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Effect of Ni and Cu Addition on Pre-Alloyed Mo Powders Designed for High Performance Applications

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Abstract: Steel powders containing Mo, Ni and Cu are widely used in the industry. Indeed, they offer excellent compressibility and mechanical properties due to their unique heterogeneous microstructure. Such alloys are also very easy to process under a wide range of sintering conditions. However, Mo-Ni-Cu powders are sensitive to the price of alloying elements, which has reached a peak few years ago. Other issues linked to the addition of Ni powder (health and product availability) make the development of free or low Ni levels grade of great interest. On the other hand, Ni is quite beneficial and offers some advantages in term of manufacturing and properties and may be impossible to eliminate totally. The objective of this paper is to evaluate the impact of addition of Ni and Cu on the mechanical properties of steel powder mixes containing pre-alloyed Mo. In particular, mixes with low addition of Ni were studied. Design of experiment (DOE) was used in order to evaluate the impact of each element and to determine optimum conditions for static and dynamic properties.

Keywords: Mechanical properties, high performance, steel powder

1. Introduction

Low-alloyed powder steels containing Mo, Ni and Cu have been widely used in the PM industry for many decades. These elements provide high mechanical strength without detrimental effects on compressibility and processibility since they have low affinity with oxygen. Mo is normally pre-alloyed while Ni and Cu are added as elemental particulates to the steel and often diffusion bonded, providing unique heterogeneous microstructures mainly through the presence of Ni-rich areas. Indeed, the addition of elemental Ni increases toughness and ductility while the Ni-rich areas also act as crack arrest regions leading to high dynamic properties. Cu also increases strength through liquid phase formation during sintering. As liquid forms and Cu diffuses, rounder pores are created. On the other hand, Mo offers various advantages such as a high contribution to hardenability, resistance to oxidation (facilitating its use as a prealloyed element) and very little impact on compressibility.

However, the future implementation of a more rigorous regulation regarding health and safety of Ni, a carcinogenic element [1], the high volatility of alloy prices encountered since 2005 (Cu, Mo, Ni)[2] as well as potential issues with product availability have pushed the industry to develop steels with lower levels of these elements [3][4] or produced with less conventional and more inexpensive elements (Si, Cr, V, Ti, Nb, Mn...)[5][6][7][8]. The use of non-conventional elements has led to the development of high strength alloys; however, these alloys produced thereof present processing challenges as they show more affinity with oxygen. They therefore require higher sintering temperatures under very reducing conditions. This has kept this alternate solution from replacing completely more conventional alloys.

In previous papers [9][10], the authors presented results obtained with Taguchi arrays elaborated using binder treated mixes or a DB master mix in order to better understand the effect of Ni, Mo and Cu. Following these trials, it was determined that pre-alloyed Mo was the most cost effective element to maximize properties as illustrated on Figure 1. However, the range investigated in these studies was quite limited for Ni (2.5 – 3.5%) and Cu (1.0 – 1.5%).

In order to better understand the effect of Ni and Cu on a higher Mo steel, a follow-up study was performed using a fixed Mo level at 0.85% (as suggested by the previous study) and wider ranges of Cu, Ni and graphite content. Although the urgency to reduce the use of Ni in traditional mixes is present, it may be difficult to completely eliminate it. Therefore, the low Ni level was always set at 1.0%.

The objective of this paper was to evaluate the effect of lower Ni and Cu addition on prealloyed Mo

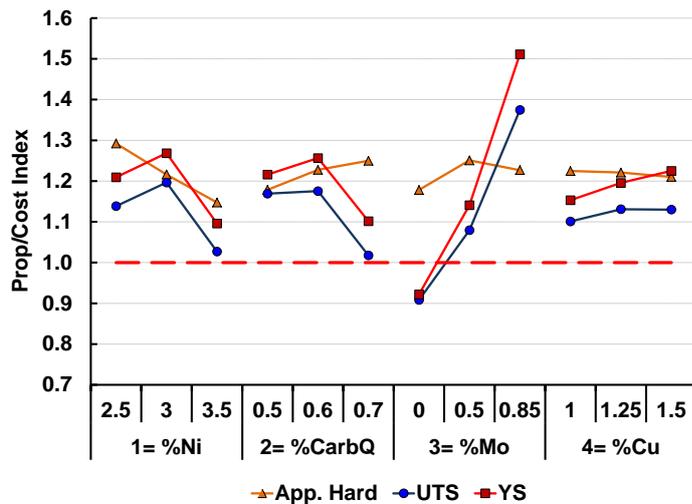


Figure 1 – Effect of Ni, graphite, Mo and Cu content on the P/C index (relative property to cost ratio) after tempering[10]

