

Improvement of Dimensional Stability of Sinter-Hardening Steel Powders

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ABSTRACT

Sinter-hardening powders are a cost effective way to manufacture high apparent hardness and high mechanical strength parts. However, these desirable properties make the use of secondary sizing operations very difficult. It is therefore of prime importance for parts manufacturers to have increased control over the dimensional change of sintered components. Enhanced control over the dimensional change quickly translates into savings for such manufacturers. Collaboration between Rio Tinto Metal Powders and Metaldyne, respectively a major powder manufacturer and a top-end American parts manufacturer, was triggered by such incentives. Over the past years, both companies have joined efforts to better understand the dimensional change behaviour of ATOMET 4601 and ATOMET 4701 under industrial production conditions.

This paper discusses in a two-fold approach the effect of the mix formulation and the sintering conditions on the dimensional change. In the first section, addition of copper and graphite is studied and the concept of using a more reactive graphite is introduced. In the second section, tests ran both at Metaldyne and RTMP demonstrate the strong impact that sintering conditions can have on the dimensional change. The effects of these changes on the process control metrics are also discussed. In conclusion, it is established that the optimisation of both the mix formulation and the sintering conditions are necessary in order to fully take advantage of the sinter-hardening powders.

INTRODUCTION

In the perpetual race towards high performance, cost effective parts, manufacturers have been introducing sinter-hardening steel powders in their processes. Such powders, combined with the proper sintering equipments, such as fast cooling capacity furnaces, permit the manufacturing of parts having high hardness and high mechanical strength.

However, a major drawback stands in the fact that sinter-hardened parts cannot be resized by secondary operations [1]. Dimensional accuracy is therefore of prime importance and this paper offers a review of conditions affecting the final size of parts made from ATOMET 4601 (powder #1) and ATOMET 4701 (powder #2), two sinter-hardening steel powders. It will be demonstrated that under industrial-scale manufacturing conditions, both the formulation of the powder premix and the sintering conditions are important in order to achieve a tight dimensional control.

An important tool to better understand the behaviour of such sinter-hardening materials through the sintering process is the dilatometer. [2-4]. It provides a detailed record of the size changes of a sample. These changes can later be explained through the metallurgical phenomena driving growth and shrinkage. Many studies have been conducted over time to understand the dimensional change behaviour of sinter-hardening powders produced by RTMP [5]. This understanding led to the introduction of a new type of graphite which offers better control over the dimensional change.

Yet, mastering the formulation of the mix remains only a portion of the equation as other factors in mass production are affecting the dimensional change behaviour of sinter-hardening powders. Differences

between the sintering profiles of furnaces can play a significant role. By comparing the different temperature profiles used throughout the tests, it is possible to understand how to optimise the temperature profile of an industrial scale sintering furnace in order to further increase the control over dimensional change.

The increased knowledge of the phenomenon of dimensional change in sinter-hardening powder formulations combined with optimised sintering profiles substantially increases the control over the final size of the parts produced.

EXPERIMENTAL PROCEDURES

Effect of Powder Formulation on Dimensional Change

Mixes of powder #1, and powder #2 containing various amount of Cu and C were prepared according to Table 1 below. For mixes containing natural graphite, standard graphite with a carbon concentration comprised between 96% and 97% was used. The D_{90} of this natural graphite is about 25 μm . Mix G was prepared using high purity synthetic graphite with a carbon concentration above 99% and a D_{90} of 15 μm . One inch long bars were pressed from all the mixes and delubricated in a Lindberg furnace at 600°C for 15 minutes and under a pure nitrogen atmosphere. The bars were sintered in a Theta dilatometer (Dilatronic) with a maximum sintering temperature of 1600°C. The sintering atmosphere was argon based with 5% H_2 and the heating rate varied between 10°C min^{-1} and 20°C min^{-1} . Table 1 shows the different samples used throughout this experiment.

Table 1: Composition of test samples and sintering parameters.

Sample	Base	Cu (%)	Graphite (type)	Graphite (%)	Heating Rate (°C min^{-1})
A	Powder #1	0.0	Natural	0.0	10
B	Powder #1	0.0	Natural	0.6	10
C	Powder #1	0.0	Natural	0.9	10
D	Powder #1	2.0	Natural	0.9	10
E	Powder #1	2.0	Natural	1.0	10
F	Powder #2	2.0	Natural	0.9	10
G	Powder #1	2.0	Synthetic	1.0	10
H	Powder #1	2.0	Natural	1.0	20

A typical dilatometry curve is shown in Figure 1. This curve demonstrates the sequence of events leading to the final dimensional change from the green compact to the sintered compact. As the temperature increases, the iron matrix changes from α Fe to γ Fe causing a contraction of the matrix. Upon further heating, graphite diffusion begins which leads to growth (noted as C growth). At 1083°C copper melts, wets the iron particles, and then starts to diffuse to grain boundaries, thus causing growth (Cu growth). When the maximum temperature is reached, sintering takes place and the formation of sintering necks and the accompanying reduction in pore volume causes contraction [3]. Cooling begins after this isotherm and the phase change from γ Fe to α Fe causes further growth. The final dimensional change is simply the sum of all the changes indicated.

