Effect of Process Variables on the Dimensional Change of 434L Stainless Steel

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ABSTRACT

The ferritic grades of stainless steel (400 series) undergo greater amounts of dimensional change (shrinkage) during sintering when compared to the austenitic grades (300 series) of stainless steel. Prediction and management of dimensional change is highly essential in order to meet the dimensional and density requirements of the sintered components. The most commonly utilized powder and process parameters for management of dimensional change are particle size distribution of the starting powder, green density, and sintering temperature. This study examines the relative influences of these three variables on the dimensional change of 434L stainless steel in 100% hydrogen atmosphere sintering. Sintering temperature was found to be the most significant variable controlling dimensional change and sintered density. Particle size distribution and green density were found to have less significant influence on dimensional change.

INTRODUCTION

The phenomenon of sintering is primarily driven by the lowering of the free-energy of a powder aggregate. This, in effect, is achieved by the reduction of the total surface area of the powder particles in the aggregate. As sintering necks develop between adjacent powder particles and voids shrink to lower the total surface area of the aggregate, the outer dimensions of the powder aggregate are reduced. Shrinkage is typically observed with most solid state sintering. In some materials other phenomena taking place in parallel during sintering could tend to expand the powder aggregate; this can counter the shrinkage from sintering, and may even lead to a net growth. Examples of metallurgical phenomena occurring during sintering that lead to expansion are: Kirkendall pore formation (e.g., Cu-Ni, and Fe-Cu alloys), expansion of entrapped gases, and formation of low density phases (e. g., H_2O from reduction of oxides, and chromium nitride formation in stainless steels). Nevertheless, dimensional change occurring in a powder compact is widely accepted as a measure of the degree of sintering.

In PM component manufacture, dimensional change plays a crucial role. It is essential to manage the dimensional change occurring in the sintering process in order to meet the required part dimension. Inability to achieve the dimensional requirements can have significant impact on the economics of the process due to a high rate of rejection of sintered parts and employment of secondary operations, such as coining and machining. Additionally, since dimensional change directly influences the sintered density, it also plays an important role in cases where a minimum sintered density is specified.

Dimensional change is influenced by both the powder properties and the process parameters. Powder properties that influence dimensional change include powder composition (including alloy type, carbon and oxygen contents), particle size distribution, particle morphology, as well as, lubricant and other additives. Ferritic (bcc) alloys exhibit greater amounts of shrinkage in comparison to austenitic alloys (fcc), owing to their more open crystal structure which facilitates a higher rate of atomic diffusion during sintering [1]. Surface oxides that are inevitably present on water atomized powders are largely reduced in the early stages of sintering. Excessive amounts of surface oxides, if present, can prolong the reduction process and reduce effective sintering time. The total surface area of a powder compact is determined by the particle size distribution and the particle morphology. Smaller particles have a larger specific surface areas (surface area per unit mass), and hence promote faster sintering. Conventional powder property determinations cover the mass percentage of particles that are smaller than 44 micrometers in diameter (<325 screen mesh). However, this measurement does not accurately describe the amount of 'super-fines' (less than 20 micrometers in diameter) which have the most significant influence on dimensional change. A powder that has a highly irregular particle shape will have a larger specific surface area compared to one that is nearly spherical in shape. Particle morphology is not an easily quantifiable powder property. However, the apparent density (A D) data can be used to compare particle morphologies of two or more powders that have similar particle size distribution. If two powder lots have very similar particle size distribution but have different apparent densities, then the one having the lower apparent density would be considered to be the more irregularly shaped (higher specific surface area) powder. Lubricants and other additives present in the powder can sometimes influence the rate of sintering, and hence can have an effect on the dimensional change.

Processing variables that influence dimensional change include green density, completeness of delubrication, composition and dew point of the sintering atmosphere, sintering temperature, sintering time, heat up rate and cooling rate [2]. While the primary compaction related parameter, namely the green density, can be easily quantified, not all of the sintering related parameters can be easily quantified. Sintering variables that are more difficult to measure and control are: the dew point of the sintering atmosphere, heat up rate, cooling rate, and the time at sintering temperature. The exact composition of the sintering atmosphere can also vary from time to time if the pre-heat section or the cooling section of the furnace (or the end curtains) is supplied with a different type of gas than the hot zone. Sintering temperature and sintering time are the two major process variables that influence the degree of sintering. Control of these two variables, in addition to that of the green density, is essential for the achievement of a desired dimensional change and sintered density.

Stainless steels undergo significant amounts of shrinkage during sintering compared to low alloy and plain carbon steels. A large majority of the 400 series stainless steels are intended for structural components, which require relatively high sintered densities (>7.2 g/cm^3). The need for close control of dimensional change, combined with the requirement of a high sintered density, poses a significant challenge to the parts maker.

Dimensional change can be expressed either as "green-to-sinter" linear size change, or as "die-to-sinter" linear size change. The latter is more commonly used in the US PM industry for practical reasons. The "green-to-sinter" dimensional change, on the other hand, is a true representation of physical changes taking place during sintering; hence it is more appropriate for a scientific study.

The object of this study was to determine the relative effects of the major powder and process variables on the dimensional change of 434L. The variables included in the study are the fines content (<44 micrometers in diameter) of the powder, green density, and the sintering temperature. These three variables not only exert the strongest influences on dimensional change, but also are the ones that are more frequently modified.

MATERIALS

Stainless steel 434L is a popular ferritic grade of stainless steel, both in wrought and powder metallurgy. It combines adequate mechanical strength and moderate corrosion resistance and is significantly lower in cost compared to the austenitic grades of stainless steel. The 434L powder used in the study was a commercially available, water atomized, and annealed powder having a nominal particle size of minus100 mesh (<149 micrometers). Table 1 lists the chemical composition, apparent density (A D) and the fines (<44 micrometers in diameter) content of the powder.

Table 1: Properties of 434L base powder used (mass %)

Alloy	Fe	Cr	Mo	Si	Mn	P	S	C	N	O	A D, g/cm^3	<44 μm fraction
434L	Bal	16.7	0.93	0.82	0.12	0.010	0.010	0.023	0.044	0.31	2.80	45

The study utilized three powder blends that differed from each other in their particle size distributions. The starting powder (Table 1) was modified by sieving and re-blending to produce the three different powder blends. The particle size distributions of the three powder blends are shown in Table 2, along with their apparent densities and oxygen contents. The goal was to utilize powder samples with three distinctly different fines content, matching closely with the most commonly available range of fines content in stainless steel powder, namely 35 to 50%. Since all three samples were derived from the same starting lot of powder, they are expected to be similar with regards to their chemical composition and particle morphology. All powder samples were lubricated with 1.0% (by weight) Acrawax C.

