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Dilatometric analysis of pre-alloyed high hardenability PM steels containing elemental Cu additions.

I. Bailon-Poujol(1), V. Paserin(1), S. Sainz(2), A. Veiga(2) and F. Castro(2)
(1) Rio Tinto Metal Powders (QMP), Quebec, Canada
(2) CEIT, San Sebastian, Spain

ABSTRACT

A selection of Fe-based powders containing Mn-Ni-Mo in pre-alloyed form plus additional copper and nickel in elemental form have been sintered at 1120ºC for 15 min for obtaining high performance PM steels containing 0.6%C in solution. An exhaustive dilatometry study combined with interrupted sintering experiments from selected temperatures has been carried out in order to determine, not only their hardenability response as expressed by the corresponding CCT curves, but also the micromechanisms involved in microstructural development due to nickel redistribution and copper spreading and penetration through the austenite grain boundaries. Special attention has been paid to the determination of the influence of these elements on dimensional changes related to copper swelling for different Cu/C ratios and martensite formation. Mechanical properties of the sintered materials have also been determined.

INTRODUCTION

Over the years, and amongst other factors associated with new developments in furnaces, presses and processes, the growth of ferrous PM has been particularly linked to the development of new powders and powder blends (1, 2). Generally PM requires a higher concentration of alloying elements than wrought counterparts in order to achieve similar characteristics. But due to solid solution hardening using high amounts of alloying elements leads to low compressibility powders (3). Hence, hybrid alloying methods based on combining pre-alloyed powders with admixed alloying elements (4-7) or master alloys (8-11) is alternatively used to adjust the final chemical composition of these PM steel grades while still keeping convenient compressibility. One of the most favoured alloy systems for high loading applications is based on blends prepared by diffusion bonding Ni and Cu particles onto Fe-Mo pre-alloyed powders (12-15). These steels are classed as sinter-hardening grades and exhibit heterogeneous microstructures after sintering at any temperature within the practical industrial range.

It is well known that during sintering, admixed copper melts at around 1083°C and is redistributed throughout the steel compact by spreading of the liquid phase followed by grain boundary diffusion and ultimately by volume diffusion into the iron lattice. In contrast Ni redistribution takes place by solid state events involving surface diffusion over Fe-particle surfaces, diffusion through austenite grain boundaries and finally Fe-Ni inter-diffusion with preferential transport from Fe into the Ni-containing regions (16-19). Consequently Ni-rich areas are commonly observed in sintered parts caused by the slow dissolution of steel particles into Ni. Such Ni redistribution mechanisms are sequentially active at increasing temperatures from around 850-900ºC.

It is therefore apparent that both, Cu and Ni, have diffusion paths in common, but must also be pointed out that for Ni these events take place at much lower temperatures than that for Cu melting. Hence, as suggested by several authors (20-24) the interaction of these elements during sintering determine, both, dimensional changes and properties of PM steels containing admixed Ni, Cu and C.

Based on the analysis of microstructural development, the present work further explores the behavior of admixed Ni, and Cu during sintering of hybrid PM steels containing low amount of pre-alloyed Ni. The results are compared against a PM grade containing all Ni in pre-alloyed form and admixed copper. The influence of these elements on hardenability and mechanical properties are also studied.

EXPERIMENTAL PROCEDURE

As the main objective in this work is to study the influence of nickel during sintering, added either in pre-alloyed form or a combination of pre-alloyed and elemental admixing, several powder mixtures were prepared containing variable elemental Ni additions (Table 1). In all cases graphite and copper additions were kept constant at 0.6 and 2wt%, respectively. Cold die pressed green compacts were obtained to reach densities around 7.05 g/cm^3. Specimens were sintered at 1120ºC for 30 min in a N_2/H_2 gaseous atmosphere and cooled down at cooling rates <1ºC.

For obtaining the Continuous Cooling Diagrams (CCT curves) a series of cylindrical samples (6mm in diameter and 10mm height) were used for dilatometry experiments. These cycles consisted of holding the samples at 1120ºC during 15 mins in argon followed by cooling at constant cooling rates ranging from 0.08 to 34ºC/s. Prior to the dilatometry experiments, and in order to avoid copper dripping in the dilatometer chamber, the specimens were pre-sintered in a separate furnace at 1120ºC for 15 min.