Effect of Sintering Conditions on Dimensional Change

To verify the effects of the sintering conditions on the dimensional change, several production lots of powder #2 were sintered at RTMP and at Metaldyne. At RTMP, TRS bars one inch in length were sintered at a temperature of 1120°C for a minimum of 25 minutes in a 90% N_2 / 10% H_2 atmosphere. At Metaldyne, sintering was done on both 123 mm long bars and sprockets with an approximate diameter of 138 mm at a green density of 6.8 g cm^{-3} under a 95% N_2 / 5% H_2 atmosphere.

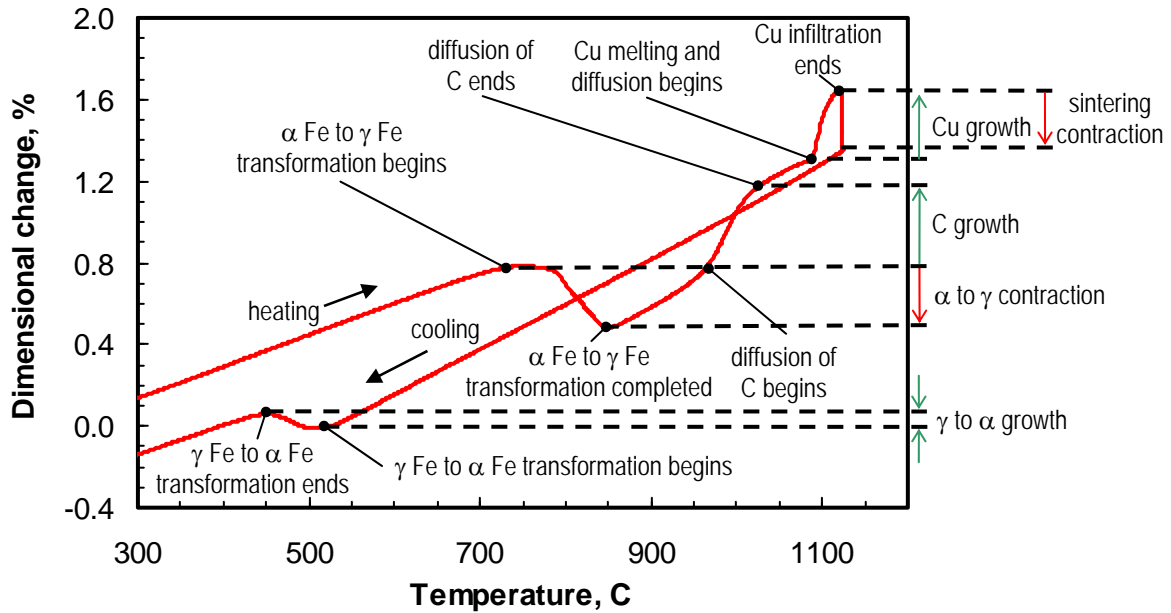


Figure 1: Typical dilatometry curve and the associated metallurgical transformation during sintering.

RESULTS AND DISCUSSION

Effect of Cu and C on Dimensional Change

Figure 2 shows the effect of an increased concentration of graphite in a powder #1 based-material. It can be seen that with no graphite (curve A), there is no growth associated with the diffusion of carbon into the iron matrix. As the graphite concentration is increased, diffusion occurs and can be observed on the curve by the swelling of the samples at temperatures ranging from 925°C to 975°C. Growth increases with the carbon concentration (curves B and C).

The effect of an addition of copper can be seen in Figure 3 where curves D and E show a significant swelling starting at around 1100°C. This growth is due to the copper melting and migration to the grain boundaries. Curve D shows a greater growth than curve E even at equal concentration of copper. This is due to the limited amount of graphite available to diffuse which then promotes growth through copper melting and copper diffusion.

As a result, both copper and graphite concentration have a significant effect on the dimensional change. Very little can be done to increase or reduce the amount of growth contributed by the phase change of the base material. The control of the dimensional change therefore partially depends on the copper and graphite added to the mix.