Table 2: Particle size distributions, A D, and oxygen contents of the three powders

Mesh fraction	Low fines powder	Medium fines powder	High fines powder
+100 mesh	2.0%	2.1%	2.1%
-100 / +150	8.6%	7.6%	6.8%
-150 / +200	16.9%	15.5%	12.8%
- 200 / +325	33.5%	30.0%	27.5%
- 325 Mesh	39.0%	44.9%	51.1%
A D, g/cm^3	2.77	2.79	2.80
Oxygen content, ppm	3087	3045	3004

PROCESSING

Test specimens used in the study were in the form of Transverse Rupture Strength (TRS) test bars, having the dimensions specified in MPIF Test Method 44 (nominally 31.7 mm x 12.7 mm x 6.4 mm, 1.25 in. x 0.50 in. x 0.25 in.).

From each of the three powder samples, three sets of green TRS bars each having a different green densities were compacted. The three green densities were 6.28 (+/-0.01) g/cm^3, 6.43 (+/- 0.01) g/cm^3, and 6.57 (+/- 0.01) g/cm^3.

Three replicate specimens were used for each combination of powder and process variables. The dimensions and densities of the as compacted test bars were determined. The compacted specimens were delubricated in a 100% hydrogen atmosphere, at a temperature of 538 °C (1000 °F) for 15 minutes. Sintering was carried out in a programmable batch furnace under an atmosphere of 100% hydrogen. Specimens representing each powder sample and green density were sintered in the same furnace batch at the selected temperature. Three sintering temperatures were employed: 1149°C, 1232°C, and 1288°C (2100°F, 2250°F and 2350°F). The time at sintering temperature was kept at 30 minutes in all cases. The heat up rate, soak times, hold times, and the cooling rates were kept the same for the three sintering runs. The average cooling rate from the sintering temperature to 538°C (1000°F) was 0.70°C/sec. (1.26 °F/ sec.).

Sintered specimens were measured for determination of dimensional change. Sintered density was determined by water immersion per MPIF Test Method 42. Samples from each furnace run were analyzed for carbon, oxygen, and nitrogen contents.

RESULTS AND DISCUSSION

Table 3 lists the compacting pressures used and the spring back observed for all groups of samples. Spring back is the physical difference between the actual length of the green specimen and the corresponding dimension of the die cavity.

Comparing the pressure required to arrive at a given green density, it is found that the 45% fines containing powder had the best compressibility. This is not surprising since this powder sample, being identical to the original powder lot, had a normal particle size distribution ('bell' shaped curve). The much lower compressibility seen with the 51% fines containing material is partially due to the lower compressibility of the large fraction of fines present in this powder. The spring back data more or less parallel the tonnage used to achieve the targeted green density.

Table 3: Compacting pressures used and spring back observed

Fines content	Compaction Pressure and Spring back	Green Density, g/cm^3		
		6.28	6.43	6.57
39%	Compaction Pressure, MPa (TSI)	563 (40.8)	640 (46.4)	745 (54.0)
	Spring back, mm (in.)	0.1003 (0.00395)	0.1016 (0.00400)	0.1092 (0.04300)
45%	Compaction Pressure, MPa (TSI)	563 (40.8)	623 (45.2)	728 (52.8)
	Spring back, mm (in.)	0.0800 (0.00315)	0.0813 (0.00320)	0.0876 (0.003450)
51%	Compaction Pressure, MPa (TSI)	557 (40.4)	645 (46.8)	750 (54.4)
	Spring back, mm (in.)	0.0775 (0.00305)	0.0825 (0.00325)	0.0889 (0.00350)

Table 4 lists the typical carbon, oxygen and nitrogen contents for each of the three sintering temperatures – determined only on the 6.57 g/cm^3 G D test bars made from the 45% fines containing powder. It is noted that as the sintering temperature is increased the rate of reaction between the carbon and the oxygen present in the lubricated powder becomes more rapid, leading to a more efficient reduction of both of these interstitials. Nitrogen contents of the sintered samples decreased as the sintering temperature was increased; this follows from the lower limit of solubility of nitrogen in the steel at higher temperatures.

Table 4: Interstitial content of sintered samples

Interstitial	Sintering Temperature °C (°F)		
	1149 (2100)	1232 (2250)	1288 (2350)
Carbon, wt%	0.0245	0.0125	0.006
Oxygen, ppm	3738	3607	3033
Nitrogen, ppm	111	52	47

Table 5 shows the green density, sintered density, and dimensional change of all sample sets. All dimensional change determinations were based on the long dimension of the specimen (31.7 mm, 1.25 in). Dimensional change was determined both as 'green-to-sinter' and 'die-to-sinter', hereafter referred to as D C-gs and D C-ds, respectively. Data shown are the average values of dimensional change for each set of three samples. Dimensional change was calculated using the two equations listed below.

Dimensional change 'green-to-sinter' or "D C-gs" (%) =
(Sintered dimension – Green dimension) ÷ (Green dimension) x 100 %

Dimensional change 'die-to-sinter' or "D C-ds" (%) =
(Sintered dimension - Die dimension) ÷ (Die dimension) x 100 %

For all data analyses and correlation, only the D C-gs data were used. Since, the green dimension equals die dimension + spring back, theoretically D C-ds equals D C-gs + (spring back ÷ green dimension). In all cases, sintering led to shrinkage of the specimen, hence resulting in negative values for DC-gs.

Figures 1(a, b, and c) are plots of dimensional change versus sintering temperature for the low, medium and high green densities, respectively. Figures 2 (a, b, and c) are plots of dimensional change versus fines content for the low, medium and high green densities, respectively. Figures 3(a, b. and c) are plots of dimensional change versus green density for the low, medium and high fines contents, respectively. Figures 4(a, b, and c) thru Figures 6(a, b, c) show the dependence of sintered density on the three process variables.

In all three plots of Figures 1 (a, b, and c), the relationship between the dimensional change and sintering temperature is not exactly linear but the line does curve slightly downwards at the 1288 °C (2350 °F) temperature mark, indicating that at this higher temperature there was a more rapid reduction of surface oxides, leading to longer effective sintering duration. This effect is also reflected in the sintered density versus sintering temperature plots (Figures 4 a, b, and c). Here the line curves upwards..

The effect of each of the three variables on the dimensional change was determined from the slopes of their respective plots in the Figures 1, 2 and 3. For example, the slope of the line drawn thru the 45% fines data in Figure 1(a) was used to represent the effect of sintering temperature on the dimensional change for the low green density samples (which turned out to be 0.167% D C-gs per 10 °C). Similar data were determined for the medium and high green density sample groups having 45% fines content.