TABLE 1.- Chemical composition of the experimental powder mixtures used in this work. Graphite additions were kept constant at 0.6wt%.

Powder Grade	**Pre-alloyed (wt%)**				**Elemental Additions (wt%)**	
	Fe	**Mn**	**Mo**	**Ni**	**Ni**	**Cu**
ATOMET 4601	Bal	0.2	0.55	1.80	---	2.0
ATOMET 4201	Bal	0.3	0.6	0.45	---	2.0
ATOMET 4201 a	Bal	0.3	0.6	0.45	0.55	2.0
ATOMET 4201 b	Bal	0.3	0.6	0.45	1.35	2.0

In order to follow the microstructural development during sintering, interrupted sintering cycles were designed consisting of heating to selected temperatures followed by immediate cooling at 0.17°C/s. Mechanical properties like Impact energy, TRS and Tensile strength were assessed by standard methods. Microstructural characterization of specimens at various stages, that is, after sintering, dilatometry and interrupted sintering experiments was carried out by optical microscopy.

RESULTS AND DISCUSSION

Figure 1 shows the CCT curves for a fully pre-alloyed 4601 steel grade and for 4201-based steels with varying elemental Ni additions.

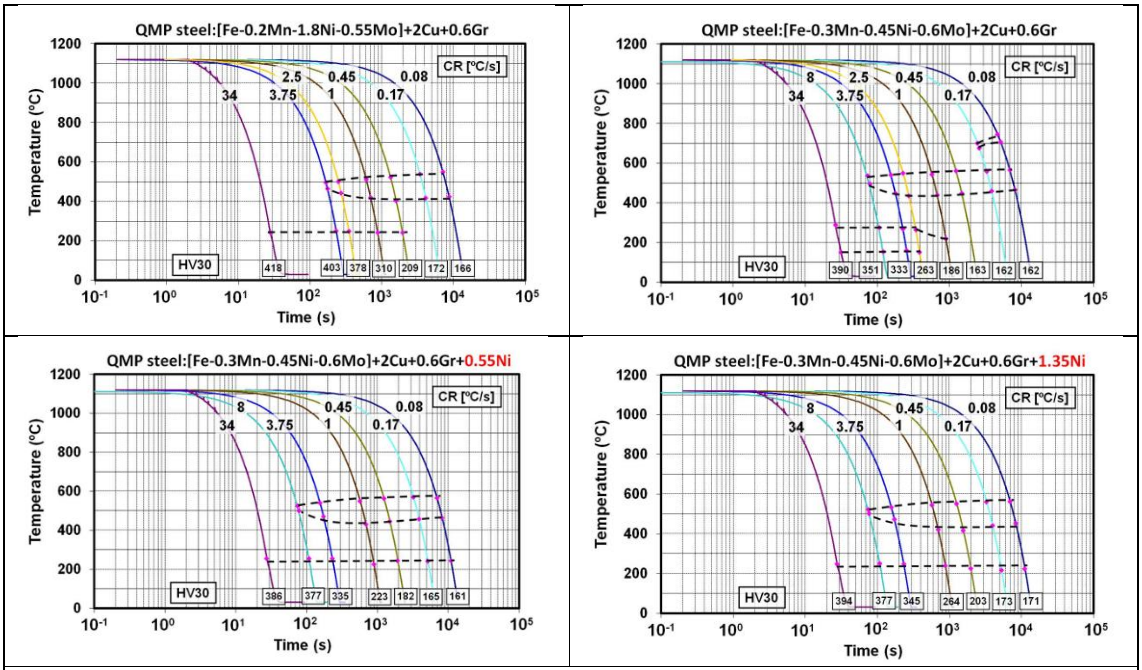

Figure 1.- CCT curves for (a) fully pre-alloyed 4601 steel grade, and for 4201-based steels with various elemental Ni additions: (b) 0% Ni, (c) 0.55%Ni and (d) 1.35%Ni. In all cases graphite and copper additions were kept constant at 0.6 and 2%wt respectively.