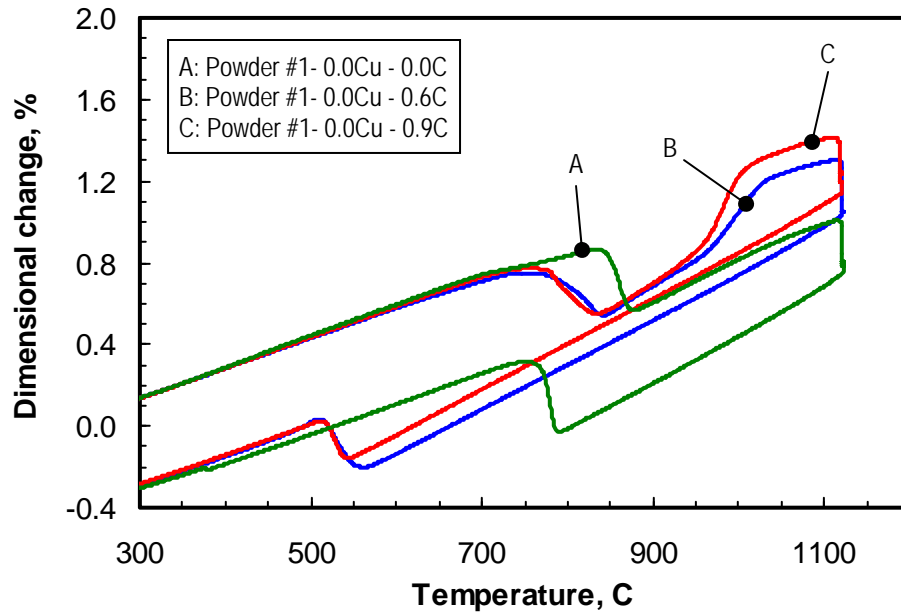


Figure 2: Dilatometry curves showing the effect of graphite content on the dimensional change related to the diffusion of graphite.

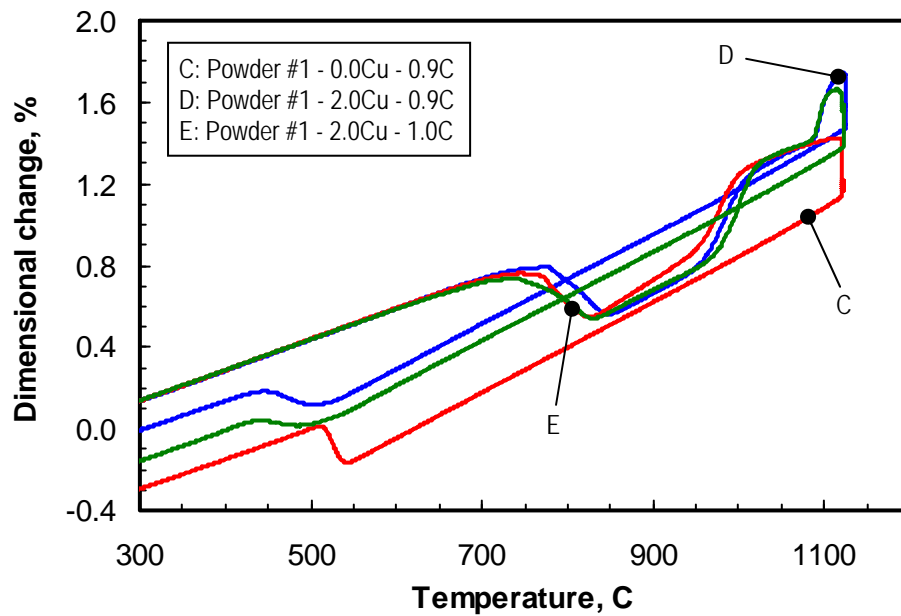


Figure 3: Dilatometry curves showing the effect of Cu addition to a formulation already containing graphite.

Effect of Base Powder on Dimensional Change

Even though both base powders considered in this study are sinter-hardening grades, they both have different responses to graphite and copper addition. This is mainly due to their chemical composition and intrinsic properties. Table 2 shows the chemical composition of each steel powder grade along with its hardenability index. The hardenability index is a value derived from Grossman's method for the

determination of hardenability. As this method is used to calculate the ideal critical diameter, the adapted method rather provides with a theoretical index by dropping the factor usually applied to the concentration of carbon [6].

Table 2: Chemical composition and hardenability index of powder #1 and powder #2.

Grade	Ni (%)	Mo (%)	Mn (%)	Cr (%)	O (%)	Hardenability Index
Powder #1	1.8	0.55	0.2	0.05	0.10	8.5
Powder #2	0.9	1.0	0.5	0.5	0.20	25

Figure 4 shows the difference between the two sinter-hardening powders, powder #1 and powder #2. Curve F represents powder #2 and, as shown, the graphite diffusion occurs later in comparison with curve D, which represents powder #1. It can also be noted that the copper melting occurs before the graphite is totally diffused in the matrix. This is in part explained by the higher oxygen content which needs to be reduced prior to the graphite diffusion [2]. The time required for this reduction impedes the diffusion of graphite which in turn yields higher copper related growth.

