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Design of Low Cost High Performance Diffusion-alloyed Powders

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Abstract

With the volatility of alloy prices encountered in recent years, high performance lean alloys are of great interest to many part producers. Common PM grades such as the diffusion-alloyed powders often contain relatively high levels of nickel, copper and molybdenum. While they remain very efficient in regard to mechanical properties, the levels of these alloys could be better optimized to balance property requirements with costs.

This paper presents the results of a study on the optimization of properties and costs of diffusion-alloyed powders based on a FD-0208 chemistry (0.5%Mo-1.75%Ni-1.5%Cu). Design of experiment was used to evaluate the effect of nickel, copper and molybdenum contents on green and sintered static properties. A model was developed in order to optimize the materials chemistry in regard to cost and properties.

Keywords: Lean alloys, cost, diffusion bonded

Introduction

Diffusion-alloyed powders containing Mo, Ni and Cu are widely used in the PM industry for the production of high performance parts. Indeed, these alloys offer very good compressibility and unique heterogeneous microstructures. In addition, the partial diffusion of Ni and Cu obtained during the second annealing step provides excellent bonding, resulting in low segregation and dusting of Ni and Cu and high stability during powder handling and part production [1]. However, in recent years, alloy prices such as Ni and Mo have at some point reached more than four times their historic prices [2]. This variation in alloy prices has rendered the use of alloyed steels very costly and the development of lower cost alternatives with similar properties a priority.

Many approaches were taken over the years in order to improve part properties, i.e. the use of microalloying or non-traditional alloys replacing higher cost alloys requiring smaller quantities (Nb, V, Ti, Si and Mn) [3] [4] [5], heat treating of sintered parts [6] [7] and increasing the density of materials [8] [9].

The objective of this work was to develop lower cost alternatives to ATOMET DB46, a diffusion-alloyed powder with 0.5%Mo-1.75%Ni-1.5%Cu (MPIF FD-0208 [10]) produced by Rio Tinto Metal Powders. In order to achieve that goal, a study was undertaken to determine and quantify the effect of Ni, Cu, Mo and graphite content on properties and develop a model for mix optimization taking into account the cost similarly to what was done a few years ago with a FD-0405 formulation [11]. To maintain the excellent attributes of DB46 outlined earlier and ease the production of various formulations, the approach taken was to produce a unique master diffusion-alloyed powder richer in Ni and Cu and dilute this master powder with atomized steel powders with various levels of Mo to reach the desired Ni, Cu and Mo content. Only the TRS properties obtained with a moderate cooling rate are presented in this paper. However, it is the objective to obtain the tensile and fatigue properties for these sintering conditions and also with a much faster cooling rate. This information was not yet available at the time of writing this paper.

Experimental Procedure

A master diffusion-alloyed powder (DB powder) made of ATOMET 4001 admixed with 6.2% Ni and 5.0% copper was produced in laboratory using the same manufacturing conditions as ATOMET DB46. The master DB powder was then admixed with various levels of steel atomized powders AT1001, AT4001 and AT4401 in order to reach predetermined levels of Mo, Ni and Cu in the final mix. Excellent Ni and Cu bonding was obtained for each mix due to the use of a master DB powder. Indeed, the level of bonding was similar to that obtained with the ATOMET DB46, which is about 8 times higher than the bonding obtained when Ni and Cu are admixed with a base steel powder. The chemistry of the steel atomized powders and DB master powder are given in Table 1. The main difference between AT1001, AT4001 and AT4401 is the amount of pre-alloyed Mo which is 0%, 0.55% and 0.85%, respectively.