As mentioned before both PM steels contain admixed graphite and copper. As expected, the minimum critical cooling rate (around 3.75ºC/s) corresponds to the pre-alloyed grade which after copper diffusion into the Fe-lattice presents all the elements in solid solution. On the other hand the rest of PM steels exhibit the same critical cooling rate (8ºC/s) independently of the change in the overall Ni-concentration. It must also be noticed that simultaneously these steels exhibit martensite coexisting with bainite, even at cooling rates as low as 0.08ºC/s whereas the pre-alloyed grade requires at least 0.45ºC/s. This result may be clearly appreciated in the diagrams shown in Figure 2 for two PM steels with almost identical overall chemical composition. This Figure also shows that the progressive formation of martensite with increasing cooling rate, is faster for the pre-alloyed grade. This result is understandable because of the higher degree of chemical homogeneity in the pre-alloyed grade together with some heterogeneity in copper re-distribution into the steel particles.

On the other hand the material with elemental Ni additions can be seen as two interpenetrating materials with different chemical composition and local hardenability. Martensite in this material can only be formed in areas containing nickel, unless a cooling rate > 8ºC/s is imposed. In that case the core of the Fe-based particles, which have a lower hardenability as they do not contain nickel (17-19), will also reach their critical cooling rate.

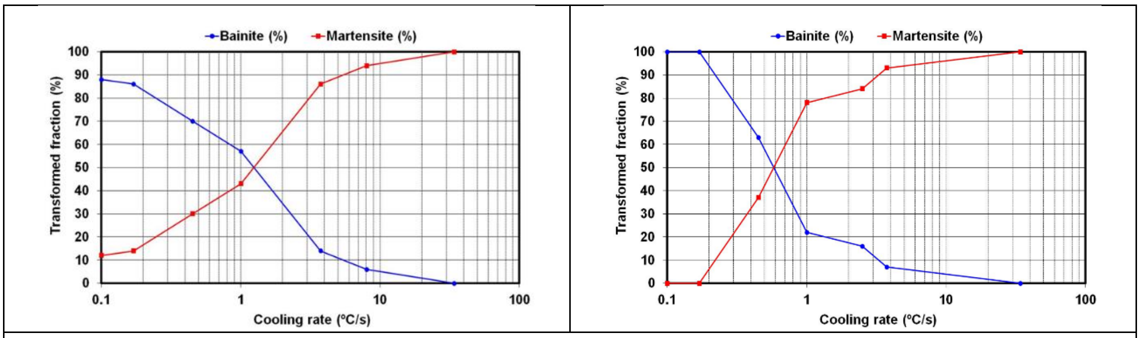

Figure 2.- Phase quantification as a function of cooling rate for (a) 4201+1.35%Ni+2%Cu, and (b) fully pre-alloyed 4601+ 2%Cu steel grades.

Figure 3 shows the microstructures for these materials at two cooling rates. In agreement with Fig. 2, after slow cooling (0.17ºC/s) the material containing elemental Ni additions exhibits a mixed microstructure consisting of nickel-martensite and bainitic Fe-based grains, whereas the pre-alloyed material is fully bainitic. As expected, increasing the cooling rate to 1°C/s causes an increase in the amount of martensite formed in both materials but the volume fraction formed is nearly twice as much for the pre-alloyed grade (Fig. 2). For that material the only possible compositional gradient may be due to copper.

