2002-01-0668

Effect of Mix Formulation on the Dimensional Stability of Sintered Automotive Components.

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ABSTRACT

The P/M industry is being challenged with increasingly demanding applications requiring high mechanical strength as well as very high dimensional stability. Synchronizer hubs, sprockets and gears are examples of such applications in the automotive industry. The dimensional stability of P/M sintered parts is influenced by a number of factors including the powder mix formulation, the selection of additives, the blending procedures, the handling, compaction, sintering and post-sintering operations.

A study was conducted to evaluate and quantify the effect of a few of these factors, namely the mix formulation and type of additives on the dimensional stability of parts made with high performance materials. Statistical tools were used to identify the significant parameters affecting the dimensional stability and quantify their effects.

INTRODUCTION

The development of new materials combined with the improvement of manufacturing processes during the last decades have lead to a significant increase in the level of strength that can be reached in P/M sintered parts. This has markedly contributed to an increase in the number of P/M parts used in the automotive industry. However, the achievement of very consistent and stable sintered dimensions within a part and from part to part is of prime importance to further increase the use of P/M materials in high precision components such as gears, sprockets and synchronizer rings. Amongst the numerous merits of a better dimensional change (DC) control are:

- Reduction of the manufacturing costs by avoiding post sintering sizing and machining steps.
- Increased usage of high hardness materials that cannot be machined or calibrated to adjust the final size after sintering.
- Reduction of scrapped parts due to failure to meet dimensional specifications.

Several factors affect the dimensional change during sintering, and thus, the part-to-part dimensional scattering of P/M components. Table I lists some of these important factors [1]. Materials selection is of course of prime importance. In particular, the distribution of the alloying elements including carbon within and between parts is crucial for dimensional stability. Alloying elements can be added either to the melt prior to atomization (pre-alloyed), during the annealing treatment (diffusion bonded) or in the powder mixes as elemental additives. Pre-alloyed powders give a very homogeneous distribution of the alloying elements within P/M parts but their compressibility may be adversely affected. On the other hand, the addition of elemental alloying additives in the mixes has little effect on compressibility but the risk of segregation is significantly increased. Diffusion bonding reduces segregation [2] by partially bonding alloying elements such as Cu and Ni to the steel particles with little effect on compressibility. However, the cost of these materials is significantly higher than regular mixes of similar compositions.

Table I. Factors affecting the dimensional change of sintered P/M parts.

Group	Factors
Materials	Base powder (type and chemistry), alloying technology, formulation, type of additives, consistency, flow
Blending	Homogeneity, blending technology.
Handling	Segregation, feeding system
Compaction	Filling conditions (shoe), die cavity complexity, density variation within and between components.
Sintering	Temperature, time at temperature, heating and cooling cycle, atmosphere (carbon and oxygen potential)

Binder treatment, which consists in adding an organic bonding agent during the mixing operation, is another route to reduce the segregation at a lower cost [3]. The role of the binding agent is to increase the bonding of elemental alloying, graphite and lubricant additives to the steel particles, therefore helping to reduce segregation and dusting that may occur during powder handling and die cavity feeding [4,5]. The binder treatment also improves the flowability of mixes, improving the ease of feeding and the homogeneity of the powder mix within the die cavity [6].

The significant improvement in powder flow rate obtained by binder treatment allows for the use of very fine additives that would otherwise yield mixes with very poor flow rates or no flow [6]. It was shown in different studies that using finer additives is beneficial to the final sintered properties. However, their influence on the dimensional stability of sintered components is complex and not well known. For instance, use of fine copper particles in regular mixes is more susceptible to segregation than coarser particles, while copper with a more irregular shape is less prone to segregation [1].

The object of this paper is to determine the effect of using copper and graphite additives of different sizes and shapes on the sintered properties and, more specifically, on the dimensional stability of parts pressed from binder-treated mixes of a Mo pre-alloyed steel powder with elemental Cu, Ni and graphite additives. The effect of varying the density on the dimensional change was also investigated, since a variation of density within and between parts is known to contribute to dimensional scattering.

