USING BINDER-TREATMENT TECHNOLOGY FOR HIGH PERFORMANCE STEEL POWDER MIXES

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ABSTRACT

FLOMET technology is a binder treatment blending technique that consists of bonding fine particles of graphite, metallic additives and lubricants to the coarser iron particles using a solid organic binder. The main advantages of binder-treated mixes compared to conventional mixes are better flow, improved productivity and part consistency and reduced dusting and segregation. These attributes make binder-treated mixes well suited for high performance PM applications as well as other types of applications requiring mixes with excellent die filling characteristics.

QMP introduced a family of binder-treated mixes in the mid 1990's. Since then, R&D efforts were pursued to continuously improve the properties of this type of mix and to develop better performing binder-treated mixes for specific applications. This paper reviews the physical, green and sintered properties of binder-treated materials. Particular attention is paid to the processing characteristics of these materials.

INTRODUCTION

The PM industry is continuously trying to expand its market either by improving the PM part production and process capability and efficiency to increase its competitiveness or by developing new PM applications. In particular, the development of new PM applications requires the continuous development of new, higher performance products and processes.

It is well recognized that the use of finer additives such as very fine graphite grade and metallic additives in iron-base powder mixes contributes to improve their diffusivity in the iron matrix during sintering, which in turn improves the final sintered properties of the parts. Nevertheless, very fine additives are more prone to segregation during powder handling. In addition, they have a significant detrimental effect on the mix flowability, one of the key powder characteristics during part compaction. Indeed, the flowability behavior of the mix determines its die cavity filling performance, especially in the dump or gravity filling mode. Poor die cavity filling performance resulting from the poor flow of mixes containing fine additives may result in lower production rates, higher variability in weight, larger density gradients within the part and less dimensional consistency after sintering. Of course, all these drawbacks contribute to increase the percentage of rejected parts and the total cost of production, which in turn, reduce the economic competitiveness and advantages of the PM process.

In this regard, a new bonding technology called FLOMET was introduced in the 1990's in order to improve the flow behavior of mixes for demanding applications or difficult die cavity filling conditions and significantly reduce segregation during powder handling and compaction. The FLOMET technology is a binder-treatment blending technique in which the common additives used in PM pre-mixes are bonded to the iron particles using a patented polymeric solid binder [1,2].

In addition to the significant improvement in flow obtained with this bonding technology, the other main advantages of binder-treated mixes compared to conventional mixes are:

- Efficient particle bonding that ensures better chemistry homogeneity within part and from part-to-part as well as less segregation during powder handling.
- Reduced dusting, which results in a much cleaner environment where the powder is used.
- Improved part consistency, which results in fewer rejected parts and better process capability indices.

More importantly, binder-treatment allows the use of very fine additives. This paper reviews the characteristics and performance of bonded materials produced with the FLOMET binder-treatment technology.

PARTICLE BONDING

Figure 1 illustrates the flow diagram of the binder-treatment process. The binder is dissolved in a volatile solvent, which acts as a carrier and is then sprayed into the homogenized base ferrous mix. After homogenization of the solution in the powder mix, the solvent is dried out, leaving a thin coating of binder on the surface of the powder particles. This thin organic film bonds the finer particles of graphite, metallic additives and iron to the coarser iron particles. Agglomeration of fine additives is also possible during the binder-treatment.

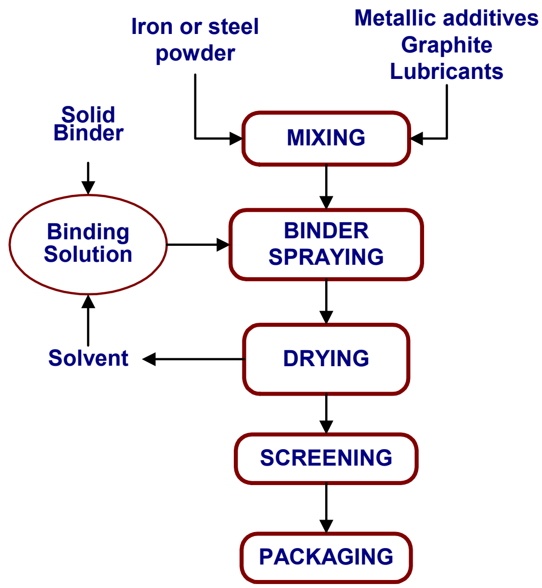

Figure 1. Process flow diagram of the binder-treatment technology.

Figures 2 and 3 show different micrographs of the powder particles after conventional and binder-treatment blending respectively. Micrographs were obtained on a scanning electron microscope (SEM) in the back-scattered (BS) and secondary (S) electron image modes. The mix formulation was FN0208 made with ATOMET 1001, a steel powder with 0.18% Mn and admixed with, 2% Ni, 0.85% graphite and 0.75% EBS wax or equivalent in the case of the binder-treated mix.

It can be seen that in the case of the regular non-bonded mix a significant proportion of the graphite and lubricant (appears dark in the BS mode) and nickel (appears white, dendrite-like) are free and not attached to the iron particles. Nevertheless, a certain proportion of graphite, lubricant and even nickel are attached to the iron particles. This dry-bonding is mainly associated with the van der Walls (VDW) adhesion forces that take place between particles. Electrostatic forces could also play a role in the case of the lubricant. The magnitude of the VDW force is increased as the difference in size between two particles increases. In the case of binder-treated materials, the proportion of graphite, lubricant and nickel not attached to the iron particles is significantly lower. In fact, most of these additives are bonded to the iron particles.