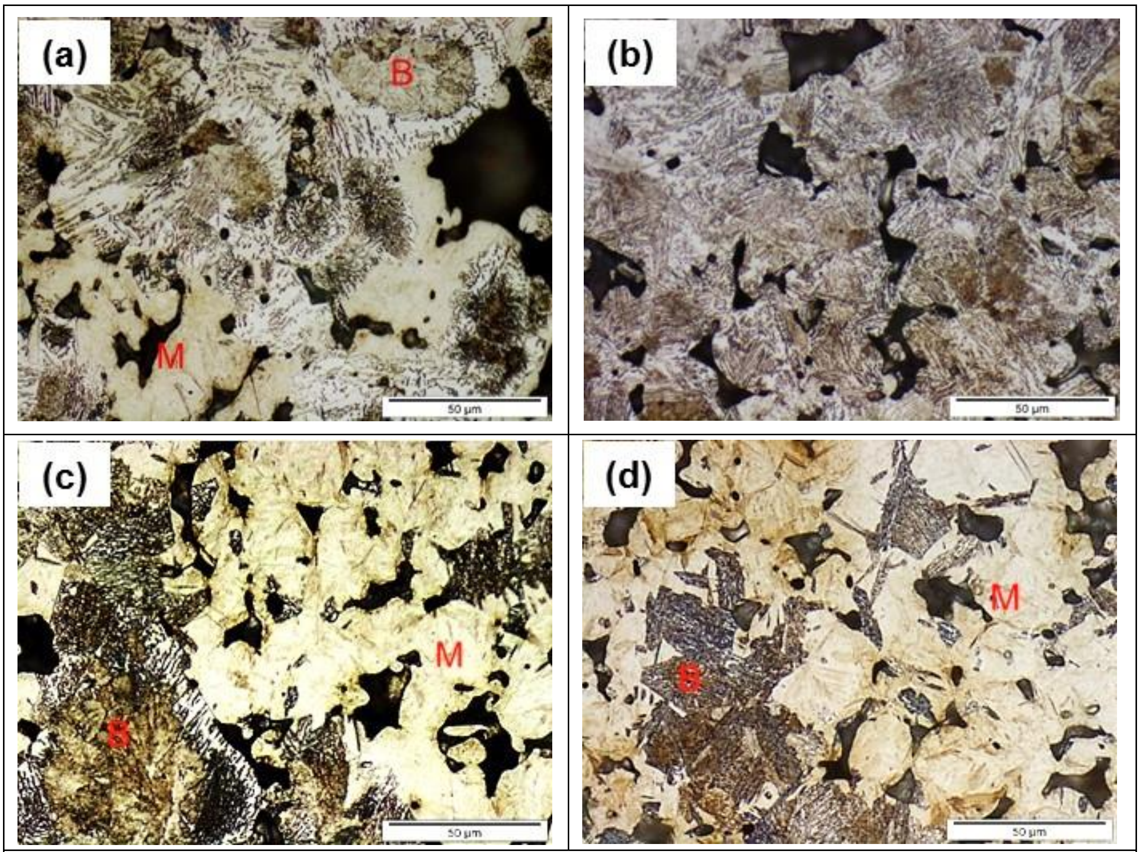

Figure 3.- Microstructures after 1120ºC, 15 min for 4201+1.35%Ni (left column) and 4601 (right column). Cooling rates (a, b) 0.17ºC/s above and (c, d)1.0ºC/s.

On the other hand, for the material with elemental Ni additions, the dissolution of the Fe-based particles (mainly containing Fe, Mo and C) into the Ni-containing regions is a slow process. Furthermore, at slow cooling rates the amount of martensite possibly formed in those materials is totally dependent on the amount of elemental nickel added. As an additional consequence the remnants of bainite in these materials (Fig. 3 at 1ºC/s) clearly exhibit a distinct morphology which also reflects the difference in chemical composition. These statements are supported by the observation of the microstructural evolution during sintering of these materials. Figure 4 shows two images corresponding to the pre-alloyed material after interrupted sintering experiments at 1076 and 1090ºC. At 1076 and after cooling at 0.17ºC/s the microstructure is mainly bainitic as expected from the corresponding CCT diagram. As minor amounts of ferrite are also observed it is deduced that the stage of carbon diffusion (after graphite dissolution) may have not finished yet. This is consistent with previous observation (25). In addition the original copper particles initially admixed with the powder mixture are still clearly noticeable and do not exhibit any signs of melting.

