



## Regular article

## Determination of atomic diffusion coefficient via isochronal spark plasma sintering

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## ABSTRACT

During spark plasma sintering (SPS), it is widely argued that the densification mechanism of powder particles can be correlated with some specific physical quantities; however, an atomic diffusion coefficient  $D$  has yet to be derived. In this work, we report on the establishment of a framework, which can be used to derive the value of the  $D$  and further provide significant insight into the densification mechanisms that are active during powder sintering. We validate the framework by comparing the densification behavior of the atomized and milled  $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{37.5}\text{Ni}_{9.4}\text{Sn}_{3.1}$  metallic glass powders during SPS, and clarifying the underlying densification mechanisms.

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Powder sintering is a technique used for bonding powder particles together into a coherent bulk solid structure. In general, powder shrinkage and densification mechanisms are influenced by various physical parameters [1], such as surface energy ( $\gamma$ ), average particle size ( $L$ ), viscosity ( $\eta$ ), etc., especially during the early stage of powder shrinkage, which is typically characterized by neck formation between powder particles. In the case of powder sintering during spark plasma sintering (SPS), the corresponding powder shrinkage and densification mechanisms are particularly interesting given its specific physicochemical mechanism [2]: spark generation and sputtering effects during neck formation between powder particles [3]. In essence, densification mechanisms are analytically correlated with specific physical quantities determined by the aforementioned physical parameters, including densification rate ( $\dot{\rho}$ ) [4,5], activation energy ( $Q$ ) [6–10], stress exponent ( $n$ ) [8,9], comprehensive impact factor ( $f$ ) [10]. In fact, the individualized scientific issue in SPS is the diffusion behavior of atoms induced by spark generation under high-density pulsed electric current [2]. Recently, this viewpoint has been substantiated by quantitative reaction diffusion rate coefficient of titanium-copper diffusion couples using isothermal heat treatment of SPS [11]. Unfortunately, as a direct physical quantity that represents the ability of mass transfer governing densification mechanism of powder particles, an atomic diffusion coefficient ( $D$ ) during SPS has heretofore never been attempted analytically and derived quantitatively.

As a promising metallic material, metallic glasses have attracted increasing interest during the past two decades [12]. Interestingly, inspection of the published literature shows that the diffusion behavior in the supercooled liquid region is poorly understood [13,14]. Concomitantly, metallic glass powders are frequently consolidated via SPS to fabricate novel bulk alloys with finer grains [15–17], such as: fully amorphous [15], equiaxed ultrafine-grain [16], and bimodal [17] microstructures, to name a few examples. Qualitatively, the formation mechanism of the finer-grain microstructures has been attributed to the individual diffusion of atoms in a relative short SPS time [1–11,15–17].

In light of the above questions, the objective of this study is to quantitatively derive a coefficient  $D$  during SPS of metallic glass powders, which has heretofore never been attempted. In our study, we first attempt to establish a framework that can be used to derive the value of a coefficient  $D$ , which can clarify the underlying densification mechanism during SPS of  $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{37.5}\text{Ni}_{9.4}\text{Sn}_{3.1}$  metallic glass powders. Interestingly, as will be discussed below, the value of the as-derived  $D$  for the atomized metallic glass powder is always lower than that of the milled counterpart.

During powder sintering, the instantaneous relative density  $\rho$  (%) of the sintered compacts can be expressed as:

$$\rho = \frac{H_0}{H} \rho_0 \quad (1)$$

where  $\rho_0$  (%) refers to the initial relative density,  $H_0$  (m) the initial height of the compacts in the die, and  $H$  (m) the instantaneous height corresponding to the relative density of  $\rho$  (%). Then, the instantaneous

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densification rate  $\dot{\rho}$  ( $\text{s}^{-1}$ ) of the sintered compacts is estimated by [7]:

$$\dot{\rho} = \frac{d\rho_i}{dt_i} = \frac{\rho_i - \rho_{i-1}}{t_i - t_{i-1}} \quad (2)$$

where  $\rho_i$  (%) is the instantaneous relative density at time  $t_i$  (s), and the time interval ( $t_i - t_{i-1}$ ) is 2 s.

