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DEVELOPMENT OF COST EFFECTIVE ORGANIC-BONDED MO-NI-CU STEEL POWDERS EQUIVALENT TO DIFFUSION-BONDED POWDERS WITH THE FLOMET PROCESS.

***S. Saint-Laurent* [1], *P. Francois* [2]**

[1] Rio Tinto Metal Powders, 1655 route Marie Victorin,
Sorel-Tracy, Canada, J3R 4R4, e.mail: sylvain.st-laurent@qmp-powders.com

[2] Rio Tinto Metal Powders, Mergenthalerallee 79-81,
D-65760 Eschborn, Germany, e.mail: philippe.francois@riotinto.com

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ABSTRACT

The diffusion-bonded process is an efficient method to partially alloy metallic elements to the iron particles and it is particularly used for the mass production of high performance Mo-Ni-Cu steel powders. However, the cost of these powders is significantly higher due to the manufacturing cost. The binder-treatment is another method that efficiently bonds Ni and Cu to the steel powders in a cost effective way. In recent years, Rio Tinto Metal Powders has improved and optimized its proprietary binder-treatment process called FLOMET™ and introduce Organic-Bonded powders equivalent to the diffusion-alloyed grades available in the market.

Organic-bonded powder offers several advantages compared to diffusion-bonded grades. One of the major advantages is its great versatility. Indeed, it is very easy to modify the formulation by changing the base powder grade and/or the type and levels of alloying additives. This allows developing lower cost alternative powders that meet application needs, which is particularly interesting in today’s environment.

The key characteristics of the Organic-Bonding as well as the properties of various grades of Mo-Ni-Cu diffusion-alloyed and organic-bonded powders are presented in this paper. Properties of optimized leaner organic-bonded versions developed for each grade are also presented.

Keywords: *powder manufacturing, alloying techniques, organic bonding, mechanical properties.*

INTRODUCTION

Pre-alloyed Mo steel powders admixed with Ni and Cu are widely utilized by the PM industry for the production of high performance parts mainly because of their unique microstructure, static and dynamic properties. Diffusion-alloyed process is certainly the most widely used method to produce such type of powders. In this process, the Ni and Cu are partly diffused to the steel powder through a second annealing step. This results in an excellent Ni and Cu metallurgical bond to the steel particles, which is believed to help maintaining higher level of homogeneity within the part and from part-to-part and provide slightly different microstructure compared to conventional admixing methods. The excellent bonding obtained from this process also results in very low Ni and Cu dusting during handling and compaction, which is of prime importance for health and environment [1]. This process is however more costly due to the second annealing step. The partial diffusion of Ni and Cu in iron also affects the compressibility to a certain level, even if annealing conditions are such to limit the detrimental effect on compressibility. Finally, it is very difficult, if not impossible, to modify the final powder chemistry to target a given application. Indeed, due to evident processing constraints, only few different chemical grades are produced by the PM powder producers and available in the market.

The binder-treated route is another method that allows to bond efficiently the Ni and Cu to the iron particles. The bonding is obtained by a chemical agent. This process, which is less costly than the diffusion-alloyed process, provides better Ni and Cu bonding than the conventional admixing route but not like the diffusion-alloyed route. The organic-bonding process, a modified version of the Rio Tinto Metal Powders patented binder-treatment method called FLOMET™, was recently developed to provide increased Ni and Cu bonding. In fact, the Ni and Cu bonding achieved with the organic-bonding process is quite similar to that of the diffusion-alloyed process as shown in Figure 1. Organic-bonded process can be used to produce any grade of powder equivalent to the existing diffusion-alloyed powders available in the market.

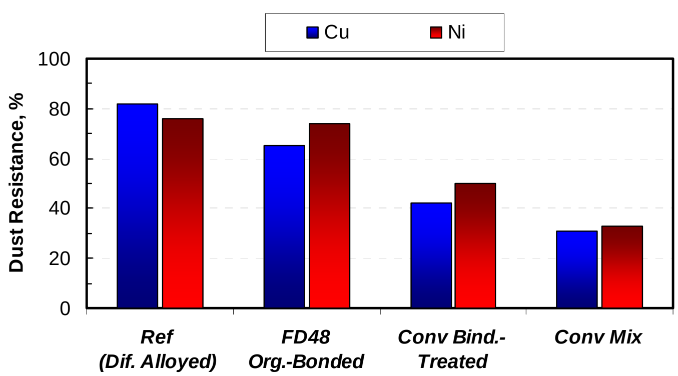

Figure 1. Ni and Cu dust resistance of various type of 4Ni-1.5Cu-0.5Mo steel powders.