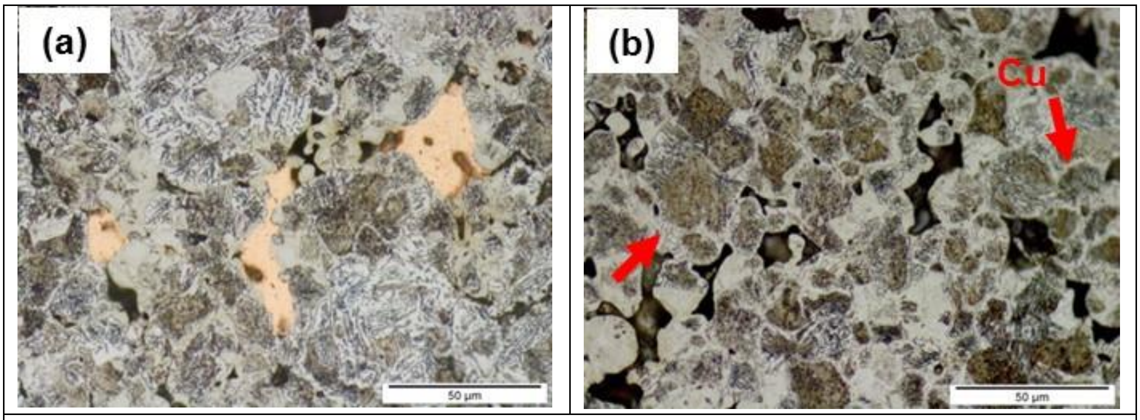

Figure 4.- Microstructural evolution for AT4601+2Cu as revealed by interrupted sintering experiments at (a) 1076 and (b) 1090ºC followed by cooling at ~0.17ºC/s.

Raising temperature to 1090ºC (that is 14ºC higher), the microstructure does not show any signs of free or prior un-melted copper particles. Additionally the noticeably smaller grain size surrounded by rims are clear indications of Cu spreading around steel particle surfaces as well as through the austenite grain boundaries. In contrast to previous reports (26, 27) this observation, which suggests that the wettability of Fe-based particles by liquid copper is not significantly reduced by the presence of carbon, is in agreement with previous works (23, 25). Comparison of micrographs in Figs. 4b and 3b indicates a rapid chemical homogenization during sintering at 1120ºC. This is aided by fragmentation of steel-particles caused by copper penetration into the grain boundaries which consequently produces an important decrease in diffusion distances.

For the material with elemental Ni additions, Figure 5 serves as an illustration of the microstructural evolution during sintering from 900 to 1120ºC. During heating a powder mixture and after the debinding stage several diffusion events take place under the thermal activation tending to reduce surface area by forming necks between the particles and smoothing out chemical gradients. In the hybrid [Fe-Mo]-C-Ni-Cu alloy system the first events taking place are graphite dissolution and carbon diffusion. The $\alpha\rightarrow\gamma$ transformation occurs out of equilibrium conditions at relatively low temperatures, typically between 700-800ºC. As revealed by the microstructure at 900ºC (Fig.5a) the microstructure is consequently bainitic and at this stage the original copper and nickel (arrowed) particles are clearly visible. Increasing the sintering temperature the copper particles remain unaltered but the nickel particles start coalescing (yellow arrow in Fig. 5b). Simultaneously Ni spreading through the microstructure by solid state surface and grain boundary diffusion may be observed (recognized as white halos engulfing Fe-based grains; white arrows in Figs. 5b and c). Also indicated by white circles some Ni-rich areas start forming as illustrated in Fig.5c. At 1090ºC (Fig. 5d), thus after copper melting, some of these areas provide evidence that copper is incorporated by dissolution in Ni. This is not surprising considering, as mentioned before, that Cu and Ni, have diffusion paths in common (steel particles surfaces and austenite grain boundaries). However, as Ni is present in those places before copper melting, the interaction mainly takes place with liquid copper. Interaction between Cu and Ni in the solid state is not clearly evidenced, (e.g. Fig. 5c), at least under the experimental conditions, mix formulations and particles sizes used in this work.

In all areas where Ni is present after Ni particle coalescence and Ni surface and grain boundary diffusion, subsequent microstructural evolution, even before copper melting, takes place by diffusion of Fe into Ni, that is, the steel particles are progressively dissolved in Ni. In this way those Ni-containing regions are progressively enriched in Fe, Mo and C. Copper meanwhile, after reaching its melting temperature, is not only incorporated in Ni but can also diffuse into the

Fe-based particles. Finally, at 1120ºC those Ni-regions having reached the right chemical composition (mainly balance between Fe/Ni/C) according to the constitutional diagram of Ni-steels (Guillet diagram) will transform to martensite upon cooling (Fig. 5e). As noticed by the diagrams in Fig. 1 these are regions of very high hardenability. Otherwise, Ni-regions with a too high Ni-content will remain austenitic as Ni acts as an austenite stabilizer. These areas consist of un-transformed austenite, are consequently relatively soft and are the so called Ni-rich areas.