According to the Frenkel model as adapted for glassy materials in the case of formation and growth of sintering neck by viscous flow, the densification behavior of powder particles during isothermal sintering is determined by [18]:

$$\frac{\Delta H}{H_0} = \frac{3\gamma}{4L\eta} t \quad (3)$$

where  $\Delta H/H_0$  is the shrinkage of the powder,  $\gamma$  ( $\text{J/m}^2$ ) the surface energy,  $t$  (s) the time,  $L$  (m) the average particle size, and  $\eta$  ( $\text{Pa}\cdot\text{s}$ ) the viscosity of the powder materials.

In general, viscous flow occurs in the early stage of powder shrinkage [1,2,6–10], specifically in the supercooled liquid region for a glassy materials during powder sintering [6,7]. As such, we can correlate the coefficient  $D$  with the viscosity  $\eta$  through the Stokes-Einstein relation [19]:

$$\eta = \frac{kT}{3\pi D\delta} \quad (4)$$

where  $D$  ( $\text{m}^2/\text{s}$ ) is the atomic diffusion coefficient;  $\delta$  the atom diameter,  $3.61 \text{ \AA}$  specific for Ni,  $T$  (K) the absolute temperature, and  $k$  ( $1.38 \times 10^{-23} \text{ J/K}$ ) the Boltzmann constant.

Simultaneously, the coefficient  $D$  is dependent of the temperature and follows an Arrhenius relationship [14]:

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \quad (5)$$

where  $D_0$  ( $\text{m}^2/\text{s}$ ) is the pre-exponential factor,  $R$  ( $8.314 \text{ J/K/mol}$ ) the universal gas constant,  $Q$  ( $\text{kJ/mol}$ ) the activation energy for atomic diffusion. In an isochronal experiment, the relationship between temperature  $T$  and time  $t$  can be expressed as:

$$\frac{dT}{dt} = c \quad (6)$$

where  $c$  ( $\text{K/s}$ ) is heating rate. Subsequently, by differentiating Eq. (3) with respect to  $T$  and applying Eqs. (4)–(6), the powder shrinkage rate under isochronal heating condition can be estimated by:

$$\frac{d\left(\frac{\Delta H}{H_0}\right)}{dT} = \frac{9\pi\gamma\delta D_0}{4Lkc} \frac{\exp\left(\frac{-Q}{RT}\right)}{T} \quad (7)$$

Rearranging and taking the logarithm of both sides, Eq. (7) can be written as:

$$\ln\left(T \frac{d\left(\frac{\Delta H}{H_0}\right)}{dT}\right) = \ln\left(\frac{9\pi\gamma\delta D_0}{4Lkc}\right) - \frac{Q}{RT} \quad (8)$$

Thus, the atomic diffusion activation energy  $Q$  and the pre-exponential factor  $D_0$  at a specific heating rate can be deduced from the slope and the intercept respectively from plots of  $\ln(Td(\Delta H/H_0)/dT)$  versus  $1/T$  (Eq. (8)). Finally, the atomic diffusion coefficient  $D$  can be determined using Eq. (5).