However, even if organic-bonding technology offers few advantages over the diffusion-alloyed process such as lower cost and better compressibility, its great versatility and flexibility is certainly the most interesting feature of that process in today's highly competitive environment. Indeed, it is very easy to modify the formulation and/or select other additive grades since binder-treatment occurs at the blending stage. This allows developing powders that meet application needs at the lowest possible cost. Such flexibility is not possible with the diffusion-alloying process.

It is therefore the objective of this paper to capitalize on this advantage and present a cost effective and leaner alternative to the diffusion-alloyed powder containing 0.5Mo-4Ni-1.5Cu. This paper presents first the results of a Taguchi L9 study carried to better quantify the influence of pre-alloyed Mo levels in steel powder and Ni, Cu and graphite additions on the properties and cost of organic-bonded powders. An expert program, developed with the data acquired, enables to determine the composition of a system that matches a set of desired sintered and mechanical properties at the lowest possible cost. The properties of such a lean organic-bonded powders are also presented and compared to that of ATOMET DB48 admixed with 0.6% graphite.

1. EXPERIMENTAL PROCEDURE

a. Taguchi L9 plan

A design of experiment Taguchi L9 was used to evaluate the effect of 4 factors at three levels. Table 1 describes the mixes prepared according to this L9 matrix. The 4 factors investigated were Ni addition (2.5, 3 and 3.5%), graphite addition (0.5, 0.6 and 0.7%), level of Mo pre-alloyed in steel powder (0.0, 0.5 and 0.85%) and Cu addition (1, 1.25 and 1.5%). Since binder-treatment has no direct influence on sintered properties, mixes were prepared by conventional admixing method. 0.6% EBS wax was added in each mix. A reference mix was also prepared with the diffusion-alloyed grade ATOMET DB48. This grade contains 0.5%Mo pre-alloyed in the steel and 4%Ni and 1.5%Cu diffusion-alloyed. The L9 matrix was developed in order to minimize the interactions such as Ni-Cu and also minimize the overall cost of these powders. This explains why levels of Ni and Cu were kept lower compared to the reference diffusion-alloyed grade DB48, the average concentration in Ni and Cu for the 9 powders prepared being 3% and 1.25% respectively compared to 4 and 1.5% for the reference ATOMET DB48 powder. The same grade of Cu as the one used for the diffusion-alloyed powder was used while a finer Ni grade, T110D, produced in the past by Inco was used. This Ni grade is not anymore available. However, internal studies showed that this very fine Ni powder was very similar in properties compared to the conventional T123 grade. A high purity graphite grade called CarbQ was used for all the mixes. Steel powder grades ATOMET 1001, 4001 and 4401 produced by Rio Tinto Metal Powders (QMP) were used for the 0.00, 0.50 and 0.85% pre-alloyed Mo levels, respectively.

A relative cost index was calculated for each mix and is reported in Table 1. This cost index was obtained by dividing the alloying, additive and processing costs of a given system by that of the reference mix. Of course, cost index depends on the market price of additives and one would expect the Cost Index to vary with time. Two cost indexes per material are reported in Table 1. The first one was established based on price paid for alloying and additives during the first quarter of 2008 when the project was initiated, and the second one was calculated based on a more recent data available (second quarter of 2009). The Cost Index for the reference material was established as 1. The cost index for mixes 1 to 9 varies from 0.58 to 1.00 when Q1-2008 prices are used while it varies from 0.69 to 0.96 when the most recent prices are used. Even if a significant drop in alloying price is obtained at the end of 2008, it can be seen that the average cost index was very similar, 0.84 versus 0.81, and remains significantly lower compared to the reference. The drop in alloying price between Q1-2008 and Q2-2009 was beneficial for powder mixes made with 0.85% Mo steel powder and detrimental for powder mixes containing no Mo.

Table 1. Description of mixes prepared (Taguchi L9). All mixes contain 0.6% EBS wax.

Mix	Base Power	Admixed Ni, %	Admixed Graphite, %	Pre-alloyed Mo, %	Admixed Cu, %	Cost Index	
						Q1-2008	Q2-2009
1	AT1001	2.5	0.5	0	1	0.58	0.69
2	AT4001	2.5	0.6	0.5	1.25	0.75	0.78
3	AT4401	2.5	0.7	0.85	1.5	0.87	0.84
4	AT4001	3	0.5	0.5	1.5	0.83	0.85
5	AT4401	3	0.6	0.85	1	0.92	0.89
6	AT1001	3	0.7	0	1.25	0.66	0.77
7	AT4401	3.5	0.5	0.85	1.25	1.00	0.96
8	AT1001	3.5	0.6	0	1.5	0.75	0.85
9	AT4001	3.5	0.7	0.5	1	0.89	0.90
AVG	**-**	***3***	***0.6***	***0.5***	***1.25***	***0.81***	***0.84***
Ref	DB48	4	0.6	0.5	1.5	1.00	1.00