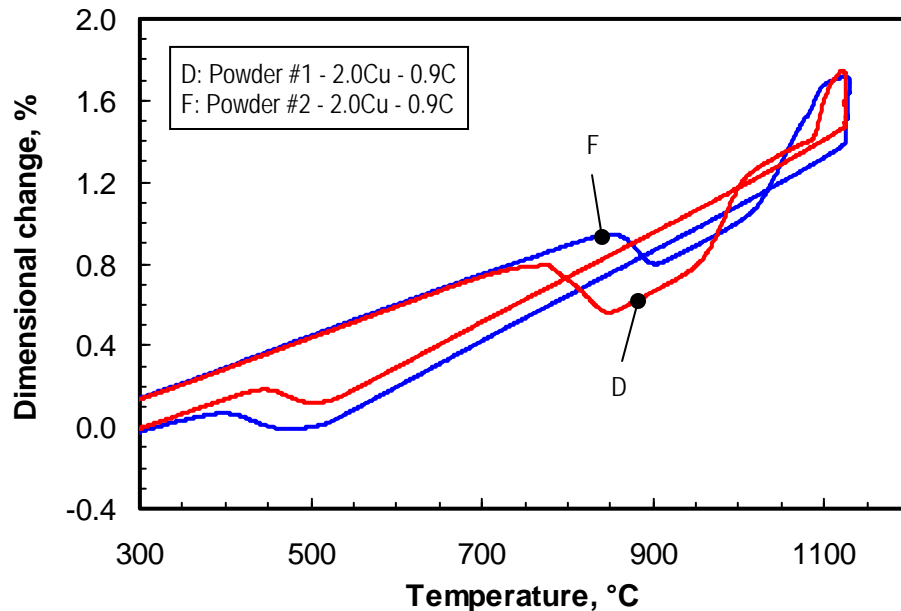


Figure 4: Dilatometry curves showing the effect of the type of powder on diffusion of alloying elements.

Effect of graphite type

As seen earlier, copper-melting growth is favoured at higher temperatures and one way to limit this growth is by either reducing its concentration or by increasing the matrix saturation with carbon. For the latter to occur, the graphite must dissolve and diffuse readily into the matrix. Figure 5 shows the effect of a synthetic graphite type which has a much finer particle size distribution. This graphite begins to infiltrate into the matrix at a much lower temperature. Curve G in Figure 5 demonstrates that at a temperature of about 950°C, the graphite has completely dissolved in the matrix. When the sample reaches the copper melting temperature of 1083°C, very little growth occurs; a consequence of already saturated grain boundaries. Curve E shows the copper induced growth occurring at 1083°C.

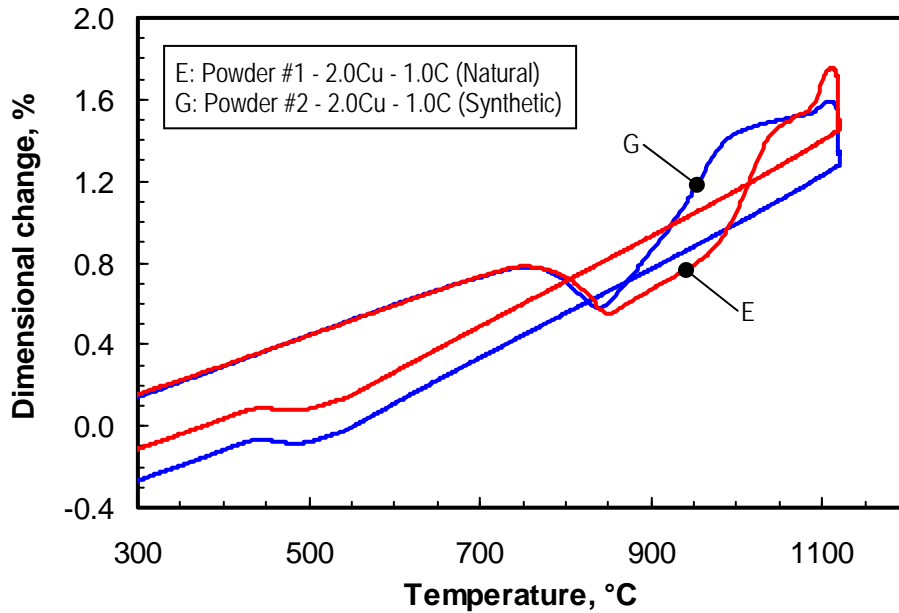


Figure 5: Dilatometry curves illustrating the rapid diffusion of the fine synthetic graphite into the iron matrix and its corresponding effect on dimensional change.

This demonstrates that some factors that have an influence on the dimensional change depend on the mix formulation. The presence of graphite induces growth when it diffuses to the grain boundaries. In the same fashion, copper adds to the total growth by diffusing as well. Using a different sinter-hardening grade also affects the dimensional change due to the later onset of graphite diffusion. Furthermore, using various types of graphite with different dissolution rates also has an effect on the dimensional change, as suggested by Danninger *et al.* [7].