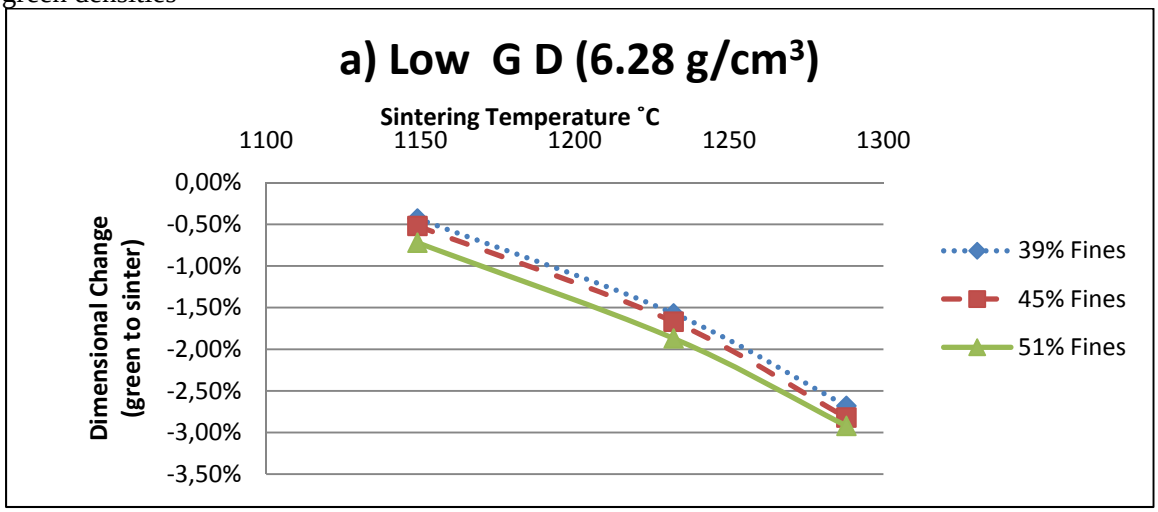
For the determination of the effect of fines content on the dimensional change, slopes of the plots in Figures 2 (a, b, and c) were obtained to represent, respectively, the low, medium, and high green densities. These determinations were based on the 1232 °C (2250 °F) data only.
For the determination of the effect of green density on the dimensional change, slopes of the plots in Figures 3 (a, b, and c) were obtained to represent, respectively, the low, medium, and high fines contents. These determinations were also based on the 1232 °C (2250 °F) data only.

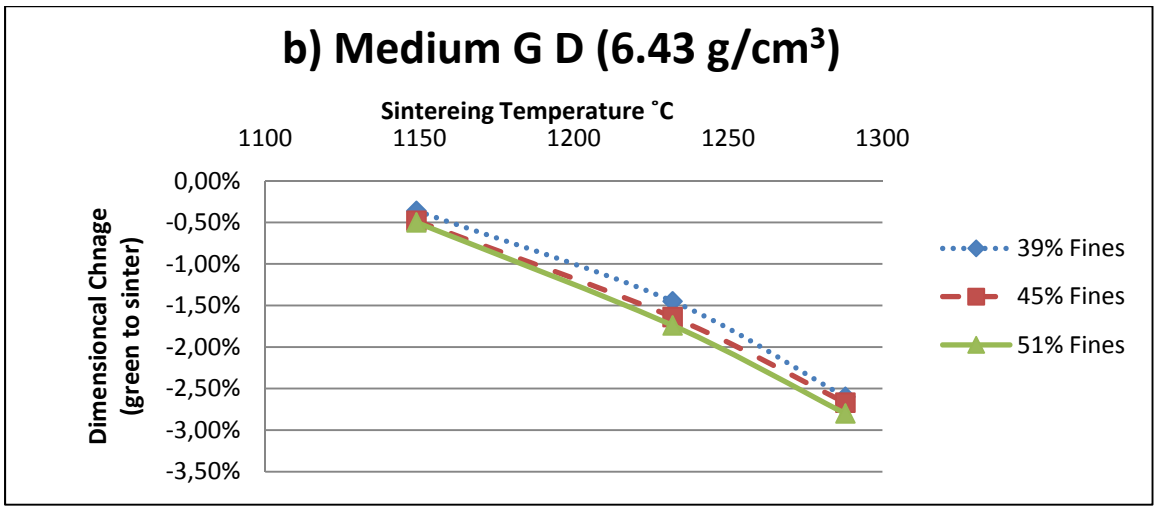
Based on the above calculations, the response of dimensional change to a measurable change in each of the controlling parameters (sintering temperature, fines content, and green density) were determined, as shown in Table 7. Table 7 also shows the amount of adjustment needed for each of the three controlling parameters to effectively shift dimensional change by 0.10%.

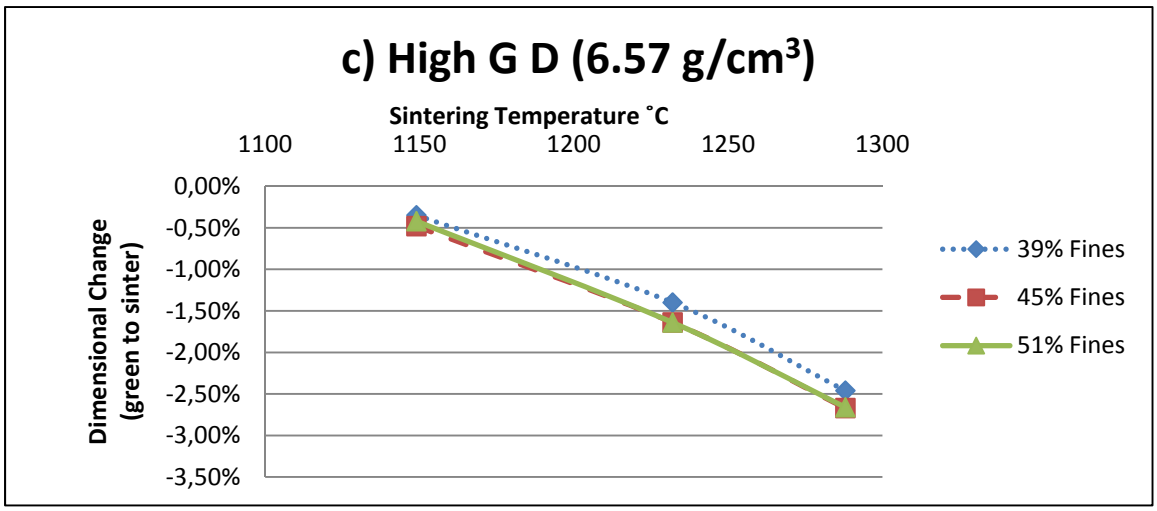
Table 5: Summary of dimensional change, green density and sintered density data for the various process parameters studied.

