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Analysis of compaction and sintering behavior of 316L stainless steel nano/micro bimodal powder

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ABSTRACT

Nano powder had various advantages on powder metallurgy process. However, because of its high price and difficulties in treatment, nano powder cannot be easily applied to the field. As a result, nano/micro bimodal powder has been introduced to overcome such problems. In this study, the effects of nano powder ratio in nano/micro bimodal powder on powder metallurgy process have been investigated. The master sintering curves for the bimodal powders were also developed for the first time. With micro, nano and 3 different bimodal powders, compaction behavior was investigated, and dilatometric sintering was carried out to analyze the densification behavior during the sintering process. The results showed bimodal powders had relatively high green density, and the highest value was obtained with 25% nano bimodal powder. The powder also provided the highest densification parameter. Based on the dilatometer data, the master sintering curves of each powder were constructed, and all curves were consistent with experimental data.

1. Introduction

316L stainless steel is one of the most widely used materials in powder metallurgy (PM) from agricultural to aerospace field [1]. Since it can provide excellent corrosion resistance, this alloy is also appropriate for biomedical, chemical and nuclear plants applications [2–4]. Although various powder processing methods, such as spark plasma sintering, powder injection molding and additive manufacturing, have been developed many studies are still being conducted with traditional PM process, and 316L stainless steel powder occupies the large portion of them [2–7].

Recently, many researchers in PM field have been dealing with nano powder because it provides various advantages, such as more isotropic shrinkage, better surface and green strength. Because of its small diameter, nano powder has large specific surface area [8]. Since the large surface area increases surface energy, nano powder has low sintering temperature with low activation energy [9–10]. However, at the same time, the large surface area results in strong agglomeration and high interparticle friction. These characteristics decrease packing density and induce defects in green bodies [11–12]. Thus, additional treatments are sometimes required, such as preheating or milling [12–14]. Explosive oxidation of metal nano powder and the high price of nano powder are also critical issues for applying nano powder to PM process. These disadvantages can be minimized by using nano/micro bimodal powder. Bimodal powder is a mixture of two different sized powders. By mixing nano powder with micro powder, the drawbacks of nano powder decrease while its merits are preserved. Nano/micro bimodal powder can provide higher green density since nano particles can fill the interparticle space of micro particles [15–17]. It is also known that the samples fabricated with nano/micro bimodal powder provide better mechanical properties [18–19].

Sintering is one of the most important steps in PM process. During sintering, densification of a porous green body takes place by the thermally activated diffusion process, and as a result, the density of samples increases [20–22]. Since the density of parts directly influences the properties of the whole, comprehension of densification behavior during sintering is crucial. Therefore, various sintering models, which can describe the densification behavior, were suggested [23–27]. Among the models, master sintering curve (MSC) model, developed by Su and Johnson [28], has been widely applied to sintering of various materials from metals (Stainless steel [22], Nickel [29], Tungsten alloy [29–31]) to ceramics (Alumina [21,28,32], Zirconia [21,28]). Sintering behavior of nano powders was also described with the MSC model [33–36]. Recent studies of the MSC model even covered experimental factors. V. Pouchly et al. [37] developed two-stage MSC by considering two-step sintering process, and phase transformation MSC model was reported as well by K. Maca et al. [38] and I.D. Jung et al. [39]. The MSC model enables to predict the densification behavior with minimal set of preliminary experiments [34]. Since the construction of the MSC depends on only experimental data rather than theoretical mechanisms, the MSC model is more practical and convenient for industrial fields.

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Although MSC model was applied to various materials, most studies dealt with unimodal powder, and MSC with nano/micro bimodal powder has not been reported yet. In this study, the effects of nano powder ratio in bimodal powder have been examined with 316L stainless steel powders. The compaction and sintering behaviors of the powders have been analyzed, and the master sintering curve was developed for each powder.

2. Master sintering curve model

Although the development of the MSC is reliant on experimental approaches, the formulation of the MSC model is derived from combined stage sintering model [28]. The model relates the linear shrinkage rate of a compact to grain boundary and volume diffusion coefficients, surface energy and microstructure [34]. The instantaneous linear shrinkage rate in the model is given as:

$$-\frac{dL}{Ldt}=\frac{\gamma\Omega}{kT}\left[\frac{\Gamma_v D_v}{G^3}+\frac{\Gamma_b \delta D_b}{G^4}\right] \tag{1}$$

where, γ is the surface energy,
Ω is the atomic volume, k is the Boltzmann constant, T is the absolute temperature, G is the mean grain size, D is the diffusion coefficient and Γ is the lumped geometric scaling parameter. The subscripts, v and b, represent volume diffusion and grain boundary diffusion, respectively.