was developed in order to characterize the effect of each parameter. A 2³ factorial design was elaborated with the three parameters being Ni, Cu and graphite. The level of Mo was fixed at 0.85% (pre-alloyed); base powder ATOMET 4401 was used for all mixes. The chemistry of the base powder is shown in Table 1. The three factors and two levels of each factor used in the DOE are listed in Table 2. Factorial design was built with these combinations and resulted in 8 mixes being produced with levels of Ni of 1 and 3%, Cu levels of 0.5 and 2.5% and graphite levels of 0.5 and 0.7%. Moreover, central points were added in order to determine the linearity of the relation between the two levels of each factor. Therefore, two more mixes (same composition) were produced at intermediate levels of Ni, Cu and graphite of respectively 2, 1.5 and 0.6%. All mixes were admixed with 0.75% ZnSt as the lubricant and graphite KS15 was used.

TRS and tensile specimens were pressed to a green density of 7.0 g/cm³ and sintered at 1130°C for 20 minutes and cooled at a rate of 0.6°C/s in the range of 600 to 315°C in a 90% nitrogen 10%

Table 1 - Chemistry of the base powder

Powder grade	Mn (%)	Mo (%)	Ni (%)	Cu (%)
ATOMET 4401	0.15	0.85	0	0
ATOMET DB48	0.15	0.50	4.0	1.5

Table 2 - Factors and levels used for the DOE

Ni (%)	Cu (%)	Graphite (%)
1	0.5	0.5
3	2.5	0.7

3. Results

Results are detailed in Table 3. The DOE was analysed in order to identify the most important factors influencing the different properties. The pareto charts illustrated on Figure 2 show the relative impact of each factor on dimensional change, apparent hardness, TRS and UTS. DOE allows for the determination of the impact of all interactions when using full factorial design. In Figure 2, only the impact of Ni, Cu, graphite and the Ni/Cu interaction were plotted since the interaction between Ni/graphite and Cu/graphite and the triple order interaction were all statistically non-significant. Removing non-significant terms allows for the development of a more precise model. In the case of dimensional change only Cu and Ni are statistically significant. Although the most significant terms can be identified using these diagrams, their positive or negative effects can only be determined using the

powders. A factorial design was constructed in order to evaluate the effect of each element, Ni, Cu and graphite, on mechanical properties. The use of factorial designs instead of Taguchi arrays permits a better understanding of the different factors' interactions. This analysis was used to build a model assisting in the development of optimum mixes matching a FD-0405 reference (0.5% Mo, 4.0% Ni and 1.5% Cu).

2. Experimental Procedure

DOE (design of experiment) was used and a factorial design was developed in order to characterize the effect of each parameter. A 2³ factorial design was elaborated with the three parameters being Ni, Cu and graphite. The level of Mo was fixed at 0.85% (pre-alloyed); base powder ATOMET 4401 was used for all mixes. The chemistry of the base powder is shown in Table 1. The three factors and two levels of each factor used in the DOE are listed in Table 2. Factorial design was built with these combinations and resulted in 8 mixes being produced with levels of Ni of 1 and 3%, Cu levels of 0.5 and 2.5% and graphite levels of 0.5 and 0.7%. Moreover, central points were added in order to determine the linearity of the relation between the two levels of each factor. Therefore, two more mixes (same composition) were produced at intermediate levels of Ni, Cu and graphite of respectively 2, 1.5 and 0.6%. All mixes were admixed with 0.75% ZnSt as the lubricant and graphite KS15 was used. TRS and tensile specimens were pressed to a green density of 7.0 g/cm³ and sintered at 1130°C for 20 minutes and cooled at a rate of 0.6°C/s in the range of 600 to 315°C in a 90% nitrogen 10% hydrogen atmosphere. The samples were tempered at 205°C for one hour in air. A FD-0405 mix containing 0.6% graphite (ATOMET DB48) was processed under the same conditions as a reference. The composition of this reference mix is depicted in Table 1. Mechanical strength (TRS and UTS) apparent hardness and dimensional change were characterised.