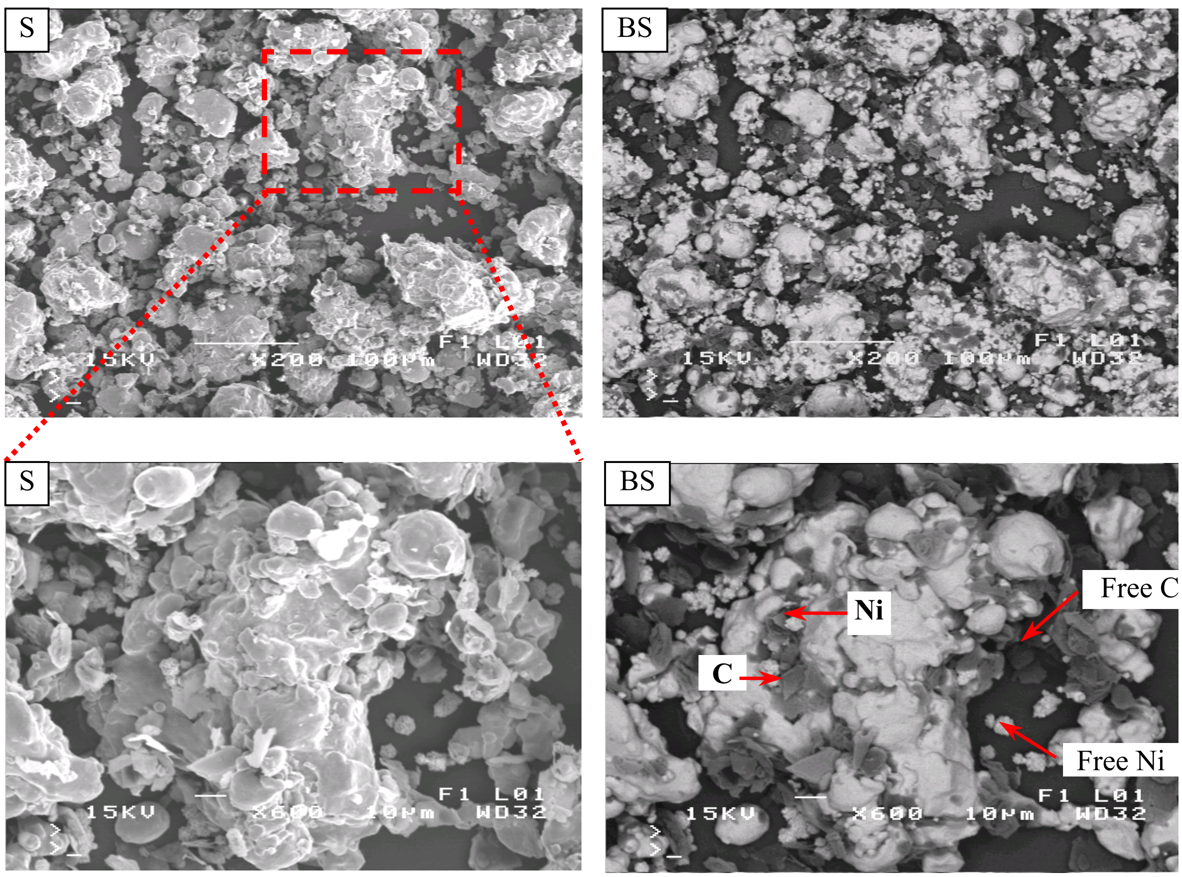

Figure 2. SEM micrographs of particles from a regular pre-mix made of ATOMET 1001, 2% Ni, 0.85% graphite and 0.75% wax. C represents either graphite or lubricant.
S is for secondary electron mode image and BS is for back-scattered electron mode image.

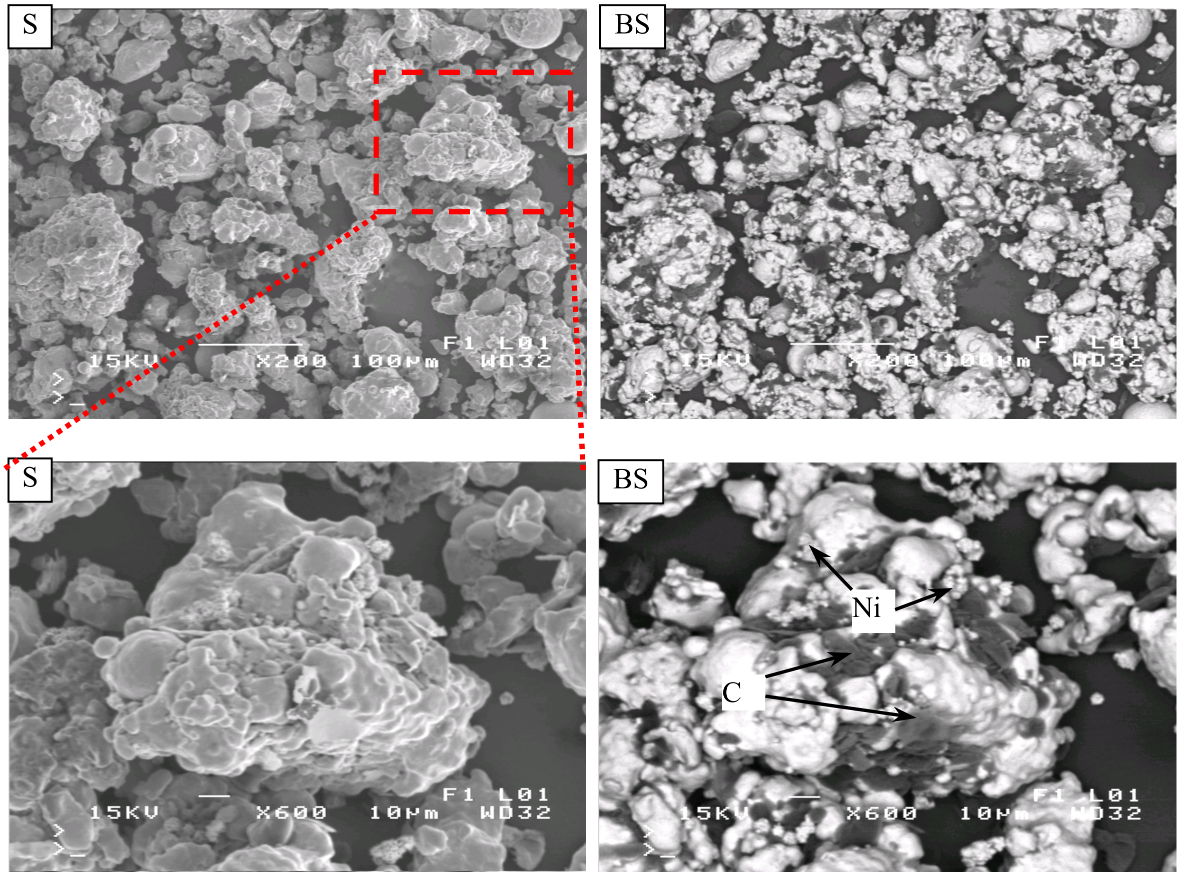

Figure 3. SEM micrographs of particles from a binder-treated mix made of ATOMET 1001, 2% Ni, 0.85% graphite and 0.75% wax+binder. C represents either graphite or lubricant. S is for secondary electron mode image and BS is for back-scattered electron mode image.

