Densification of W–Ni–Fe powders using laser sintering

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A B S T R A C T

In this paper, Laser Sintering (LS) of 90%W–7%Ni–3%Fe (wt.%) powders have been investigated, with the goal to understand the influence of final density by laser power, scanning speed, laser trace width, and the number of scanning passes. The results suggest that the laser power and scanning speed are the most important factors influencing density; the influence of trace width and number of scanning passes are not significant. With the increase of laser power and decrease of scanning speed, higher density can be achieved. The microstructure analysis indicated that the porosity changed from open porosity to closed porosity with higher laser energy input. Energy-Dispersive X-ray Spectroscopy (EDX) analysis shows that during the sintering process, W was not melted but dissolved into the Ni–Fe matrix. Contact flattening and grain accommodation of W grains have been observed. It suggests that both rearrangement and solution-precipitation mechanisms are responsible for the densification. The sintered density with respect to laser power and scanning speed was modeled by continuum modeling theory and compared with experimental results.

1. Introduction

Tungsten Heavy Alloys (WHA), such as W–Ni–Fe, W–Cu, W–Ni–Mo, W–Ni–Cu, are widely used as kinetic-energy penetrators [1], counter-balance weights [2], projectiles, and medical radiation shields [3]. W–Ni–Fe is a WHA which is conventionally fabricated through Liquid Phase Sintering (LPS), owing to refractoriness of tungsten (melting point at 3420 °C) [4]. Nickel and iron are commonly added to tungsten to form a ductile solid solution matrix of W–Ni–Fe [5]. The nickel to iron ratio of 7:3 avoids intermetallic precipitation on cooling [6]. Laser sintering (LS) and Laser Melting (LM) enable the fabrication of three-dimensional objects from powder materials by selectively heating and fusing particles using a laser beam. Compared to conventional LPS, there is no need to fabricate the die to compact powders; therefore rapid manufacturing can be achieved with flexibility to manufacture complex geometries. Depending on the laser processing parameters, the binding mechanism in LS ranges from fully melting of all phases to melting of only low melting temperature phases which act as binders [7,8,9]. The binding mechanism determines the densification and the final density. For LS of W–Ni–Fe, both fully melting, in which W, Ni, and Fe are all heated to above their respective melting point; and liquid phase sintering, in which only Ni and Fe are melted while W still remains as solid phase, have been reported [10]. Density is one of the

most critical factors to influence the mechanical properties and dimensional accuracy for LS/LM processes. In conventional LPS, the densification process of W–Ni–Fe has been studied extensively [11,12]. It is a well-established theory that there are three stages in conventional LPS: (1) liquid formation and resultant particle rearrangement; (2) solution-precipitation; (3) solid state sintering of the solid skeleton. Each stage has a different densification mechanism which is responsible for different densification rates [13,14]. Contrasting to conventional LPS, LS is a significantly faster process due to the high energy density irradiated by a focused laser beam which scans at fast speed. As a result, it is important to find out what laser parameters are crucial to the final density. Moreover, the mechanism responsible for densification in LS of W–Ni–Fe should be understood in order to develop models that can predict the sintered density. This paper aims to understand the factors that influence the density during laser sintering, the densification mechanism, and develop a model to predict the density of LS of W–Ni–Fe.

2. Experimental procedures

The powders used in this study are premixed from Aerojet Rocketdyne. After magnetic separation, size distribution measurements were acquired for W powder and Ni/Fe powder optically via an automated microscopy and image analysis tool (Malvern Morphologi G3). Fig. 1 shows the Circle Equivalent (CE) diameter of W and Ni–Fe. The compositional analysis results show that the mixed powder has 89.98 wt.% W, 7.1 wt.% Ni, and 2.92 wt.% of Fe.