Table 1. Chemistry of the base powders

Powder	Cu (%)	Ni (%)	Mn (%)	Mo (%)
DB Master	5.0	6.2	0.13	0.49
AT 1001	---	---	0.20	---
AT 4001	---	---	0.15	0.55
AT 4401	---	---	0.15	0.85

Design of experiment (DOE) was used in order to evaluate the effect of key factors while maintaining the number of experiments at a practical number. A Taguchi L9 array with 3 factors at three levels each was developed as detailed in Table 2. The cost index for each formulation is also given. The cost index represents the ratio of the costs of the test formulation over the DB46 reference when considering composition, processing and additives. A ratio of 1 represents a mix with the same cost as DB46. The equation was developed using the average alloy prices for the first quarter of 2012. Although this ratio varies through time following alloy prices fluctuation, a study of prices variation of the most alloyed mix showed less than 10% difference over 8 years. The factors studied were Mo level (0.30, 0.50 and 0.75%), Ni level (1.5, 1.0 and 0.5%) and graphite addition (0.4, 0.6 and 0.8%). The desired Mo and Ni concentrations were obtained by admixing the DB master powder mix with different levels of AT1001, AT4001 and AT4401. Synthetic graphite KS15 from Timcal was admixed to the chosen level. 0.75% Zn stearate was also admixed to all blends. It should be noted that copper content was not included in the Taguchi array as it varies linearly with the amount of nickel. The levels of copper corresponding to each nickel concentrations are 0.4, 0.8 and 1.2%. The final mixes are detailed in Table 3. For the last series of mixes (G, H and I), AT1001 was admixed to obtain an equal concentration of molybdenum of 0.75% and obtain a valid Taguchi array. The addition of ATOMET 1001 would likely result in lower mechanical properties and higher chemical heterogeneity than what would be obtained using only AT4401. The Taguchi array therefore simulates the worst case scenario.

Table 2. Taguchi L9 experiment

Experiment	Mo (%)	Ni (%)	Graphite (%)	Cost Index
A	0.3	1.50	0.4	0.79
B	0.3	1.00	0.6	0.71
C	0.3	0.50	0.8	0.62
D	0.5	1.50	0.6	0.83
E	0.5	1.00	0.8	0.75
F	0.5	0.50	0.4	0.66
G	0.75	1.50	0.8	0.87
H	0.75	1.00	0.4	0.78
I	0.75	0.50	0.6	0.70

Rectangular bars (31.7 mm X 12.7 mm X 6.35 mm) were pressed to a density of 7.0 g/cm³. The samples were sintered at 1120°C for 25 minutes under an atmosphere of 90% N2 – 10% H2. Post-sintering cooling rates of 0.8°C/s in the temperature range of 650 to 400°C were used. Some samples were tempered at 205°C for 1 hour in air. All samples were tested in the as-sintered condition as well as in the tempered conditions.

Green, sintered and tempered properties (compressibility, sintered strength, apparent hardness, dimensional change) were measured and a model was developed in order to predict the transverse rupture strength, hardness and dimensional change as a function of the mix formulation. An equation was also developed to estimate a cost index as described earlier. This cost index will be used as a tool for the optimization model later. This model was developed to optimize the properties of a mix while minimizing its cost. Equivalent mixes to DB46 with 0.4%, 0.6% and 0.8% graphite, respectively, were determined and tested to confirm the predicted properties. Mixes at 0.8% carbon were optimized using both as-sintered and tempered properties while the other two were optimized using only as-sintered properties.

Table 3. Detailed mix recipes

Mix	DB master mix (%)	AT1001 (%)	AT4001 (%)	AT4401 (%)	Graphite (%)	Lubricant (%)
A	24.3	40	35.3		0.4	0.75
B	16.2	40	43.2		0.6	0.75
C	8.1	40	51.1		0.8	0.75
D	24.3		75.1		0.6	0.75
E	16.2		83.0		0.8	0.75
F	8.1		91.5		0.4	0.75
G	24.3	1.0		79.9	0.8	0.75
H	16.2	4.7		78.7	0.4	0.75
I	8.1	7.8		83.5	0.6	0.75

Results and discussion

Fig. 1 illustrates the effect of each parameter on compressibility, dimensional change (from die size), transverse rupture strength (TRS) and apparent hardness in the as-sintered condition. The red dotted line represents the average value for all tests in the L9 matrix for the corresponding property while the green dotted line represents the average value of the DB46 reference at 0.6% graphite.

