EFFECT OF COPPER ADDITIONS ON PROPERTIES OF
1.5% Mo SINTERED STEELS

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ABSTRACT

Alloying elements are generally required to improve the mechanical properties of P/M steels. These can be either pre-alloyed (i.e. added to the liquid steel melt prior to atomization), diffusion alloyed or admixed to the ferrous base powder using regular or binder-treated blending techniques. Pre-alloyed elements often reduce the compressibility of the powder due to their strengthening effect on the ferritic matrix of iron or steel powders. However, the use of molybdenum as a pre-alloying element represents an interesting avenue to improve mechanical properties of P/M steels with only a moderate impact on the compressibility of the powder.

A study was conducted to characterize the sintered properties of a 1.5% Mo low alloy steel powder. Mix formulations were prepared with graphite and copper concentrations varying from 0.38 to 0.98% and 0 to 2% respectively. Test specimens were pressed to 6.9 g/cm^3 and sintered 25 minutes at 1135 or 1160°C in a nitrogen based atmosphere, followed by post-sintering cooling rates of either 1.85 or 0.65°C/s in the temperature range of 650 to 400°C. Sintered properties were evaluated in the as-sintered condition and after tempering 60 minutes at 200°C.

Results showed that with proper additions of copper and graphite and the use of fast post-sintering cooling rates, the 1.5% Mo low alloy powder can be used for sinter hardening applications. Indeed, specimens containing 2% Cu and 0.7% combined carbon, exposed to a post-sintering cooling rate of 1.85°C/s achieved apparent hardness values above 40 HRC. Apparent hardness of 34 HRC, tensile strength of 980 MPa (142 ksi) and yield strength of 680 MPa (98.5 ksi) have been achieved after tempering 60 minutes at 200°C.

INTRODUCTION

Sinter hardening is defined as a process in which martensitic transformation occurs when the P/M parts are cooled from the sintering temperature. The main advantage of this process is the elimination of a post-sintering heat treatment. Therefore, sinter hardening can offer a significant cost advantage over the quench-and-temper process by reducing the number of steps to reach the required levels of strength and hardness [1]. To achieve high apparent hardness after sintering, base powders used in sinter hardening applications usually contain alloying elements such as nickel, manganese, molybdenum and chromium, which are added to the melt prior to atomization to improve hardenability. As illustrated in Figure 1, manganese, molybdenum and chromium are the most efficient elements to improve hardenability while copper and nickel, below 2.5%, have weaker effect on hardenability. Also, manganese and chromium are the less expensive elements to enhance hardenability but are susceptible to oxidation during water atomization. On the other hand, both nickel and molybdenum oxides are easily reduced during annealing but these elements are more expensive.

Another important aspect in achieving high mechanical properties is the powder compressibility, which determines the green density that is reached at a given pressure. As shown in Figure 2, of the four most popular elements used to improve the hardenability of water atomized powders, molybdenum is the least detrimental on powder compressibility. Therefore, the use of a proper addition of this element in the melt combined with fast post sintering cooling rate could be an interesting avenue for sinter hardening applications where density is an important parameter for mechanical properties.

Therefore, the objective of this study is to evaluate the effect of graphite and copper additions as well as the post-sintering cooling rate on the sintered and tempered properties of a 1.5% Mo low alloy steel powder.
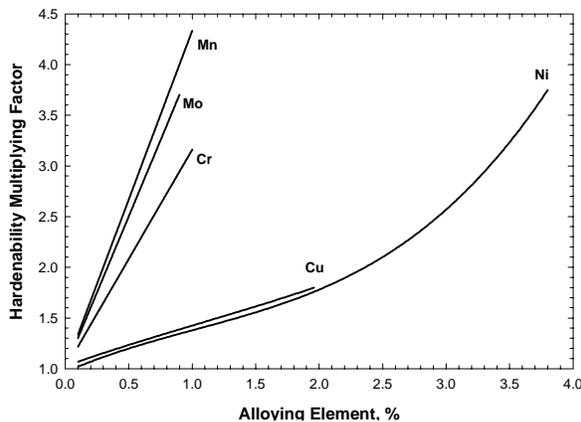
Figure 1. Hardenability multiplying factors of manganese, molybdenum, chromium, copper and nickel [2].
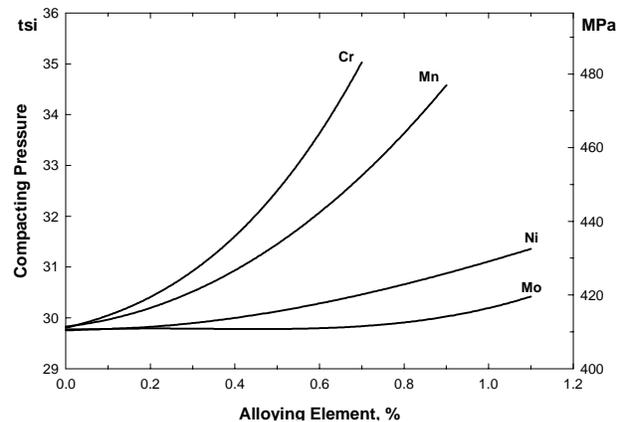
Figure 2. Effect of alloying elements on the compressibility of pre-alloyed powders (mixes with 0.5% graphite and 0.75% lubricant pressed to 6.8 g/cm) [3].