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The relative density of the samples is defined as:

$$\rho = \frac{\rho_m}{\rho_T} \quad (1)$$

where ρ_m is the measured density of the sintered sample; ρ_T is the theoretical density of fully dense sample. The relative density of tapped powders was determined to be 48.2%. Cubic samples with 8 mm length were sintered by a Concept Laser M2 machine under an argon protective atmosphere.

In order to determine if scanning trace width (the track width of the melt-pool of single laser scanning [15]) and repetitive heating can impact the final density, in the first experiment, samples were sintered with trace width of 0.1 mm, 0.125 mm, and 0.15 mm, at different combinations of laser power and scanning speed.

At each set of LS parameters, the relative density of the resultant samples was measured using Archimedes method. In the second experiment, repetitive scans on same trace were conducted to understand the impact of the number of scanning passes on the sintered density. After sintering, the samples were removed from the build plate by Electrical Discharge Machining (EDM). The samples were polished by sand paper, enabling microstructure and composition samples to be analyzed using a JEOL 6390 scanning electron microscope equipped with EDX.

3. Results and discussion

3.1. Density

The specific laser energy input to the powder bed can be described as [16]:

$$P_a = \frac{P}{vdh} \quad (2)$$

where P is the laser power input (W), v is the scanning speed (mm/s), h is the distance between scanning traces (mm), and d is the thickness of each layer (mm). Since the layer thickness and scan spacing were

constant in this study, the specific energy input to the powder bed per unit length (J/mm) is:

$$P_u = \frac{P}{v}. \quad (3)$$

The density of sintered samples with different laser scanning parameters is summarized in Table 1. Trace Width (TW) with various specific energy P_u is plotted in Fig. 2. The results indicate that the influence of trace width to density is within 4%, which is not technically significant. The laser energy range evaluated in this study is enough to melt Ni-Fe to facilitate densification by W grain rearrangement and solution-reprecipitation (confirmed by the microstructure analysis in the next section), therefore the trace width has minimal impact on the final density.

The density of sintered samples with single and double shot is summarized in Table 2. The relative density of single shot vs double shot (the laser beam scans the same trace twice) is plotted in Fig. 3. There is no significant difference in final density by using double shot at the same trace. This suggested that after the first laser scan, the densification by W grain rearrangement and solution-reprecipitation is completed; further heating is not helpful for further densification, unless further processing to assist solid state sintering, such as conventional sintering or Hot Isostatic Pressing (HIP).

3.2. Microstructure

Microstructures provide evidence of the processing and densification mechanism during processing. Fig. 4(a) shows the optical image of the sample with lower energy input (0.362 J/mm), which has a relative density of 66.7%; Fig. 4(b) is a sample with higher energy input (1.31 J/mm), which has a relative density of 88.1%. With lower energy, it can be seen that most of the pores are connected. As the relative density increases, the pores become isolated and closed. The protective atmosphere argon in this study has no solubility or diffusivity through the matrix; therefore the trapped pores show no mobility while being dispersed in the solid and liquid phases, preventing further

Fig. 1. Particle size distribution.

Table 1

Sintered density of the samples with different trace width.

Power P (W)	Scanning speed v (mm/s)	P/v	Density with TW = 0.1 (mm)	Density with TW = 0.125 (mm)	Density with TW = 0.15 (mm)
230	300	0.77	83%	86%	87%
230	635	0.36	82%	78%	81%
310	300	1.03	86%	86%	84%
393	300	1.31	86%	88%	87%
393	470	0.84	82%	85%	84%

densification [17]. There are no dendrite structures in the micrographs confirming that there is no full melting or solidification of W, which has been reported in literature [10]. The liquid phase has penetrated into the grain boundary of W. From the thermodynamics point of view, the surface tension and capillary forces are the driving factors for densification during the rearrangement stage of liquid phase sintering. Therefore, the pores are closed and rounded in Fig. 4(b).