Part Density Group	Sintering Temp $^0C(^0F)$	Fines Content	Green Density g/cm^3	Sintered Density, g/cm^3	D C - Die to Sinter	D C - Green to Sinter
Low Density	1149 (2100)	39%	6.27	6.31	-0.39%	-0.43%
		45%	6.28	6.35	-0.40%	-0.52%
		51%	6.28	6.37	-0.48%	-0.72%
	1232 (2250)	39%	6.29	6.52	-1.37%	-1.57%
		45%	6.29	6.56	-1.35%	-1.67%
		51%	6.28	6.60	-1.58%	-1.87%
	1288 (2350)	39%	6.29	6.72	-2.42%	-2.68%
		45%	6.28	6.76	-2.64%	-2.82%
		51%	6.29	6.83	-2.68%	-2.92%
Medium Density	1149 (2100)	39%	6.42	6.46	-0.25%	-0.36%
		45%	6.42	6.48	-0.37%	-0.48%
		51%	6.42	6.50	-0.42%	-0.50%
	1232 (2250)	39%	6.43	6.65	-1.20%	-1.45%
		45%	6.44	6.70	-1.40%	-1.64%
		51%	6.43	6.73	-1.48%	-1.74%
	1288 (2350)	39%	6.43	6.86	-2.46%	-2.60%
		45%	6.43	6.91	-2.50%	-2.67%
		51%	6.43	6.95	-2.54%	-2.80%
High Density	1149 (2100)	39%	6.58	6.60	-0.30%	-0.35%
		45%	6.58	6.62	-0.34%	-0.39%
		51%	6.56	6.63	-0.40%	-0.42%
	1232 (2250)	39%	6.58	6.82	-1.30%	-1.40%
		45%	6.58	6.84	-1.41%	-1.48%
		51%	6.57	6.88	-1.50%	-1.64%
	1288 (2350)	39%	6.58	6.99	-2.32%	-2.46%
		45%	6.57	7.03	-2.35%	-2.52%
		51%	6.57	7.08	-2.48%	-2.66%

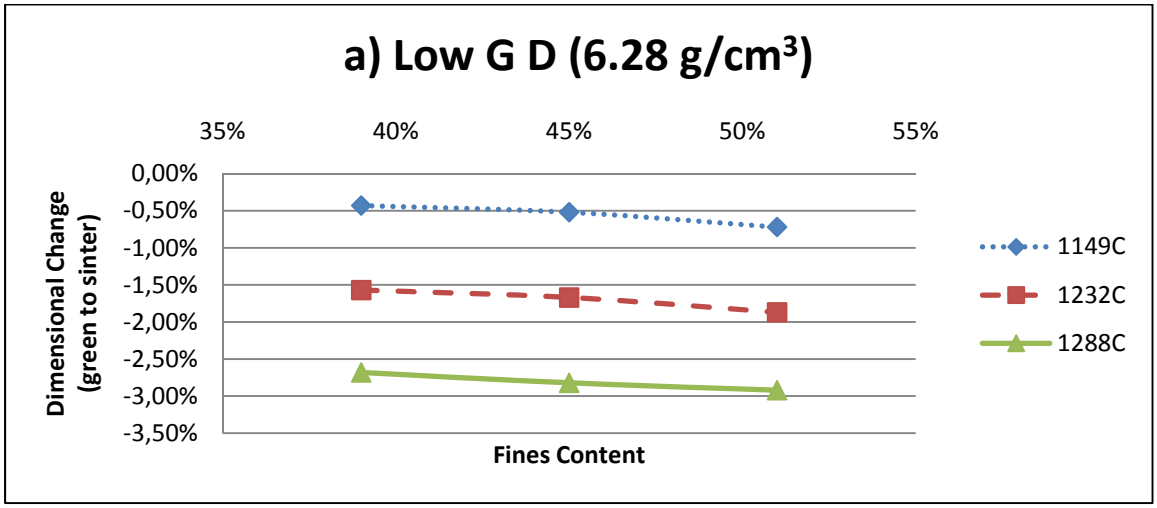
Figures 1(a, b, and c): Dimensional change versus sintering temperature for the three different green densities