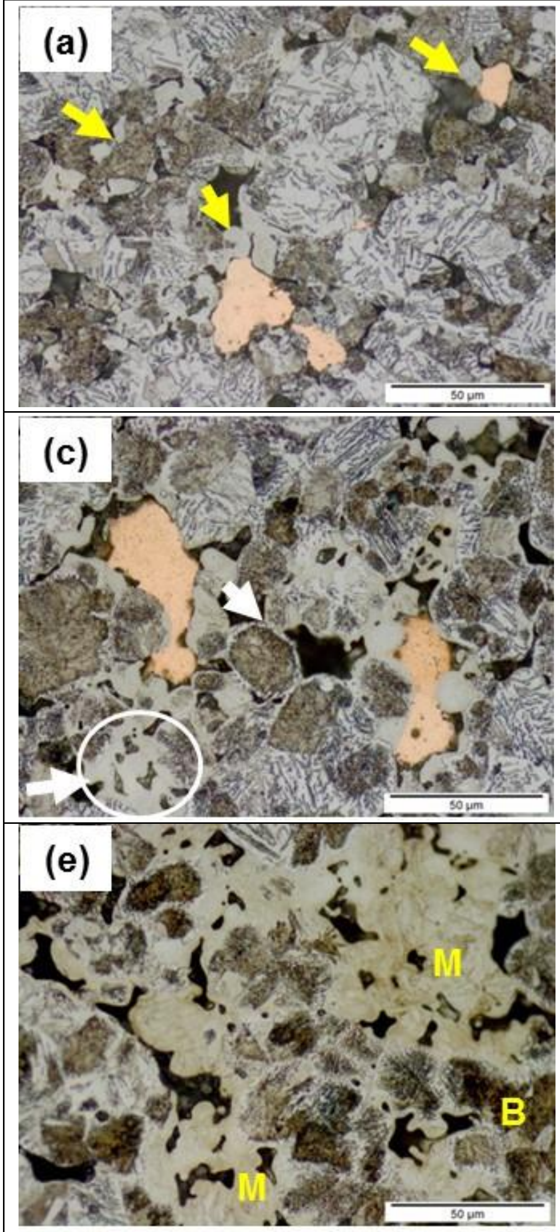

Fig 5.- Microstructural development for AT4201+1.35Ni+2Cu as revealed by interrupted sintering experiments at (a) 900, (b) 1000, (c) 1076, (d) 1090 and (e) 1120ºC followed by cooling at ~0.17ºC/s.

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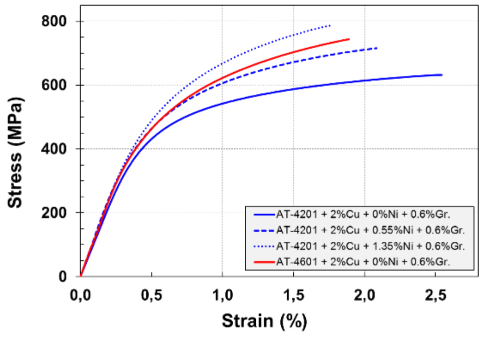

Figure 6.- Tensile curves for the indicated powder mixtures.

In terms of mechanical properties and dimensional changes Fig.6 and Table 2 present a summary that allows analyzing the influence of the amount of elemental Ni added as well as establishing a comparison with the pre-alloyed material. Firstly, hybrid premixes containing elemental Ni all show better compressibility than their pre-alloyed counterpart. In addition, it may be seen that increasing the Ni content produces a systematic increase in properties such as, impact energy, apparent hardness, TRS, yield and tensile strength. In contrast, this increase in Ni does not seem to alter sintered density and does not exert any influence on springback. In terms of dimensional changes it may be seen that in all cases, including the pre-alloyed grade, the final net effect is swelling, however, the minimum value is obtained for the specimens with highest admixed Ni. Comparing the pre-alloyed grade against that containing 1.35wt%Ni (hence identical overall Ni content) an interesting combination of properties is revealed as the admixed-Ni PM steel exhibits the highest value in UTS and yield stress together with highest impact energy, while still offering better compressibility.