b. Characterization of Mixes

Compressibility was evaluated by pressing standard transverse rupture strength (TRS) specimens at three compacting pressures at room temperature on a 100 Ton hydraulic press. The transverse rupture strength, apparent hardness and dimensional change were estimated by pressing TRS specimens at 7.0 g/cm³ and sintering them at 1130°C for 25 min in a Nitrogen based atmosphere containing 10% Hydrogen. The cooling rate achieved was ~0.8°C/sec from 650 to 400°C. Dog bone specimens were also pressed and sintered under the same sintering conditions to evaluate tensile properties. For fatigue evaluation, TRS specimens were used to characterize plane bending fatigue resistance at a load ratio of R=0.1. The fatigue limit at 50% survival was determined by the staircase method with a run out limit of 2.5 millions cycles. The values are reported in terms of maximum stress. Finally, TRS, tensile and fatigue properties reported in this paper were all determined after a tempering carried out at 200°C for 1 hr in air.

Sintered properties under faster cooling conditions were also estimated by sintering TRS specimens pressed at three compacting pressures in a production furnace with fast cooling capability. Sintering was done at 1120°C for 20 minutes in a nitrogen based atmosphere with 10% Hydrogen. Cooling rate was ~1.25°C/sec from 650 to 400°C.

2. RESULTS

a. Effect of Ni, Graphite, Mo and Cu Contents on Compressibility

Figure 2 shows the compressibility curves for the mixes studied and the reference. Data were grouped by level of Mo in order to simplify the graph. As expected, all mixes showed better compressibility than DB48. Typically, the difference in pressure at 7.0 g/cm³ was around 40 MPa (3 tsi). It is worth noting that increasing the Mo content in base powder had almost no effect on compressibility.

Figure 3 illustrates the individual effect of each factor on green density at 415 and 690 MPa. The average density for Mixes 1-9 and the reference are given by the red and green dashed lines respectively. As seen in Fig. 3, Mo has little effect on density. Ni had a slight beneficial effect on density at 415 MPa but almost no effect at high pressure. The opposite trend is observed with graphite, which has no effect at 415 MPa but is detrimental on density at high pressure. This is due to the low specific gravity of graphite and its effect on the maximum theoretical density (pore free density). It is also interesting to note that the amplitude of the effect of each factor is less than the difference between the average density for these mixes and the reference, especially at low compacting pressure. The difference between mixes 1-9 and reference becomes smaller as pressure increases.

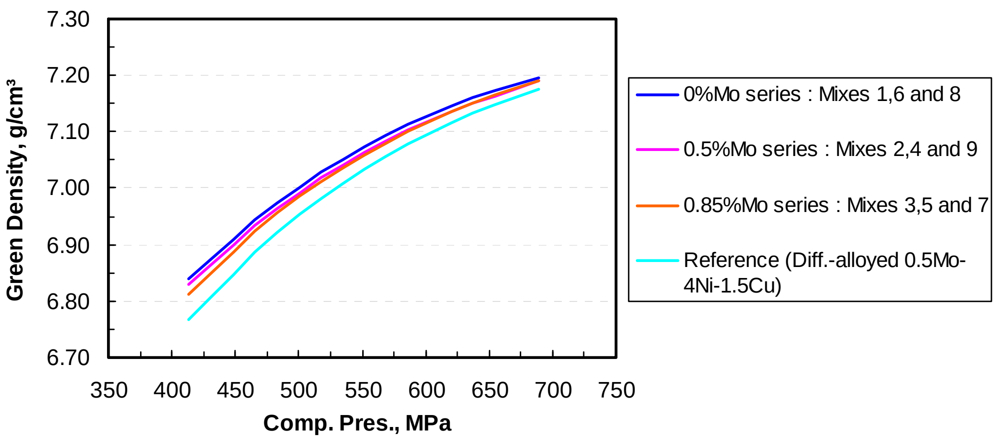

Figure 2. Compressibility curves for mixes regrouped by level of pre-alloyed Mo.