Table 3 - Results from TRS and tensile tests

Mix	Nickel (%)	Copper (%)	Graphite (%)	TRS (MPa)	Dim. Ch. vs.die(%)	Hardness (HRA)	UTS (MPa)
A	3	2.5	0.7	1657	0.20	63.3	980
B	1	2.5	0.7	1519	0.50	62.3	928
C	3	2.5	0.5	1494	0.31	59.0	840
D	2	1.5	0.6	1482	0.10	59.7	827
E	3	0.5	0.7	1541	-0.16	61.3	912
F	1	2.5	0.5	1341	0.57	56.3	766
G	3	0.5	0.5	1444	-0.15	56.3	798
H	1	0.5	0.5	1127	0.01	50.0	595
I	1	0.5	0.7	1221	0.04	54.3	682
J	2	1.5	0.6	1500	0.09	59.3	649

mean effects plots of Figure 3. These graphs show the effects of each element when taken alone. The relation indicated by the black line shows the impact created when going from the low level of one factor to the high level. The red dot indicates the effect obtained with the central points. This indicates if the relationship is linear or if there is curvature.

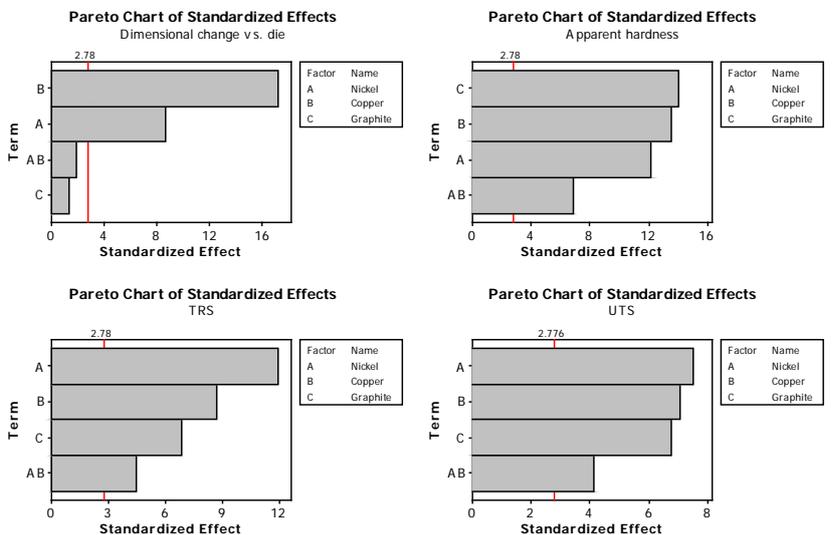


Figure 2 – Relative impact of Cu, Ni and graphite on dimensional change, apparent hardness, TRS and UTS

