Simulation of the Sintering Densification and Shrinkage Behavior of Powder-Injection-Molded 17-4 PH Stainless Steel

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This study simulates the sintering behavior of powder-injection-molded 17-4 PH stainless steel to predict the geometry of the sintered components. Sintering is considered as the viscous deformation process of a porous body under the influence of sintering stress. Consequently, modified constitutive equations applicable to linear viscous, compressible material, based on a continuum-mechanics approach, were utilized in simulating the sintering kinetics, with grain-boundary diffusion as the dominant densification mechanism. Quenching and other experiments were conducted to quantify the densification and grain-growth behavior of the powder-injection-molded 17-4 PH samples during sintering, to determine the material parameters required for the constitutive model. The predictive capability of the model was verified by comparing the theoretical calculations with the experimentally observed variation in sintering shrinkage of the samples determined by dilatometry. The predictions underestimate shrinkage above 700 °C, a factor related to the volume change from the phase transformations observed during the sintering.

I. INTRODUCTION

POWDER injection molding (PIM) is a near-net-shape manufacturing technology for the mass production of small and complex-shaped metal or ceramic components. The PIM process is composed of four sequential steps: mixing of the powder and organic binder, injection molding, binder removal (debinding), and sinter densification. Mechanical properties of a well-processed powder-injection-molded material are indistinguishable from cast and wrought material.\(^\text{[1]}\)

The 17-4 PH stainless steel is a precipitation-hardening martensitic stainless steel widely used in the PIM industry for medical, automotive, and aircraft components due to its high strength, high toughness, and moderate corrosion resistance.\(^\text{[1,2,3]}\) Understanding the densification behavior and modeling the shrinkage of 17-4 PH stainless steel powder shaped by PIM during sintering is valuable for process and tool design. Considerable effort has been directed at developing the constitutive equations for the sintering densification and grain growth of ceramic powders.\(^\text{[4–9]}\) The efforts on the sintering densification and grain growth of metal powders during conventional metal powder processing are limited, because of the large particle sizes (greater than 50 \(\mu\)m) that do not undergo significant densification by pressureless sintering. But, the particle size of metal powders for the PIM process is small (2 to 15 \(\mu\)m) and, consequently, the constitutive equations for fine powder material can be applied to analyze their densification and grain-growth behavior.

The present article reports on the sintering densification and grain growth of PIM-produced components molded with a feedstock composed of gas-atomized 17-4 PH stainless steel powder. Our effort is focused on modeling the sintering kinetics, to enable us predict the final component size and shape. In this process, it is important to consider grain growth, because the grain boundary provides the dominant path for atomic motion.\(^\text{[3]}\) A new grain-evolution equation is proposed to model the experimentally determined grain-growth behavior. Further, the creep-densification equations proposed by Kwon and Kim\(^\text{[10]}\) were simplified. Such a simplification leads to determining a single, unique, experimentally determined material parameter that enables application of the model for practical uses such as process control.

II. EXPERIMENTAL

Gas-atomized 17-4 PH stainless steel powder with an average particle size of 10.2 \(\mu\)m was used in this work. The chemical composition of the powder is given in Table I. The powder was mixed with an agar-based binder with a 55 pct volume fraction of powder.\(^\text{[3,10]}\) The feedstock was injection molded as tensile bars of 75.0 mm in length, 7.6 mm in width, and 7.6 mm in thickness, with a 42.0-mm gage length in a standard plastic molding machine. The tensile bars were thermally debound at 5 °C/min to 600 °C for 1 hour in hydrogen with a dew point of −67 °C. Samples for quenching experiments and dilatometry, with dimensions of 6.7 mm in height, 7.6 mm in width, and 7.6 mm in thickness, were cut from the debound tensile bars.

The samples were sintered in a vertical alumina tube furnace at 1120 °C, 1220 °C, 1270 °C, and 1320 °C for 1, 10, 20, and 60 minutes in hydrogen with a dew point of −67 °C. The heating cycle was 10 °C/min to 1010 °C for 1 hour, with subsequent heating at 2 °C/min to the sintered temperature and cooling rapidly by quenching in water after holding at the sintering temperature for the desired time. The sintered density was measured by the Archimedes method.\(^\text{[11]}\)

The sintered samples were cut, mounted in Bakelite, and polished to a 0.3-\(\mu\)m surface finish for metallographic
examination. The polished samples were chemically etched using Kalling’s reagent to observe the microstructure and quantify the grain size. The grain size \( G \) was obtained by measuring the average linear-intercept length \( G_i \) on the polished cross section of a sample with the following relationship:\(^{[12]}\)

\[
G = 1.571G_i
\]  

where the average linear-intercept length was measured from at least 400 grains. Where applicable, the average linear-intercept length was measured by assuming that regions of martensite surrounded by \( \delta \)-ferrite constituted the same grain.

A vertical pushrod dilatometer was used to determine the shrinkage vs temperature during sintering. Dilatometry was conducted in hydrogen at 10 °C/min to 1010 °C for 1 hour, then the sample was heated at a rate of 2 °C/min to 1365 °C for 1 hour, followed by cooling to room temperature at a rate of 10 °C/min.