EXPERIMENTAL PROCEDURE

The base powder used in this study was ATOMET 4901, a steel powder prealloyed with 1.5% Mo and 0.2% Mn. As illustrated in Figure 3, this powder retains good compressibility in spite of its relatively high content of alloying elements. At a compacting pressure of 620 MPa (45 tsi), a green density in excess of 7.0 g/cm³ can be achieved. This good compressibility makes possible the production of large parts and/or achieves high sintered density at a reasonable compacting pressure.

Mixes containing 0.75% zinc stearate were prepared with various additions of graphite and copper as reported in Table 1. Transverse rupture strength and dog bones specimens were pressed to 6.9 g/cm³. These were sintered in mesh belt furnaces in a 90% nitrogen based atmosphere. Half of the specimens were sintered 25 minutes at 1160°C, followed by a post-sintering cooling rate of 0.65°C in the temperature range of 650 to 400°C. The balance of the specimens were sintered 25 minutes at 1135°C, followed by a post-sintering cooling rate of 1.85°C/s in the temperature range of 650 to 400°C. A tempering treatment was then carried out at 200°C for 60 minutes on one half of each series of specimens. Apparent hardness, dimensional change from die size and tensile properties were determined according to MPIF Standards 43, 44 and 10 respectively. Microstructural characterization was performed by optical microscopy.
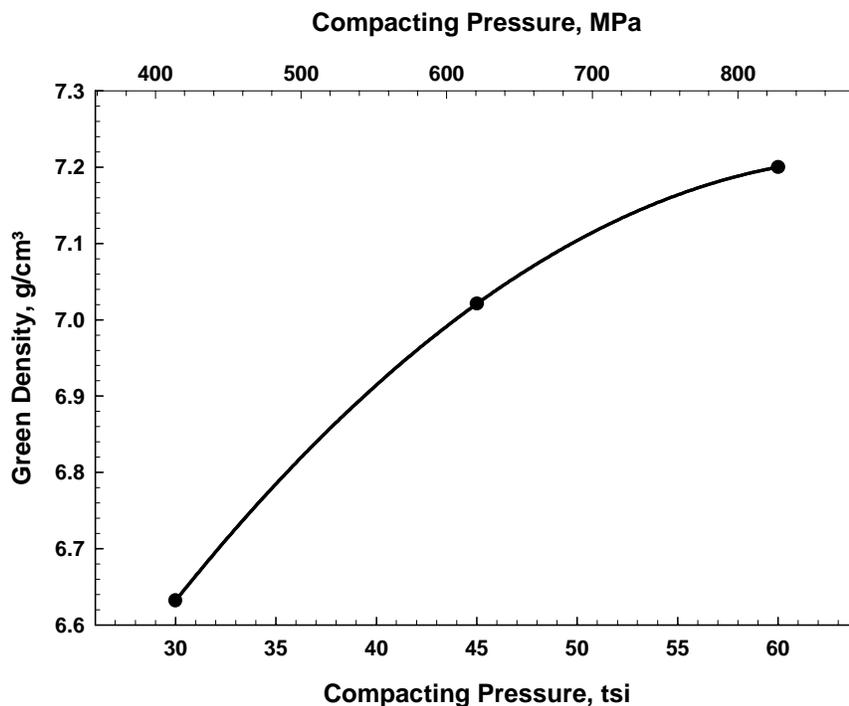
Figure 3.   Compressibility of ATOMET 4901 (mixes with 0.75% zinc stearate).

Table 1
Mix compositions used in this study.