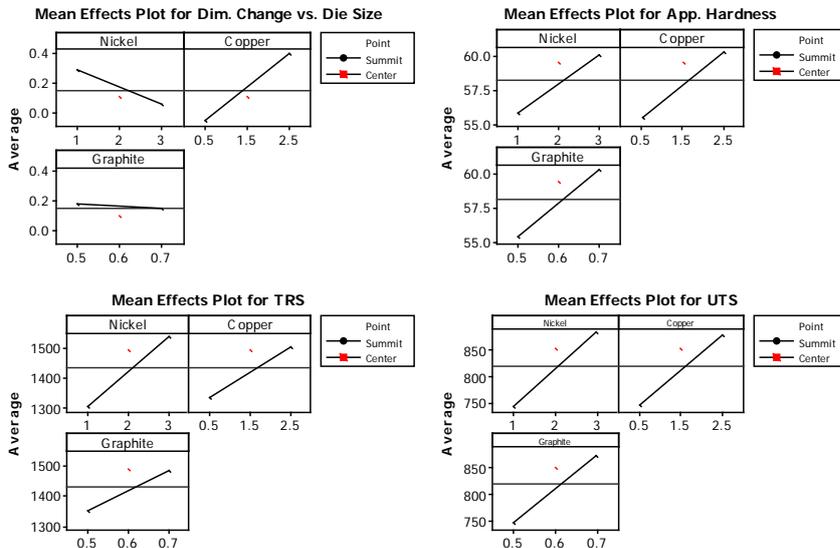


Figure 3 – Mean effect plots for dimensional change, apparent hardness, TRS and UTS

As observed in both Figure 2 and Figure 3, the parameters having the most effect on dimensional change are Cu and Ni, which was expected. Cu is the element with the largest effect. Increasing Cu from 0.5 to 2.5% resulted in growth of more than 0.4%. The effect of increasing Ni from 1 to 3% was two times lower but in the opposite direction, ~ -0.2%. It would be expected to see a strong interaction between Ni and Cu but the influence of the two factors is so strong that the interaction remains negligible. In this case the central point is near the linear relation indicating that the relation is linear. In the case of apparent hardness, TRS and UTS, an increase in all elements increases these properties. However, the red central point clearly shows that the relation is not linear for all factors. Indeed, the effect of increasing the Ni, Cu or graphite content is more pronounced in the first half of the range than in the second half, where the TRS, hardness and

UTS tend to level off.

Figure 4 shows the interaction plots that illustrate the potential interactions between Ni, Cu and graphite. Interactions exist when lines are non-parallel. As discussed previously, it appears that Ni/Cu and Cu/graphite have small interactions with regards to dimensional change. However, it was not statistically significant. On the other hand, the interaction Ni/Cu is important enough to have a significant impact on apparent hardness, TRS and UTS. This interaction means that when mixes contain a low level of Ni, the increase of Cu has a more significant impact than when the level of Ni is high.

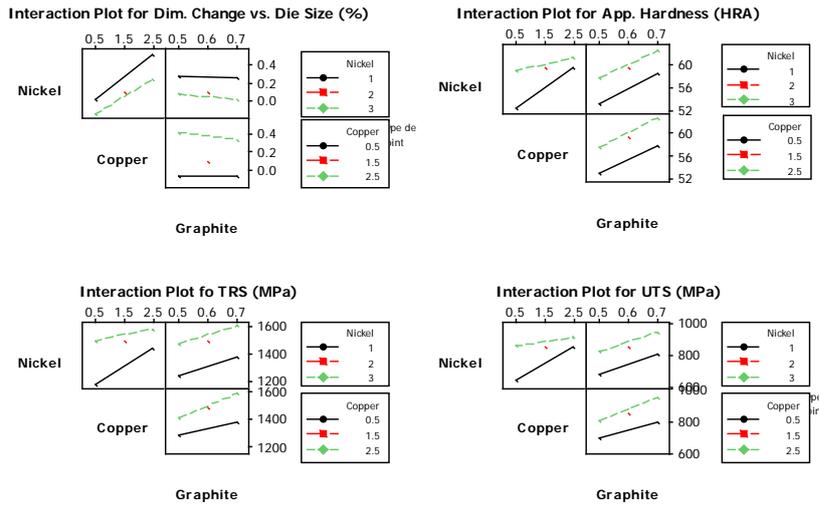


Figure 4- Interaction diagrams for dimensional change, apparent hardness, TRS an UTS

Based on these results it would be easy to conclude that increasing the level of Ni, Cu and graphite will result in better properties. However, the non-linearity relation between these elements and the mechanical properties indicate that the beneficial effect of increasing these elements is less and less important as their level increases. Also, the effect of each element on cost must also be considered. In order to determine which element has the most beneficial effect on properties with regards to cost, a property to cost ratio was calculated. This ratio (Equation 1) is built by comparing the effect of increasing properties on cost compared to that of the reference mix (FD-0405). The calculated cost takes into account process and alloy costs as calculated at the end of 2013.

