

SINTERING OF PIM Fe-2Ni-0.8C

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ABSTRACT

The use of water atomized powders in powder injection molding processes has long been an area of interest because of the cost savings afforded by the water atomization process over gas atomization and chemical methods. In this study, water atomized Fe-2Ni powder is investigated for sintering response in the milled and as-received conditions. Variations in particle size, carbon content, heating rate, sintering temperature, and atmosphere were studied. The findings indicate that, aside from sintering temperature, the most important factors influencing the sintered density are the particle size, heating rate, and surface chemistry. Milling alters the surface chemistry and decreases the particles size, both of which serve to increase sintered density.

INTRODUCTION

A common alloy that has been widely used in the powder injection molding (PIM) process is Fe-2Ni [1]. This alloy has traditionally been made by admixing carbonyl Fe and Ni powders. Carbonyl iron powders are chemically produced powders with small size and spherical shape, both attributes being attractive in the PIM process. Lin et al. [2] have reported a sintered density of 96 % theoretical by optimizing the process variables for carbonyl powders. Carbon control in Fe-2Ni systems have been achieved by debinding and sintering in nitrogen based atmospheres, or by the use of a carbon control step during presintering with CO/CO₂ gas mixtures [3].

Sintering difficulties have been encountered with larger water atomized prealloyed Fe-2Ni powder and near full density is not achieved at the same sintering temperatures as carbonyl based systems. The primary goal of this research was to attain maximum densification with a desired level of carbon using water atomized Fe-2Ni, and gain a more thorough understanding of the sintering barriers in these powders.

BACKGROUND

Nickel is a common alloying element in ferrous materials due to its positive effect on hardenability, strength, and toughness. Zhang and German [4] found that densification in the carbonyl Fe-Ni system was maximized at a 2 wt. % Ni admixed addition. This composition gave a significant increase in the

strength, hardness, and ductility over unalloyed carbonyl iron. Zhang et al. [5] found that most of the densification takes place prior to the $\alpha \rightarrow \gamma$ phase transformation and that the processing conditions inherent to PIM affect the final properties through the three dominant factors of density, grain size and carbon content. Lin et al. [6] found that temperature is the primary factor and time is the secondary factor in affecting the final sintered density in the Fe-2Ni system. The final carbon content depends on the chemistry of the starting powder (such as carbon and oxygen content), as well as the debinding and sintering conditions and has an influence on the strength of the product.

Zhang and German [7] concluded that the sintering of this class of materials can be divided into three stages, from 570 to 730°C, 730 to 880°C, and above 880°C. They found that most of the sinter densification occurred below 1000°C and that microstructure development above this temperature has an important influence on the mechanical properties. High densities are possible by sintering carbonyl powders below the $\alpha \rightarrow \gamma$ phase transformation. For example, a sintered density of 7.38 g/cm³ (94% theoretical) is reported after heating Fe-2Ni to 880°C for 1 h [8]. The bcc structure of ferrite is a more open packing structure than the close packed fcc structure of austenite. The relatively slow lattice and grain boundary diffusion and rapid grain growth associated with austenite cause sluggish sintering response in comparison to ferrite. However, the microstructure after low temperature sintering is heterogeneous, and higher temperatures are needed to solutionize and homogenize the alloy. A sintered density of 7.6 g/cm³ (96% theoretical) is achieved after heating to 1250°C for 1 h. The tensile properties are much improved at this temperature because strengthening by Ni and C in solution requires the formation of austenite. Thus, the mechanical properties are improved as a result of a homogeneous microstructure. There is, however, a trade-off between strength and ductility at high temperature sintering (over 1200°C). The strength increases due to pore shrinkage, pore spheroidization, and nickel homogenization, while the ductility decreases due to microstructural coarsening. For a typical carbonyl Fe powder, grain size increases six times between 900°C and 1250°C [8]. Hence, there is little gain in densification in spite of carbon dissolution and homogenization at higher temperatures.

Previous investigations have shown that mechanical properties of sintered Fe-Ni alloys are sensitive to several factors including porosity, pore size, pore shape, carbon content, and homogeneity, and the densification and homogenization events are controlled by several factors including Ni powder morphology and temperature [4, 6-14]. Dixon et al. [15] demonstrated that a homogenization parameter could be used to predict mechanical properties. As long as the homogenization parameter was above a certain value, a simple relationship between porosity and tensile strength was valid. In less homogenous materials, the equation over-predicted the tensile strength. Zhang et al. [7] demonstrated that ductility is inversely affected by grain growth and that the large austenitic grains usually result in a coarse pearlite structure, which degrades both strength and ductility. Lin et al. [6] showed that densification by hot isostatic pressing after sintering demonstrated superior properties by elimination of residual porosity, adjustment of carbon level, and control of grain growth.