The effect of alloying was small on compressibility. Indeed, a difference of only 40 MPa was seen between the more compressible and less compressible mixes. Nevertheless, graphite had the largest effect, as an increase in graphite lowered the compressibility. Furthermore, molybdenum had very little impact as expected. This is one of the advantages of using this alloying element for strengthening. Molybdenum content had the largest effect on dimensional change. However, the effect was not seen between 0.3 and 0.5% Mo. This could be explained by the low level of dilution with AT1001. However, when a large quantity of high Mo AT4401 is added, the effect of Mo on dimensional change is more important. Ni had only a very little effect on dimensional change. Normally, reducing the Ni content is linked to less shrinkage. However, it must be kept in mind that each variation in Ni content results in a variation of the same ratio of the Cu content since both elements originate from the DB master mix. The effect of nickel and copper on the dimensional change when taken separately is very well known. Indeed, copper tends to promote growth when entering the iron body after melting while nickel promotes shrinkage. Normally, the higher the concentration, the more important is the effect. The same behavior is observed when Ni and Cu are both present in the mix, even if the resulting dimensional change is affected by the interactions of both elements, which are completely soluble in one another [12]. The result obtained in that study confirmed that the level of both elements had no significant effect as long as the Ni/Cu ratio remains unchanged.

It is with no surprise that an increase in Mo, Ni and graphite all resulted in an increase in TRS. Moreover, Mo and graphite, at the levels chosen, had a very similar impact on the strength of the material. The effect of Ni (and thus Cu) is slightly less important, in line with the results of the study from St-Laurent and Gelinas [11], confirming that pre-alloyed Mo has a higher effect on mechanical strength than admixed Ni and Cu. A similar trend was observed for the as-sintered apparent hardness, except that the effect of graphite is more important than that of the other two parameters. Indeed, the Taguchi analysis indicates that the effect of graphite counts for almost 50% of the overall variation in apparent hardness as indicated in the lower right section of Fig. 1.

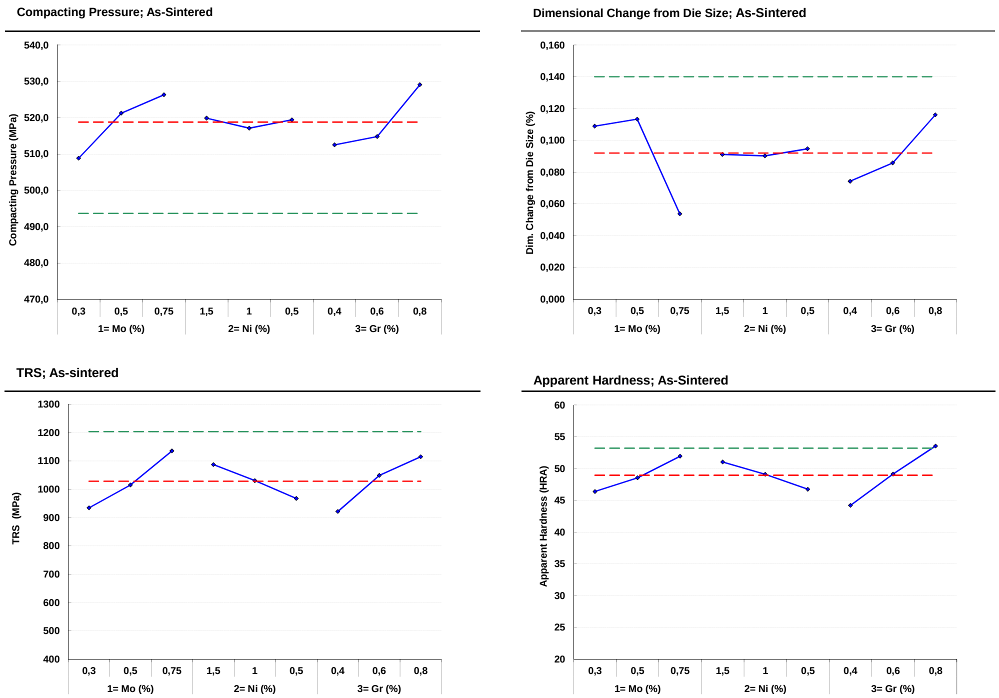

Fig. 1 – Effect of Mo, Ni and graphite on green and sintered properties at 7.0 g/cm³.