Mix number	Graphite, %	Copper, %
1	0.38	0
2	0.58	0
3	0.78	0
4	0.98	0
5	0.38	1
6	0.58	1
7	0.78	1
8	0.98	1
9	0.38	2
10	0.58	2
11	0.78	2
12	0.98	2

RESULTS AND DISCUSSION

Figure 4 illustrates the effect of combined carbon, copper concentration and sintering temperature on the sintered density of specimens pressed to 6.9 g/cm³. The density of the specimens sintered at 1160°C is on average 0.03 g/cm³ higher than that of those sintered at 1135°C. The lowest sintered density, 6.78 g/cm³ is observed at low carbon content and 2% copper. This is explained by the significant expansion occurring during sintering for this mix formulation. This is well illustrated in Figure 5, which shows the effect of combined carbon, copper concentration, sintering temperature, post-sintering cooling rate and tempering treatment on the dimensional change from die size of specimens pressed to 6.9 g/cm³. Similar trends are seen for both sintering cycles. Dimensional change increases with carbon content at 0% copper, remains relatively stable at 1% copper and decreases at 2% Cu. These results are in accordance with previous studies and are related to the diffusion of carbon and to the difference in the behavior of copper in low and high carbon alloys [4, 5, 6]. Indeed, in low carbon alloys, the molten copper tends to penetrate into the iron grain boundaries, thus causing growth of the specimen. The dimensional change of specimens sintered at 1160°C is on average 0.14% lower than that of specimens sintered at 1135°C. This can be related to the better densification occurring at higher sintering temperature. It is also worth noting that with the exception of formulations with 2% Cu and 0.67 and 0.87%C, the tempering treatment does not affect the dimensional change for specimens cooled at 0.65°C/s. This is an indication that no significant amount of martensite is produced at this post-sintering cooling rate. Indeed, when martensite is tempered, the iron lattice shrinks, resulting in a smaller dimensional change [5]. With a post-sintering cooling rate of 1.85°C/s, there is a difference in the dimensional change before and after tempering at 0% Cu and a carbon content of 0.88% and, 0.5, 0.69 and 0.88% C for copper concentrations of 1 and 2%. This indicates that a larger amount of martensite has been produced with the fastest cooling rate.
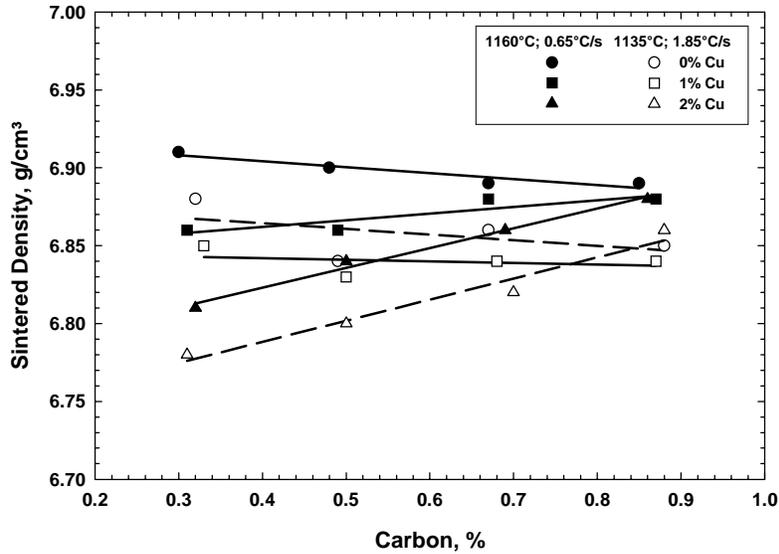
Figure 4   Effect of combined carbon, copper concentration and sintering temperature on the sintered density of specimens pressed to a green density of 6.9 g/cm³.

<center>a</center>

<center>b</center>
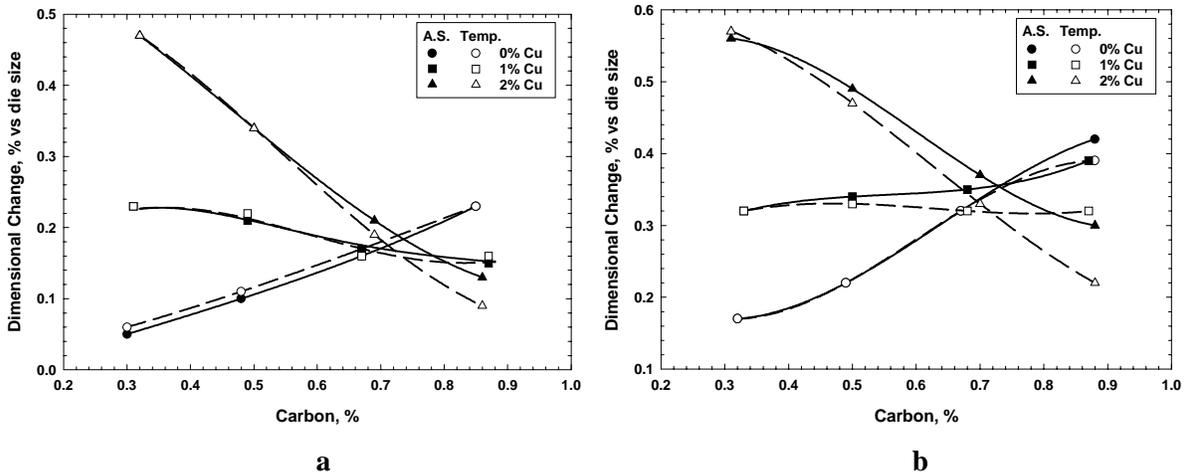
Figure 5.   Effect of combined carbon, copper concentration and tempering at 200°C on the dimensional change from die size of specimens pressed to 6.9 g/cm³ and sintered 25 minutes at:
a) 1160°C and cooled at 0.65°C/s in the temperature range of 650 to 400°C.
b) 1135°C and cooled at 1.85°C/s in the temperature range of 650 to 400°C.