Water atomized and gas atomized prealloyed powders have been employed in powder injection molding for years, particularly in 316L and 17-4PH stainless steel grades [16, 17]. Gas atomized powders are more spherical in shape than water atomized powders, and typically possess greater yields of $>20\mu\text{m}$ powder, due to the slower cooling rate of the gas atomization process. Over the years, special techniques have improved the yield of fine particles by the water atomization process [18]. Water and gas atomized stainless steel powders are often mixed to achieve improved or equal performance at a lower cost than pure gas atomized powder. Spherical particles tend to mold better and allow for higher solids loading, while rounded irregular particles produce compacts with better strength in the debound condition [19, 20]. Water atomized powders have also been used in injection molding without blending with gas atomized or carbonyl powders [21, 22, 23]. Changes in binder formulation can improve the moldability of water atomized powders by decreasing powder-binder separation [24]. Miura et al. [25] compared the use of 12

μm water atomized Fe-2Ni powder and blended carbonyl and Ni powder for injection molding. Because a density of only 93% was attained with the water atomized powder, mechanical properties were superior in the blended carbonyl and Ni system.

EXPERIMENTAL PROCEDURE

The powders were characterized for particle size distribution and shape, pycnometer density, surface chemistry, and bulk chemistry. The surface chemistry analysis was performed using X-ray photoelectron spectroscopy (XPS). The chemical analyses of the powders were carried out using ICP-AES. A sample of Fe-2Ni powder was ball milled under argon cover gas with stainless steel media and heptane for 24 h to break down the surface oxides and reduce the particle size. DSC/TGA was performed on the milled and as-received powders by heating at $5^\circ\text{C}/\text{min}$ to 1475°C in high purity N_2 . A 635 sieve ($20\ \mu\text{m}$) was used to affect the particle size of a sample of as received powder, in order to evaluate the effect of particle size on sintering response. A sample of as-received powder was mechanically strained by pressing at 10 tsi without binder, and breaking back down into powder, in order to measure the effect of mechanical straining on sintering response.

Test pellets for sintering experiments over a range of compositions and processing conditions were prepared by mixing powders with 2 wt.% paraffin wax by heating in an air oven at 70°C for 20 min. and compounding the mixture by hand every 5 min. The powders were compacted with a Carver hand press into pellets nominally 12.8 mm in diameter and 3 mm in height such that the green density of the pellets was 56% of the theoretical density. Several samples were pressed to 60% density to determine the effect of packing density on sintered density. Torque rheometry was used to determine the proper solids loading for the as-received Fe-2Ni powder. The as-received Fe-2Ni powder was compounded in a twin screw compounder using a solids loading of 56% and a binder system consisting of 50% paraffin wax, 30% polypropylene, and 20% modified polyethylene. Tensile bars were injection molded in an Arburg 55 ton injection molding machine at 20 mm/s with a 450 bar holding pressure, at an injection temperature of 170°C and a mold temperature of 25°C .

The green cylinder compacts were presintered at 700°C for 1 h in 80:20 N_2 : H_2 atmosphere to provide handling strength and to burn off the binder. Molded tensile bars were debound at 350°C and 450°C , then presintered at 900°C in 80:20 N_2 : H_2 atmosphere for handling strength. The samples were sintered in dry H_2 and an 80:20 N_2 : H_2 atmosphere in a CM horizontal tube furnace. Five samples were tested for each condition. The effect of heating rate was examined by changing the heating rate in the temperature range of 1150°C to 1300°C . The heating rates used were 1, 5, and $10^\circ\text{C}/\text{min}$. The samples were held at 1300°C for 1 h and cooled at $10^\circ\text{C}/\text{min}$ to room temperature in a horizontal alumina tube batch type furnace. Dilatometry was performed in an Anter vertical dilatometer in an 80:20 N_2 : H_2 atmosphere by heating at $5^\circ\text{C}/\text{min}$ to 1400°C for 1 h. Heat treating of tensile bars was performed by reheating to 900°C for 20 minutes and quenching in oil, then reheating to 350°C for 1 h in an 80:20 N_2 : H_2 atmosphere.