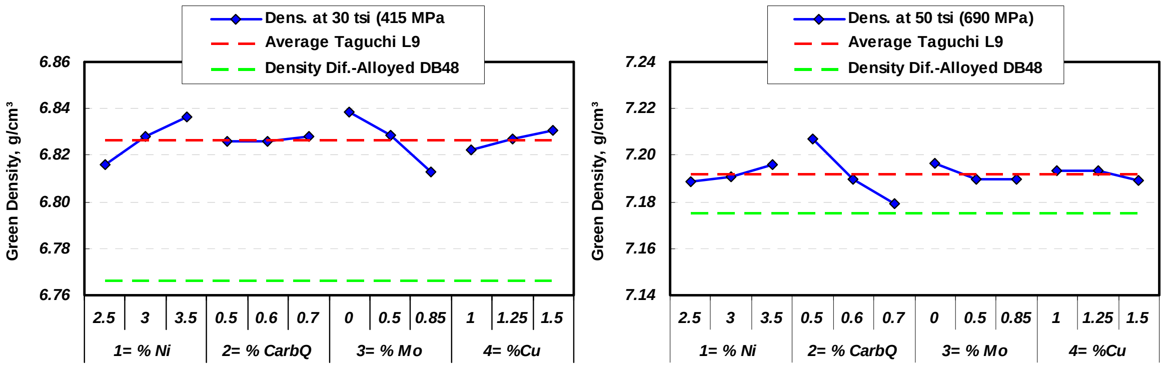

Figure 3. Effect of parameters on compressibility at 415 and 690 MPa (30 and 50 tsi).

b.Effect of Ni, Graphite, Mo and Cu Contents on Sintered Properties

The effect of each factor on the apparent hardness, dimensional change, TRS and tensile properties for specimens pressed to 7.0 g/cm³ and sintered under standard conditions is illustrated in Figure 4. The compacting pressure required to achieve 7.0 g/cm³ was between 495 and 520 MPa for Mixes 1 to 9 and 540 MPa for the reference. It is important to take note that the slopes illustrated in Figure 4 do not reflect the real slope as quantified by regression analysis since X axis is not linearly scaled. However, the amplitude or change obtained when a given factor is increased within the limit of that study are real and it is quite easy to determine which factor has the highest influence on each property.

No real surprise was observed for dimensional change. Indeed, increasing Ni content led to more shrinkage as illustrated by the more negative dimensional change obtained. The opposite trend was observed with Cu content, which led to more growth. Increasing graphite and Mo content also led to slightly more shrinkage. Nevertheless, the strongest effect on dimensional change was obtained from the Cu, with counts for 42% of the total variation in dimensional change measured within the limit of that study.

Sintered strength and apparent hardness were affected in a similar way, except for small differences. Both properties increased with the Ni, graphite and Mo contents. However, in terms of magnitude and rate of change, Mo content had the strongest effect on both properties, contributing for 68% and 53% of the total changes in TRS and hardness respectively. Increasing the Cu content also led to a slight increase in apparent hardness but had no significant affect on TRS. Finally, as it was the case for TRS, Mo showed the greatest beneficial effect on ultimate tensile strength (UTS) and yield strength (YS), its relative contribution being 81% and 100%, respectively. Only Mo was found to have a statistical influence at 95% confidence on the YS while graphite was the only other factor that had a statistical influence on UTS. Indeed, increasing graphite content from 0.5% to 0.6% was beneficial for the UTS but not above 0.6%. Ni and Cu contents had no significant effect on UTS and YS with a confidence limit of 95% within the limit of this study. However, the effect of Ni and Cu on UTS becomes statistically significant if a confidence limit of 90 and 82% is used respectively. Higher number of tensile specimens would be required to assess the real effect of these factors on UTS.