The knowledge gained through dilatometry experiments enabled adjustments to the formulation of the ATOMET 4701 based mix provided to Metaldyne. By replacing the natural graphite used in the original formulation with finer, faster reacting graphite, the standard deviation of the outer diameter of the sprockets was greatly reduced and the overall dimensional change stability notably improved. Figure 6 shows the statistical variation of the outer diameter of sprockets manufactured out of ATOMET 4701 with natural graphite on the left and the statistical variation of the outer diameter of the same part when the mix contained CarbQ, a faster diffusing graphite, on the right.

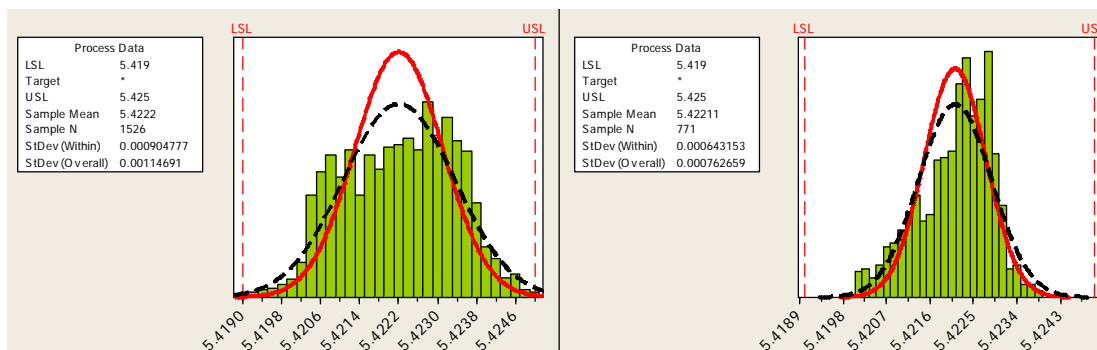


Figure 6: Statistical data showing the improvement in dimensional change control after replacing natural graphite with CarbQ.

However, improving the dimensional change behaviour of the powder formulation has limitations. Although the part-to-part size consistency was greatly improved, the correlation between the dimensional

change measured on TRS bars at RTMP and the dimensional change measured on long test bars at Metaldyne remained poor. This is clearly demonstrated in Figure 7 which shows the difference between lots of powder #2 with 1.7% copper, 0.85% graphite and 0.5% MnS sintered in both a laboratory-scale furnace and an industrial furnace. Lot D shows a much larger dimensional change than the other lots when sintered under industrial conditions. However, this increased dimensional change could not be detected when the laboratory furnace was used. This implies that sintering conditions indeed affect the dimensional change and that controlling the mix formulation is not sufficient to meet tight dimensional change tolerances.

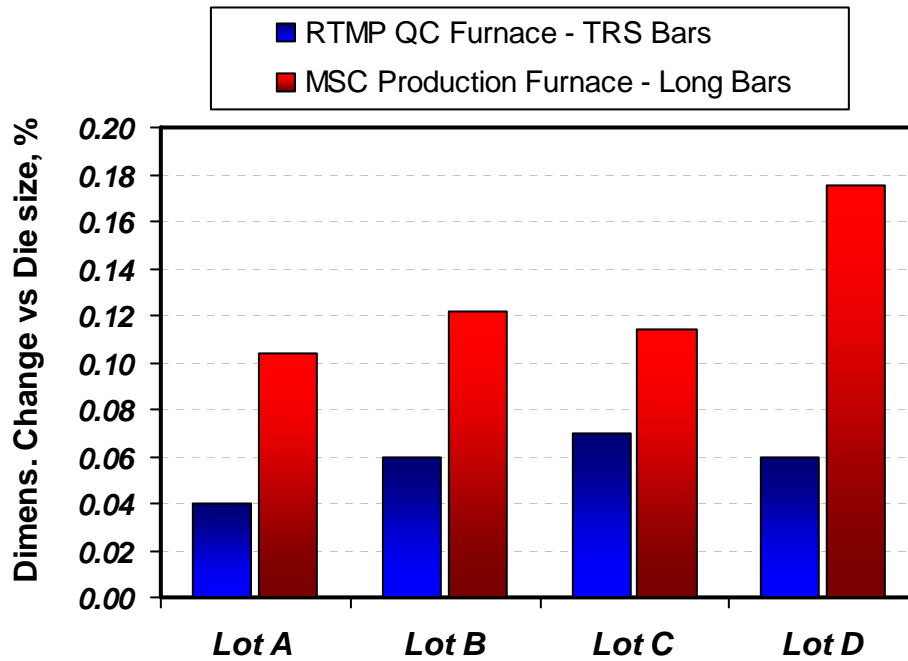


Figure 7: Difference in dimensional change between samples sintered at both RTMP and Metaldyne.