EXPERIMENTAL PROCEDURE

A water-atomized FL-4400 low alloy steel powder containing 0.15% Mn and 0.85% Mo, ATOMET 4401, was selected as the base powder for this study. The powder was admixed with 3.70% nickel, 2.65% copper and 0.60% graphite. An EBS-type lubricant was also added and the mixes were binder-treated. The total amount of lubricant and binder was 0.80% in all the mixes. The nickel and different types of copper and graphite that were used in the study are described in Table II. Two graphite additives were used: a synthetic grade and a natural grade, the former being purer and finer. Three copper additives produced by different techniques were used: a fine, medium and coarse grade. It is worth noting that these copper powders also have different particle shapes. The same fine nickel powder was used for all mixes. The four binder-treated mixes prepared with these additives are described in Table III with their apparent density and Hall flow rate. An apparent density in the 3.10 to 3.15 g/cm³ range with a Hall flow rate in the 29 to 31 s/50 g range were obtained. It is worth noting that the binder treatment improved the Hall flow rate of the mixes by about 6.5 seconds or 18%.

Table II. Description of the elemental additives used in the binder-treated mixes.

Additive	Size	Features
Graphite:		
Natural	D_{50} < 9 µm	< 3.4% Ash
Synthetic	D_{50} < 6 µm	< 0.1% Ash
Copper:		
Fine	D_{50} < 9 µm	Electrolytic, dendritic
Medium	D_{50} < 20 µm	Atomized, irregular
Coarse	D_{50} < 50 µm	Atomized, irregular
Nickel	$D_{50} \approx 5$ µm	Spiky shape with a dendritic surface

Table III. Type of graphite and copper used in the binder-treated mixes with their apparent density and flow rate (0.85% Mo steel powder with 3.7% Ni, 2.65% Cu and 0.6% Graphite).

Mix	A	B	C	D
Graphite	Natural	Natural	Synthetic	Synthetic
Copper	Coarse	Medium	Fine	Coarse
A.D., g/cm³	3.08	3.16	3.14	3.16
Hall flow, s/50 g	31.2	29.7	30.9	28.9

Mixes A, B and C were used to evaluate the effect of the type of additives on the dimensional stability. Mixes B and D were used to study the consistency and stability of the sintering process and to validate the method developed for the measurement of the ring diameters.

Sintered properties of the mixes were determined on standard TRS bars pressed to densities ranging from 6.7 g/cm³ up to 7.1 g/cm³ on a 100 Ton hydraulic press with floating die. Specimens were sintered for 25 min at 1120°C (2050°F) in a 90%N_2/10%H_2 atmosphere and tempered for 1hr at 205°C (400°F) in air. The proportion and size of pores in specimens pressed to 7.1 g/cm³ were evaluated on polished specimens using an image analyzer and an optical microscope at a magnification of 200X.

For the evaluation of the dimensional stability and distortion, a thin wall ring was selected since it is more susceptible to distortion than a TRS bar during sintering. Rings with an outside and inside diameter of 2.06” and 1.69” and a thickness of 0.49” (5.2 cm OD by 4.5 cm ID and 1.2 cm thick) were compacted to a density of 7.0 g/cm³ on a 100 Ton press with floating die. The position of rings with respect to the tooling was clearly identified in order to assure that the measurements were done according to the same reference point. Rings were sintered in a laboratory belt furnace for 25 minutes at a temperature of 1120°C in a 90%N_2/10%H_2 atmosphere. The rings were sintered five per boat with the bottom side facing down. The top and bottom outside diameters of green and sintered rings were measured at three different positions along the circumference: 0°, 120° and 240° from the reference point. As illustrated in Figure 1, a positioning fixture was used with a high precision digital indicator with a resolution of 0.0001" (0.0025 mm) in order to improve the accuracy and reproducibility of the measurement. The diameters were measured 0.25 cm below the top surface and 0.25 cm above the bottom surface. The mean top and bottom outside diameters were calculated from these values. The dimensional changes from green size were calculated from these mean diameters. For the purpose of this work, the parts distortion or dimensional stability was evaluated by calculating the difference in dimensional change between the top and bottom of the rings.