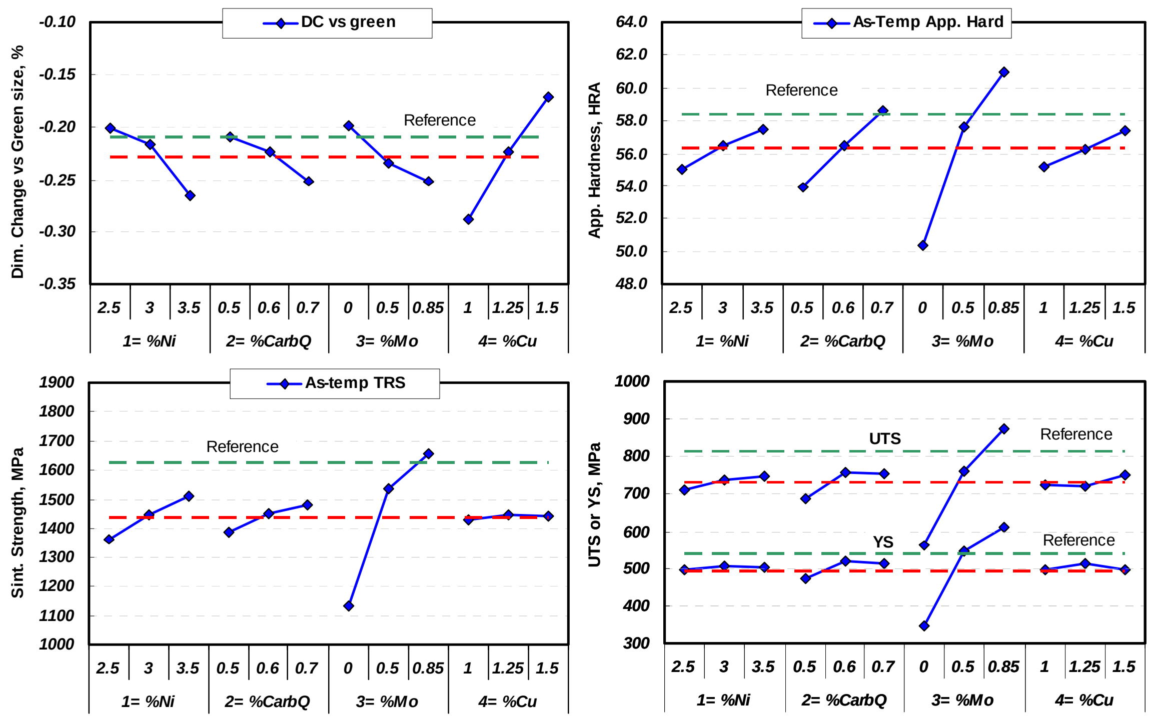

Figure 4. Effect of Ni, graphite (CarbQ), pre-alloyed Mo and Cu content on as-tempered properties at 7.0 g/cm³. Specimens were sintered at 1130°C and cooled under normal cooling rate (0.8°C/sec).

c. Effect of Ni, Graphite, Mo and Cu Contents on Fatigue Limit

The effect of Ni, graphite, Mo and Cu content on the fatigue limit at 50% for standard TRS specimens pressed to 7.0 g/cm³, sintered under standard conditions and tempered at 205°C for one hour, is illustrated in Figure 5a. All factors had a beneficial effect on the fatigue limit, graphite and Mo content having the highest effect and accounting for about 73% of

the total change in fatigue limit. On the other hand, Ni content had the smallest effect, its influence being statistically significant only if a confidence limit of 89% is used.
According to the Taguchi analysis carried out in this study, the Mo content has a strong influence between 0 and 0.5% but no effect beyond 0.5%. This result is somewhat surprising based on a previous study carried out in 2003 [2]. Indeed, it was shown in that study that increasing the Mo content from 0.5 to 0.85% was beneficial on the axial fatigue limit (at R=-1) for powders containing 4%Ni-1.5%Cu-0.6% Graphite. This apparent discrepancy between the current study and the previous one is likely due to the use of a fractional design of experiment (Taguchi L9), which reduced significantly the information from interactions.

Finally, a very good fit was obtained between fatigue limit and apparent hardness. This is illustrated in Fig. 5b, which gives the relation between the fatigue limit and apparent hardness and the Ni, graphite, Mo and Cu contents. Fatigue limit and apparent hardness are expressed by a ratio obtained by dividing the value measured for a given condition and mix by the average value measured for the 9 mixes. Except for Mo, where slight differences are observed, apparent hardness and fatigue limit vary almost identically when the level of each factor is increased.

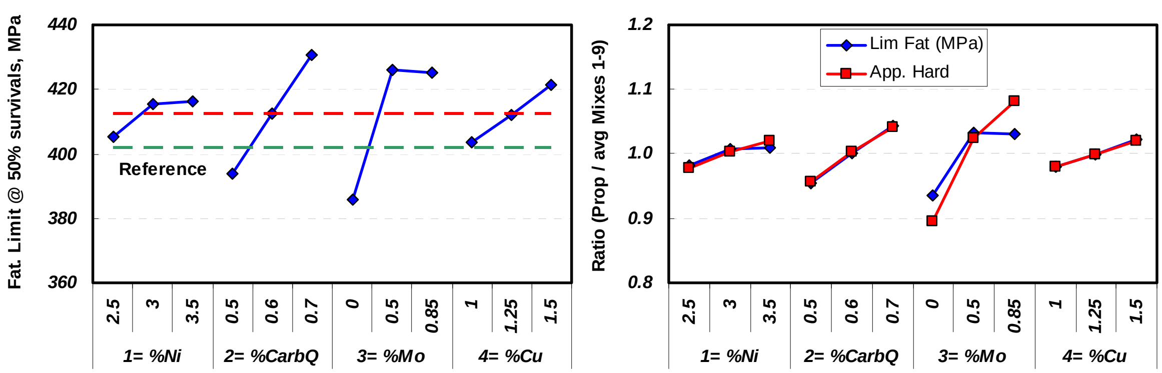

Figure 5. Effect of mix formulation on fatigue limit and apparent hardness.
a) Fatigue limit at 50% survival. b) Fatigue limit and apparent hardness ratio.
Fatigue limit is the maximum stress at R= 0.1.