Effect of Sintering Conditions on Dimensional Change

Figure 8 shows the temperature profiles of the quality control laboratory furnace, the production sintering furnace and the dilatometer profiles at the heating rates of $20^{\circ}\text{C min}^{-1}$ and $25^{\circ}\text{C min}^{-1}$. The production sintering furnace has a much shorter temperature plateau than the other furnaces. Figure 9 compiles the time spent between 870°C and 1080°C for each profile. As demonstrated with the dilatometry experiments, graphite diffuses between 870°C and 1080°C , prior to copper melting, as illustrated in Figure 10. In this experiment, the heating rate of the dilatometer was increased from $10^{\circ}\text{C min}^{-1}$ to $20^{\circ}\text{C min}^{-1}$. This change in the heating rate enables the sample to spend more time in the graphite diffusion temperature range since this zone is reached more quickly. In the quality control furnace, the parts spend a considerable amount of time in this temperature range. This leaves enough time for most of the graphite to diffuse and therefore reduces copper growth. The production furnace has a profile limiting this time to only 6 minutes.

The production sintering furnace profiles were therefore optimised in such a way that the time spent in the graphite diffusion temperature range (870°C to 1080°C) would be increased. Two different modified profiles were tested. Figure 11 shows the dimensional change of a selection of powder #2 lots sintered in the laboratory furnace and in the production furnace with different temperature, including the standard mass production profile. Due to the very long time spent in the graphite diffusion zone of the laboratory furnace, the dimensional change of each lot is very small and shows limited variation from one lot to another. The standard production profile, however, resulted in a much greater dimensional change for all lots. The variation in the dimensional change obtained from one lot to another is also noticeable. By using

modified profiles with longer times spent in the graphite diffusion temperature range, not only was the dimensional change significantly reduced, but so was the standard variation from one lot to another.

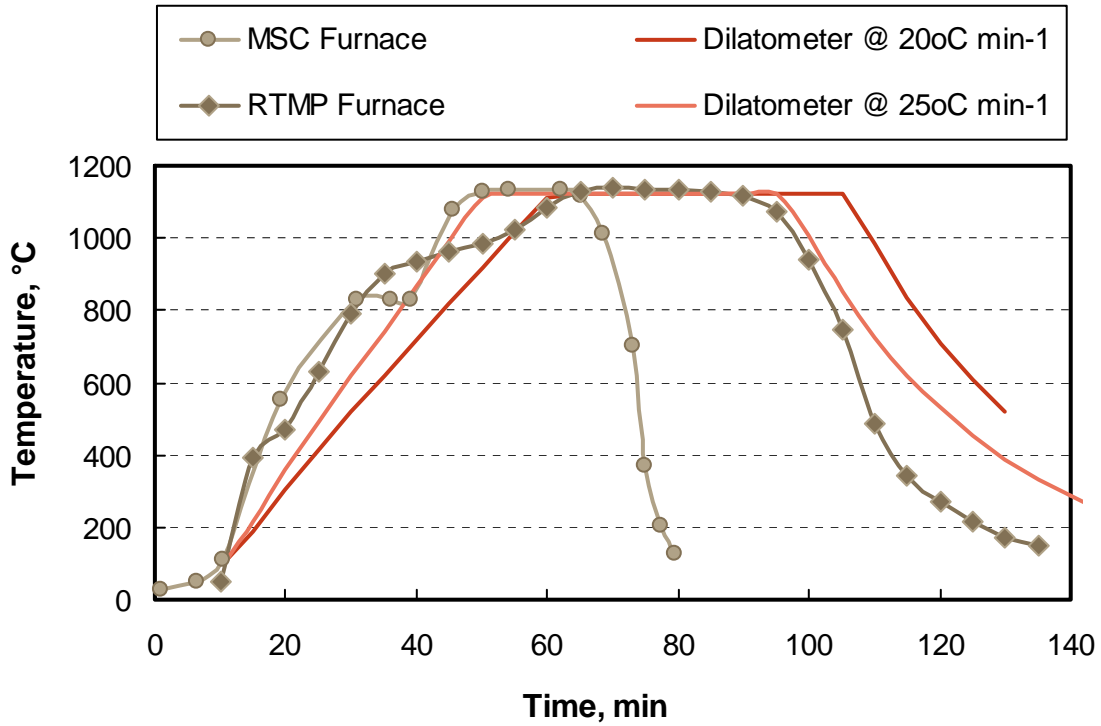


Figure 8: Sintering profiles of the quality control furnace, the production sintering furnace and the dilatometer at 2 different heating rates.