Figure 6 illustrates the effect of combined carbon, copper concentration and post-sintering cooling rate on the apparent hardness of TRS specimens in the as-sintered condition and after tempering 60 minutes at 200°C. The apparent hardness increases with carbon and copper contents but the effect is more evident for the specimens cooled at 1.85°C/s. At 0.65°C/s, apparent hardness values superior to 30 HRC are achieved only with 2% copper and 0.87%C. However, when the specimens are cooled at a rate of

1.85°C/s, values above 30HRC are reached at 1 and 2% Cu and carbon contents of 0.7 and 0.87%. The highest apparent hardness value, 45 HRC, is observed at either 1 or 2% Cu and 0.87% C. Tempering at 200°C causes a decrease of the apparent hardness only for hardness values superior to 25 HRC, i.e. when a significant amount of martensite is produced. This is well shown in Figures 7, 8 and 9, which illustrate the typical microstructure of sintered specimens for copper concentration of respectively 0, 1 and 2% Cu.

a   b
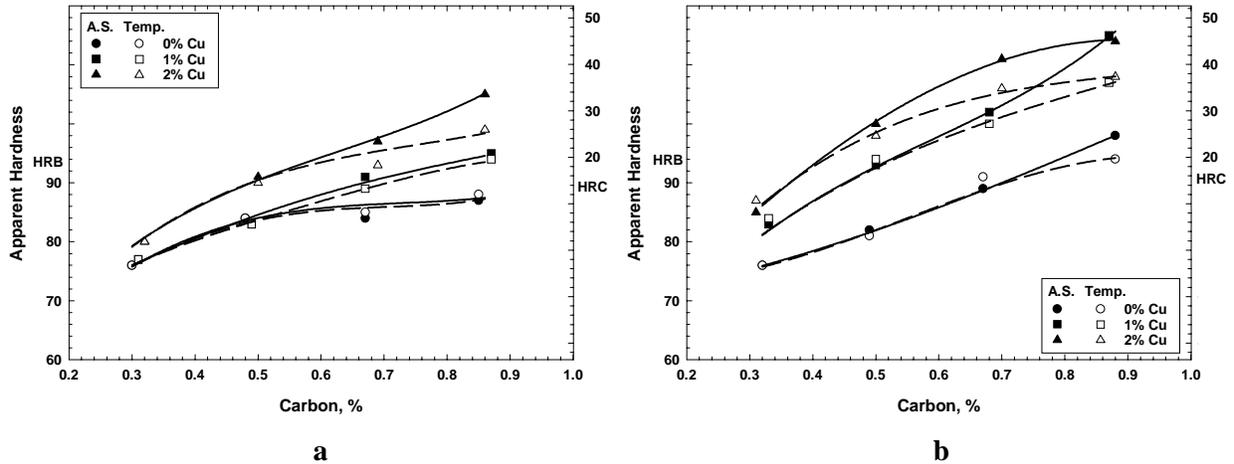
Figure 6. Effect of combined carbon, copper concentration and tempering at 200°C on the apparent hardness of specimens pressed to 6.9 g/cm³ and sintered 25 minutes at:
     a) 1160°C and cooled at 0.65°C/s in the temperature range of 650 to 400°C.
     b) 1135°C and cooled at 1.85°C/s in the temperature range of 650 to 400°C.