d. Effect of density on sintered properties

As discussed previously, organic-bonded mixes exhibit a better compressibility than diffusion-alloyed mixes as shown in Fig. 2. For instance, if a pressure of 540 MPa had been applied to all mixes (pressure required to press the reference mix to 7.0 g/cm³), density would have been ~0.06 g/cm³ higher on average. This advantage can be used to improve the sintered and mechanical properties of parts without applying higher compacting pressure. An illustration of the effect of density on the sintered properties for the three levels of pre-alloyed Mo investigated in our study is given in Figure 6. The values reported in Figure 6 were obtained for specimens sintered at around 1120°C in a fast cooling furnace as described in the experimental procedure section. The rate of improvement of sintered strength and apparent hardness is in line with expectations. Even if we did not carry out a similar study for the normal cooling rate conditions, very similar trends are expected. Based on equations calculated for each mix, the gain in apparent hardness and TRS, UTS and YS would be about 0.5 HRA and 50, 25 and 15 MPa, respectively, at an applied pressure of 540 MPa.

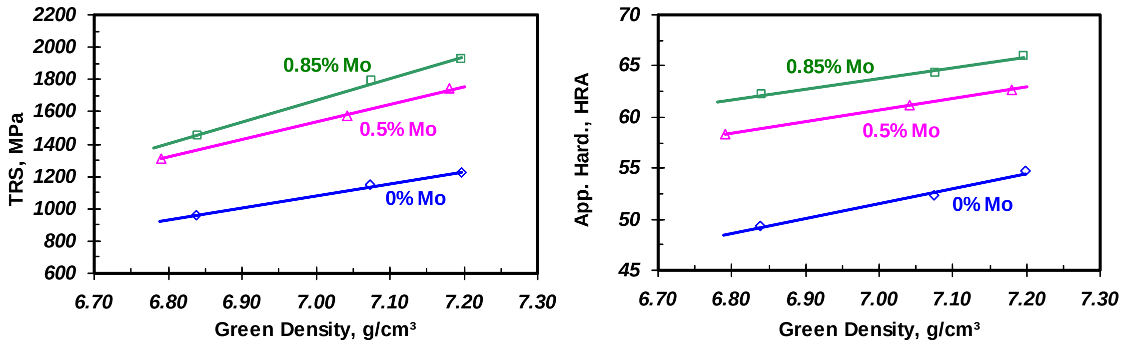

Figure 6. Effect of green density on sintered properties (fast cooling rate + tempered).

3. MIX OPTIMIZATION

a. Effect of formulation on cost and properties

The results presented in the previous section allow to evaluate the effect of mix formulation on properties. Nevertheless, when designing optimum formulation, properties are not the only factor to consider. Indeed, cost is also a key factor. Effect of each element on cost is illustrated in Figure 7. In today's environment and with the very high price of alloying, it is important to estimate if the addition of an additive is worth it. One interesting way to illustrate the effect of cost is by calculating a property-to-cost ratio and comparing it to that of the reference mix as indicated by the equation (1) below:

$$P/C\ Index = (Prop_{Mix\ i} / Cost_{Mix\ i}) / (Prop_{Ref} / Cost_{Ref}) \quad (1)$$

In this equation, the cost of mixes and reference was estimated by summing the processing cost with the cost of alloying and additives paid for the second quarter of 2009. A P/C index value of 1 for a given characteristic and mix indicates that the property-to-cost ratio is equal to that of the reference. An increase of the P/C index value when raising the level of a given factor indicates that this factor allows increasing the property in a cost effective way. In other words, this factor has a more positive effect on properties than on cost. Conversely, a reduction of the PC index value when the level of a given factor increases indicates that this factor has more effect on cost than on the property and is not cost effective. Figure 8 illustrates the effect of each factor on the P/C index for hardness, static strength and fatigue limit for standard sintering/cooling conditions with tempering. It is interesting to note that in most cases, the P/C index is advantageous (>1) compared to the diffusion-alloyed reference powder. Trends are summarized as follows:

⇒ Increasing Ni content lowers the P/C index for all properties, indicating that adding Ni is not a cost effective way to increase sintered properties.