The influence of binder-treatment on the bonding efficiency of fine particles is clearly demonstrated by the size distribution of powder mixes as evaluated with a Coulter laser diffractometer, model LS230, in Figure 4. The size distribution of the base powder is given as a reference. It can be seen that the addition of fine nickel, graphite and lubricant significantly increases the proportion of fines in the regular mix. The distribution obtained corresponds quite well to the anticipated distribution of the powder mix calculated based on the weight fraction and the size distribution of each component. In the case of the FLOMET mix, size distribution is almost equivalent to that of the base powder, clearly showing that the particles below 60 µm were efficiently bonded to the larger ones or bonded together (graphite, lubricant and nickel) to form larger size agglomerates.

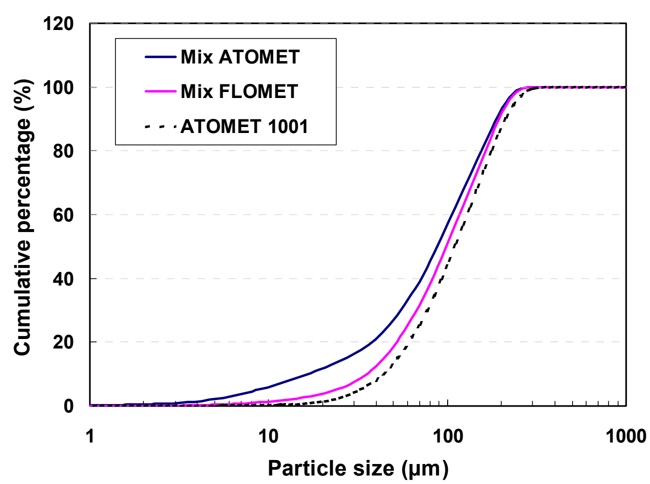

Figure 4. Particle size distribution of regular and binder-treated FLOMET mixes (laser particle analyzer). ATOMET 1001 + 2%Ni + 0.85% C + 0.75% EBS wax

DUSTING RESISTANCE

As shown earlier, the solid polymeric film formed during the binder-treatment process is highly efficient to bond the fine particles of graphite, lubricant and metallic additives to the larger iron particles. Nevertheless, the thin film that bonds the fine particles must also be strong enough to maintain the fine particles, when the mix is subjected to movement or strong air flow. Figure 5 illustrates the difference in dusting between regular and binder-treated mixes, confirming the high strength of the bonding film formed during the binder-treatment.

The difference in dusting was quantitatively measured with the experimental assembly shown in Figure 6. 10 to 25 g of powder is placed in a Hall cup and then poured into an Erlenmeyer flask. An aerosol dust monitor, which is connected via a tube to the flask, extracts the air at a rate of 2 liter/min and counts the number of particles below 10 µm (mg/m³). Figure 7 shows the results obtained with a F0008 mix. It can be seen that the amount of fine particles is strongly reduced with the binder-treated material, the peak being around 4 times lower.

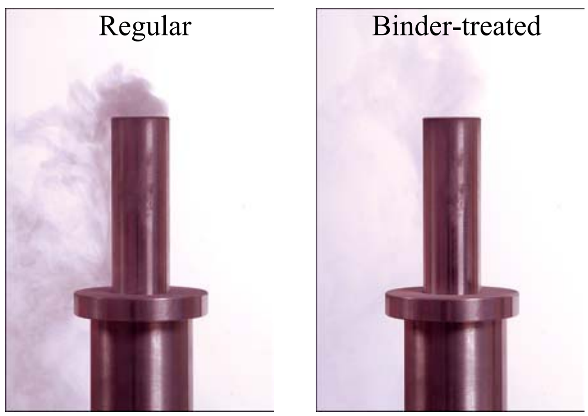

Figure 5. Dust produced with regular and binder-treated mixes in an apparatus used to measure resistance to dusting (6 liter/min air flow through a 25 mm diameter tube).

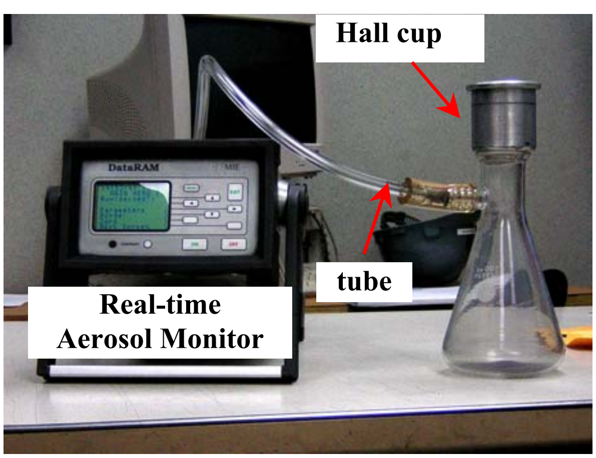

Figure 6. Experimental assembly used to evaluate the dust created during the flow of powder mixes.

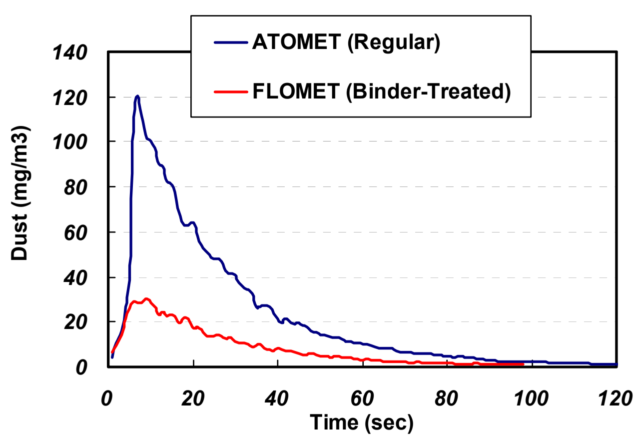

Figure 7. Quantity of dust (particles < 10 µm) created by a regular and a binder-treated F0008 mixes.

Another method to evaluate the efficiency of bonding is to measure the level of retention of fine additives such as graphite, lubricant, Ni and Cu after the powder mix is subjected to a strong flow of air for a given period of time. A test was developed where 25 or 50 g of powder is poured into a 25 mm cylindrical tube and a flow of air is forced into the tube at a rate of 6 liter/min for 5 minutes. The flow of air is strong enough to partially fluidize the powder. The powder before and after the test is analyzed and the dust resistance of a specific element is determined as followed:

$$\text{Dust resistance} = \text{wt\% after test} / \text{wt\% before test} * 100$$

Table 1 gives the typical carbon, copper and nickel dust resistance obtained. Typically, the dust resistance of each element is increased by a factor of 2 after a binder-treatment. This confirms that the thin bonding film formed during the binder-treatment is strong enough to withstand high turbulence flow. It should be noted that the carbon dust resistance reported is related to the overall percentage of retention of graphite and lubricant.