Density measurements were made using the Archimedes principle of water immersion. Carbon analysis was performed using a Horiba EMIA 8200 sulphur/carbon analyzer and oxygen analysis was performed using a Horiba EMGA oxygen/nitrogen analyzer. Metallographic polishing was achieved with a series of SiC grinding papers followed by a $3\ \mu\text{m}$ diamond polish. A final polish was obtained with colloidal silica suspension of size $0.3\ \mu\text{m}$. To enhance the contrast, the samples were etched for 5 to 10 s with 6% nitric acid (HNO_3) in methanol.

RESULTS

The particle attributes of the as-received Fe-2Ni and the 24h milled Fe-2Ni powders are detailed in Table I. The surface area increased from 0.47 to 0.58 m²/g as a result of milling. Figure 1 illustrates the SEM micrograph of the as-received and milled Fe-2Ni powders. It is observed that the as-received particles are rounded in shape, which is typical of fine water-atomized powders. There are a fair number of satellites on the powder particles. The particle shape after milling remains rounded. Many of the satellites have broken away from the particles, which contributed to the reduction in the particle size, increase in surface area, and increase in tap density.

Table I outlines the XPS surface chemistry analysis data for the as received and milled powders. It is observed that there is a significant reduction in the silicon (4.2 to 1.7wt. %) content on the surface of the milled powder. No nickel is detected on the surface of the powders. All elements are present as oxides. The oxygen and carbon values in XPS measurement represent mainly adsorbed organics and are therefore excluded from the results. The ICP chemical analysis results for both the as received and milled powders indicate that there is a considerable carbon and oxygen pickup as a result of milling. This was determined to be the result of contamination from the milling jar. A considerable change in the content of other elements is not observed.

Table I: Particle attributes, surface chemistry, and bulk chemistry of the as-received and milled Fe-2Ni.

Attribute	As Received	24 h Milled
Tap Density (g/cm ³)	4.26 (53% Theoretical)	4.42 (56% Theoretical)
Powder Size (μm)	D ₁₀ = 8 D ₅₀ = 15 D ₉₀ = 28	D ₁₀ = 5 D ₅₀ = 12 D ₉₀ = 22
Oxygen content (wt %)	0.49	0.58
Surface Area (m ² /g)	0.47	0.58
XPS Surface Chemistry – Si (at. %)	4.2	1.7

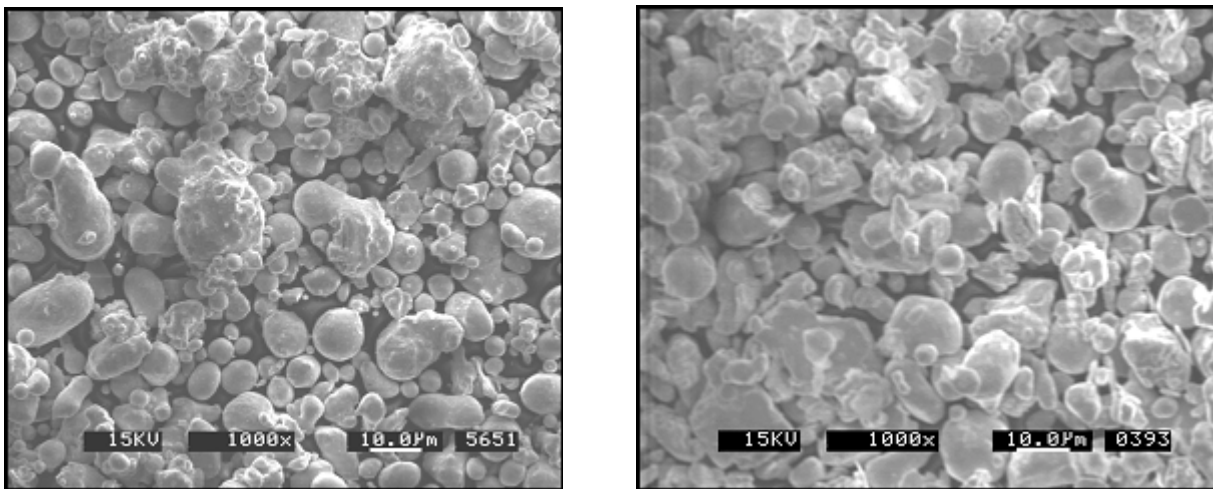


Figure 1. SEM micrographs of the as-received Fe-2Ni powder (left) and the 24 h milled powder (right).