⇒ Increasing Mo level is highly beneficial for the static strength (TRS, UTS and YS). It has a smaller effect on apparent hardness and fatigue limit. Overall, even if costly, Mo allows to increase sintered properties in a cost effective way.

⇒ Increasing graphite level is beneficial for all properties.

⇒ Cu is basically neutral, P/C index remaining quite constant when Cu content is increased.

⇒ Except for graphite, none of the factors allows increasing hardness in a cost effective way.

In summary, this analysis showed that Mo, Ni and graphite are the key elements in terms of properties and cost: a high Mo level and low Ni level are preferable to maximize properties. A graphite content of 0.7% is preferable while Cu is quite neutral, which means that increasing its content has basically the same effect on the properties and cost. The level of Cu should thus be adjusted as a function of desired properties.

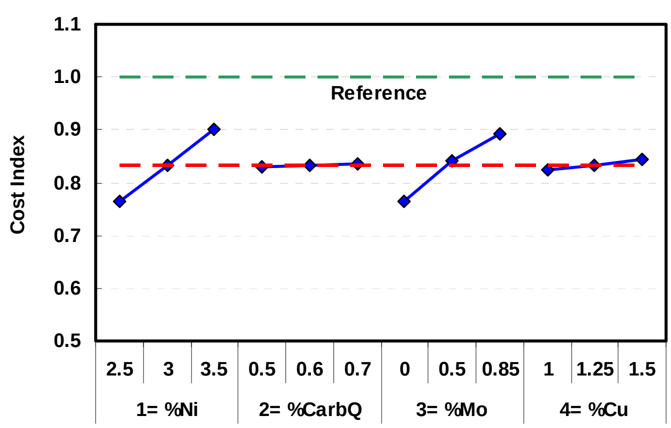

Figure 7. Effect of formulation on Cost index.

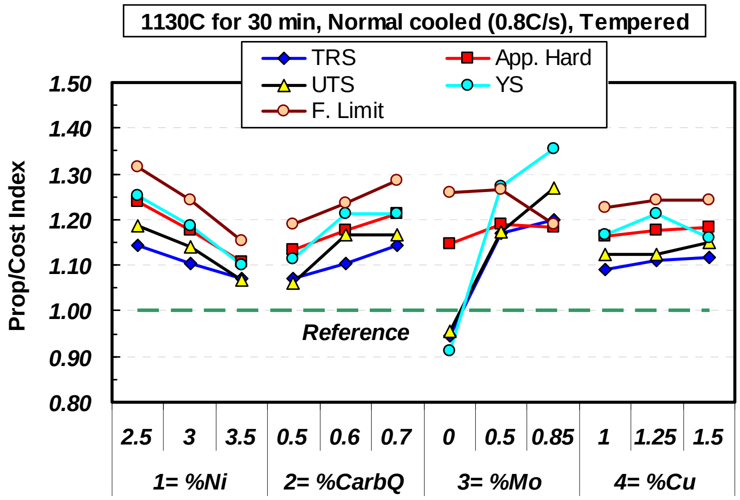

Figure 8. Effect of Ni, graphite, Mo and Cu content on the P/C Index (relative property to cost ratio) for standard sintering/cooling conditions after tempering.

b.Optimization of Mix Formulation

One of the objectives of this study was the development of leaner alternatives to FD-0405. To achieve this objective, an expert program was developed with the data acquired. First of all, first or second degree equations were calculated for each property. An equation for the material cost taking into account the processing, alloying and additives costs was also developed. With all these equations, a program was developed which allows determining by iteration an optimized mix formulation meeting a desired set of sintered properties at the lowest possible cost. This model was used to determine a lean formulation equivalent to the reference diffusion-alloyed product (DB48 with 0.6% graphite). The following criteria were used in the model:

Table 2. Criteria used to determine a lean formulation equivalent to DB48+0.6%C

TRS: ±34 MPa vs. Ref	App. Hard: -1/+3 HRA vs. Ref	Dim. Change : ±0.02% vs. Ref

The formulation proposed by the model was: ***AT4401 (0.85 Mo), 2.3% Ni, 1.15%Cu and 0.6% graphite***. A mix (F48Lean) was prepared according to this formulation using the organic-bonding technology and properties were compared to those of the reference. Specimens were pressed at 540 MPa, sintered under standard sintering/cooling conditions and tempered. The properties measured and estimated from the model are given in Table 3. Only fatigue limit is missing, tests being not completed yet. It is seen that, as estimated by the model, the proposed formulation gave equivalent or slightly higher sintered properties compared to the diffusion-alloyed powder. In general, a very good match was obtained between the measured and estimated properties, except maybe for UTS and elongation, which were significantly over-estimated by the model for both powder systems. Such discrepancies can be explained by differences in the sintering and tempering conditions (time and temperature). The organic-bonded mix also showed a much better flow rate (~5 sec/50 g) than the diffusion-alloyed mix. Finally, the proposed formulation represents a cost saving for alloying and processing of ~20% compared to the diffusion-alloyed powder. A cost saving of up to 25% could be obtained by using a standard Ni grade and wider dimensional change criteria (±0.10%).