The size of the additive has a key influence on the dust resistance after binder-treatment. Indeed, the finer the additive, the more efficient the bonding and dust resistance. For example, it was shown by Azzi et al [*3*] that using an extra fine Nickel grade (D50 ~ 2 µm) increased the Ni dust resistance up to 97%. On the other hand, using additives with a lower amount of fine particles may also increase the dust resistance. For example, the copper dust resistance of typical –200 mesh grade available in the market is 90% or higher. Figure 8 illustrates the influence of the average equivalent diameter D_{50} on the dust resistance.

Table 1. Typical dust resistance of carbon, copper and nickel in mixes.

Type of mix	Carbon, % [1]	Copper, % [2]	Nickel, % [3]
Regular (ATOMET)	50-65	20	25
Binder-Treated (FLOMET)	85-95	50	60

1. Lubricant and graphite
2. –325 mesh grade.
3. Carbonyl grade, D50 ≈ 8-10 µm

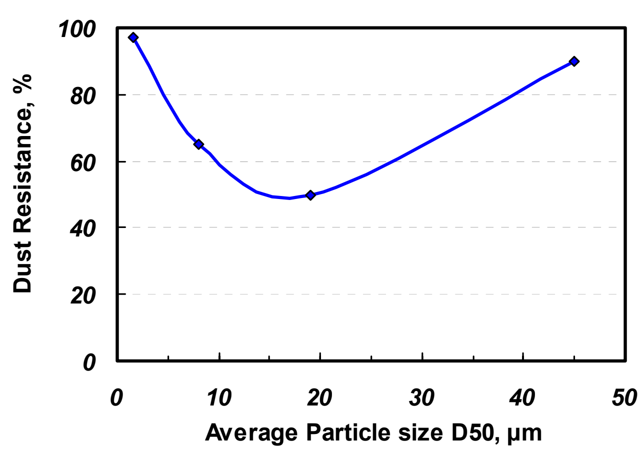

Figure 8. Effect of mean particle size D_{50} of metallic additives on the dust resistance after binder-treatment.

FLOWABILITY AND DIE FILL CAPABILITY

I. FLOW BEHAVIOR

As mentioned earlier, bonding fine particles to the coarser ones helps to improve the flow. In general, improvement in flow obtained by binder-treatment is typically in the order of 4 to 10 s/50g, depending on the mix formulation. Normally, the slower the flow rate for the regular mix, the larger the gain in flow rate after binder-treatment. The improvement in flow rate may be significantly higher when the amount of very fine additives is substantial.

II. DIE FILL BEHAVIOR IN REAL COMPACTION CONDITIONS

In order to measure the die filling capability of regular and FLOMET materials, different tests were performed on mechanical production presses. Table 2 shows the formulation and physical properties of the mixes evaluated. The flow rate of the binder-treated materials was 4 to 8 sec faster depending on the formulation. It should be noted that a regular –200 mesh copper grade was used for the regular mixes and a finer -325 mesh copper grade was used for the FLOMET mixes. The same grades of graphite, Ni and EBS wax were used. Tests were done in two different modes: (1) gravity or drop fill and (2) suction or withdrawal fill. Figure 9 illustrates schematically these two modes of filling in a press. In the gravity mode, the bottom punch is already located at its lowest position in the die, when the shoe feeder is brought over the cavity. In the suction fill mode, the bottom punch is in its upward position when the shoe is brought over the cavity. The bottom punch is then moved (done by the platen moving upward) to its lowest position before the shoe is removed over the cavity. Because of the entrapped air in the cavity, the filling in the gravity mode is more difficult, usually resulting in larger part-to-part weight variation.

Table 2. Formulation and physical properties of mixes evaluated on production presses.

<table>
<tr><th>Test #</th><th>Mix ID</th><th>Formulation (1)</th><th>A.D., g/cm³</th><th>Hall Flow, s/50g</th></tr>
<tr><td rowspan="3">1</td><td>FC0208-Reg</td><td rowspan="2">ATOMET 1001 - 2Cu - 0.9C - 0.75 wax</td><td>2.96</td><td>36.5</td></tr>
<tr><td>FC0208-BT</td><td>3.05</td><td>31.5</td></tr>
<tr><td>F40B-BT</td><td>ATOMET 4001 - 4Ni - 1.5Cu - 0.6C - 0.75 wax</td><td>3.13</td><td>30.4</td></tr>
<tr><td rowspan="2">2</td><td>FLNC4405-Reg</td><td rowspan="2">ATOMET 4401 - 1.75Ni - 1.5Cu - 0.6C - 0.75 wax</td><td>3.08</td><td>36.0</td></tr>
<tr><td>FLNC4405-BT</td><td>3.20</td><td>27.8</td></tr>
<tr><td rowspan="3">3</td><td>FC0208-Reg</td><td rowspan="3">ATOMET 29M - 2Cu - 0.85C - 0.75 wax</td><td>2.99</td><td>37.7</td></tr>
<tr><td>FC0208-BT 1</td><td>3.01</td><td>31.8</td></tr>
<tr><td>FC0208-BT 2</td><td>2.86</td><td>29.1</td></tr>
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(1) The wax used was Acrawax C atomized. A -200 mesh Cu grade was used in regular mixes (Reg) and a -325 mesh Cu grade was used in Binder-treated mixes. (BT)

