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EFFECT OF POWDER MIX FORMULATION AND SINTERING CONDITIONS ON THE DIMENSIONAL STABILITY OF SINTER HARDENING POWDERS

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ABSTRACT

The production of high strength and high apparent hardness parts with sinter hardening steel powders sintered in furnaces with fast cooling capabilities is a cost effective method that is widely used in PM. However, due to the high levels of martensite formed after sintering, it is very difficult to correct the size of parts by secondary operations. The dimensional control of components is therefore of prime importance. A lot of effort has been devoted over the past years to better understand the behavior during sintering of ATOMET 4601 and ATOMET 4701, two sinter-hardening powders produced by Rio Tinto Metal Powders. The ultimate goal of these studies was to develop optimized sinter-hardening formulations with excellent dimensional accuracy in order to reduce as much as possible the cost related to quality issues resulting from dimensional variation.

The key materials and processing factors affecting the dimensional change are discussed in this paper. More precisely, the effect of mix formulation and type of additives on dimensional change occurring during sintering is presented in the first section. The dimensional consistency of optimized powder formulations and sintering conditions is discussed in the second part of the paper.

INTRODUCTION

Several parts with high mechanical strength and hardness are produced at a competitive cost by sintering high performance steel powder grades in furnaces equipped with fast cooling units without using post-sinter heat treatments. This is the case for ATOMET 4601 and 4701, two sinter-hardening powders produced by RTMP.

Due to the high apparent hardness reached after sintering, a very tight control of final dimensions of the parts is necessary, since it is almost impossible to adjust the final size by secondary operations [1]. A very good understanding of the behaviour of sinter-hardened powders during the sintering cycle is essential in order to achieve such a tight dimensional control in mass production. In that regard, dilatometry is a very powerful tool to study the sintering behaviour of materials [2-7] and many dilatometry studies were carried out during the last decade to better understand and quantify the dimensional change of ATOMET 4601 and 4701 [8]. The results of these studies have led to the development of a graphite grade used to improve dimensional consistency of pre-mixes. The effort has been mainly focused in the most recent years on the optimization of sintering conditions.

It is the objective of this paper to review the effect of graphite and copper on the dimensional change behaviour in the first section and discuss the dimensional performance of optimized materials under standard and optimized mass production conditions in the second section.

EXPERIMENTAL PROCEDURES

Table 1 gives the chemical composition of ATOMET 4601 and 4701. Sintered properties were measured on standard TRS specimens pressed either at 6.8 or 6.9 g/cm³. Sintering was performed in a mesh belt furnace at around 1140°C for 25 min in a 90%/10% nitrogen/hydrogen atmosphere. The cooling rate achieved in the temperature range 650°C to 400°C was ~ 0.8°C/sec. The dimensional response was evaluated either with a Theta dilatometer model DILATRONIC 1600°C or Linseis dilatometer model L75. For all tests, the specimens were heated between 10 to 20°C/min to reach 1120°C for 40 minutes, and then cooled at the maximum capacity of the dilatometers in an atmosphere consisting of pure Argon, Argon with 5% H_2 or 90%N_2/10% H_2. All samples were previously treated at 600°C in a nitrogen atmosphere to remove the lubricant.

TABLE 1. Chemical composition of ATOMET 4601 and 4701.

Grade	Ni, %	Mo,%	Mn,%	Cr,%	O,%
ATOMET 4601	1.8	0.55	0.2	0.05	0.10
ATOMET 4701	0.9	1.0	0.5	0.5	0.20

The effect of sintering conditions in mass production was evaluated at Metaldyne Sintered Components in USA in 61 cm wide mesh belt furnaces equipped with fast cooling units. Tests were performed with ATOMET4701 admixed with 1.7% copper, 0.85% graphite CarbQ, 0.5% MnS and lubricant. Tests were carried out either on rectangular bars 12.3 cm long or on sprockets with a diameter of ~ 138 mm pressed to a density of about 6.8 g/cm³. For each test, parts were sintered under steady-state sintering conditions in a N_2/5%H_2 atmosphere.

EFFECT OF POWDER FORMULATION ON DIMENSIONAL BEHAVIOR

Cu-graphite interactions during sintering

Figure 1 illustrates the variation of dimensional change as a function of sintered carbon content for 0, 1 and 2% copper for ATOMET 4601 and 4701 for conventional cooling rate. Similar trend is obtained when fast cooling rate and/or tempering are applied on parts. The dimensional response as a function of sintered carbon is highly dependant on the copper content. In particular, the dimensional change is highly affected by the sintered carbon content above 0.5% for both powders when 2% copper is added. Indeed, dimensional change varied by about -0.01% for each increment of 0.01% in sintered carbon. Variation in dimensional change is significantly reduced at 1% copper which appears to be a more appropriate level in term of size consistency. However, formulation is not solely dependant on the dimensional response but mainly on the strength and hardness desired. A very good understanding of the Cu-graphite interaction during sintering is therefore needed and dilatometry was used to acquire that understanding.