$$\frac{P}{C} index = \frac{Prop_{mix} / Cost_{Mixi}}{Prop_{Ref} / Cost_{Ref}} \quad [1]$$

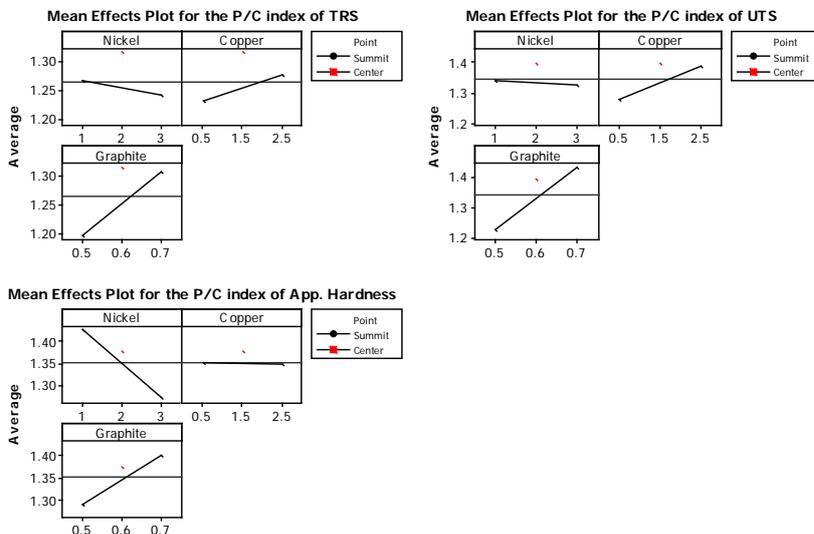


Figure 5 – Effect of Ni, Cu and graphite content on the P/C index

(relative property to cost ratio)

The mean effect plots

based on the P/C index are illustrated in Figure 5. A property to cost ratio of 1 indicates that the property to cost ratio is equal to that of the reference (FD-0405). As the property to cost ratio grows, it means that the increase of this factor increases the property in a cost effective way. On the other hand, when the trend of the P/C index is downward, it means that this factor does not increase the property in a cost effective way. Trends are very similar for TRS and UTS and they show that an increase of Cu or graphite will improve properties while maintaining costs lower than in Ni mixes. In fact, increasing the Ni is not a cost effective way to increase properties.

This analysis was then used to build a model predicting each property. Indeed, it was possible to come up with an equation relating each property with regards to Ni, Cu, graphite and the Ni/Cu interaction. The following equations can be used to calculate apparent hardness, TRS and UTS.

$$\text{TRS} = 544.3 + (180.8 \times \text{Ni}) + (171.1 \times \text{Cu}) + (666.0 \times \text{Graph.}) - (43.2 \times \text{Ni} \times \text{Cu}) \text{ [MPa]} \quad [2]$$

$$\text{App. hard.} = 32.0 + (3.94 \times \text{Ni}) + (4.79 \times \text{Cu}) + (24.58 \times \text{Graph.}) - (1.21 \times \text{Ni} \times \text{Cu}) \text{ [HRA]} \quad [3]$$

$$\text{UTS} = 89.0 + (127.7 \times \text{Ni}) + (142.9 \times \text{Cu}) + (629.0 \times \text{Graph.}) - (38.5 \times \text{Ni} \times \text{Cu}) \text{ [MPa]} \quad [4]$$

Although the central points showed that the relations are not linear, linear equations were drawn since the amount of information was insufficient to adequately calculate quadratic relations. Only surface response design could give adequate quadratic relations. In addition, taking into consideration the interaction, the equations allow us to obtain calculated values that correlate very well with the measured value as illustrated in Figure 6. Indeed, all mixes were predicted within 50 MPa of the measured data and within 1 HRA in the case of apparent hardness.