DSC/TGA results of as-received and milled powders are shown in Figure 2. A liquid formation appears to occur around 1400°C in both powders. The milled powder has a weight loss at 250°C, most likely due to the burnoff of the milling jar polypropylene contamination. Dilatometry results of milled and as-received powders are given in Figure 3. It is observed that the milled powder shrinks more than the as-received powder at lower temperatures. The difference continues to widen until approximately 1375°C - 1400°C, where rapid shrinkage occurs in both powders. This is likely due to a formation of a small amount of liquid as confirmed by DSC.

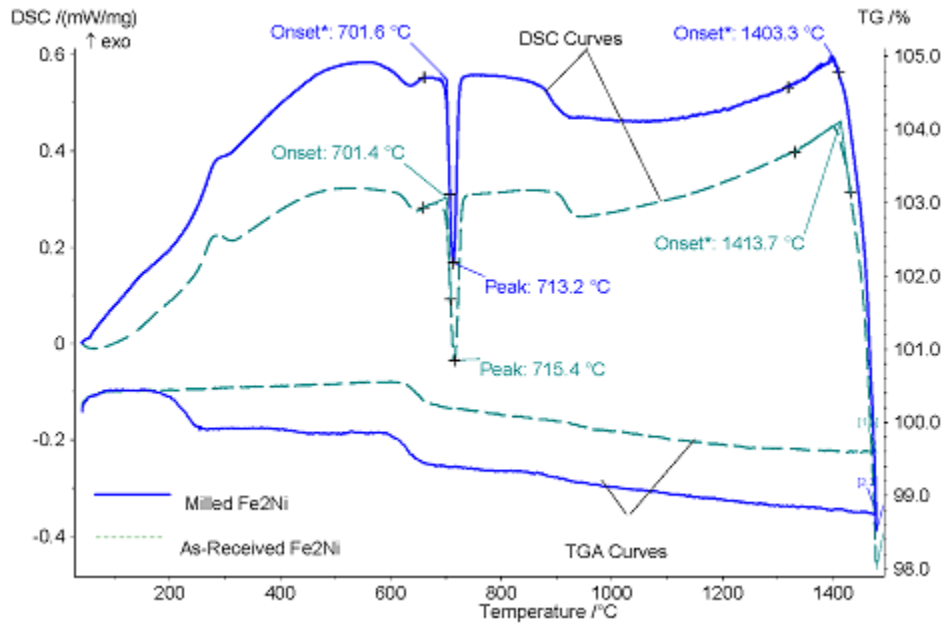


Figure 2. DSC and TGA curves for milled and as-received Fe-2Ni powders.

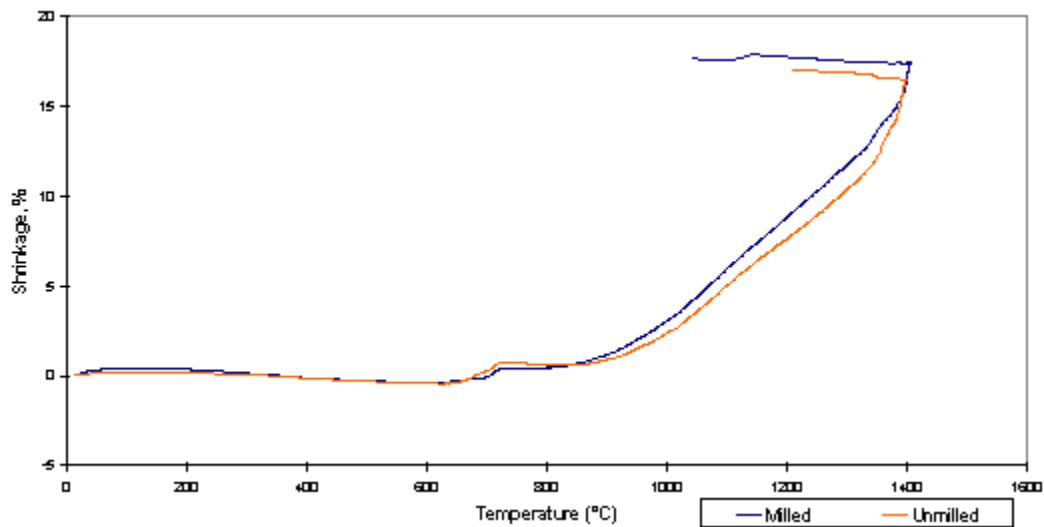


Figure 3. Dilatometry of milled and unmilled Fe-2Ni powder, samples heated at 5°C/min to 1400°C for 1 h in 80% N₂ / 20% H₂.