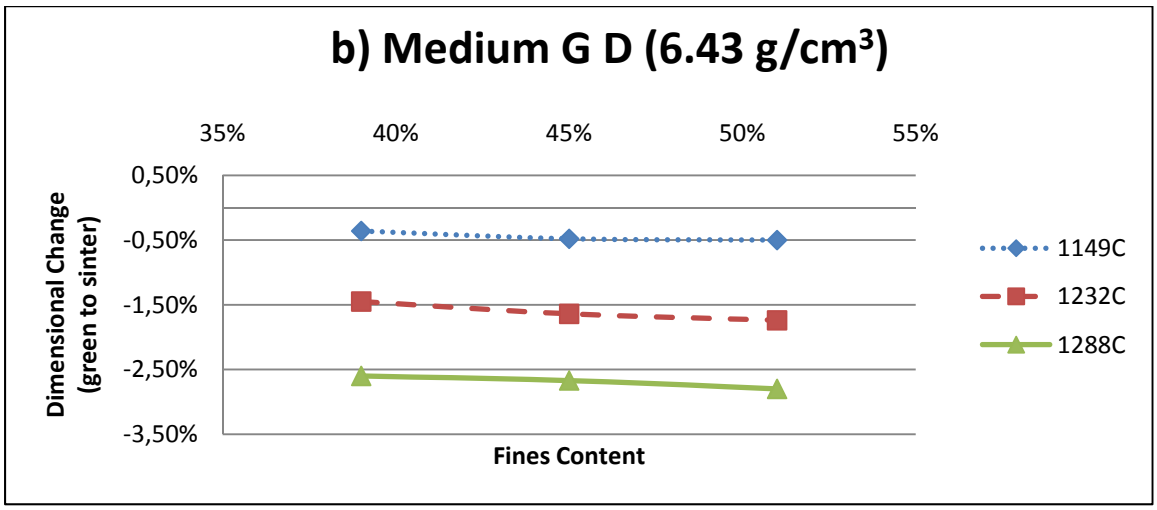


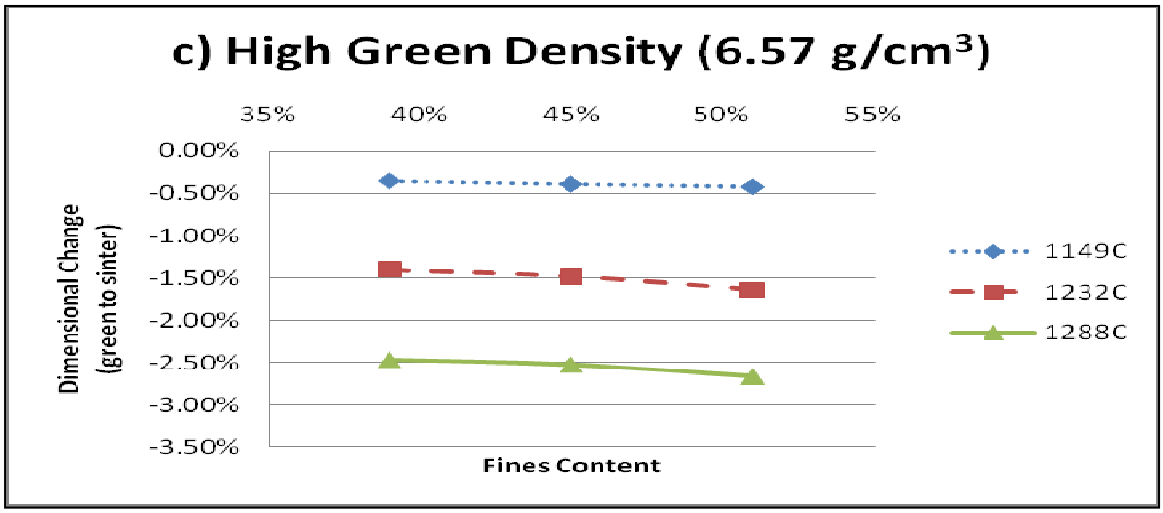




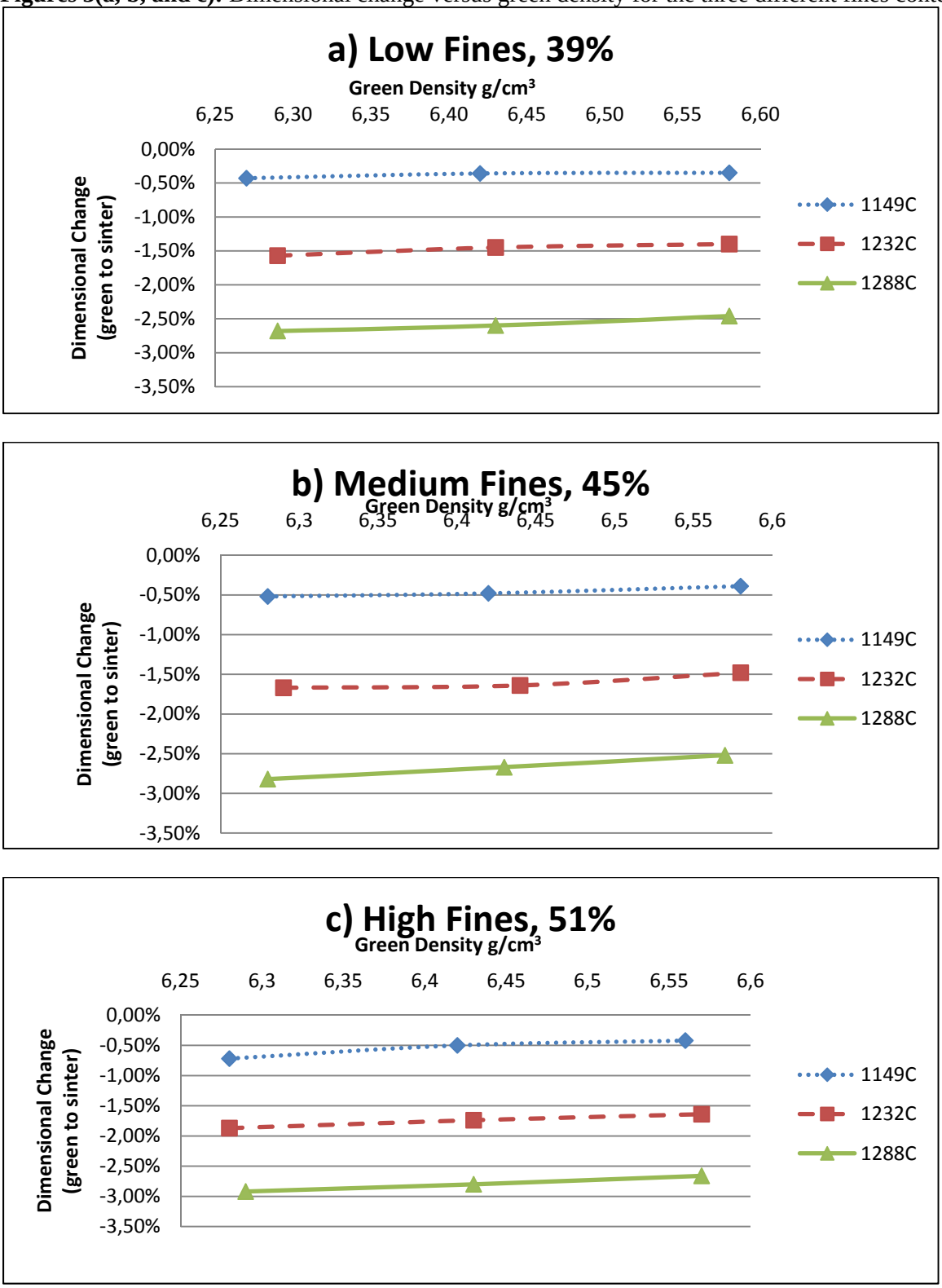
Figures 2(a, b, and c): Dimensional change versus the fines content for the three different green densities