At 0% Cu, there is no martensite in the 0.87% C specimens cooled at 0.65°C/s. The microstructure is predominantly composed of upper bainite and divorced pearlite. Raising the cooling rate to 1.85°C/s results in a 30-40% martensite structure, the balance being a mixture of upper and lower bainite.

a   b
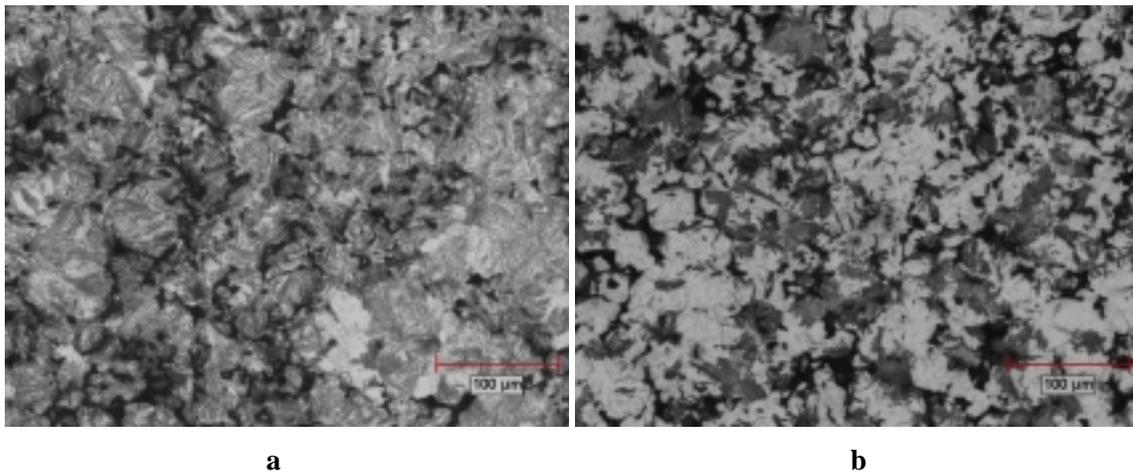
Figure 7. Microstructure of specimens containing 0.87% C and 0% Cu (Nital etched):
     a) 1160°C, cooled at 0.65°C/s in the temperature range of 650 to 400°C.
     b) 1135°C, cooled at 1.85°C/s in the temperature range of 650 to 400°C.

At 1% Cu and 0.87% C, Figure 8, there is no martensite in the specimens cooled at 0.65°C/s and upper bainite is the primary constituent. The amount of martensite is however significantly increased in the specimens cooled at 1.85°C/s, reaching almost 95%, the balance of the microstructure being bainite.

a   **b**
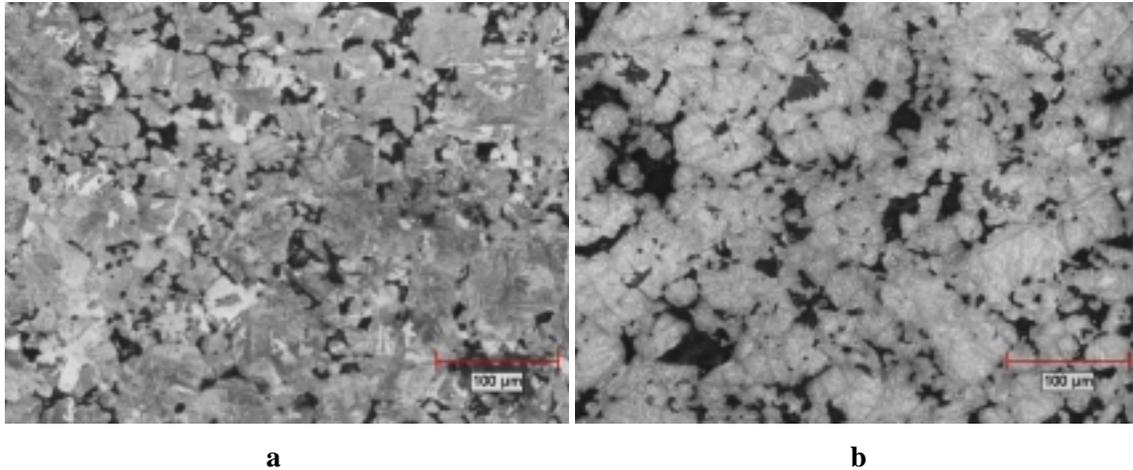
Figure 8.   Microstructure of specimens containing 0.87% C and 1% Cu (Nital etched):
a) 1160°C, cooled at 0.65°C/s in the temperature range of 650 to 400°C.
b) 1135°C, cooled at 1.85°C/s in the temperature range of 650 to 400°C.