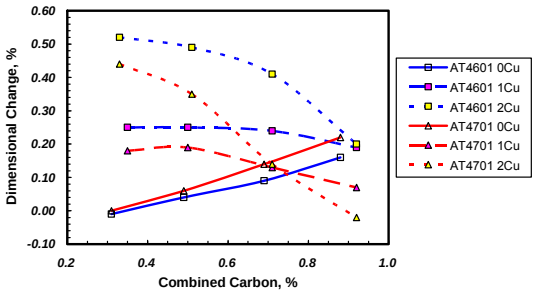

Figure 1. Dimensional change as a function of carbon and copper content.
Density: 6.9 g/cm³, cooling rate: 0.8°C/sec

Figure 2 illustrates a typical dilatometry curve of ATOMET4601 with 2% copper and 0.9% graphite. Five major transformation events can be observed during the heating/cooling cycle as

described in the legend. It was determined that the two phenomena having the strongest effect on the final dimension were the carbon diffusion (event 2) and the copper melting (event 3) [1, 9]. In particular, the growth associated with the copper melting, called copper growth, is a function of both the concentration of copper and carbon. Larger copper growth is obtained when copper content increases and/or sintered carbon content decreases [1, 9].

Series of experimental tests have shown that the copper growth was also affected by the diffusion behavior of graphite, which is mainly a function of the type and size distribution of graphite and the nature of the steel base powder. Example of that is illustrated in Figure 3 for ATOMET4601 with 2% copper and 1.0% graphite. The carbon diffusion starts and ends at a much lower temperature in the case of synthetic graphite. Even if the total growth associated with the carbon diffusion prior to the copper melting is basically the same for both types of graphite, the copper growth was strongly reduced with synthetic graphite. The lower copper growth obtained with synthetic graphite is likely related to a better iron diffusion and inter-particle necking prior to the copper melting.

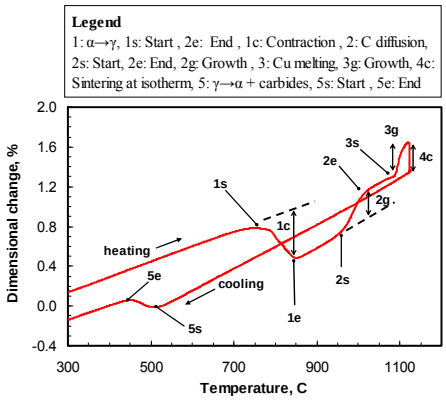

Figure 2. Typical dilatometry curve for ATOMET4601 with 2%Cu and 0.9%C.

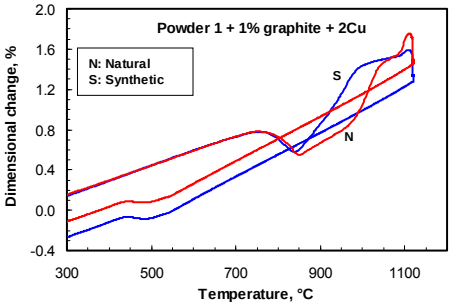

Figure 3. Effect of graphite type on carbon diffusion and copper growth.

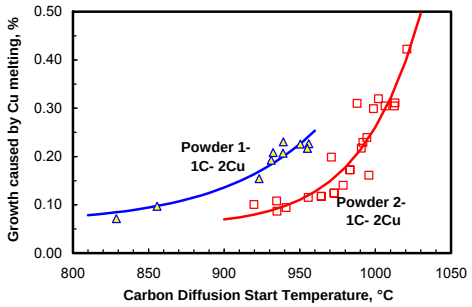

Figure 4. Effect of carbon diffusion start temperature on copper growth.

The effect of carbon diffusion on the copper growth is illustrated in Figure 4 at 2% copper and 1% graphite. As shown, a reduction of the temperature at which carbon starts to diffuse leads to a reduction and stabilization of the copper growth. It is thus quite obvious that the use of graphite with excellent carbon diffusion characteristics would result in a greater dimensional stability. This is even more important for ATOMET4701 for which the diffusion of graphite is a little bit more difficult, likely due to the higher level of oxygen for this powder grade.