Figure 4 is a comparison in sintering response between the water atomized Fe-2Ni and carbonyl Fe + 2 wt% Ni. Samples were sintered for 1 h at maximum temperature in 80% N₂ / 20% H₂. The carbonyl powder has an average particle size of roughly 4 μm. It is observed that carbonyl Fe + 2 wt% Ni undergoes significant densification at lower temperatures as compared with the larger water atomized powder. Figure 5 depicts microstructures of water atomized Fe2Ni sintered at 1300 and 1350°C.

Sintering in H₂ atmosphere resulted in decarburization to a sintered carbon level of ~0.3 wt% after sintering at 1300°C for 1 h. Sintering in 80:20 N₂:H₂ atmosphere resulted in better carbon control, leading to sintered carbon contents of ~0.8 wt% for the same sintering cycle. Addition of 0.2 wt% carbon increased the final carbon by ~0.2 wt% in either H₂ or 80:20 N₂:H₂.

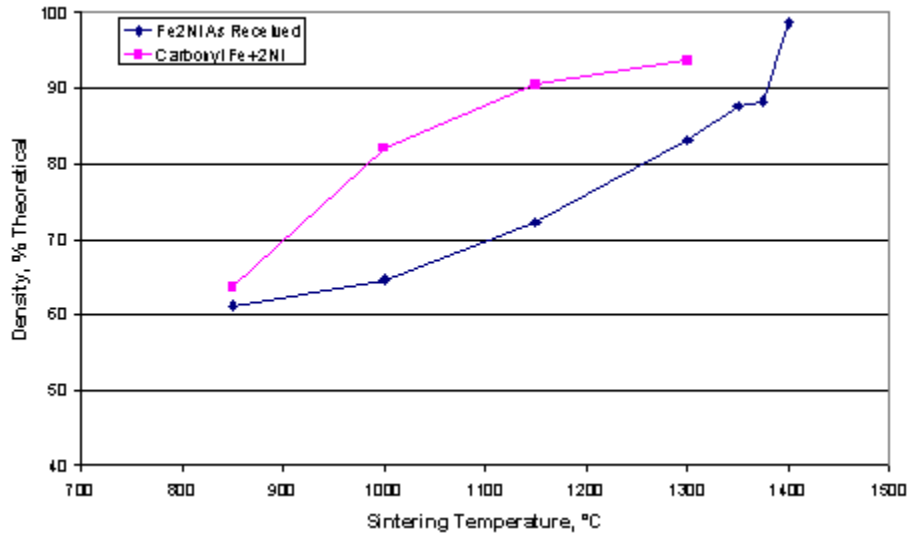


Figure 4. Comparison in sintering response between water atomized Fe-2Ni and carbonyl Fe + 2Ni. Samples were sintered for 1 h at maximum temperature in 80% N₂ / 20% H₂.

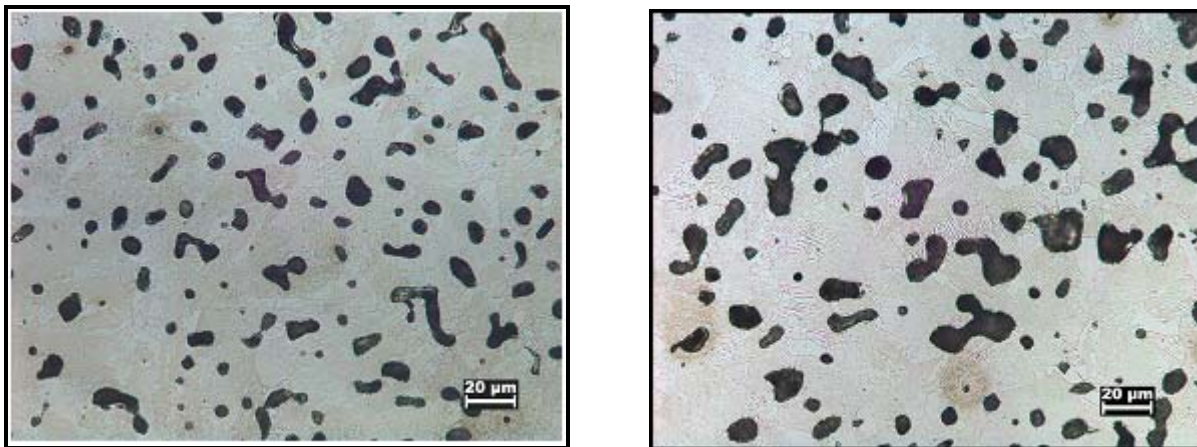


Figure 5. Optical micrographs for the Fe-2Ni powder sintered at 1300°C (left) and 1350°C (right). The heating rate was 5°C/min and atmosphere was a mixture of 80% N₂ and 20% H₂.