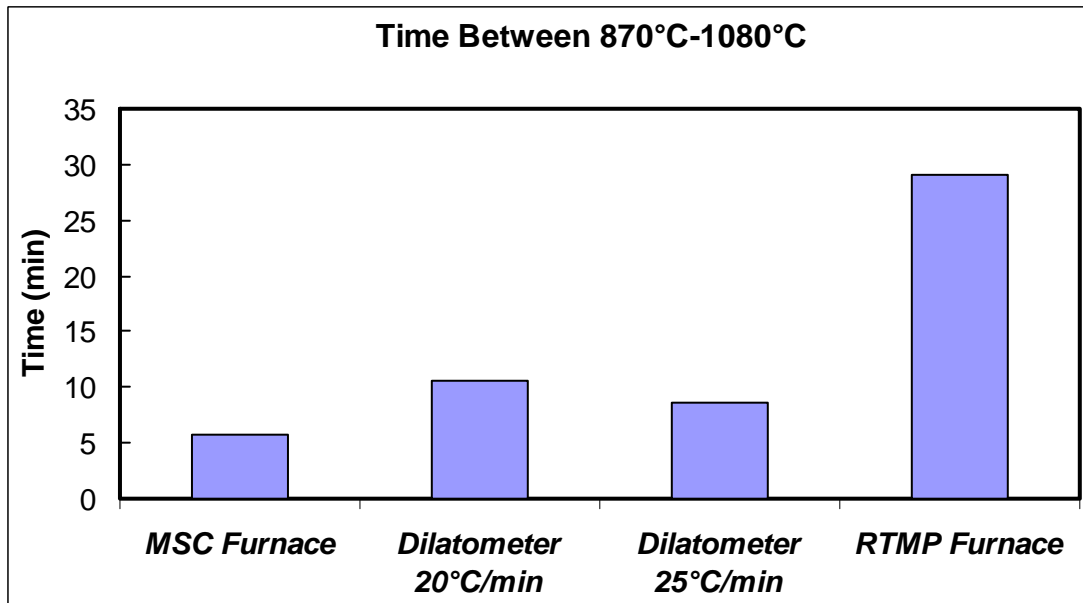


Figure 9: Histogram representing the total time available for graphite diffusion in each furnace profile.

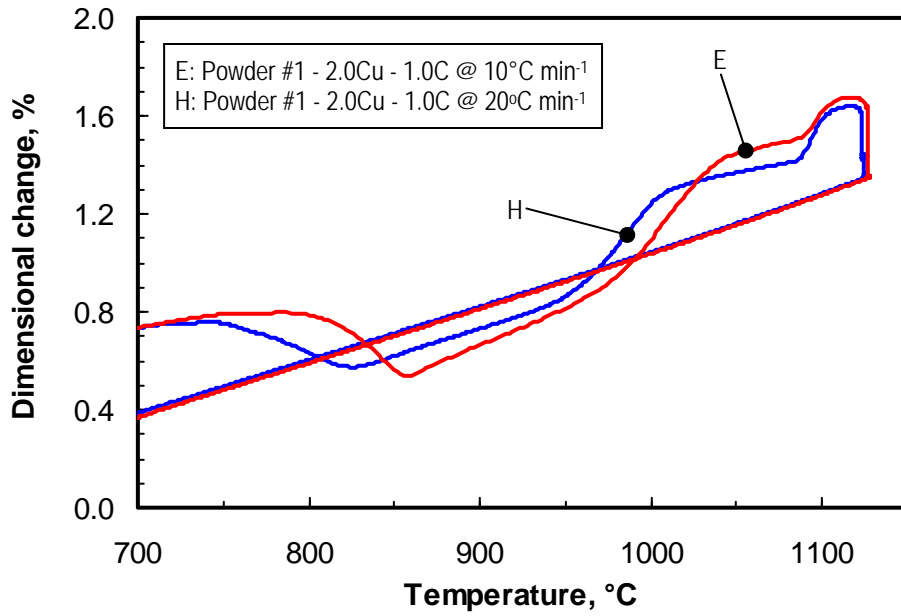


Figure 10: Dilatometry curves showing the effect of heating rate on the diffusion of graphite and subsequent copper melting growth.