DIMENSIONAL CONSISTENCY IN MASS PRODUCTION

Optimization of Mixes Formulation

In light of results of dilatometry studies, a new grade of graphite, CarbQ, with excellent diffusion behavior and lower cost compared to synthetic grades was developed. More details on CarbQ can be found in reference 9. CarbQ was mainly introduced in pre-mixes containing

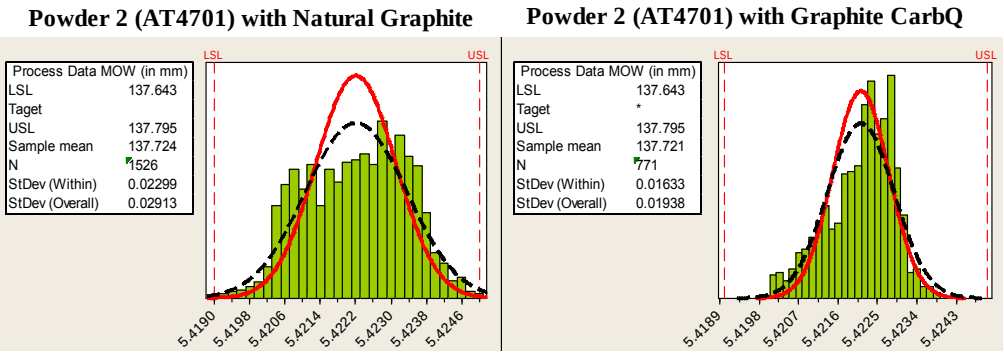

Figure 5. Statistical variation of outer diameter (MOW) of sprockets produced with ATOMET 4701 admixed either with natural graphite or CarbQ (Mix: 2%Cu -0.9%C). MOW is in inch.

ATOMET 4601 and 4701. For both powders, the standard deviation on dimensional change as-measured in laboratory was typically reduced by about 40% when using CarbQ instead of natural graphite. Using CarbQ was also extremely beneficial for the dimensional consistency of heavy parts processed in mass production as illustrated in Figure 5. Indeed, the standard deviation of the outer diameter as measured with the "measurement over wire" method (MOW), for ATOMET 4701 is significantly reduced with CarbQ, resulting in a significant improvement of the PpK (Critical Process Capability) from 1.03 to 1.5.

Optimization of Sintering Conditions in Mass Production

Despite the significant improvement of the part-to-part size consistency achieved with CarbQ, the sintering performance of sprockets produced with ATOMET 4701 was not yet optimal and as good as that obtained with ATOMET4601 for two reasons. First, the correlation between the sintered size achieved in laboratory and the size achieved on production parts was not always good as illustrated in Figure 6 for different lots of

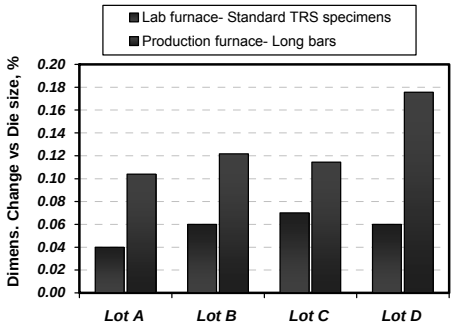

Figure 6. Dimensional change measured in lab and production-scale conditions (AT4701).

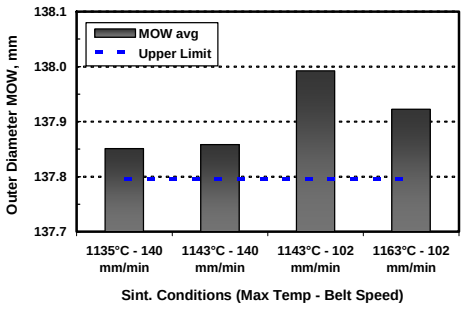

Figure 7. Effect of sintering conditions on size for sprockets produced with AT4701.

a pre-mix with 1.7% copper, 0.85% graphite, and 0.5% MnS. Indeed, lot D gave larger dimensional change than the other lots under mass production conditions even if no difference was found in laboratory. Secondly, the material did not behave necessarily as expected when adjusting sintering temperature and/or time in some cases. An example of that is shown in Figure 7 for lot D where increasing temperature and/or lowering belt speed did not allow reducing the outer diameter as normally observed. There was thus a need to understand the

reason for such a behavior and find ways to improve the dimensional consistency of ATOMET 4701 under mass production conditions.

As a first step, dilatometry was performed at a rate of 20°C/min with lots A and D (Fig. 6) to verify if there was some difference between these two materials. Dilatometry curves for these two powders are shown in Figure 8. The two lots behave in a very similar way, their behavior being that of a mix with CarbQ. In both cases, graphite diffusion ended prior to copper melting. As a result, very similar copper growth, between 0.10 and 0.13%, and shrinkage at the sintering temperature were obtained for both powders. The difference in size as illustrated in Fig. 6 could thus not be explained by a difference in material characteristics.

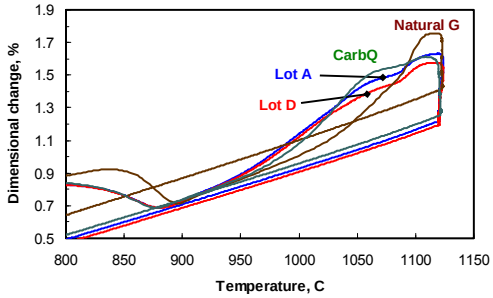

Figure 8. Dilatometry curves for Lot A and D (Powder 2 + 1.7Cu + 0.85C + 0.5MnS).