In the W–Ni–Fe system, the solubility of W in the Ni–Fe matrix is about 23 wt.% [18]. To understand if W has been dissolved into Ni–Fe, higher magnification Scanning Electron Micrographs (SEM) and EDX analysis have been conducted. From Fig. 5(a), it can be seen that the W grains have remained solid; EDX analysis from Fig. 5(b) confirmed that the grain is 100% W. Fig. 5(d) EDX analysis on the Ni–Fe matrix indicated that W has been dissolved into the matrix. Contact flattening between W grains has been observed in all samples, as shown in Fig. 6. From classical LPS theory, this signature indicates that solution-reprecipitation has happened during the laser sintering process. The stress at the intergranular contact point, due to the capillary force from the wetting liquid, causes preferential dissolution of the solid at the contact point with reprecipitation at regions removed from the grain contacts [18,19]. The rearrangement of W grains and shape accommodation are responsible for the densification, similar to conventional LPS. A second possible explanation is the pre-melting of W grain boundaries which has been confirmed by experiments using High Resolution Transmission Electron Microscopy (HRTEM) during conventional sintering [20,21,22]. However, it is still subject to further experimental study to confirm what mechanism is driving the dissolution of W into Ni–Fe matrix. A sintering kinetics study would reveal the mechanism beyond doubt by measuring the shrinkage rate and calculating the sintering exponents, as in supersolidus liquid phase sintering [23]. However, due to the extremely fast speed of densification in laser sintering, it is impractical to perform such experiment. Solid state sintering was not present during the laser sintering process, as evidenced by the lack of neck formation in the microstructure. There is no significant grain growth, which is also attributed to the short sintering time.

Fig. 2. Sintered density of different Trace Width (TW).**Table 2**

Sintered density of the samples with single and double shot.

Density of single shot	Density of double shot	Power P (W)	Scanning speed v (mm/s)	P/v
87%	82%	230	300	0.77
81%	79%	230	635	0.36
84%	85%	310	300	1.03
87%	87%	393	300	1.31
84%	84%	393	470	0.84

4. Modeling of densification

The density of various P/v ratios was plotted in Fig. 7. The highest density of the resultant sample is about 94.7%. With higher laser input, the higher temperature of the melt pool resulted in longer solidification time under which the Ni–Fe phase remains liquid. Longer time above liquidus will help the rearrangement and result in higher density. According to LPS theory, 35% volume fraction of liquid is necessary to achieve full density by rearrangement mechanism [19]. The volume fraction of the liquid phase in this study is 20%, which is not sufficient to fully densify by the particle rearrangement mechanism.

One of the important objectives in optimizing LS process is to predict the final density. In this study, continuum modeling approach developed by Olevsky and Skorohod [24] was applied. In continuum modeling, the mechanical response of a porous body with linear viscous behavior is described by a rheological (constitutive) relation that interrelates the components of a stress tensor σ_{ij} and strain rate tensor $\dot{\epsilon}_{ij}$ [25]:

$$\sigma_{ij} = 2\eta_0 \left[\varphi \dot{\epsilon}_{ij} + \left(\psi - \frac{1}{3} \varphi \right) \dot{\epsilon} \delta_{ij} \right] + P_L \delta_{ij} \quad (4)$$

where φ and ψ are the normalized shear and bulk viscosity moduli, which depend on porosity θ . η_0 is viscosity of the material; P_L is capillary sintering stress; δ_{ij} is the Kronecker symbol, and $\dot{\epsilon}$ is the first invariant of the strain rate tensor, which is:

$$\dot{\epsilon} = \dot{\epsilon}_{11} + \dot{\epsilon}_{22} + \dot{\epsilon}_{33}. \quad (5)$$

Physically, $\dot{\epsilon}$ represents the local volume change rate of a porous body. The porosity θ is defined as:

$$\theta = 1 - \frac{\rho}{\rho_T} \quad (6)$$

Fig. 3. Sintered density of single shot vs double shot.