Since price of mixes are dependent on the market price of additives, and thus changed constantly overtime, we have estimated the cost index of F48Lean at different quarter starting from 2004 to 2009, Figure 9. It is seen that, on average, the cost index of this leaner formulation was varying from 0.76 to 0.96, with an average value at ~0.85. It can thus be concluded that the optimum formulation F48Lean maintained its economical advantage for the entire period considered, with a cost saving of about 15% compared to the reference DB48 material.

Table 3. Estimated and measured properties for a lean organic-bonded and a diffusion-alloyed powder containing 0.5Mo-4Ni-1.5Cu. Conditions: 540 MPa, standard sintering and tempering.

Mix ID	Process	Chemistry	Cost Index	AD, g/cm³	Flow, s/50g		S. Dens., g/cm³	TRS, MPa	Hard., HRA (HRC)	DC vs green, %	UTS, MPa	YS, MPa	Elong., %
Ref	Diff-Alloyed	0.5Mo-4Ni-1.5Cu-0.6C	1.0	3.10	37	M *	6.99	1570	59.0 (18.2)	-0.22	725	517	1.1
						E *	6.98	1626	58.4 (17.1)	-0.21	788	520	2.2
F48 Lean	Org.-bonded	0.85Mo-2.3Ni-1.15Cu-0.6C	0.80	3.04	32	M *	7.05	1600	59.0 (18.2)	-0.20	757	659	0.5
						E *	7.03	1622	59.6 (19.3)	-0.22	906	636	1.3

* M stands for measured properties and E for estimated properties with the model

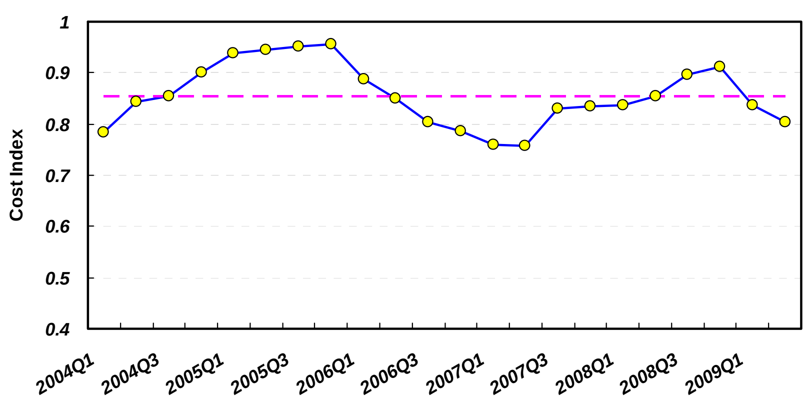

Figure 9. Variation of the cost index of F48Lean between the first quarter of 2004 and the second quarter of 2009.

CONCLUSION

The effects of Ni, graphite, Mo and Cu contents on the properties and cost of organic-bonded powders were investigated using a Taguchi L9 plan of experiments. The major conclusions of the study are summarized below:

⇒ A significant gain in density is obtained when using organic-bonded powders instead of diffusion-alloyed powder, Mo content in the steel powder having only a little effect on compressibility.

⇒ Mo was found to be the element having the strongest effect on sintered properties and increasing its content in steel powder is a cost effective way to improve sintered properties.

⇒ On the contrary, Ni had more effect on cost than on performance and increasing its content has more effect on price than on properties. It is thus not recommended to increase its content.

⇒ The effect of copper was mainly neutral while graphite content wad beneficial for most of the properties.

⇒ A model proposing optimized formulations as a function of green and sintered performance and cost was developed from the data generated in this study.

⇒ This model was successfully used to design a leaner version of the 0.5Mo-4Ni-1.5Cu diffusion-alloyed powder with equivalent properties: The optimum formulation suggested was a 0.85% pre-alloyed Mo steel powder organic-bonded with 2.3% Ni, 1.15% Cu and 0.6% CarbQ. A cost saving of 15% would be achieved with such a formulation between 2004 and 2009.

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