With the assumption of isotropic shrinkage and mass conservation, the relationship between sintering shrinkage rate and densification rate should follow the equation below.

$$-\frac{dL}{Ldt}=\frac{d\rho}{3\rho dt} \tag{2}$$

Here, L is the length of the sample and ρ is the relative density. Therefore, Eq. (1) can be expressed as the following equation:

$$\frac{d\rho}{3\rho dt}=\frac{\gamma\Omega}{kT}\left[\frac{\Gamma_v D_v}{G^3}+\frac{\Gamma_b \delta D_b}{G^4}\right] \tag{3}$$

If sintering behavior is governed by only a single diffusion mechanism (either volume diffusion or grain boundary diffusion), and G and Γ are functions of the density, Eq. (3) can be simplified with Arrhenius equation [28,40–41].

$$\frac{d\rho}{3\rho dt}=\frac{\gamma\Omega(\Gamma(\rho))D_0}{kT(G(\rho))^n}\exp\left(-\frac{Q}{RT}\right) \tag{4}$$

Here, Q is the apparent activation energy and R is the gas constant. D_0 is the diffusion coefficient of the dominant diffusion mechanism. If the dominant mechanism is volume diffusion, $D_0=(D_v)_0$ and $n=3$ are satisfied, whereas if grain boundary diffusion is dominant, then $D_0=(\delta D_b)_0$ and $n=4$.

The combined stage sintering equation provides the relationship between densification rate and diffusional sintering. However, measurement of the lumped geometric scaling parameter (Γ) and the diffusion coefficient (D) requires much effort [29]. Therefore, Su et al. [28] rearranged the equation and divided it into density dependent group and process dependent group.

$$\int_{\rho_0}^{\rho}\frac{kG^n}{3\gamma\Omega\rho D_0\Gamma}d\rho=\int_{t_0}^{t}\frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt \tag{5}$$

The left-hand side includes microstructural parameters and material properties.

$$\Pi(\rho)=\int_{\rho_0}^{\rho}\frac{kG^n}{3\gamma\Omega\rho D_0\Gamma}d\rho \tag{6}$$

The right-hand side of Eq. (5) depends on only activation energy (Q) and time-temperature profile. It is commonly referred as the work of sintering (Θ).

$$\Theta(t,T)=\int_{t_0}^{t}\frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt \tag{7}$$

The MSC is the relationship between ρ and Π. However, it is difficult to obtain Γ and D as mentioned above. Whereas, the work of sintering (Θ) can be calculated by numerical integration with a heating cycle of the sintering process. Since $\Theta(t,T)=\Pi(\rho)$ is satisfied by Eq. (5), the MSC can be established as the relationship between ρ and Θ.

D.L. Johnson et al. [42] suggested a polynomial function for the MSC. However, M.H. Teng et al. [43] and D.C. Blaine et al. [29] found a sigmoidal function was better to describe the MSC. The sigmoidal function of the MSC can be expressed as a function of the relative density and the work of sintering.

$$\rho=\rho_0+\frac{1-\rho_0}{1+\exp\left(-\frac{\ln\Theta-a}{b}\right)} \tag{8}$$

Here, ρ is the relative density, ρ_0 is the initial relative density and the constants, a and b, are the parameters of the sigmoidal function. To calculate the sigmoidal parameters, linearization of the MSC model is required [20]. The densification parameter (ψ) and the densification ratio (Φ) need to be defined for linearization.

$$\psi=\frac{\rho-\rho_0}{1-\rho_0}=\frac{1}{1+\exp\left(-\frac{\ln\Theta-a}{b}\right)} \tag{9}$$

$$\frac{1}{\psi}-1=\exp\left(-\frac{\ln\Theta-a}{b}\right)=\frac{1}{\Phi} \tag{10}$$

The densification ratio can be expressed as:

$$\Phi=\frac{\rho-\rho_0}{1-\rho}=\left(\frac{\Theta}{\Theta_{\mathrm{ref}}}\right)^n \tag{11}$$

where, Θ_{ref} is the work of sintering in half way of densification and n is the power law exponent. From Eqs. (10) and (11), the equation below should be satisfied.

$$\ln\Phi=\frac{1}{b}(\ln\Theta-a)=n(\ln\Theta-\ln\Theta_{\mathrm{ref}}) \tag{12}$$

Therefore, the parameters of the sigmoidal function, a and b, can be calculated from linear fitting of ln Φ vs. ln Θ.

3. Experiments

3.1. Materials and methods

The powders used in this study were 316L stainless steel. Commercially available 4 μm (Atmix, Japan) and 100 nm (Nano technology, Korea) powders were used. The powders were mixed by turbula mixer (KMC, KMC-T21) for 40 min to fabricate nano/micro bimodal powders. 3 different bimodal powders were formulated with nano powder of 25, 50 and 75 vol%. The powders were observed by scanning electron microscopy (JEOL, JSM-6390LV), and characterization of each powder was conducted. Pycnometer density was measured by automatic helium pycnometer (Micromeritics, Accupyc 1330), and tap density was measured by tap density volumeter (Bettersize Instruments Ltd., BT-300). Particle size distribution was also analyzed by particle size analyzer (HORIBA, LA-960).