Figure 1. Fixture used to measure the outside diameters of green and sintered rings.

VALIDATION OF THE MEASUREMENT METHOD – In order to validate the precision and the accuracy of the method, the bottom and top diameters of green and sintered rings were also measured using an industrial coordinate measuring machine (CMM). This type of machine is used in the industry to precisely determine the size of parts of different shapes. For the purpose of this work, nine contact points equally distributed along the circumference were read. From these nine readings, the CMM calculates an ideal diameter that minimizes the sum of the squares of distances between these measured points and the calculated ideal diameter points. Measurements were done on two series of 15 rings pressed from materials B and D. Figure 2 illustrates the relation between the mean outside diameters measured using the two methods. An excellent correlation factor (R^2) of 0.9796 was obtained between the two sets of data, clearly indicating that the method developed in the lab and used in this study was very precise even though the in-house method was found to give slightly lower values than the CMM method: a difference of about 0.0015" for both green and sintered parts. The difference may be related to the fact that measurements were done at different positions relative to the bottom and top surfaces (0.16 cm below the top and above the bottom surfaces for the CMM method).

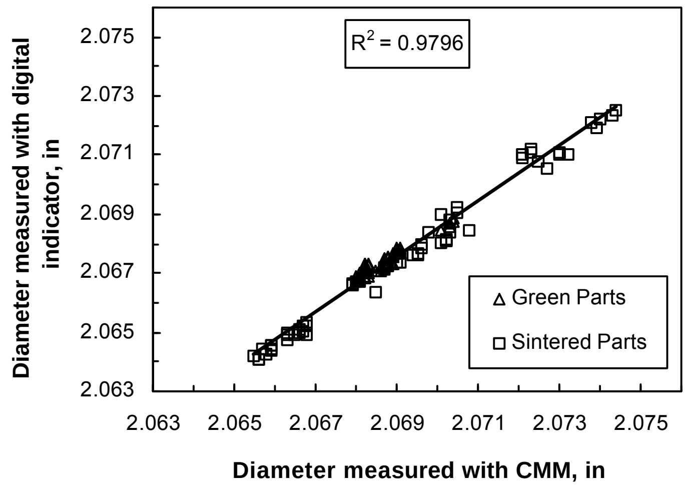

Figure 2. Relation between outside diameters measured using two different methods.

RESULTS AND DISCUSSION

EFFECT OF DENSITY AND ADDITIVES FINENESS ON SINTERED PROPERTIES (BARS) – The sintered properties before and after tempering were evaluated on bars pressed to different densities. Figure 3 shows the effect of green density on the dimensional change measured after sintering and tempering and the transverse rupture strength after tempering for materials A, B and C. The dimensional change after tempering was about 0.02% to 0.04% more negative than after sintering for all the mixes. Also, the use of finer additives, mainly fine copper, resulted in a more negative dimensional change, the difference between mixes A and C being around 0.28% at a given density.

Increasing the density resulted in a linear increase of the dimensional change, the variation being similar for all the mixes, i.e., an increase in dimensional change of about 0.05% for each increment of 0.1 g/cm³ in density. This shows that the size and shape of additives have no significant effect on how the dimensional change varies with density. Therefore, it appears that the use of finer additives may not improve the dimensional stability of parts in which the density is not homogeneously distributed.

The use of very fine copper and graphite was also beneficial to the rupture strength. Indeed, the TRS was 20 to 40 kpsi higher for mix C than for mixes A and B. However, no significant difference in TRS was obtained between mixes A and B at 6.7 g/cm³ and 6.9 g/cm³ even if there was a significant difference in the size of copper. It is interesting to note that the rupture strength of mix A started to level off between 6.9 g/cm³ and 7.1 g/cm³