A very similar tendency is observed for the as-tempered properties as illustrated on Fig. 2. The only slight difference between the as-sintered and as-tempered conditions is the rate of variation of the TRS between 0.6 and 0.8% graphite. Indeed, in the as-sintered state, the rate on increase is less than in the as-tempered state. This is explained by the lower TRS values obtained at 0.8% graphite in the as-sintered state for the more highly alloyed materials (G) as illustrated in Fig. 3. This result can be explained by the microstructure developed for such a formulation, which contains higher level of brittle martensite than the other materials. It is known that formation of martensite tends to limit or even reduce the TRS and UTS values in the as-sintered state. However, strength is normally increasing quite significantly after tempering, as shown in Fig. 3. On the other hand, tempering has only very little effect on the strength when martensite is absent or only slightly present, such as for mixes at 0.4% and 0.6% graphite. This explains why the TRS increases more between 0.6 and 0.8% in the as-tempered state.

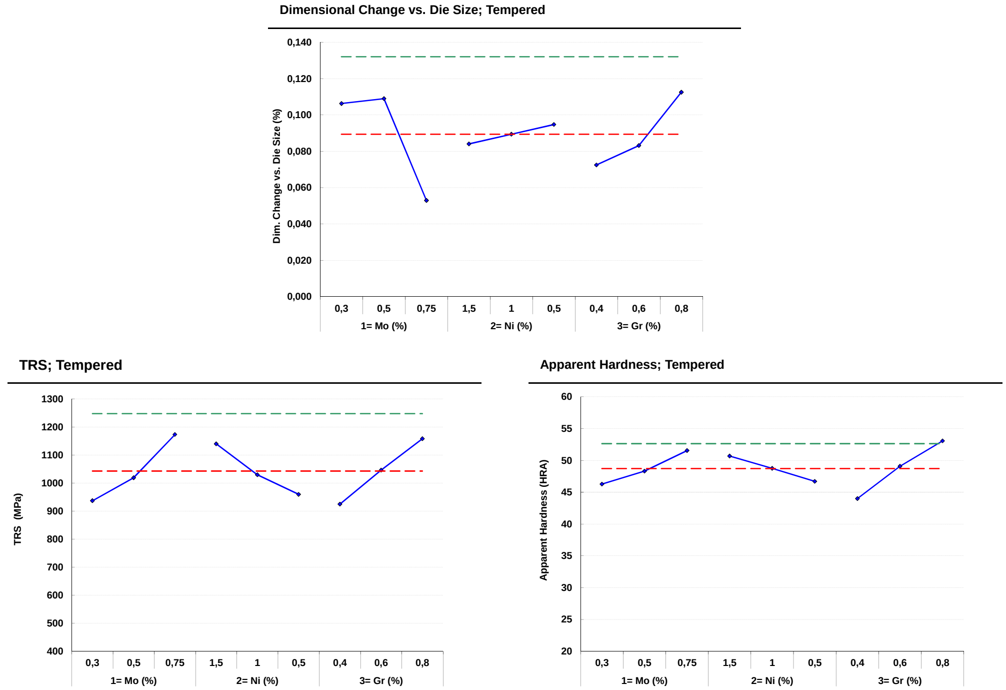

Fig. 2 - Effect of Mo, Ni and graphite on the tempered properties at 7.0 g/cm³.