TABLE 2.- General characteristics and mechanical properties of the studied powder mixtures in the green and sintered states (TRS specimens).

Property	***4201 (0.45%Ni pre-alloyed)***			***4601 (1.8%Ni pre-alloyed)***
Additions	**+1.35%Ni+2%Cu**	**+0.55%Ni+2%Cu**	**+0%Ni+2%Cu**	**+2%Cu**
Total Ni content (%)	1.8	1.0	0.45	1.8
Compacting press. (MPa)	565	575	578	694
Green density (g/cm^3)	7.05±0.00	7.05±0.00	7.05±0.00	7,05±0.00
Springback (%)	0.29±0.00	0.29±0.00	0,29±0.00	0,32±0.00
Sintered density (g/cm^3)	6.97±0.00	6.96±0.00	6,96±0.00	6,97±0.00
Dim. Ch. vs Die Size (%)	0.52±0.01	0.60±0.01	0,54±0.00	0.57±0.01
TRS (MPa)	1.419±41	1.282±42	1.211±15	1.379±40
Hardness (HRB)	94±1.0	88±1.0	83±1.0	90±3.0
Yield strength (MPa)	575±31	513±19	480±17	528±10
Tensile strength (MPa)	784±12	713±20	633±8	747±17
Impact enery (J)	18	15	14	14

CONCLUSIONS

PM steels in the Fe-Mo-Ni-Cu-C alloy system containing constant amounts of admixed Cu and C and variable amounts of Ni, up to 1.8wt%, were studied. Ni was added, either, in elemental form or pre-alloyed with the Fe-Mo basic powder. Interrupted sintering experiments specially designed to follow microstructural evolution during heating revealed that:

<u>*In the pre-alloyed grade*</u>,

1.- Apart from neck formation and the $\alpha \rightarrow \gamma$ transformation, the main microstructural changes are due to C and Ni diffusion in the solid state and Cu by LPS mechanisms.

2.- Liquid Cu penetration into the austenite grain boundaries is not significantly reduced in the pre-alloyed grade. Hence the reason for observing less Cu-swelling in PM steels with high carbon contents cannot solely be a decreased wettability of Fe-based particles and grain boundaries by liquid copper. Instead, it is considered that progressive carbon incorporation during heating, increasing sinter-activity and therefore promoting shrinkage, counteracts copper swelling. Evidently, this effect is more pronounced for higher carbon contents, hence, as carbon is increased less shrinkage is observed in steels (any Fe-based, Cu>1%, C mixture) with the same amount of copper.

<u>*For the admixed-Ni grades*</u>,

3.- Microstructural changes, again, apart from neck formation and the $\alpha \rightarrow \gamma$ transformation which is not essentially altered by Ni being, either, in pre-alloyed or elemental form, are associated to the redistribution of C, Ni and Cu. After graphite dissolution, carbon diffusion is progressive during heating even up to the sintering temperature. In parallel Ni redistribution by solid state, surface and grain boundary diffusion is observed coming to a halt at high temperature. At this stage tendency to chemical homogenization takes place by the dissolution of steel particles into these nickel areas (i.e due to preferential diffusion of Fe into Ni).

4.- Upon cooling at relatively slow cooling rates martensite is only formed in those Ni-containing areas where the right balance of Fe/Ni/C is reached. Areas with excessively high Ni due to insufficient Fe diffusion will remain austenitic. Those regions are soft and correspond to the so called Ni-rich areas. In contrast, the remaining steel particles contain much less nickel in solid solution and require cooling rates higher than the critical to transform to martensite.

5.- Very limited Ni-Cu interaction is observed in the solid state (i.e. below Cu-melting temperature). Upon melting Cu is preferentially dissolved in solid Ni, previously located in particle surfaces and grain boundaries. Copper diffusion into steel particles also occurs.

6.- Due to the typical microstructure consisting in bainitic Fe-based particles, Ni-martensite and untransformed austenite (soft Ni-rich regions) this grade exhibits the highest toughness of the materials under study. This is attractively combined with the highest values of yield stress and UTS along with better compressibility.

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