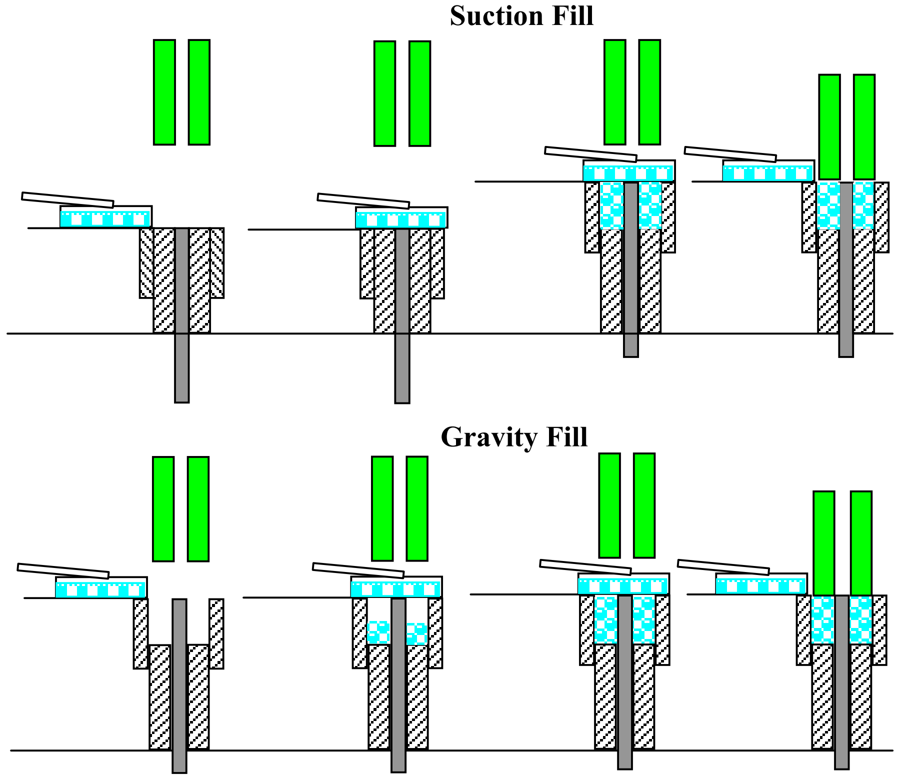

Figure 9. Illustration of the two modes of die cavity filling used in a mechanical press.

1. Test 1: Easy Die Cavity Filling Conditions

A first series of tests was carried out on a ring-die with an outside diameter (OD) of 6.10 cm (2.4 in) and an inside diameter (ID) of 3.56 cm (1.4 in), for a wall thickness of 1.27 cm (0.5 in). The fill height was fixed at ~ 2.5 cm, which represents relatively easy filling conditions. Two tests were carried out: test-A simulates filling conditions achieved at 14 strokes per min (SPM) and test-B simulates filling conditions achieved at 20 SPM. The filling time obtained was respectively 1.4 and 1.0 sec. In addition, to make filling conditions slightly more difficult, the core rod was brought up at the beginning of the feeding process for test-B. The results of these tests are given in Figure 10. All mixes gave very similar part weight variation, which increases slightly with test-B. This increase is thought to be mainly due to the difference in the movement of core rod during the feeding stage. In addition, the average part weight dropped by ~ 2% only. These results indicate that for relatively easy filling conditions, and when the suction fill mode is used, there is no real advantage to use a binder-treated material in term of weight consistency.

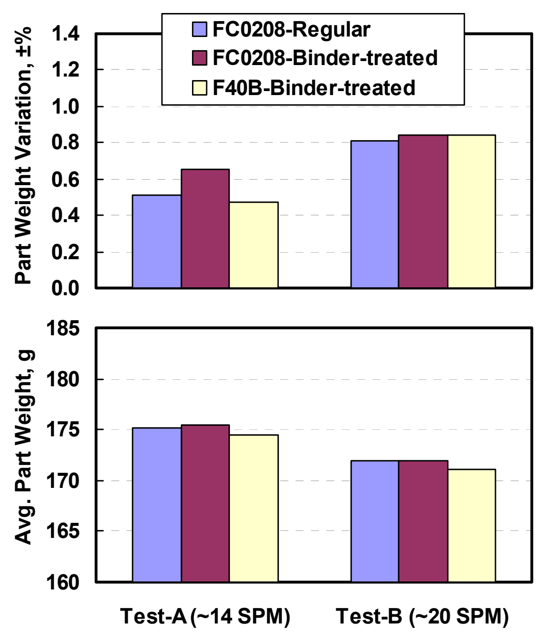

Figure 10. Results of test #1 carried out under easy filling conditions (Suction fill, fill height/wall thickness = 2).

2. Test 2: Difficult Filling Conditions

A second series of tests was carried out with more difficult filling conditions. A ring-die having an OD of 5.25 cm (2.068 in) and an ID of 4.34 cm (1.710 in), giving a wall thickness of 0.45 cm (0.18 in) was used for these tests. The die filling height was fixed to 3.81 cm (1.5 in). The filling conditions for these tests were significantly more challenging than for the previous test, with a height to wall thickness ratio more than 4 times higher. In addition to that, core rod was fixed during these tests. In other words, the core rod always remained in the same position relative to the die platen. This was done to make the filling even more difficult. Normally, in actual production runs, the core rod is down during the filling and moves upward to its compaction position at the end of the feeding stage, in order to ensure better cavity filling and part weight consistency.

Figure 11 shows the part weight variation as obtained in the suction fill mode at a compaction rate of ~22 SPM. The fill time was set to 1 and 0.8 sec. Contrary to the results obtained in the previous test, the binder-treated mix gave much lower part weight variation, 66% and 105% lower compared to the regular mix at 1 and 0.8 sec respectively. This result clearly indicates that in the case of more difficult filling conditions, and even if suction fill mode is used, the use of binder-treated materials can reduce part weight variability and/or increase production rate.

Figure 12 shows the part weight variation and the average part weight as a function of the filling time for tests carried out in the gravity filling mode. Compaction was done at 10 SPM and the filling time was varied from 1.2 to 1.8 sec. It can be seen that the weight variation was significantly lower with the binder-treated materials, up to 600% at 1.8 sec and between 20 and 60% at 1.2 and 1.4 sec. In addition, the drop in weight, when the filling time was reduced, was less significant with the binder-treated material.

Both results confirmed the superior feeding property of the binder-treated material. Again, in difficult feeding conditions where a portion of the part or the entire part must be fed in the gravity mode, using binder-treatment should result in better weight control and increased production rate.

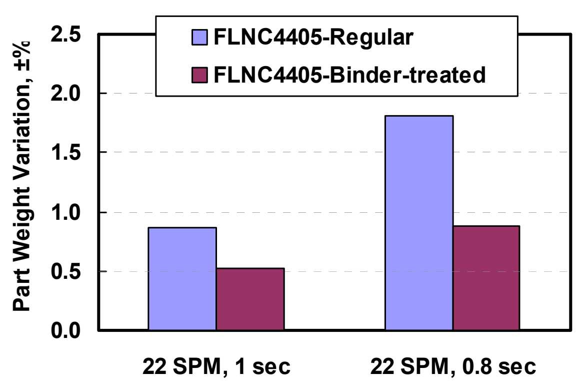

Figure 11. Variation in part weight obtained during test #2 carried out in ***suction fill mode*** under more difficult filling conditions (fill height/wall thickness = 8.2).