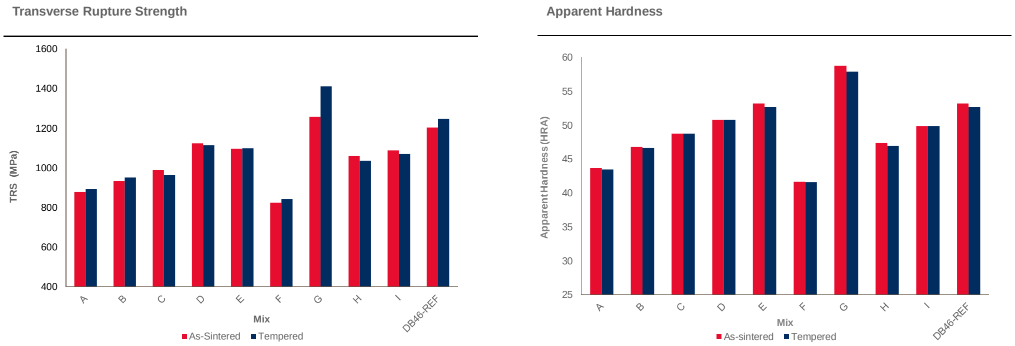

Fig. 3 - Effect of tempering on the TRS (left) and apparent hardness (right) of the different mixes tested

Fig. 4 shows the as-sintered microstructure of low (Mix A), medium (Mix E) and highly (Mix G) alloyed formulations compared to the DB46 reference at 0.6% graphite. All microstructures are heterogeneous and typical of diffusion-alloyed materials but vary depending on the formulation. The microstructure of Mix A in Fig. 4A, which contains low Mo and carbon levels, is constituted of a ferritic microstructure with some areas of pearlite. A discontinuous network of Ni-rich areas (with Cu) can be observed. The microstructure of Mix E (Fig. 4B), which contains medium levels of Ni and Mo and 0.8% graphite exhibits a fine pearlite microstructure with a network of Ni-rich areas. The Ni-rich areas are expected to contain some martensite and retained austenite. Mix G (Fig. 4C) however is the more highly alloyed mix, containing the highest levels of Ni, Mo and graphite. Its microstructure consists of a pearlitic microstructure with bainite in the high Mo particles. A thick network of Ni-rich areas is visible, which is likely constituted of martensite and retained austenite. This network appears to be thicker than the one observed with the DB46 reference (Fig. 4D), even though it contains less nickel than the standard. This is believed to be linked to the higher level of graphite and Mo in mix G.