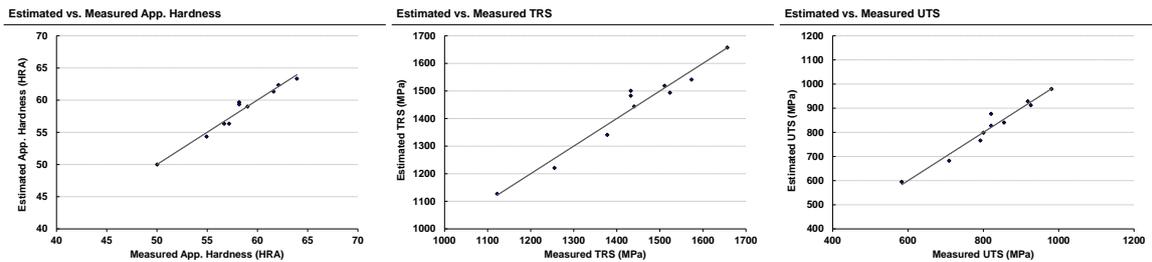


Figure 6 – Estimated vs. measured values for app. hardness, TRS and UTS

This model was used to obtain an optimised mix in the range of -25/+75 MPa of the reference for the UTS, -2.5/+5 HRA for apparent hardness and -50/+75 MPa for TRS at the lowest possible cost. The optimised mix as suggested by the model is illustrated in Figure 7. As described earlier, the model

Optimal D	Nickel	Copper	Graphite
0.99103	3.0	2.50	0.70
	[1.2057]	[2.50]	[0.70]
	1.0	0.50	0.50

UTS			
Target: 850.0			
y = 924.3857			
d = 0.61849			
App. Har			
Target: 60.0			
y = 62.3052			
d = 0.94006			
TRS			
Target: 1575.0			
y = 1526.0513			
d = 0.67964			
Cost			
Minimum			
y = 0.6993			
d = 1.0000			

Figure 7 - Optimised mix with regards to cost

chose to maximise the Cu and the graphite in order to reach the requested properties in a more cost effective way. The Ni was then adjusted as needed and remains the factor closer to its minimum value. Indeed, as discussed in the previous section, the Ni presented the least cost effective way to increase properties and therefore needs to be minimised. As indicated in the figure, it was possible to match the mechanical properties of a FD-0405 at a cost ratio of 0.70 by optimising the additives present. This was attained by increasing the amount of Mo (as determined by a previous study), lowering the Ni content and increasing the Cu content. By increasing the range of Ni and Cu vs. the previous study, it was possible to further decrease cost by another 10%. Indeed, as lower Ni levels and higher Cu levels were studied, the optimum mixes were reached with higher cost reduction. The chemistry and properties of the optimised mix vs. the reference are detailed in Table 4. Dimensional change can be difficult to match as indicated in the table.

Table 4 - Estimated properties for an optimised mix compared to the reference

Mix	Mo (%)	Ni (%)	Cu (%)	Graph. (%)	TRS (MPa)	Hardness (HRA)	UTS (MPa)	DC vs. Die (%)	Cost index
Ref (FD-0405)	0.50	4.0	1.55	0.60	1575	60.0	850	-0.04	1.0
Optimised mix	0.85	1.2	2.50	0.7	1526	62.3	924	0.47	0.70
Opt. mix prev. study [10]	0.85	2.3	1.15	0.6	1622	59.6	906	N/A	0.80

4. Conclusion

This study summarises the effect of Ni, Cu and graphite on mixes produced with a high level of Mo. The main conclusions are as follows:

- Cu has the greatest impact on dimensional change followed by Ni. In the range of elements studied, the strength of the mean effects overshadowed any interactions.
- Apparent hardness is influenced mainly by the graphite content followed by Cu and Ni and the interaction Ni/Cu.
- TRS and UTS are influenced by the same elements as hardness but Ni and Cu are predominant in this case.
- The central point test confirmed that relations are non-linear. TRS, UTS and apparent hardness increase in a much faster way in the first half than in the second half for each factor.
- Interaction between Ni and Cu shows that at low Ni level, Cu has a greater impact than at a high Ni level.
- The P/C index calculated (property to cost ratio) indicates that increasing Cu and graphite will increase properties in a more cost effective way than Ni. For apparent hardness, an increase in Ni actually decreases the P/C index.
- An optimised mix matching the properties of a FD-0405 at a cost ratio of 0.70 was obtained by maximising Cu and graphite.

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