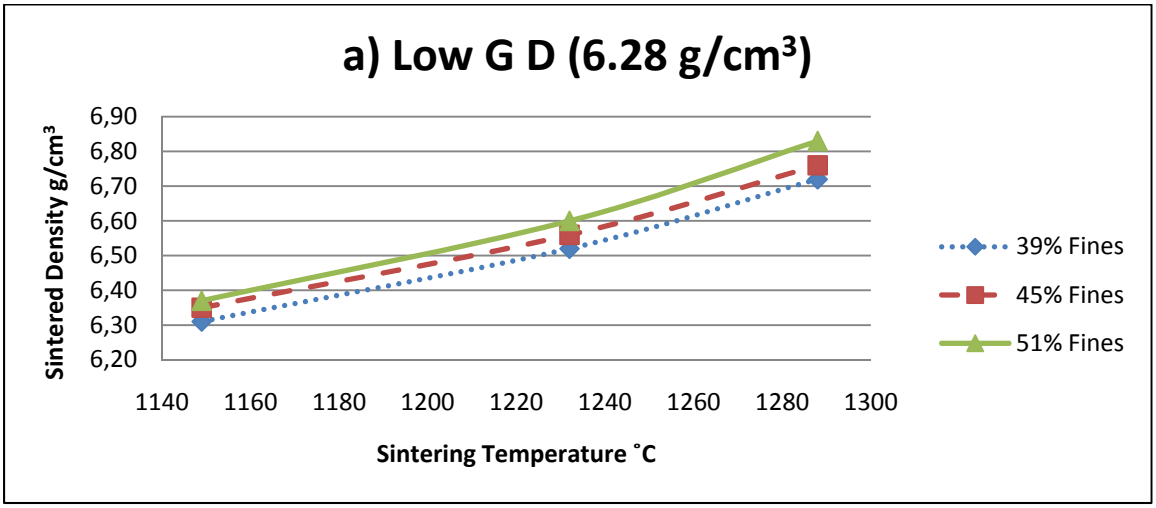


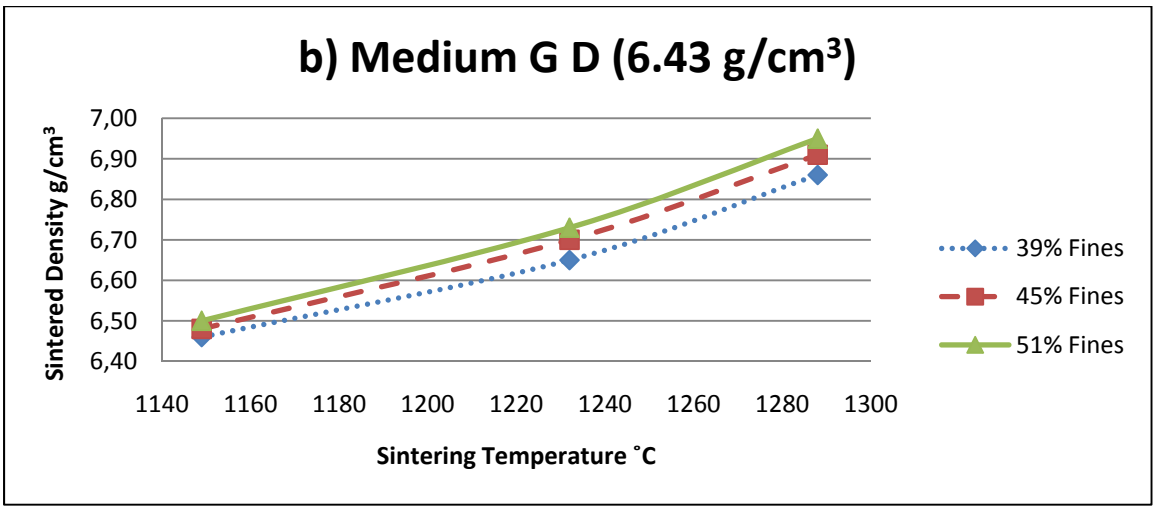


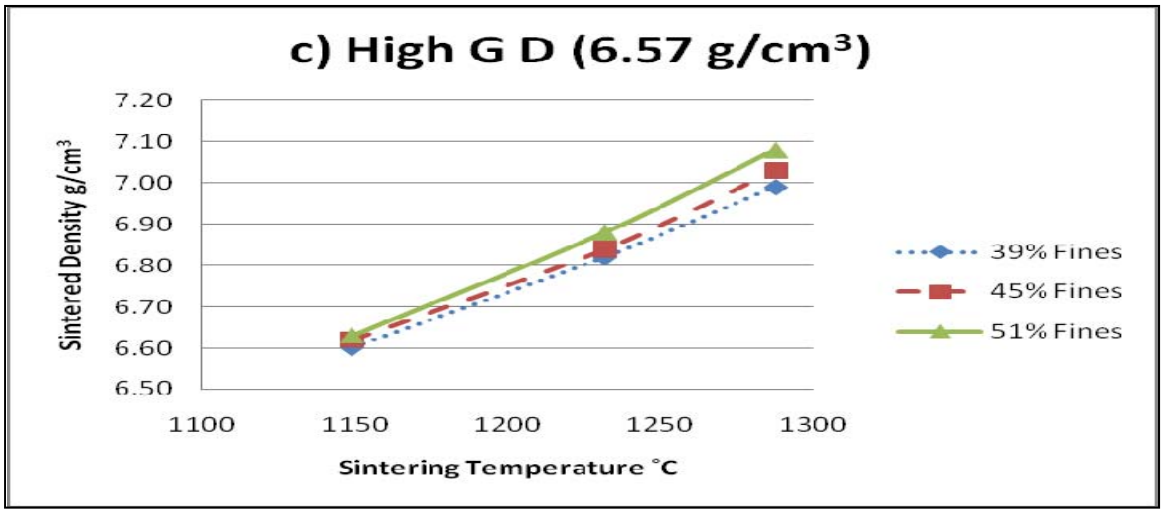
Figures 3(a, b, and c): Dimensional change versus green density for the three different fines content



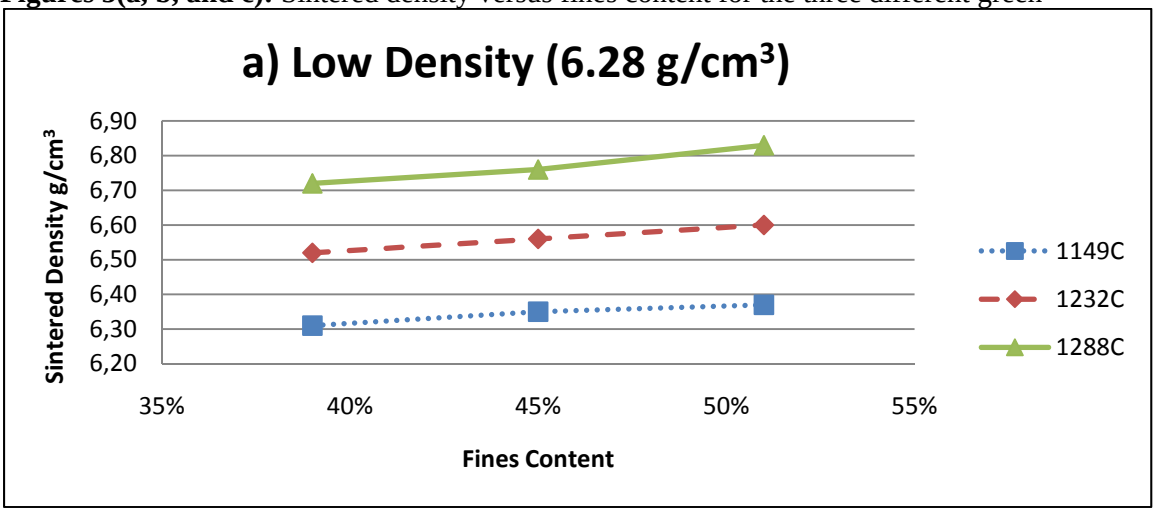
Figures 4(a, b, and c): Sintered density versus sintering temperature for the three different green densities