Studies on heating rate revealed an improvement in density with decreased heating rate in both milled and unmilled powders. Samples were presintered at 1000°C for 1 h and heated to 1150°C at 10°C/min, then heated to 1300°C for 1 h at 1°C/min, 5°C/min, or 10°C/min. The slowest heating rate of 1°C/min resulted in the highest sintered density in both atmospheres. A 91% theoretical density was obtained for the milled powder in the 80:20 N₂:H₂ atmosphere. When sintering at 1400°C, however, a density of 98% was achieved at 5°C/min, while a density of 94% was achieved at 1°C/min.

A plot of the sintered density (% theoretical) vs. particle size (D₈₀) for the Fe-2Ni, milled Fe-2Ni, and mechanically strained Fe-2Ni is shown in Figure 6. The pellets were pressed with 1 wt. % wax, presintered at 1000°C for 1 h, and heated at 1°C/min to 1300°C for 1 h in 80% N₂ and 20% H₂ atmosphere. Since milling affects the particle size, surface chemistry, and hardness of the powder, these experiments were devised to isolate each variable. Both milled and unmilled powders were sieved to + and - 635 for 5 minutes, to generate 3 particle sizes from each powder. The effect of mechanical straining is statistically insignificant, as the sintered density is less than 1% theoretical, which is within the error range. The milled powders achieved a maximum sintered density (~91% theoretical). Micrographs of samples sintered at various temperatures are given in Figures 7 and 8.

The injection molded bars were tested for hardness, ultimate tensile strength, and elongation to failure. The bars were presintered at 700°C for 1 h, and sintered for 0.5 h at 1400°C. The heating rate was 5°C/min and the atmosphere was a mixture of 80% N₂ and 20% H₂. The sintered density of the bars was 98% of theoretical and the carbon level was 0.7 wt%. The ultimate tensile strength averaged 774 MPa, with an elongation to failure of 4.3% and hardness of 22 HRC. In the heat treated condition, an average UTS of 1343 MPa was recorded, with an average elongation of 1.5% and hardness of 45 HRC. Ten bars were tested for each condition. Mechanical property and hardness data, standard deviations, and MPIF standards are given in Table II. In comparison with MPIF Standard 35 for MIM materials, the as-sintered properties are higher in hardness and UTS, and lower in % elongation, indicating the cooling rate was higher than typical. The heat treated properties are slightly below minimum values for UTS, above minimum values for % elongation, but are below the typical values for UTS, % elongation, and hardness. This is likely due to the large grain size resulting from the high sintering temperature. Microstructures of the as-sintered and heat treated tensile bars are shown in Figure 9.