At 2% Cu, Figure 9, a very small amount of martensite is observed in the specimens with 0.5% C cooled at 0.65°C/s. Again, the major constituent is bainite. The amount of martensite significantly increases with the fastest cooling rate. The microstructure is a mixture of bainite and martensite in a ratio of about 60/40. With the slow cooling rate, raising the carbon content to 0.87% for the 2% Cu addition results in a microstructure containing about 50% martensite and 50% bainite while for the fast cooling rate, martensite is the main constituent with a small amount of bainite.

Figure 10 illustrates the effect of combined carbon, copper concentration, post-sintering cooling rate and tempering at 200°C on the ultimate tensile strength (UTS). For the post-sintering cooling rate of 0.65°C/s, there is no significant difference in UTS values before and after tempering for the four levels of carbon and copper contents of 0 and 1%. The same is observed at 0.3 and 0.5% C combined with 2% Cu. For these mix formulations, the UTS increases with the carbon and copper contents. However, as a significant amount of martensite is produced i.e. at 2% Cu and 0.87% C, the UTS drops sharply from 800 MPa (116 ksi) at 0.7% C to 665 MPa (665 ksi). Tempering for 60 minutes at 200°C improves the strength by 265 MPa (38 ksi) from 665 to 930 MPa (135 ksi).

For the post-sintering cooling rate of 1.85°C/s, there is no significant difference between UTS values in the as-sintered and the tempered conditions for the four levels of carbon in the copper free specimens and at 0.3 and 0.5% C at either 1 or 2% Cu. At 1 and 2% Cu, the UTS increases with the carbon content, reaches a maximum at about 0.5% C and then decreases for carbon contents of 0.7 and 0.87%. This maximum is about 625 MPa (90.5 ksi) at 1% Cu and 750 MPa (109 ksi) at 2% Cu. The tempering treatment shifts the maximum values to about 0.7% C with UTS values of respectively 660 MPa (95.5 ksi) at 1% Cu and 980 MPa (142 ksi) at 2% Cu. This type of behavior was also observed previously in the characterization of other sinter hardening grades [5, 7].

a	b
c	d
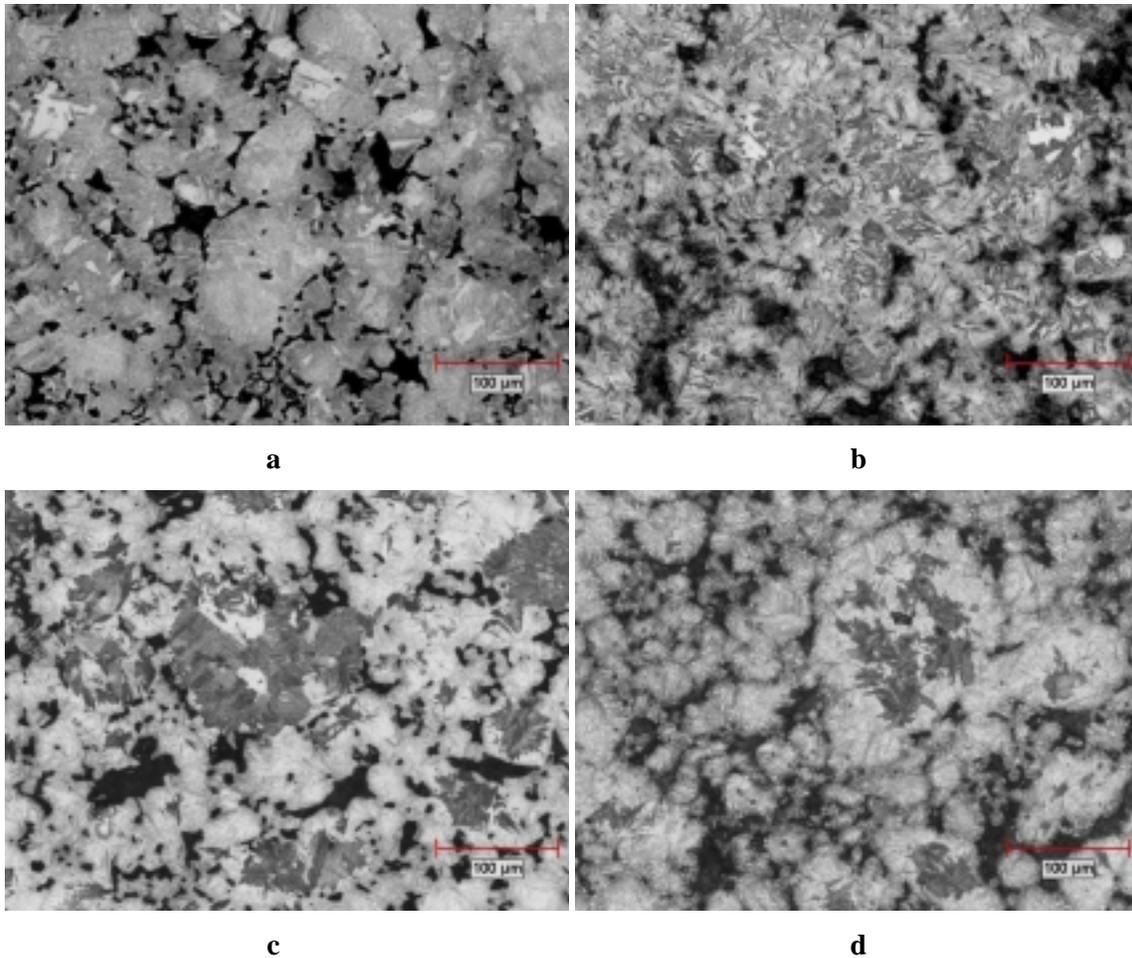
Figure 9   Microstructure of specimens containing 2% Cu (Nital etched):
a) 1160°C, cooled at 0.65°C/s in the temperature range of 650 to 400°C; 0.5%C.
b) 1135°C, cooled at 1.85°C/s in the temperature range of 650 to 400°C; 0.5%C.
c) 1160°C, cooled at 0.65°C/s in the temperature range of 650 to 400°C; 0.87%C.
d) 1135°C, cooled at 1.85°C/s in the temperature range of 650 to 400°C; 0.87%C.