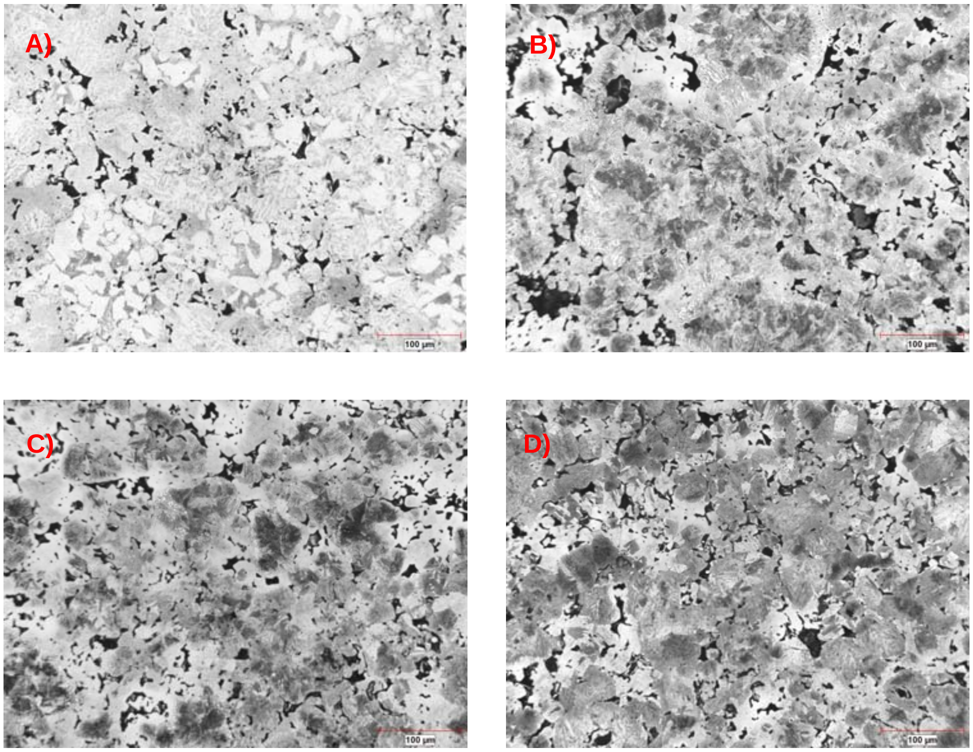

Fig. 4 - Microstructure as-sintered of A) Mix A (0.5% Mo, 1.5% Ni, 0.4% gr.); B) Mix E (0.5% Mo, 1.0% Ni, 0.8% gr.); C) Mix G (0.75%Mo, 1.5% Ni, 0.8% gr.) and D) DB46-REF (0.6% gr.)

Based on the results obtained with the nine mixes of the Taguchi array, equations were drawn for each property and a model which allows prediction of sintered strength, apparent hardness and dimensional change based on mix composition was built. An equation to estimate the cost as a function of the alloying composition, processing and additive was also built. The model does not allow determining of the tensile properties and fatigue limit since all tests were not yet completed. However, based on a previous study [11], the tensile properties should follow a very similar trend as the TRS while the fatigue limit should have a very good fit with the apparent hardness. In other words, if TRS and hardness of the optimized mix meet the DB46 mix requirements, then tensile and fatigue properties should likely be very close to that of this DB46 mix. It is the intent to complete testing at both medium and fast cooling rates to further improve the model and confirm this point.

Three laboratory mixes commonly used by the PM industry, ATOMET DB46 admixed with 0.4%, 0.6% and 0.8% graphite KS15 and 0.75% Zn stearate, were produced and tested in the as-sintered and as-tempered conditions. The mechanical properties of these reference mixes are given in Table 4. The as-tempered properties are not reported at 0.4 and 0.6% graphite since they were almost unchanged compared to the as-sintered ones. Only mix at 0.8% graphite showed some difference between as-sintered and as-tempered properties. The model developed was used to define the least expensive formulation matching the properties given in Table 4 for each of these formulations and conditions.

Table 4. Mechanical properties of the reference mixes to be matched

Mix	TRS (MPa; psi)	Hardness (HRA)	Dim. Change from Die
Ref-A	1131 (164 049)	48.4	0.159
Ref-B	1250 (181 234)	54.0	0.108
Ref-C	1190 (172 566)	58.3	0.140
Ref-C Tempered	1355 (196 466)	57.0	0.124

These targeted properties were entered in the model and constraints of ± 25 MPa for the TRS, which represents around 2% difference in strength from the standard, and ± 2.5 HRA for the apparent hardness were used. No constraint was put on the dimensional change since most of the mixes tested had dimensional changes more negative than the DB46 reference mixes. Imposing a too tight tolerance in dimension lowered significantly the possibility to obtain cost effective solutions. Therefore, the hypothesis was that if a mix was to incur a significant cost saving, it would be acceptable to replace tooling in order to match the original dimensions of the parts. The model was run to obtain the least expensive formulation matching the targeted properties within the limits of the constraints.