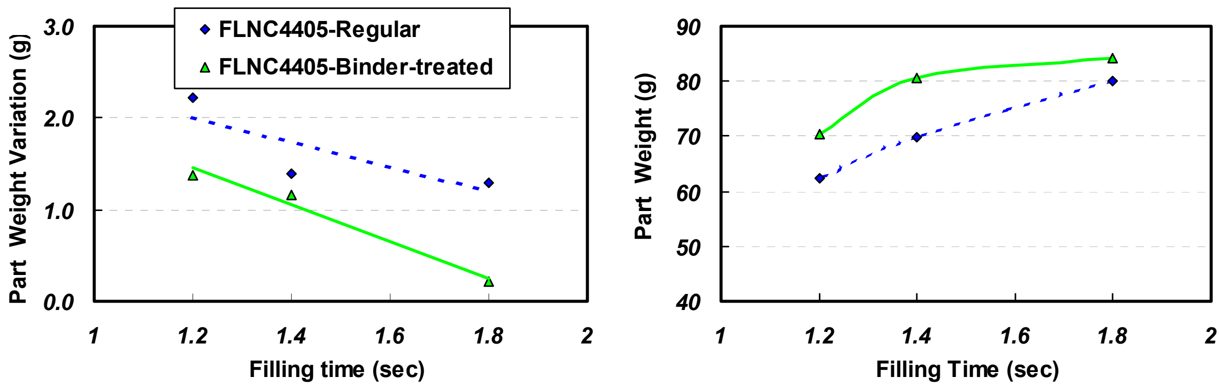

Figure 12. Results of test #2 carried out in the ***gravity fill mode*** under more difficult filling conditions (fill height/wall thickness = 8.2).

a. <u>Test 3: Production case study</u>

A trial was carried out on a small drive nut under actual industrial compaction conditions. The objectives of the test were to determine if using binder-treatment could improve the weight stability and increase productivity. A regular and two versions of binder-treated FC0208 mixes were evaluated. ATOMET 29M, a free-machining iron powder was used as the base powder. The second version of FLOMET was optimized for flowability by adding a flow agent to the binder formulation. A first series of ~ 1500 parts were produced at a rate of 21 SPM. This corresponds to the maximum compacting rate that can be used with the non-bonded mix. It should be noted that upper and lower tonnage limits were set on the press to ensure low level of rejects. The press stopped running when the tonnage exceeded these limits. A second series of ~ 1500 parts was carried out with the binder-treated mix at a rate of 27 SPM, which corresponds to the maximum compaction rate achievable with the press. It should be noted that it was not possible to run the regular mix at such a compaction rate, the tonnage constantly exceeding the lower and upper limits of the press. The type of die cavity filling was a combination of both gravity and suction fill. The lower punch was already moving downward when the shoe was brought over the die cavity.

Figure 13 shows the part weight variation obtained. For tests at 21 SPM, the two binder-treated materials gave lower part weight variation, the improvement being in the order of 15 to 22%. It should be noted that the press stopped running at least every 25-50 parts with the regular mix while the press stopped every 250-300 parts with the 1st binder-treated version and did not stop for the entire run with the 2nd binder-treated version. Considering that the press was continuously adjusted during the run with the regular mix, it can be concluded that the improvement in weight stability obtained with the binder-treated materials was in fact greater than that observed.

Increasing the compaction rate to 27 SPM did not affect the part weight stability for the 1st binder-treated version, while the part weight variation dropped by 25 % for the second version. This represents an improvement of 36% as compared to the regular mix pressed at 21 SPM. Therefore, using binder-treated materials increases the production rate by 28%, while reducing the weight variability versus a non-bonded material.

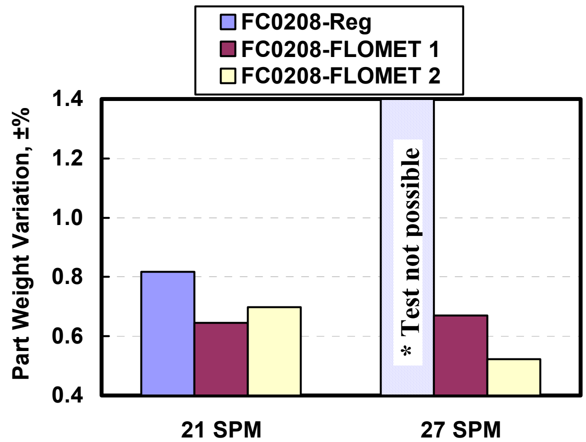

Figure 13. Part weight variation obtained during production runs with regular and binder-treated mixes. * The regular FC0208 mix was not run at 27 SPM because of a too large variation.

COMPACTION AND GREEN PROPERTIES

The primary objective of using binder-treatment is to improve flow and reduce dusting and segregation. Nevertheless, the compaction characteristics and green strength of a mix are always major concerns for PM part producers, especially for complex, high aspect ratio and high-density parts. As already discussed in a previous section, low specific gravity organic binders are used in binder-treated mixes. These binders as for the lubricant, fill more space for a given quantity than the steel powder. Therefore, it is crucial in order to maintain excellent compressibility and ejection properties to use binders with very good lubricity characteristics or that do not counteract the role of lubricant. In addition, in the case of high-density applications, it is also important to maintain the total amount of lubricant and binder as low as possible. This can be done by using very small quantity of binders and/or by replacing partially the lubricant by the binder. Again, the partial replacement of lubricant by the binder is only possible if the binder contributes to the lubrication.

Figure 14 shows the compacting pressure and green strength obtained at 6.8 and 7.0 g/cm³ for two different mix formulations. 0.65% EBS wax was used in all cases. Compaction of rectangular bars of 31.7mm-12.7mm-6.4mm was done at 60°C, which is more representative of production conditions. It can be seen that for the two formulations, the compacting pressure was slightly lower for the binder-treated materials, despite the fact that the total amount of organic is higher in these mixes. Green strength is also higher for binder-treated materials. The gain in green strength was about 14 and 20% at 6.8 and 7.0 g/cm³ respectively. These results clearly show that a proper binder treatment can be beneficial both for densification and inter-particle cohesion strength after compaction.