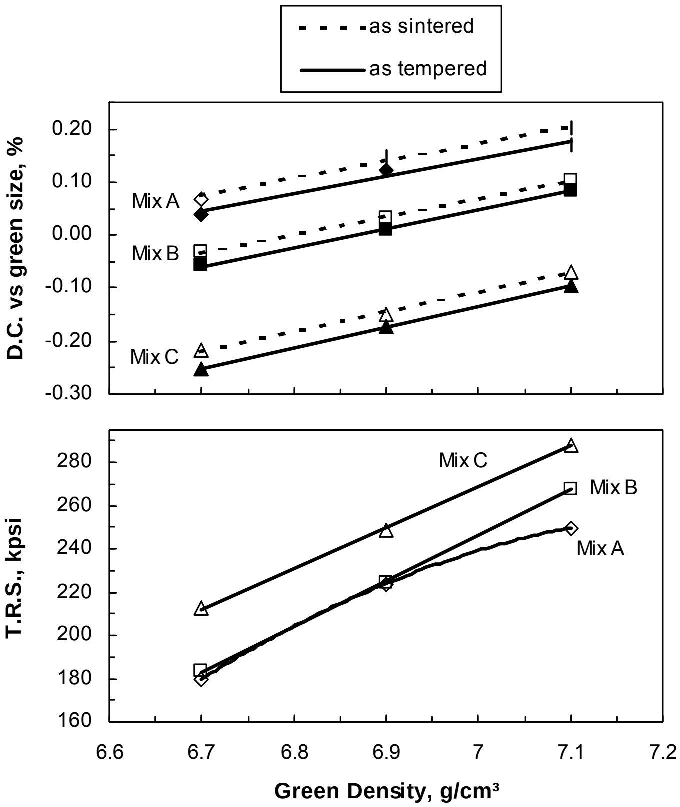

Figure 3. Influence of green density on the dimensional change and the rupture strength.

while it continued to increase linearly for mixes B and C. This difference in behavior is likely related to the porosity that was significantly different in these materials. Indeed, image analysis of pores in parts pressed at 7.1 g/cm³ revealed that the number of large pores was significantly larger for mix A than for mixes B and C, as shown in Figure 4. For instance, there was about 10 pores per mm² having a length greater than 50 µm compared to 2.3 in mixes B and C. In addition, no pore larger than

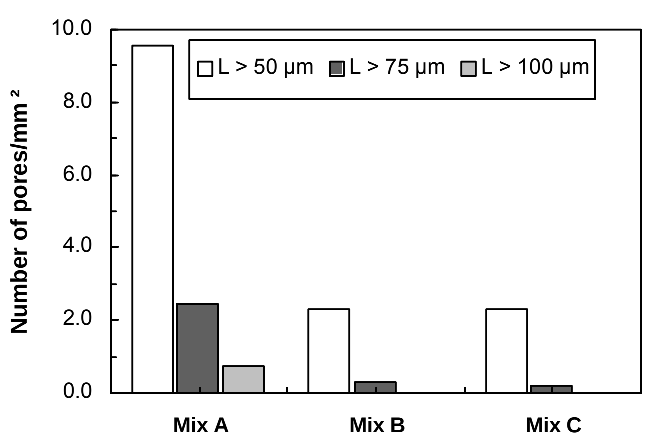

Figure 4. Number of pores having a length greater than 50, 75 and 100 µm per unit area in sintered parts pressed to 7.1 g/cm³.

100 µm was detected in mixes B and C while the longest pore analyzed in mix A was close to 250 µm. The presence of such large pores in parts made with mix A clearly reduced the beneficial effect of increasing density on strength. These large pores were likely formed by the large Cu particles that melted during sintering and penetrated the surrounding steel grain boundaries.

CONSISTENCY AND STABILITY OF THE SINTERING PROCESS – Two series of 15 rings pressed from mixes B and D were used for this preliminary test intended for assessment of the stability of the sintering treatment. Rings were loaded in groups of 5 of a given mix in a boat and fed into the sintering furnace 30 minutes apart by alternating mixes B and D. The 3 boats per mix and 5 positions per boat were numbered. The mean dimensional changes from green size were measured for the top and bottom diameters of all the rings made from mixes B and D. A statistical analysis of the DC results was made in order to find out any effect of the boat or position of the rings in the boat during sintering. A Three-Way or three factor analysis of variance (Three-Way ANOVA) was carried out with the mix, the boat and the position within the boat as the variables. The detailed results are reported in Table IV. For the statistical analysis, DF refers to the degrees of freedom or number of levels in each factor, F is the F distribution statistical test to compare the variation between and within the factors (analysis of variance) and P value is the probability of being wrong in concluding that there is a true difference between the groups.