Fig. 4. Optical micrographs of SLS parts: (a) P/v ratio of 0.362 J/mm and final density of 66.7%; (b) P/v ratio of 1.31 J/mm and final density of 88.1%.

where ρ and ρ_T are volumetric mass and theoretical density, respectively. The evolution law of porosity is given by:

$$\dot{\epsilon} = \frac{\dot{\theta}}{1-\theta}.$$

For laser sintering, the external applied stress is zero, thus Eq. (4) is the following:

$$(7) \quad \dot{\epsilon} = -\frac{P_L}{2\eta_0\psi}. \quad (8)$$

Fig. 5. (a) SEM micrograph of sintered sample with P/v ratio of 0.188 J/mm and final relative density of 58.4%; (b) EDX of the solid particle shows it is 100% W; (c) SEM micrograph where the EDX has been taken; and (d) EDX analysis of the matrix.

Fig. 6. SEM micrograph of the boundary between two W particles showing the contact flattening.

In Skorohod model, the sintering stress is:

$$P_L = \frac{3\alpha}{r_0} (1-\theta)^2 \quad (9)$$

where α is the surface tension, r_0 is the average radius of the particle. The bulk viscosity moduli from Skorohod model is:

$$\psi = \frac{2(1-\theta)^3}{3\theta} \quad (10)$$

From Eqs. (8), (1), and (10), the following can be derived:

$$\dot{\theta} = -\frac{9\alpha\theta}{4\eta_0 r_0} \quad (11)$$

Solving the differential equation of Eq. (11), the following can be obtained:

$$\theta = \theta_0 \exp -\frac{9\alpha}{4\eta_0 r_0} t \quad (12)$$

where θ_0 is the initial porosity, and t is the sintering time (assume $t_0 = 0$). As discussed before, the densification time depends on the time duration that the liquid phase exists, thus it can be assumed that:

$$t = k \frac{P}{v} \quad (13)$$

where k is a constant. From Eqs. (12) and (13), it can be derived that:

$$\theta = \theta_0 \exp -\frac{9\alpha k P}{4\eta_0 r_0 v} \quad (14)$$

The relative density is:

$$\rho = 1 - \theta = 1 - \theta_0 \exp -\frac{9\alpha k P}{4\eta_0 r_0 v} \quad (15)$$

The initial porosity was determined by experiment (see the [Experimental procedures](#) section) to be:

$$\theta_0 = 0.518. \quad (16)$$

The relationship of sintered relative density and the laser specific energy described by Eq. (15) was plotted in Fig. 7, from porosity 0.518 (relative density of 0.482) to porosity of 0.06 (relative density of 0.94). It can be seen that the model prediction trend agrees with the experimental results. Future development is ongoing to incorporate a heat transfer model with the densification model to facilitate the prediction of processing parameters.

Fig. 7. Sintered density of various P/v ratio and comparison with the master sintering curve.

5. Conclusions

From the laser sintering of 90%W–7%Ni–3%Fe (wt.%), the following conclusions can be made:

- (1) The laser scanning trace width and the number of laser scanning passes are not significant to impact the final density; while the laser power and scanning speed are significant to the final density. The highest relative density achieved was 94.7%.
- (2) It was observed that contact flattening and grain accommodation happened during densification of W–Ni–Fe. Both rearrangement and solution-precipitation mechanisms are responsible for densification. Further study is needed to confirm if solid W is dissolved into Ni–Fe matrix or if the grain boundary of W has been premelted.
- (3) Based on continuum modeling theory, a densification model was developed and compared with the experimental results. It was shown that the model agrees with the experimental results. Future development work is needed to incorporate laser processing recipes with densification model. Shape distortions can also be modeled leveraging the continuum modeling of liquid phase sintering.

Acknowledgment

The author would greatly thank the experimental support by Lawrence Livermore National Laboratory, and the support from R-IDC and College of Engineering from California Polytechnic State University San Luis Obispo. The sample preparation and SEM work has been supported Dr. Katherine Chen from Materials Engineering Department, and Dr. Richard Savage from Biomedical & General Engineering at Cal Poly.

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