Figure 15 shows the ejection curves for same mix formulations. Ejection was determined with an instrumented laboratory press, called, Powder Testing Center [*4*]. Cylindrical specimens with a diameter of ~ 9.525 mm and a height of 10 mm were pressed at 60°C and a compacting pressure of 620 MPa. For both mix formulations, it is seen that the ejection performance was improved with the binder-treated materials. Indeed, the ejection energy, which corresponds to the area under the curves, was reduced by 10% with the binder-treated materials. The stripping pressure remained almost unchanged. It should be noted that the green density achieved with the binder-treated materials was 0.01 to 0.04 g/cm³ higher, confirming the results given in Figure 13 showing an improvement in compressibility with binder-treated materials.

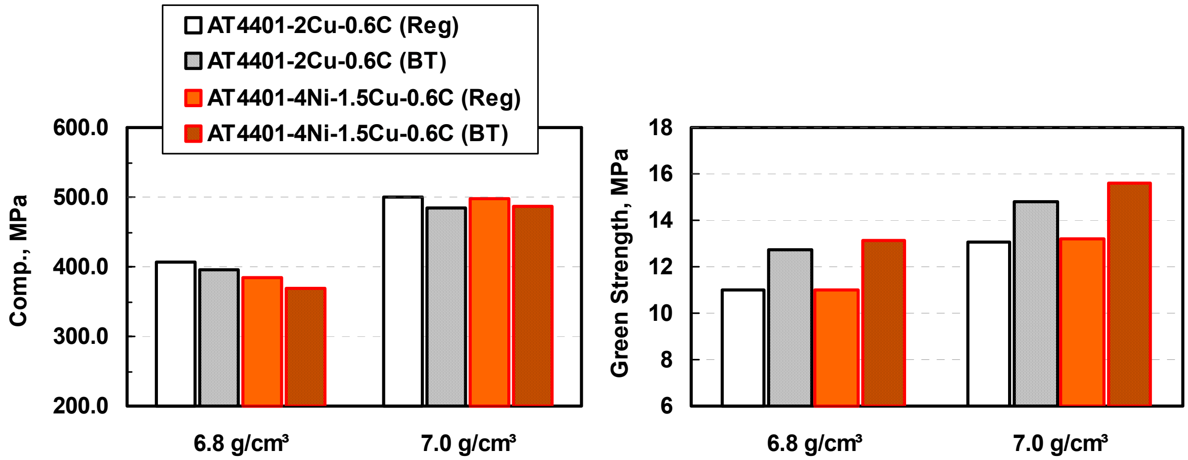

Figure 14. Compacting pressure and green strength achieved at 6.8 and 7.0 g/cm³ with two different mix formulations. Specimens pressed at 60°C.
AT1001 and AT4440 refer to ATOMET 1001 and ATOMET 4401 respectively.

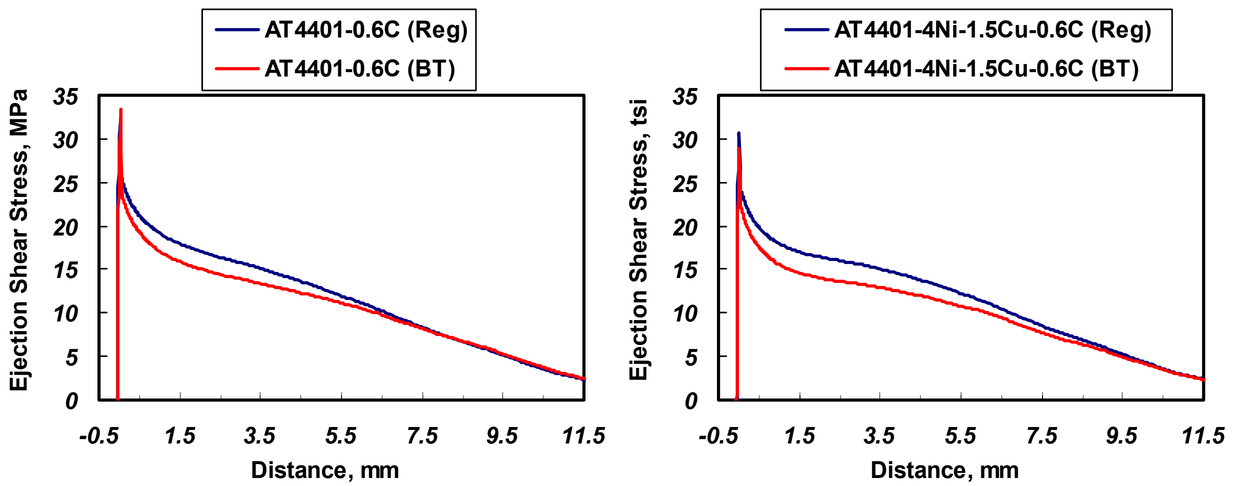

Figure 15. Ejection curves for FL-4405 and FLN4-4405-1.5% Cu mixes. EBS Wax content : 0.65%.
AT1001 and AT4440 refer to ATOMET 1001 and ATOMET 4401 respectively.

PART CONSISTENCY AND HOMOGENEITY

It was already demonstrated that using binder-treatment is an efficient method to bond fine particles of additives to the larger iron ones and the bonding film is strong enough to maintain the bonding even in high turbulence environments. As a result, it can be expected that segregation within the binder-treated mix is significantly reduced and thus, part-to-part chemistry consistency is improved.

Moreover, the binder-treatment technology allows the use of very fine additives, which normally drastically deteriorates the flow of regular mixes. The benefit of using fine copper on the distribution of copper in parts is illustrated in Figure 16. The percentage of copper was evaluated by image analysis with a color camera on specimens pressed to 7.0 g/cm³ from regular and binder-treated FC0208 mixes. Specimens were pre-sintered at 800°C for 15 min before performing image analysis. Each field analyzed was 1.06 mm² in surface area. Using fine copper greatly reduces the standard deviation from field-to-field from 0.61 to 0.19. In addition, the pore size after sintering was also considerably reduced. Both effects should lead to more consistent dimensional change.

Figure 17 clearly shows the advantage of using finer additives on the dimensional stability of thin rings made of AT4401-3.7Ni-2.6Cu-0.6C-0.75EBS wax mixes. Rings were 5.25 mm (2.07 in) OD, 4.31 mm (1.70 in) ID and 1.27 mm (0.50 in) thick. The dimensional variation reported here is the difference in dimensional change between the top and the bottom of the ring. It can be seen that using very fine copper and graphite grades resulted in a significant drop in dimensional variation. The variation from one part to another was also reduced with the extra fine copper and graphite grades.