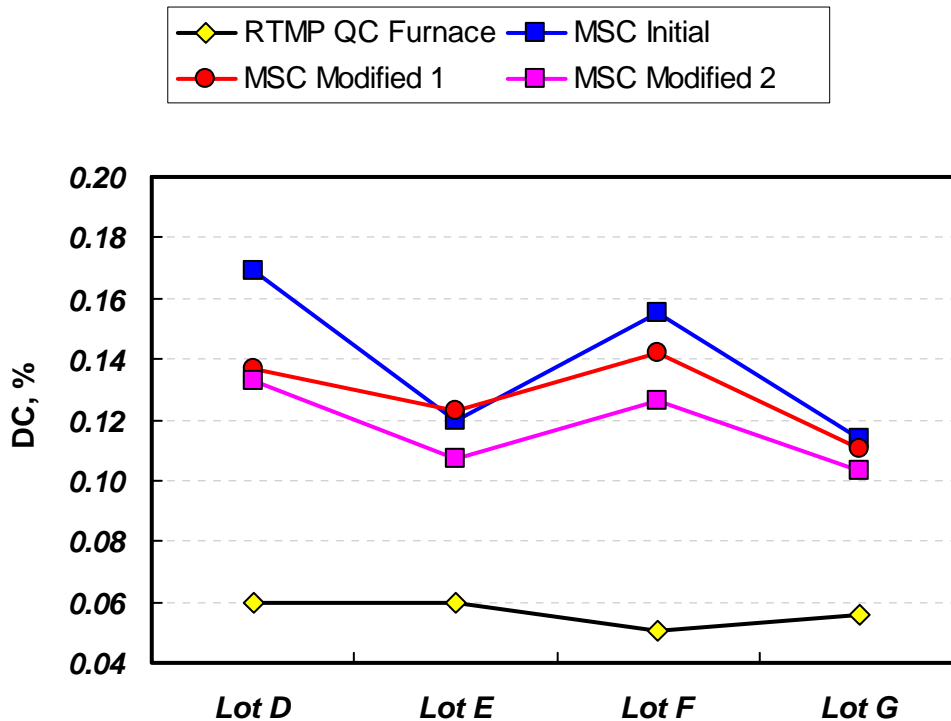


Figure 11: Comparison of dimensional change for a selection of powder #1 lots under different sintering profiles.

Overall for an ATOMET 4701 based powder containing only copper and graphite, the optimisation of the mix formulation proved very efficient in reducing the variability of the dimensional change. This is

demonstrated in Figure 12 where the use of faster diffusing, finer graphite (CarbQ) has led to a significant decrease in the standard deviation and also led to a corresponding increase in critical process capability (PpK). However, when the same change was made to a formulation containing MnS, the PpK remained low and the standard deviation was higher than for the modified MnS-free formulation. In such a case, the effects of the sintering conditions were much more important and the use of an optimised profile contributed to a significant improvement in process stability that the improvement in powder formulation could not accomplish alone.

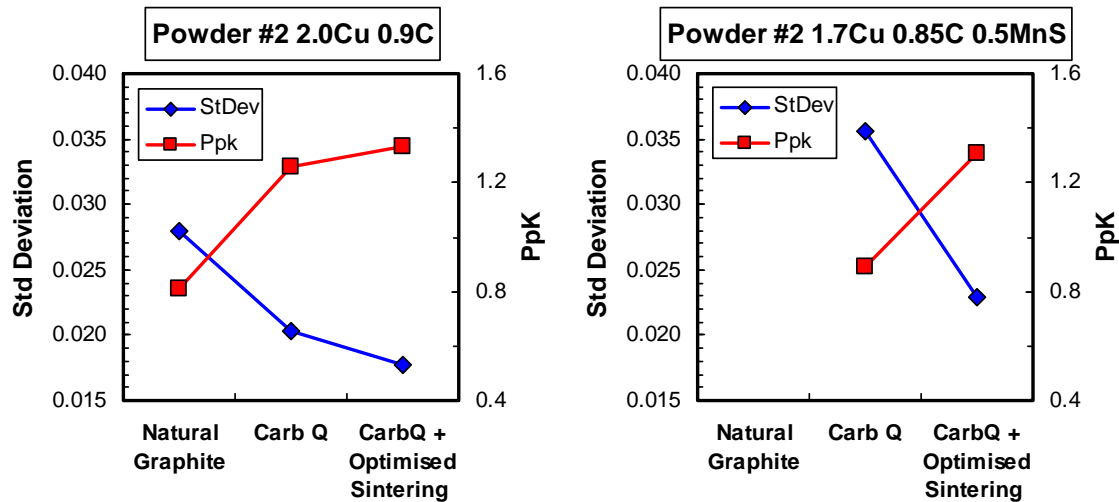


Figure 12: Improvement in process stability and control as a result of changes in powder formulation and optimised sintering profiles.

CONCLUSION

The effects of the addition of copper and graphite have a great impact on the sintering behaviour and on the final dimensional change of parts produced from ATOMET 4601 and ATOMET 4701 sinter-hardening powders. The use of the dilatometer enabled a better understanding of how these parameters interact with one another to yield the final dimensional change of a part. The replacement of natural graphite with finer, faster diffusing graphite not only contributed to a reduction in dimensional change but also significantly reduced the variability from one lot to another.

In some cases, adjustments to the mix formulation alone do not improve the dimensional change and its variability. In these cases, the effect of the sintering conditions is much more important and modifications to the temperature profile can greatly improve the dimensional change. This was the case with an ATOMET 4701 based formulation containing MnS.

The major conclusions drawn from this study are:

- Dilatometry is an excellent tool to help develop a powder formulation with increased control over the dimensional change.
- Both the graphite and copper growth can overlap which does affect the dimensional change. By controlling the diffusion of graphite, this overlap can be avoided and better results obtained.
- When modifications are made to the formulation, it can be worthwhile to also act upon the sintering conditions, as in some cases, the sintering conditions have a great impact on the dimensional change as well.
- In-depth knowledge of the behaviour of the sinter-hardening powders, coupled with interactions with other constituents of the mix and the further comprehension of the effect of sintering conditions lead to the possibility of implementing tight dimensional control for several applications.

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