Figure 11 illustrates the effect of combined carbon, copper concentrations, post-sintering cooling rate and tempering at 200°C on the yield strength (YS). In the as-sintered condition, no yield was observed for the fast cooled specimens containing 1% Cu and either 0.7 and 0.87% carbon or 2% Cu and 0.87% C. For the slowest cooling rate and copper contents of 0 and 1%, yield strength increases linearly with the carbon content and no significant difference was found between the as-sintered condition and after tempering at 200°C. At 2% Cu, the yield strength increases with the carbon content and reaches a maximum between 0.7 and 0.87% C. For these concentrations of copper and carbon, the tempering treatment at 200°C improves the yield strength by about 70 MPa (10 ksi), from 530 to 600 MPa (77 to 87 ksi).

For the fastest cooling rate, the yield strength also increases linearly with the carbon content in the copper free specimens and no significant difference was found between the as-sintered and the tempered conditions. Tempering at 200°C achieves a yield value for the entire range of carbon and copper concentrations. At 1 and 2% Cu, the yield strength increases with the carbon content to reach a maximum at about 0.7% C. The highest YS value i.e. 680 MPa (98.5 ksi) is achieved at 2% Cu.

Finally, the elongation results for the various mix formulations were below 1.6% with values generally below 1% for mix formulations with graphite contents above 0.58%. These results are typical of sinter hardened materials pressed to 6.9 g/cm³ [8].