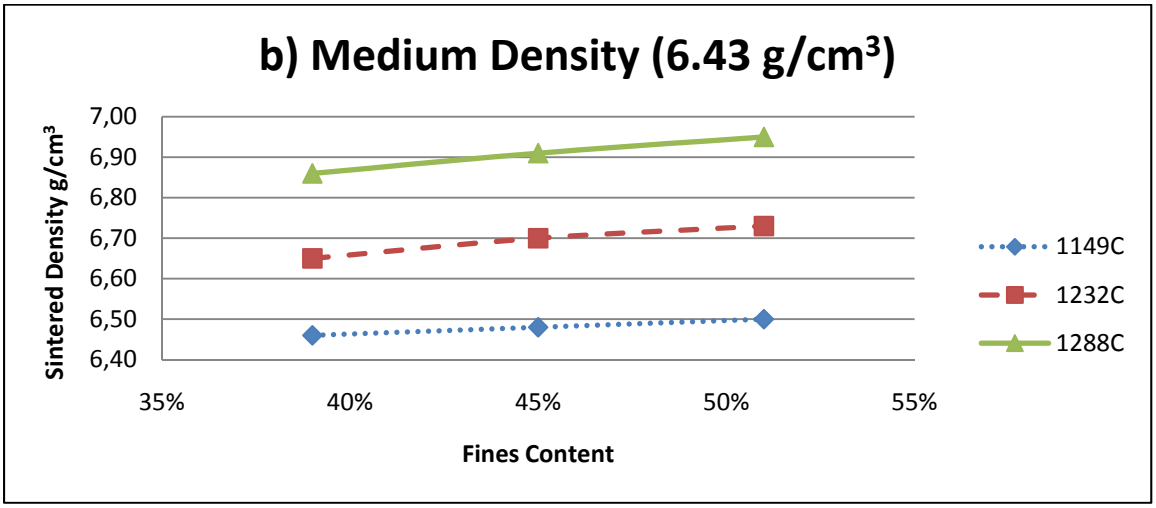


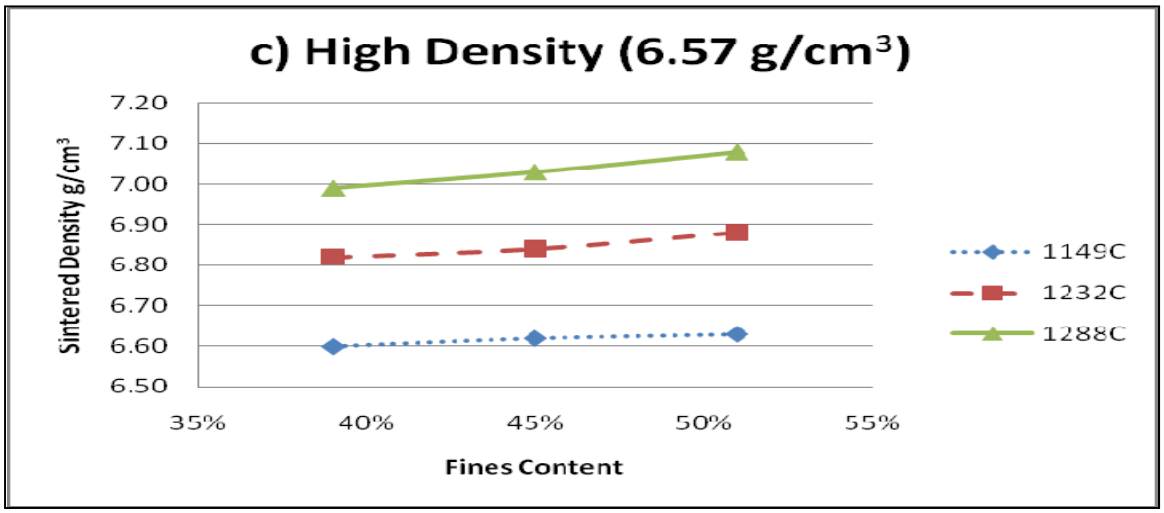




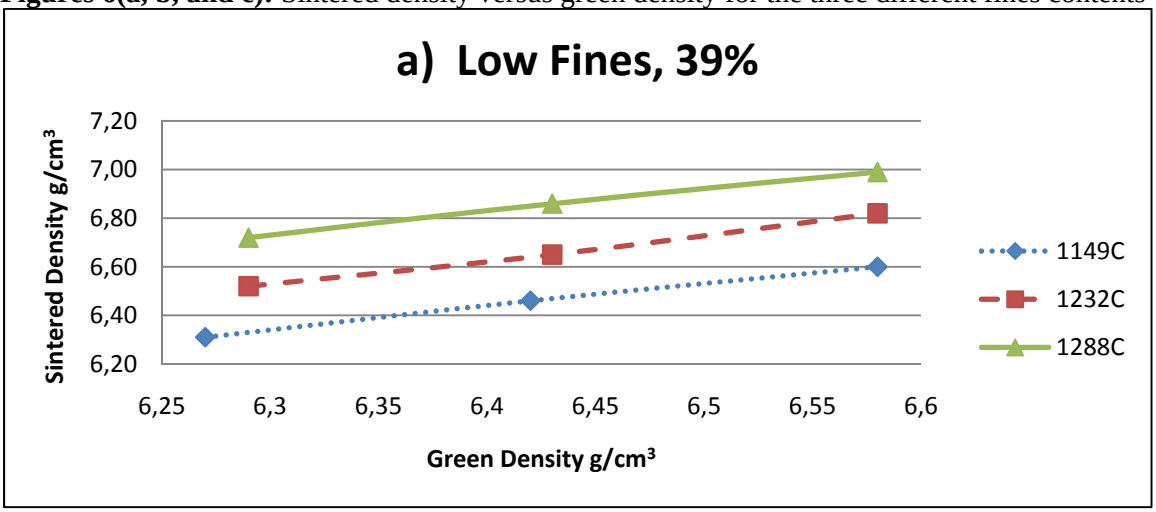
Figures 5(a, b, and c): Sintered density versus fines content for the three different green

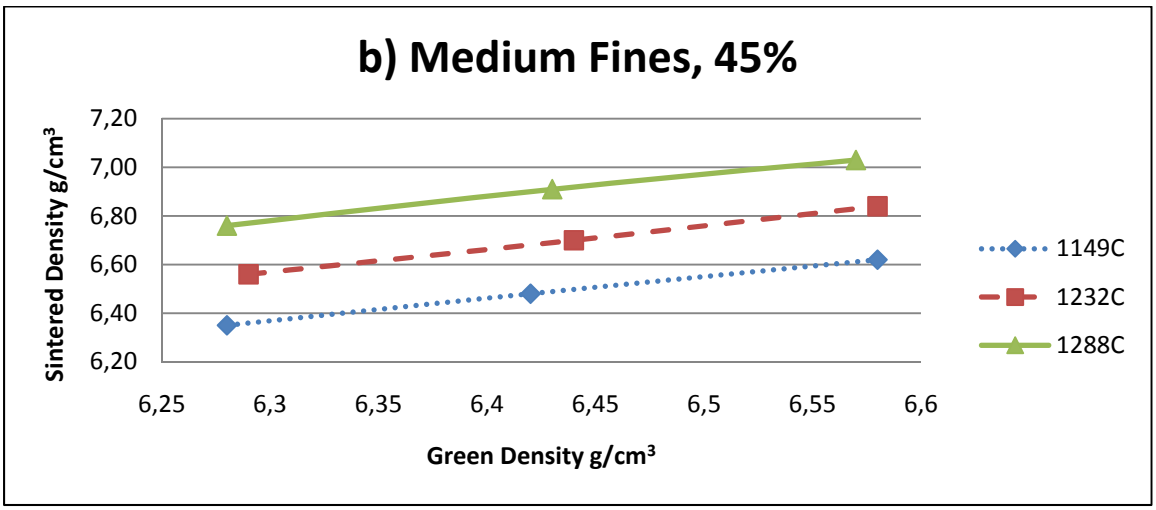






Figures 6(a, b, and c): Sintered density versus green density for the three different fines contents