The optimized mixes suggested by the program for all three references are given in Table 5 with the Ni, Cu and Mo content specified in parenthesis. In all three cases, the most cost effective mix composition was obtained by maximizing the pre-alloyed Mo content (AT4401), i.e. 0.75%. The only two parameters that vary with the three mixes are the graphite and Ni (Cu) content. In the case of mix C, two different solutions were suggested by the model, one for the as-sintered properties and one for the as-tempered properties. In order to produce only one mix corresponding to both, the choice was made to base the formulation mainly on the as-tempered properties which explains why the estimated properties of mix C have more than a 25 MPa difference with the reference. As mentioned earlier, the original mixes produced in the Taguchi array were adjusted with AT1001, AT4001 and AT4401 in order to obtain desired amounts of Mo. This was done to obtain constant levels of Mo in each formulation. However, the presence of AT1001 in the microstructure created weak unalloyed zones that should be detrimental to the mix properties. For this reason, no AT1001 was added to the validation mixes produced and tested to confirm the model. As a result, the level of Mo in the validation mixes was slightly higher than suggested by the model, up to 0.80% vs 0.75%. In all cases, the solutions suggested by the model allowed significant cost savings. The as-sintered and as-tempered (in the case of Mix C) properties were evaluated and are reported together with the properties estimated by the model in Table 6. As expected, the measured TRS values always surpassed the estimated values due to the absence of AT1001. On the other hand, the hardness and dimensional change values matched the estimated values very well confirming the very low effect of AT1001 on both these properties. As mentioned earlier, tensile and fatigue tests will be performed to optimize the model and verify the properties of the predicted mixes to their reference.

Table 5. Mixes suggested by the model

Mix	DB Master (Ni, Cu) (%)	AT4401 (Mo)(%)	Graphite (%)	Lubricant (%)	Cost Index
Mix-A	12.89 (0.80, 0.64)	86.52 (0.80)	0.6	0.75	0.75
Mix-B	15.64 (0.97, 0.78)	83.56 (0.79)	0.8	0.75	0.78
Mix-C	19.44 (1.20, 0.97)	79.76 (0.78)	0.8	0.75	0.82

Table 6. Estimated and measured properties of the three recommended mixes

Mix		TRS (MPa; psi)	Hardness (HRA)	Dim. Change from Die (%)
Mix-A	Estimated	1106 (160 549)	50.9	0.053
	Measured	1169 (169 552)	51.1	0.057
Mix-B	Estimated	1225 (177 734)	56.4	0.074
	Measured	1295 (187 967)	57.6	0.092
Mix-C	Estimated	1253 (181 806)	57.4	0.074
	Measured	1326 (192 342)	59.5	0.089
Mix-C Tempered	Estimated	1319 (191 306)	56.8	0.071
	Measured	1435 (208 142)	59.0	0.068

Conclusion

A Taguchi L9 study was performed to evaluate the effect of Ni (Cu), Mo and graphite content on the properties of mixes composed of an enriched master DB powder admixed with atomized powders with various levels of Mo. The main conclusions are given below.

- A decrease in Mo content and an increase in the graphite content caused more growth.
- No major differences in properties were obtained in the as-sintered and tempered properties except for the more highly alloyed mixes at 0.8% graphite.
- An increase in Ni (Cu), Mo and graphite results in an increase in the strength of the materials.
- Increasing the Mo is the most cost effective solution to increase TRS and hardness when compared to Ni (Cu) content.
- A model including the cost as a function of mix formulation was developed.
- According to the model, lower cost alternatives to DB46 mixes containing 0.4%, 0.6% and 0.8% graphite are obtained by maximizing the pre-alloyed Mo content and minimizing the partly diffused Ni and Cu content.
- An optimized mix with about 0.8% Ni, 0.65% Cu, 0.80% pre-alloyed Mo and 0.6% graphite showed similar strength and hardness than a DB46 mix with 0.4% graphite at 75% of its cost.
- An optimized mix with about 1% Ni, 0.8% Cu, 0. 80% pre-alloyed Mo and 0.8% graphite showed similar TRS and hardness as a DB46 mix with 0.6% graphite at 78% of its cost.
- An optimized mix with about 1.2% Ni, 1% Cu, 0. 80% pre-alloyed Mo and 0.8% graphite matched the as-tempered properties of a DB46 mix with 0.8% graphite with a cost ratio of 82%.

It is targeted to complete tensile and fatigue tests at both medium and fast cooling rates to improve the model.

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