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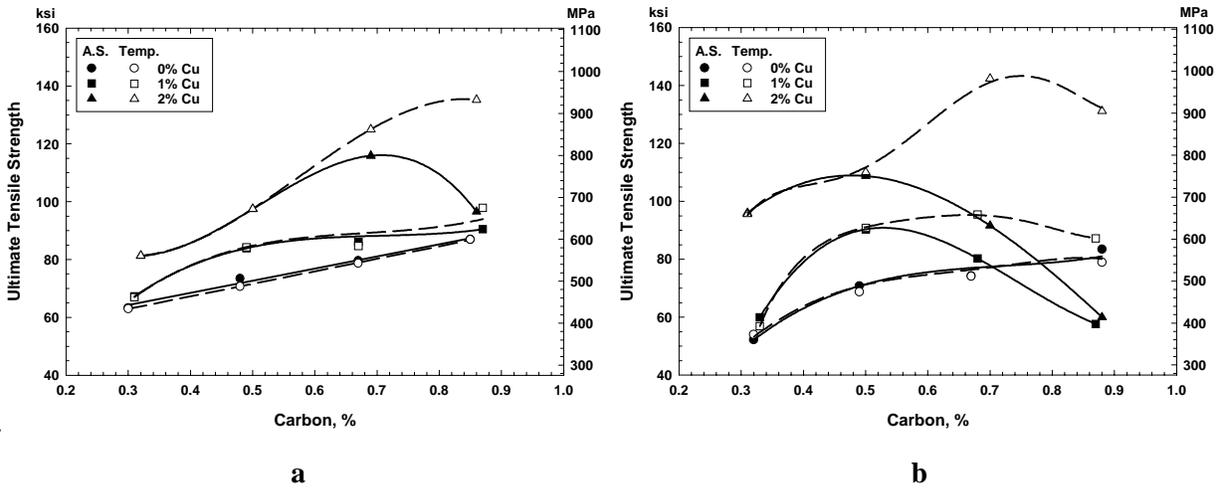
Figure 10. Effect of combined carbon, copper concentration and tempering at 200°C on the ultimate tensile strength of specimens pressed to 6.9 g/cm³ and sintered 25 minutes at:
a) 1160°C and cooled at 0.65°C/s in the temperature range of 650 to 400°C.
b) 1135°C and cooled at 1.85°C/s in the temperature range of 650 to 400°C.
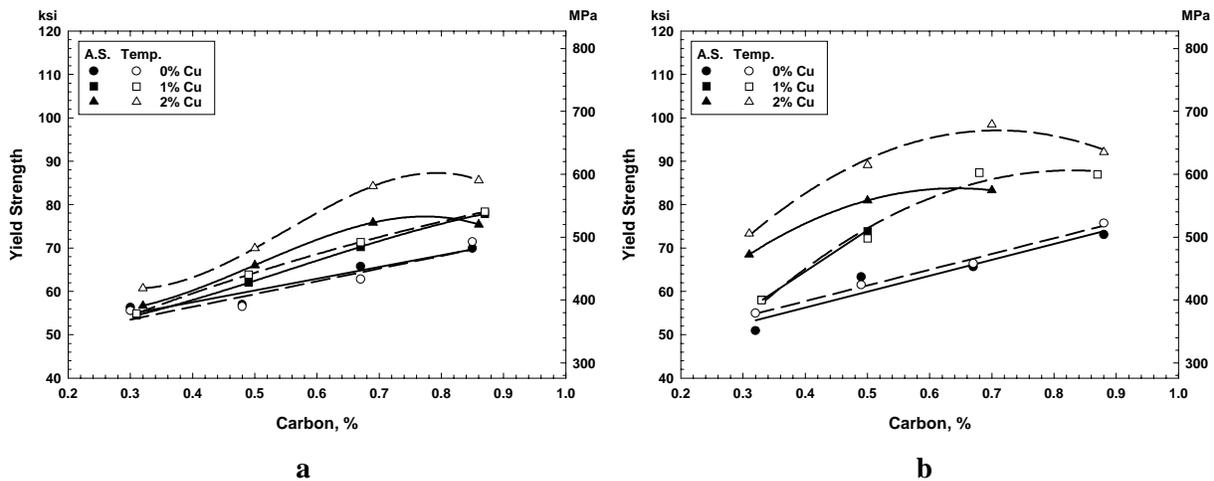
Figure 11. Effect of combined carbon, copper concentrations and tempering at 200°C on the yield strength of specimens pressed to 6.9 g/cm³ and sintered 25 minutes at:
a) 1160°C and cooled at 0.65°C/s in the temperature range of 650 to 400°C.
b) 1135°C and cooled at 1.85°C/s in the temperature range of 650 to 400°C.

CONCLUSIONS

1. The 1.5% Mo low alloy steel powder exhibited high compressibility characteristics in spite of its relatively high content of alloying elements, confirming that molybdenum is a powerful hardenability enhancer which has only a moderate negative impact on powder compressibility.

2. The dimensional change behavior of this 1.5% Mo low alloy powder grade, as a function of carbon and copper contents, was similar to that of other sinter hardening P/M grades: as the carbon content was raised, the dimensional change increased in the copper free specimens, remained relatively constant at 1% Cu and decreased at 2% Cu. The tempering treatment caused the specimens to shrink when a significant amount of martensite was produced i.e. at 0.87% C and 2% Cu for the post-sintering cooling rate of 0.65°C/s and at 0.7 and 0.87% C at 1 and 2% Cu for the post-sintering cooling rate of 1.85°C/s.

3. The 1.5% Mo powder steel required a fast post-sintering cooling rate to exhibit good sinter hardening characteristics. Indeed, apparent harness values in the range 40-46 HRC were achieved at 6.9 g/cm for a post-sintering cooling rate of 1.85°C/s with specimens containing 2% Cu and either 0.7 or 0.87% C and, 1% Cu and 0.87% C. The tempering treatment at 200°C decreased these values by about 6 to 8 HRC.

4. The best tensile strength values were reached with specimens containing 2% copper and 0.7% carbon cooled at 1.85°C/s and tempered at 200°C, with values of 980 MPa (142 ksi) for the ultimate tensile strength and 680 MPa (98.5 ksi) for the yield strength respectively.

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