Table IV. Effect of the mix, the boat and position in the boat on the DC from green size measured in top and bottom of the rings: results of the Three-Way ANOVA.

Statistical Analysis Results (95% confidence level):					
		Bottom		Top	
Variable	DF	F	P	F	P
Mix	1	27.4	0.0008	17.7	0.003
Boat	2	2.4	0.15	2.8	0.12
Position	4	0.2	0.92	0.3	0.84
Least Square Means of the DC for "Mix":					
Mix		Bottom		Top	
B		0.059%		0.037%	
D		0.108%		0.067%	

At a 95% confidence level, only the material appeared as being a statistically significant source of variation ($F>5.32$ and $P<0.05$). The boat and position in the boat had no effect on dimensional change, confirming the stability of the sintering process. Based on the mean DC values calculated for the significant source of variation, i.e., mixes B and D, it appears that the DC is larger in the bottom of the rings. Also, as expected, the DC or growth is larger in mix D containing the coarse copper, the overall average DC being 0.09% for mix D versus 0.05% for mix B containing a medium size copper grade.

The dimensional stability of these two materials was also evaluated by calculating the absolute difference between

DC in top and bottom of rings. The results are plotted in Figure 5 for the 15 rings of mixes B and D. Again, the boat and position in the boat did not have a significant effect on the DC variation at a 95% confidence level. On the other hand, the material had a significant effect. The average in DC variation (top versus bottom) with its standard deviation as well as its standard error are reported for the two mixes in Figure 6. Mix B containing the medium size copper and natural graphite exhibited a better stability in DC variation with an average of 0.022% versus 0.044% for mix D containing the coarse copper and synthetic graphite. Moreover, the standard deviation was also much smaller for mix B: 0.012% versus 0.023% for mix D. Thus, both the average and the standard deviation in DC variation were reduced by half in mix B.

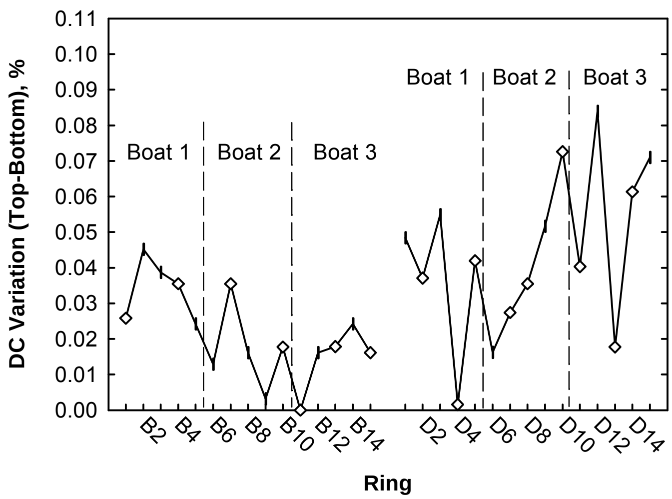

Figure 5. Difference between DC from green size in the top and in the bottom of rings made from mixes B and D.

EFFECT OF MIX FORMULATION ON DIMENSIONAL STABILITY – For this study, 5 rings were pressed from each mix A, B and C and measured (3 diameters in top and bottom). The 5 rings of a given mix were loaded in a boat and the three boats fed into the sintering furnace 30 minutes apart each other. After sintering, the diameters were measured again. The average and standard