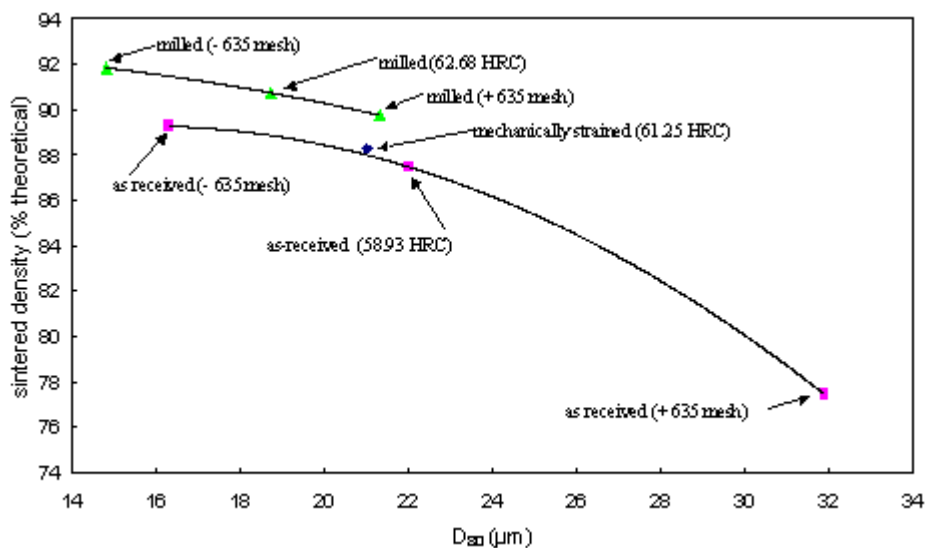


Figure 6. Plot of the sintered density (% theoretical) vs. particle size (D_{80}). The pellets were pressed with 1 wt. % wax, presintered at 1000°C for 1 h, and sintered for 1 h at 1300°C. The heating rate was 1°C/min and atmosphere was a mixture of 80% N_2 and 20% H_2 .

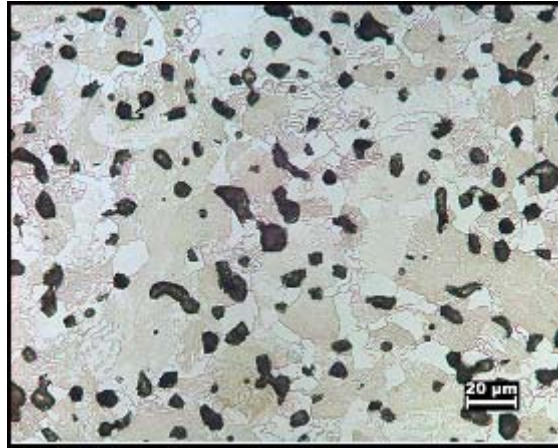


Figure 7. Optical micrograph for the milled Fe-2Ni sintered at 1300°C. The heating rate was 5°C/min and atmosphere was a mixture of 80% N_2 and 20% H_2 .

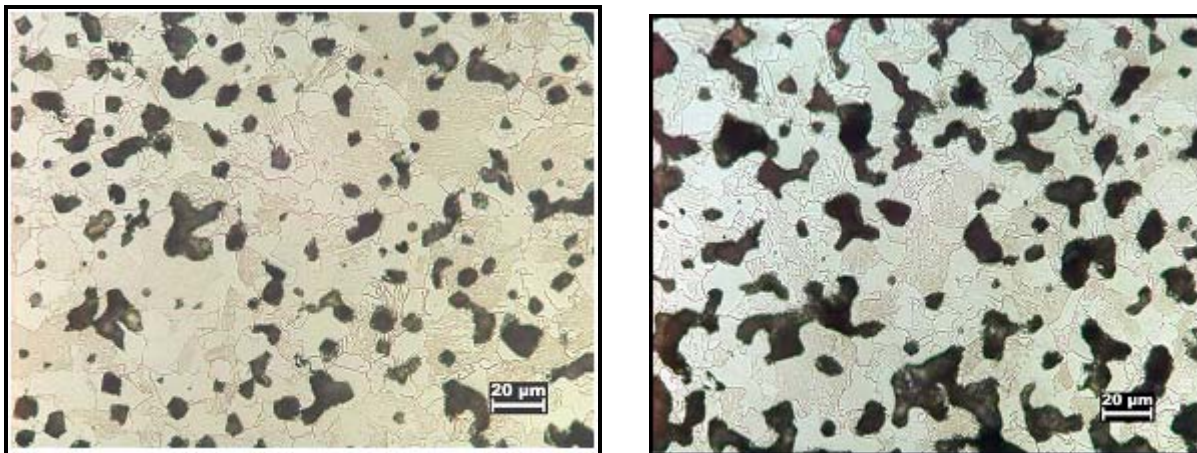


Figure 8. Optical micrographs for the -635 mesh as-received Fe-2Ni (left) and +635 mesh as-received Fe-2Ni (right) sintered at 1300°C. The heating rate was 1°C/min and atmosphere was a mixture of 80% N_2 and 20% H_2 . The compacts had carbon contents of 0.63 wt. %.

Table II: Mechanical properties of as sintered and heat treated Fe-2Ni.