To validate the framework described above, we selected irregular and spherical  $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{37.5}\text{Ni}_{9.4}\text{Sn}_{3.1}$  (at.%) metallic glass powders, prepared via gas atomization and ball milling, respectively. The spherical metallic glass powder was fabricated via an EIGA powder device of gas atomization (AMC-EIGA-50) with the following parameters: an atomization temperature of 1273 K, a spinning velocity of 5 r/min, and an argon gas pressure of 6.7 MPa. The irregular counterpart was prepared by 30 h ball milling of a mixture of high-purity (99.9 wt%) elemental powders at a rotational speed of  $4 \text{ s}^{-1}$  under a protection atmosphere of high-purity argon in a high-energy planetary ball mill (QM-2SP20; apparatus factory of Nanjing University, Nanjing, China). The phase component, thermal behavior, particle morphology, and particle size distribution of the two types of powders were characterized by X-ray diffraction (XRD; D/MAX-2500/PC, Rigaku Corp., Tokyo, Japan), differential scanning calorimetry (DSC; Netzsch STA 409C, Bavaria, Germany) with a heating rate of 20 K/min, Philips XL-30 FEG scanning electron microscope (SEM; Amsterdam, The Netherlands), and laser scattering particle size distribution analyzer (LA-960S, Horiba Corp., Japan), respectively. Especially, the phase component of the two types of powders was observed by a Tecnai G2 F30 field emission gun transmission electron microscope (TEM; FEI, USA). Subsequently, the two types of powders were sintered under the protection of argon atmosphere by spark plasma sintering system (SPS-825, Sumitomo Coal Mining Co. Ltd., Japan). To minimize deviations between the experiments, the same weight powder of 12 g was utilized in both cases and placed into a  $\phi 15 \text{ mm}$  graphite die. Detailed procedures regarding ball milling and SPS can be seen in Refs [7,16,17]. In addition, to calculate the values of  $D_0$  and  $Q$  for the two types of powders, the SPS parameters including temperature ( $T$ ), linear shrinkage ( $H$ ) and time ( $t$ ) were recorded every 2 s using standard software.

Fig. 1 shows SEM images, particle size distributions, XRD patterns, and DSC curves of the milled and atomized  $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{37.5}\text{Ni}_{9.4}\text{Sn}_{3.1}$  metallic glass powders, respectively. From Fig. 1a and b, it is apparent that the morphology of the milled and atomized powders is irregular and spherical, respectively, with a corresponding size range of 9–350  $\mu\text{m}$  (Fig. 1a inset) and 5–35  $\mu\text{m}$  (Fig. 1b inset), respectively. Meanwhile, the average particle size  $L$  is about 41.0  $\mu\text{m}$  and 15.4  $\mu\text{m}$  for the milled and atomized powders. The greater value of the  $L$  for the milled powder may yield a lower  $\gamma$  relative to the atomized counterpart [10]. As shown in Fig. 1c, XRD patterns indicate that the two types of powders reveal a completely glassy structure. However, DSC analysis in Fig. 1d reveals that compared with the milled counterpart, the atomized powder has the higher glass transition temperature ( $T_g$ ), the unchanged onset crystallization temperature ( $T_x$ ), and the lower exothermic enthalpy of crystallization ( $\Delta H$ ). Notably, the supercooled liquid region,  $\Delta T_x$ , defined as temperature interval between  $T_g$  and  $T_x$ , is 54 K for the milled powder, far higher than that (45 K) for the atomized counterpart. These results suggest that the atomized powder contains minor amount of crystalline phases, which are clearly verified by high-resolution TEM results that exhibit full glassy structure in the milled powder and yet minor amount of nano-sized crystals of approximately 4 nm embedded in a glassy matrix in the atomized counterpart. Reasonably, the greater  $L$ , smaller  $\gamma$ , larger  $\Delta H$ , and wider  $\Delta T_x$  for the milled powder would result in different densification behavior relative to the atomized counterpart.

To support this argument, and using Eq. (1), Fig. 2a presents the relative density of the milled and atomized  $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{37.5}\text{Ni}_{9.4}\text{Sn}_{3.1}$  metallic glass powders as a function of temperature for various heating rates. Apparently, the milled powders have the smaller initial relative densities ( $0.55 \pm 0.01$ ) in comparison with those of the atomized counterparts ( $0.72 \pm 0.01$ ). This may be ascribed to the larger  $L$  and more irregular geometry of the milled powder. Interestingly, the relative density of both powders increases with heating rate, and corresponding curves all exhibit a representative “double S” type of densification behavior. Specifically, these curves can be divided into two stages: the first stage (I) occurs in the temperature range of about 350–720 K and 600–750 K, followed by the second one (II) with the temperature

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