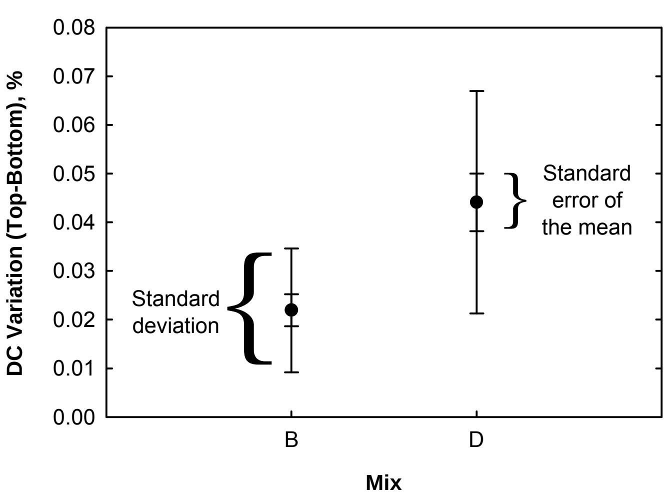

Figure 6. Mean in DC variation from top to bottom diameters with its standard deviation and standard error.

deviation of the green and sintered diameters are given in Table V. In general, the standard deviations are very small indicating a good reproducibility from ring to ring and position to position for a given mix. Green diameters are very similar for the three mixes and indicate that the top of the rings is slightly larger than the bottom. On the other hand, after sintering, the diameters vary much more from top to bottom and from mix to mix. The difference in mean diameters between top and bottom of rings increases from mix C to B to A (from finer to coarser additives in the binder-treated mix). The dimensional changes from green size measured in top and bottom of rings are reported in Figure 7.

Table V. Green and sintered mean diameters (inches) with their standard deviation in parentheses.

Mix	Top	Bottom	Difference
Green diameters			
A	2.0672 (0.0001)	2.0668 (0.0001)	0.0004
B	2.0672 (0.0001)	2.0669 (0.0001)	0.0003
C	2.0674 (0.0001)	2.0671 (0.0001)	0.0003
Sintered diameters			
A	2.0709 (0.0002)	2.0689 (0.0003)	0.0020
B	2.0682 (0.0002)	2.0666 (0.0002)	0.0016
C	2.0646 (0.0003)	2.0643 (0.0002)	0.0003

In general, and as seen on the TRS bars, the DC decreases with the fineness of the copper additive: 0.14%, 0.02% and -0.14% for the mixes containing coarse (A), medium (B) or fine (C) copper additives respectively. Contrary to the previous series of results, the DC is now slightly larger in the top of the rings indicating that the sintering was not identical. A two-way analysis of variance was carried out with the mix and position of the rings in the boat as input variables. At a

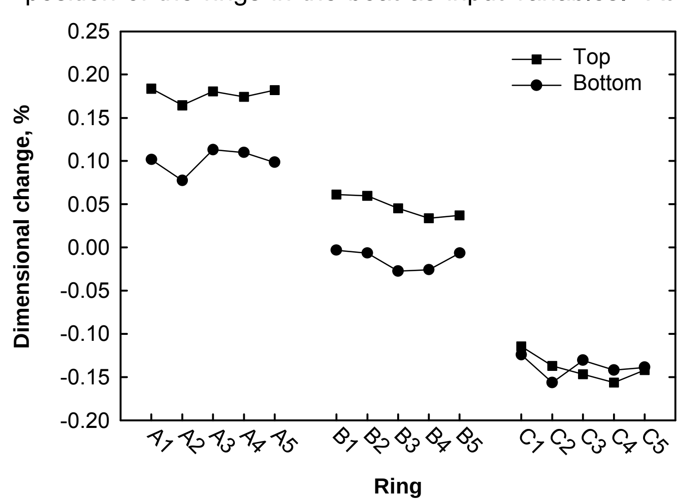

Figure 7. Dimensional change measured on top and bottom diameters of the 5 rings pressed and sintered from mixes A, B and C.

95% confidence level, only the material appeared as being a statistically significant source of variation. Another approach to evaluate the dimensional stability and part distortion is to consider the differences between dimensional changes in the top and bottom of rings. The average in absolute DC variation (top versus bottom) with its standard deviation and standard error are reported in Figure 8 for the three mixes.

