of viscosity. Isothermal studies suffer from considerable drawbacks, the foremost among them being the lack of means for obtaining sintering shrinkage as a function of temperature through a single experiment [20]. In contrast, equations pertaining to isochronal (constant rate heating) studies accurately represent the brisk shrinkages that occur during initial stages of sintering cycles when thermal equilibrium is being attained. Moreover, these studies can effectively

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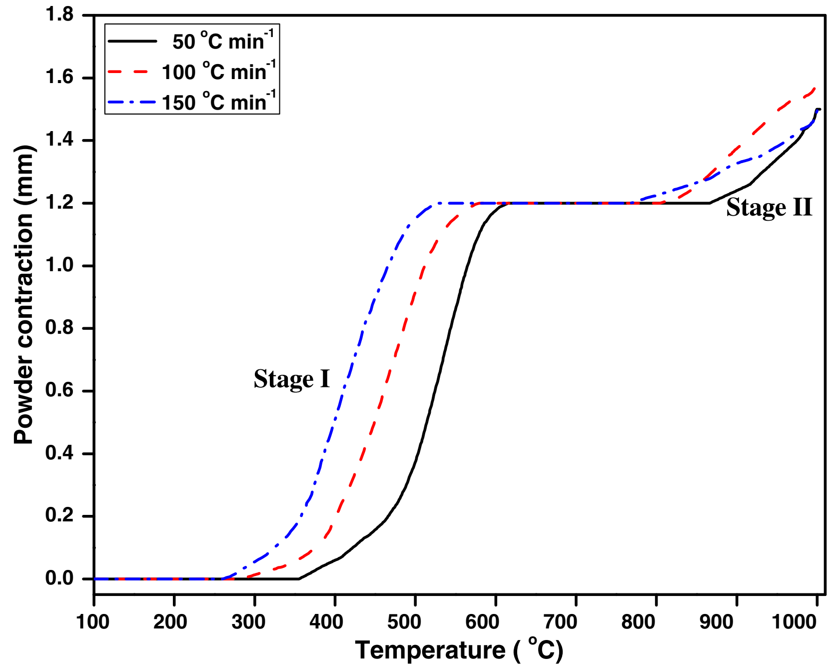

Fig. 1. Powder contraction of $Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$ amorphous alloy during SPS at heating rates of 50, 100, and 150 °C min^{-1}.

distinguish between different densification mechanisms with distinct activation energies in addition to being in better accord with industrial engineering practice [21]. In view of the above, the relationship between temperature and time in an isochronal experiment can be expressed as:

$$\frac{dT}{dt} = c \tag{4}$$

where T (K) is the temperature and c (K s^{-1}) is the constant rate of heating.

Over a small range of temperature the coefficient of viscosity of an amorphous material follows an Arrhenius equation [18]:

$$\eta = \eta_o \exp\left(\frac{Q}{RT}\right) \tag{5}$$

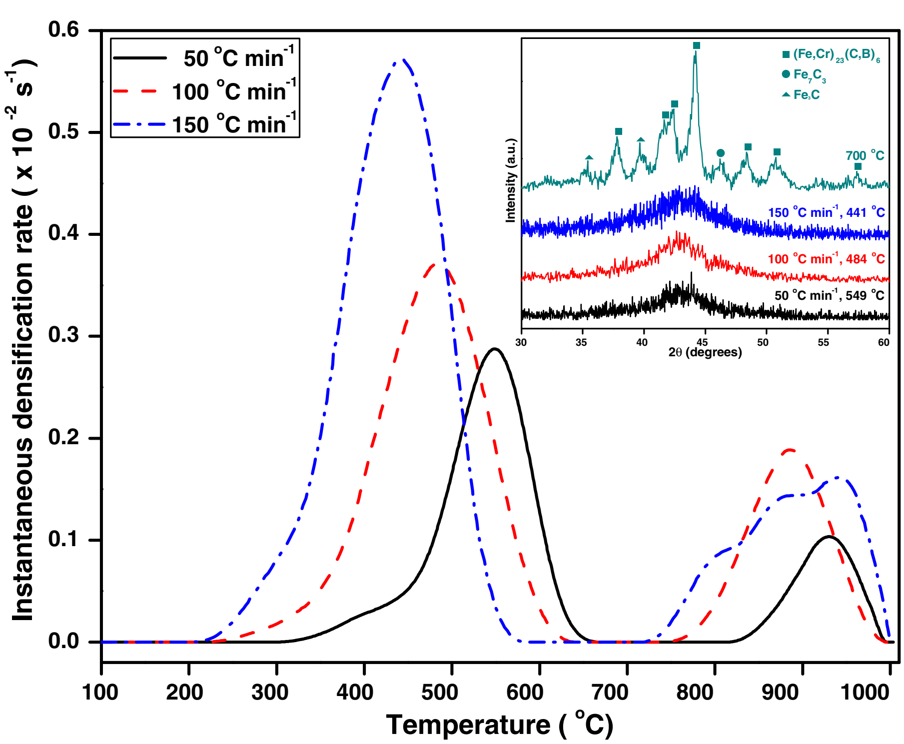

Fig. 2. Instantaneous densification rate during SPS at heating rates of 50, 100, and 150 °C min^{-1}. Inset depicts XRD spectra of specimens SP sintered up to T_p at respective heating rates and representative specimen SP sintered at 700 °C.