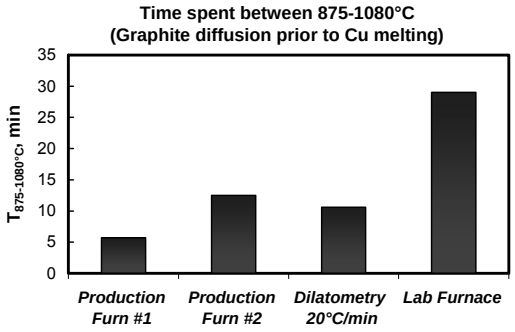

Figure 9. Time between 875 and 1080°C for different sintering furnaces.

As a second step, temperature profiles of production and laboratory furnaces and dilatometers were examined. The major difference we observed by examining the various profiles was the time between the delubing and the sintering zone. It is in this temperature range, more precisely between 875 and 1080°C that the graphite diffusion occurs. Time between 875 and 1080°C ($T_{875\text{-}1080°C}$) was calculated for each condition and is illustrated in Figure 9. $T_{875\text{-}1080°C}$ for production furnaces was very low, ~5.5 min, compared to the laboratory furnace (30 min) and dilatometry tests at 20°C/min (10 min). The time required to complete the carbon diffusion from dilatometry tests was estimated as ~ 7 min. $T_{875\text{-}1080°C}$ obtained for production furnaces was likely too short to ensure complete diffusion of graphite prior to copper melting. It is known from Fig. 4 that a lack of carbon diffusion may have a great effect in copper growth.

In order to confirm the effect of time spent between 875 and 1080°C on the dimensional change, sintering tests were run with 4 different lots of the same mix (AT4701-1.7%Cu-0.85%C-0.5%MnS), including lot D that gave much larger growth. Sprockets were sintered with conventional furnace settings and modified furnace settings to increase the carbon diffusion time. Two tests were run with modified settings to validate the effect of time

Settings	$T_{875\text{-}1080°C}$, min	Temp Max, °C	T>1095°C, min
CONV	6	1143	24
MOD-A	24.5	1132	19
MOD-B	22.2	1132	22

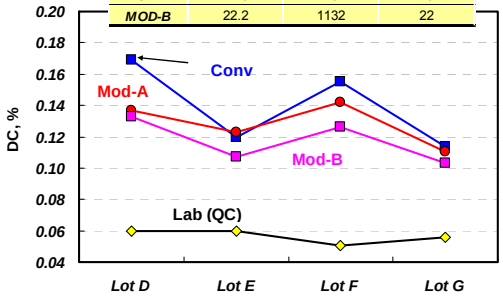

Figure 10. Effect of sintering conditions on dimensional change of different lots of ATOMET 4701 (1.7Cu-0.85C-0.5MnS).

in the sintering zone. Temperature profiles were recorded during these tests. The sintering conditions as well as the dimensional change measured for the outer diameter for these three tests are given in Figure 10. The dimensional change measured in laboratory is also included. As shown earlier, a much larger difference in size between lots was obtained with the conventional setting vs laboratory, ~0.05% vs 0.01%. The use of modified settings resulted in lower difference between lots, ~ 0.03%. In particular, the dimensional change of lot D, that showed the largest growth amongst the lots tested with conventional settings, shifted by about -0.03 to -0.04% with modified settings, even though the time above 1095°C and the maximum temperature were lower. This result confirms the importance of graphite diffusion and copper growth on the final sintered size of components.

The new furnace settings were implemented for ATOMET 4701 mixes and the process capability PpK was improved by 10 to 50% compared to the conventional sintering conditions.

CONCLUSION

The effect of graphite and copper additions as well as the effect of the sintering conditions on the dimensional behavior and consistency of ATOMET 4601 and 4701 were discussed in this paper. The major conclusions that can be drawn are:

- The graphite diffusion characteristics prior to copper melting and the copper growth are the two key factors affecting the part-to-part dimensional consistency.
- The introduction of CarbQ, a graphite grade with excellent diffusion characteristics, resulted in a reduction of the part-to-part size variation of ~55% in production.
- The diffusion of carbon in ATOMET 4701 occurs between 875 and 1025°C and takes about 7 minutes to be completed from dilatometry studies.
- The time available for graphite diffusion in steel particles prior to the copper melting point is crucial during sintering of components in mass production and must be sufficient to lower part-to-part dimensional variation.
- Modified sintering conditions to allow longer time between 875 and 1080°C and sufficient sintering time were tested positively and implemented with success.

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