### III. ANALYSIS

#### A. Creep Strain Rate

It is convenient to divide the process of densification of powder compacts into two stages,\(^{[5–8]}\) following the densification mechanism. Stage 1 is the initial stage of densification and stage 2 is the final stage of densification, with a transient from stage 1 and stage 2 at a relative density of 0.92.\(^{[8]}\) Since grain-boundary diffusion is the dominant sintering mechanism in 17-4 PH stainless steel powders,\(^{[2,3]}\) a constitutive equation for linear viscous, compressible material can be utilized to describe the sintering kinetics. The general form of the creep strain rate \( \dot{\varepsilon}_b \) for such a porous powder compact is expressed as\(^{[5]}\)

\[
\dot{\varepsilon}_b = \frac{1}{2\mu} \sigma''_y + \left( \frac{1}{3K} (\sigma_m - \sigma_y) \delta_y \right) \]  

where \( \sigma''_y \) and \( \sigma_m \) are the deviatoric and hydrostatic \( (\sigma_d/3) \) parts of the true stress \( (\sigma) \), \( \delta_y \) is the Kronecker delta, \( \sigma_y \) is the sintering potential, \( \mu \) is the effective shear viscosity, and \( K \) is the effective bulk viscosity of porous powder compacts. Both of these material parameters (shear and bulk viscosities) depend on temperature and microstructure.

In Eq. [2], the effective bulk viscosity can be represented by functions of relative density. The effective bulk viscosity during the initial stage of sintering, when dominated by grain-boundary diffusional creep,\(^{[6]}\)

\[
K = \frac{\rho (\rho - \rho_0)^2}{8(1 - \rho_0)^2} \frac{k_b T D^3}{\Omega \delta D_b}
\]  

where \( \rho, \rho_0, k_b, T, D, \Omega, \delta, D_b, \) and \( C_i \) denote the relative density, initial relative density, Boltzmann constant, temperature, particle size, atomic volume, grain-boundary thickness, grain-boundary diffusion coefficient, and a material constant. In Eq. [3], the product of the boundary thickness \( (\delta) \) and the grain-boundary diffusion coefficient \( (D_b) \) can be written as

\[
\delta D_b = \delta D_{0b} \exp \left( -\frac{Q_b}{RT} \right)
\]  

where \( \delta D_{0b}, Q_b, \) and \( R \) are the pre-exponent for boundary diffusion, the activation energy for boundary diffusion, and the gas constant.

The effective bulk viscosity during the final stage of sintering dominated by grain-boundary diffusional creep is\(^{[6]}\)

\[
K = \frac{\rho k_b T D^3}{24 C_i (1 - \rho)^{1/2} \Omega \delta D_b}
\]  

where \( C_2 \) is a material constant which can be determined from experimental data.

Measurement of the values of the atomic volume, boundary thickness, and grain-boundary diffusion coefficient in Eq. [4] and [5] are very difficult and are not known for all materials. Further, the literature values cannot be used without modifications for analysis of the densification behavior of a given powder,\(^{[9]}\) because small changes in the chemistry of the powder, residual impurities, or sintering atmospheres during heating can induce phase transformations and change the aforementioned parameters. In this work, the material parameters \( \alpha_i \) and \( \alpha_f \)—representing the effective diffusion parameters during the densification events—are utilized and expressed as

\[
\alpha_i (T) = \frac{3 C_i \Omega \delta D_b}{k_b}, \quad \alpha_f (T) = \frac{3 C_2 \Omega \delta D_b}{k_b}
\]  

From Eq. [4] and [6], the material parameters \( \alpha_i \) and \( \alpha_f \) can be written as

\[
\alpha_i = \alpha_1 \exp \left( -\frac{Q_b}{RT} \right), \quad \alpha_f = \alpha_2 \exp \left( -\frac{Q_b}{RT} \right)
\]  

where \( \alpha_1 \) and \( \alpha_2 \) are material constants that can be determined from experimental data of the relative density with time at various temperatures.

From Eq. [2], [3], [5], and [6], the effective bulk viscosity during the initial stage \( (K_i) \) and final stage \( (K_f) \) of sintering can be written as

\[
K_i = \frac{\rho (\rho - \rho_0)^2}{8(1 - \rho_0)^2} \frac{T D^3}{\alpha_i}, \quad K_f = \frac{\rho}{8(1 - \rho_0)^{1/2}} \frac{T D^3}{\alpha_f}
\]  

For continuity, the effective bulk viscosities \( K_i \) and \( K_f \) in Eq. [8] must have the same values at the transition point corresponding to a relative density of 0.92. Imposing this condition of continuity, the material constant \( \alpha_2 \) can be expressed in terms of \( \alpha_1 \) as

\[
\alpha_2 = \frac{(1 - \rho_0)^2}{0.28 (0.92 - \rho_0)^{1/2}} \alpha_1
\]