	As Sintered		Heat Treated	
	Average	Standard Deviation	Average	Standard Deviation
UTS, MPa	774	25	1343	80
UTS, PSI	112246	3694	194678	11556
% Elongation	4.3	0.9	1.5	1
Hardness, HRC	22	1.6	44.6	1.3
MPIF Standard 33				
MIM 4605	Minimum	Typical	Minimum	Typical
UTS, MPa	379	441	1483	1655
UTS, PSI	55000	64000	215000	240000
% Elongation	11	15	<1.0	2
Hardness	62 HRB	-	48 HRC	-

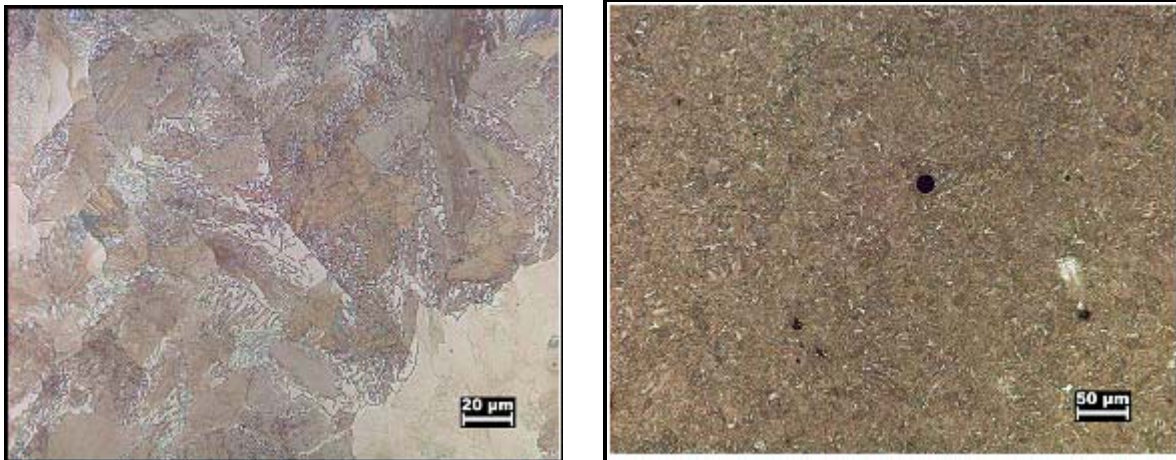


Figure 9. Microstructures of a) as-sintered and b) heat treated tensile bars, sintered at 1400°C for 30 min in 80% N₂ / 20% H₂ atmosphere to a density of 98%.

DISCUSSION

The particle size effect is illustrated by the curve in Figure 10. It is evident from the figure that there is a significant effect of particle size on sintered density. By reducing the D₈₀ particle size from 32 to 16 μm, the final density of the as-received powder increases from about 78 to 89% of theoretical density. The milled powder shows a similar trend with particle size. Milling of the powder reduced the average particle size (D₈₀ reduced from 22 to 19 μm). Therefore, the increase in sintering response from the milled powder is due in part to the decrease in particle size. If particle size were the only effect, however, the densities of the milled powder would lie along the same line as the as-received powder when plotted against particle size. The plot shows different trend lines for as-received and milled powders, indicating that the density gap between the lines is due to another mechanism. The hardness of the powder increased from 58.9 to 62.7 HRC due to milling. However, mechanical straining of the powder also increased hardness, but did not produce a significant increase in density. Milling also decreased the silicon content on the surface of the powder, which would allow for deoxidation at lower temperatures, since SiO₂ is more difficult to reduce than Fe oxides. This is evident in the dilatometry comparison, which shows that the difference in shrinkage between the two powders begins as early as 1000°C.

Dilatometry indicated that rapid densification of the as received and milled Fe-2Ni powders occurs at temperatures between 1350°C and 1400°C. This is likely due to formation of a small amount of liquid, and was confirmed by DSC. Heating rates play an important role in sintered density. By heating to

1400°C with a slow heating rate of 1°C/min, the grain boundaries break free of the pores before they are eliminated, thereby leaving pores trapped inside the grains, and the densification is limited to about 94% of theoretical. However, by heating at a rate of 5°C/min, a sintered density of 98% theoretical is achieved. At temperatures of 1300°C and below, the slower heating rates improve densification because grain growth is not as significant.

CONCLUSIONS

Sintering temperature and heating rate dictate the final density and microstructure of water atomized Fe-2Ni, and therefore the final properties of the sintered product. Slower heating rates improve final density, except in the case of liquid phase sintering, where grain growth causes a decrease in density as a result of slower heating rates. The milling of the powder had a significant effect on sintering densification. Milling removes Si oxides from the surface, and reduces particles size, both of which improve densification by allowing for more sintering to occur at lower temperatures.

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