It readily appears that the DC variation within parts is not strictly related to the extent of DC itself. Indeed, mixes A and C exhibit a DC of 0.14% during sintering (a growth in the former mix and a shrink in the latter mix) but the DC variation is much lower in the latter. For these rings, it is clear that the best dimensional stability is achieved with mix C containing the fine copper and synthetic graphite additives: lowest average and standard deviation in DC variation (0.013% ± 0.006%). The worst results were obtained with mix A containing the coarse copper and

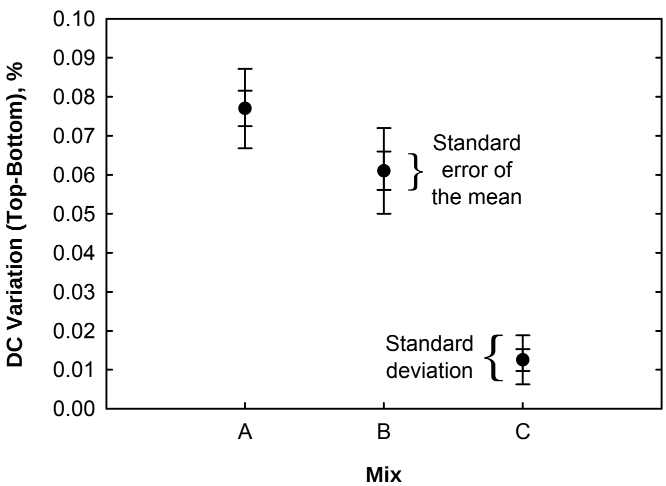

Figure 8. Difference in DC between the top and bottom diameters for rings pressed from mixes A, B and C.

natural graphite (0.077% ± 0.010%). As discussed above, the melting of such coarse copper particles during the sintering creates more disorder in the structure and consequently more distortion (more localized liquid, larger pores). By substituting such a coarse copper with a medium size copper, this phenomenon likely decreased and an improvement in DC variation was achieved (0.061% ± 0.011% for mix B).

CONCLUSION

The influence of using copper and graphite of different size and morphology on the sintered properties, especially the dimensional stability of rings made with binder-treated FLNC-4405 mixes was studied. Using fine additives resulted in much smaller dimensional variations and distortion within and between parts. It also promoted shrinkage during sintering and an improvement of the transverse rupture strength and apparent hardness. The number of large pores in sintered parts was also found to be significantly reduced by the use of fine copper. On the other hand, the size and morphology of additives had no effect on how the DC varied with density. It is therefore highly beneficial to use fine additives when tight dimensional control is required. However, the use of very fine additives is known to adversely affect the flow rate of regular mixes and binder-treatment appears to be necessary in order to get adequate flow rate and die cavity feeding. The next step in this program would be to validate the benefit of using binder-treated mixes with fine additives on the dimensional change stability of parts on a production scale.

ACKNOWLEDGMENTS

The authors thank L. Thibodeau for his collaboration and support with the experimental portion of this work.

REFERENCES

1 M. Larsson and J. Rassmus, “Higher tolerances by improved materials and processes”, Proc. 1998 P/M World Congress, Granada, EPMA, Vol. 4, pp 379-384.

2 Th. Esser and al., “Dimensional stability of iron-copper steel”, Advances in P/M, Proc. Con., Pittsburgh, MPIF, 1990, Vol. 1, pp 245-260.

3 R. Guo, “Applications of the binder treated Mo-Prealloyed premixes as alternatives to diffusion bonded powders”, Proc. 2000 P/M World Congress, JPMA, Kyoto, pp 499-502.

4 F. Gosselin, M. Gagné and Y. Trudel, “Segregation-free blends: Processing parameters and product properties”, Proc. World Con. on P/M, The institute of Metals, London, 1990, Vol 1, p. 297.

5 C. Gélinas. F. Chagnon and Y. Trudel, “Optimizing properties of binder-treated ferrous powder premixes”, Advances in P/M & Particulate Materials, Proc. Int. Conf., Seattle, MPIF, 1995, Vol. 1, pp 3-45/3-56.

6 M. Carvalho, R. Pegorer and D. Rodrigues, “Use of organic binders in powder mixes to improve dimensional stability of sintered steels”, Proc. 1998 P/M World Congress, Granada, EPMA, Vol. 4, pp 404-408.