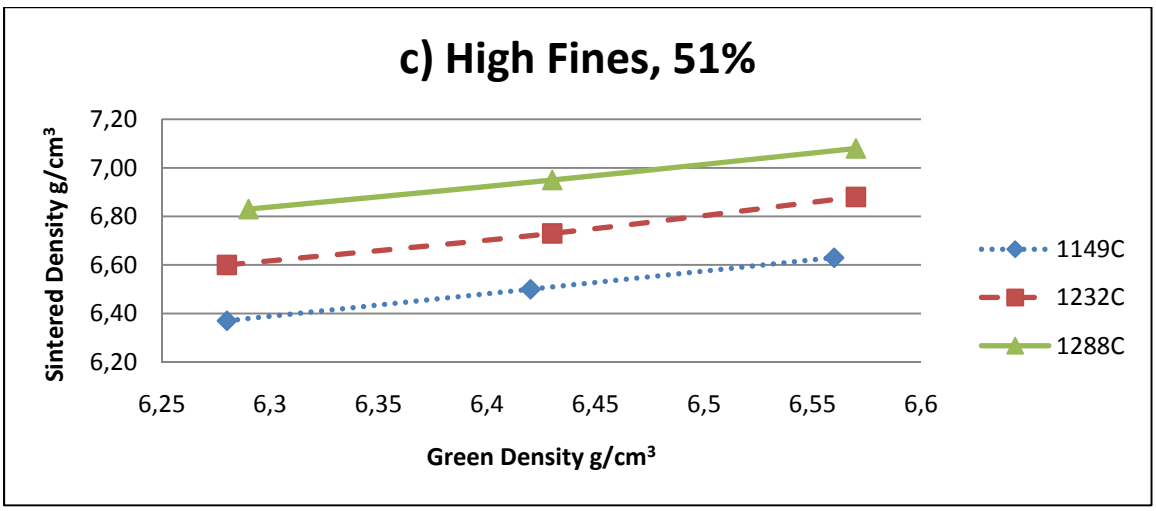


Table 7: Relative effects of the three process parameters on the dimensional change of 434L

Controlling parameter	A change in the controlling parameter by	Leads to a change in % D C-gs by			Estimates based on		Adjustment needed in the controlling parameter to change D C-gs by 0.10%		
Sintering Temperature	10 °C	0.167	0.16	0.144	Figures 1(a, b, c) 45% fines		6.0 °C	6.25 °C	7.0 °C
		low G D	med G D	high G D			low G D	med G D	high G D
Fines Content	5%	0.120	0.130	0.150	Figures 2(a, b, c) 1232 °C temp		4.20%	3.90%	3.30%
		low G D	med G D	high G D			low G D	med G D	high G D
Green Density	0.1 g/cm^3	0.077	0.061	0.058	Figures 3(a, b, c) 1232 °C temp		0.13 g/cm^3	0.16 g/cm^3	0.17 g/cm^3
		high fines	med fines	low fines			high fines	med fines	low fines

Multiple linear regressions of the data in Table 5 yielded the following relationships between the dependent variables (D C –gs and Sintered Density) and the independent variables (Sintering Temperature, Green Density, and Fines Content).

D C- gs (%) = 13.927 + (0.724 x G D) – (0.0180 x %Fines) – (0.0158 x Temperature in °C)

Sintered Density (g/cm^3) = -3.255 + (0.939 x G D) – (0.00627 x %Fines) – (0.00297 x Temperature in °C)

For the purpose of meeting a desired part dimension, D C-gs can be modified using any of these three parameters, - either individually or in some combination. However, for each of these parameters, one must consider the practicality and the secondary effects of making such a change. For example, a decrease in green density to achieve a greater amount of shrinkage (in order to meet the part dimension requirement) can lead to an undesirable decrease in the part's sintered density and hardness [3].

Similarly, adjustment of the fines content for achieving a target dimensional change has some draw backs also. The commercial water atomization process cannot be controlled to produce fines in a very narrow range from lot-to-lot. Typically, the lot-to-lot fines content of the powder can vary by about +/- 5% from a target. If frequent adjustments are made to the water atomization process for the purpose of adjusting the fines content, then some of the other properties of the powder (such as, apparent density, flow rate, compressibility, and green strength) will shift by some extent, and this can lead to undesirable side effects. Adjustment of fines content by sieving and re-blending is not only uneconomical, but it can also lead to unexpected changes in other powder properties as the particle size distribution deviates from that of a normal size distribution.

Modification of dimensional change by adjustment of the sintering temperature is found to be much more precise than what can be achieved by the adjustment of the other two parameters. For small changes in the sintering temperature (< 10°C), the side effects, i.e. changes in the sintered density and mechanical properties, would be minimal and predictable.

Based on these considerations it is concluded that modification of dimensional change is best achieved by the adjustment of the sintering temperature, rather than by the adjustment of fines content or the green density.

It may also be noted here that seemingly small variations in green density from part-to-part within a given production run can lead to undesirable variations in dimensional change, as noted in Table 7.

This study did not include the effect of sintering time on the dimensional change. However, sintering time (or the belt speed/ push rate) can be adjusted to modify dimensional change and sintered density. It has been proposed by German [4] and, by Takeda and Tamura [5], based on both experimental study and theoretical considerations, that sintering rate is closely proportional to the square root of sintering time in the case of austenitic stainless steels. If the sintering time is doubled, the dimensional change is increased by $\sqrt{2}$, or by 1.41 times. This relationship was also found to hold true for ferritic stainless steels by Klar and Samal [6]. Conversely, an inadvertent change in sintering time can lead to undesirable variations in dimensional change.

The best approach for achieving good dimensional accuracy is to first select the powder and the critical process parameters (fines content, A D, green density, sintering temperature and sintering time). Next step should be to make a sintering run with green test bars made from the selected powder using the selected process parameters. The dimensional change obtained in the test run should then be used to design the compaction tooling. Since the fines content of the subsequent production lots of powder may vary by as much as +/- 5% from the target, small adjustments to the sintering temperature should be made for each production run in order to compensate for any shift in dimensional arising from the lot-to-lot variation in the fines content.

CONCLUSIONS

1. Sintering temperature exerts a stronger influence on dimensional change in comparison to green density and the fines content of the powder.
2. Since the lot-to-lot fines content of a grade of water atomized powder can vary by as much as +/- 5%, adjustment of the sintering temperature is essential, from run to run, in order to achieve good dimensional control. The amount of adjustment needed in sintering temperature typically would be within +/- 10°C.
3. Close control of green density and sintering time are essential for achievement of consistent dimensional change.

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