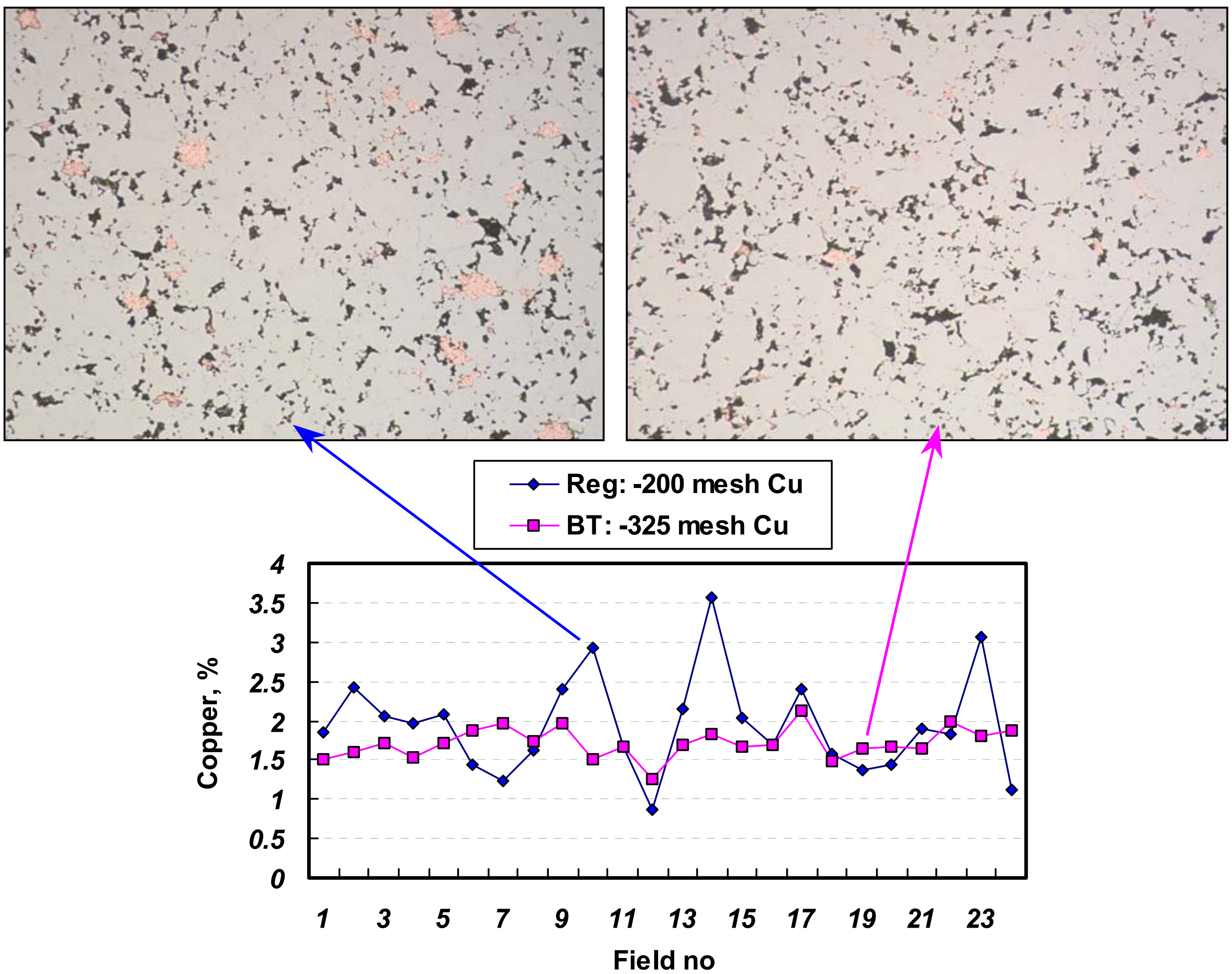

Figure 16. Distribution of copper in specimens made of FC0208 mixes. Regular mix (Reg) contains a -200 mesh Cu while the binder-treated mix (BT) contains a -325 mesh Cu grade.

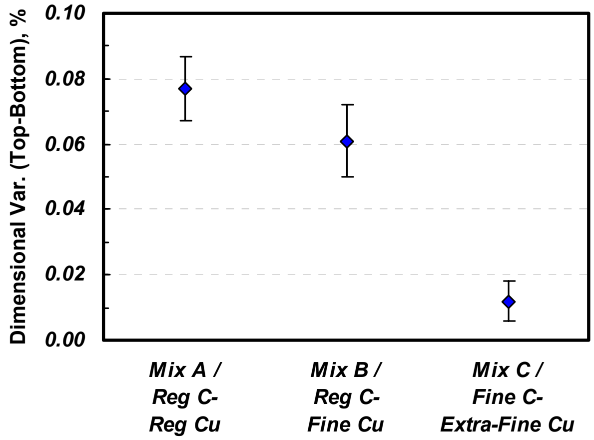

Figure 17. Dimensional variation between the top and the bottom of rings made of FLN4-4405 mixes containing different grades of Cu and graphite. Mixes contain 2.6% Cu.

CONCLUSIONS

This paper reviewed the characteristics and performances of binder-treated powder mixes using the FLOMET technology. In summary,

- The binder-treatment is an effective method to bond fine particles of additives to the larger iron particles. Virtually no difference in size distribution is seen between the regular base powder and the binder-treated materials.
- The bonding film formed during the treatment is sufficiently strong to maintain the fine particles bonded to the iron particles when powder is transferred or if the powder mix is subjected to very intense turbulence flow. For example, the amount of dust created when powder is transferred from one container to another is about 4 times lower with a binder-treated material.
- Improvement in flow obtained with the binder-treatment technology is typically in the order of 4 to 8 sec/50g.
- Binder-treated materials were found to significantly improve the part weight stability on a production press under difficult filling conditions involving long filling depth and/or gravity fill.
- Tests carried out on a small part in actual production conditions showed that binder-treated materials can improve the part weight stability by at least 20% under the same compacting conditions. Moreover, the binder-treated materials increased the productivity by 36% with no effect or slight improvement of the part weight stability.
- Finally, using binder-treatment in combination with fine or extra fine additives is an effective means to improve chemical homogeneity and dimensional stability of parts.

REFERENCES

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