EFFECT OF GRAPHITE AND COPPER CONCENTRATIONS AND POST SINTERING COOLING RATE ON PROPERTIES OF SINTER HARDENED MATERIALS.

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ABSTRACT

Sinter hardening enables the production of P/M parts with high strength and apparent hardness at lower cost than conventional heat treatment. This process is particularly attractive for parts that are difficult to quench because of their size and shape. Furthermore, the powder mix formulation can be adjusted to tailor microstructure and hence mechanical properties. With the development of sintering furnaces equipped with fast cool units, graphite and/or copper contents can be lowered while maintaining microstructures achieved with conventional cooling rates.

A study was carried out to evaluate the effect of graphite and copper concentrations as well as post-sintering cooling rate on strength, apparent hardness and dimensional change of specimens made from sinter hardening materials, in the as-sintered and tempered conditions. Test specimens were pressed to 6.9 g/cm^3 from mixes containing 0 to 2 % copper and the amount of graphite required to reach 0.3 to 0.9% combined carbon. Test pieces were sintered 20 to 25 minutes at 1120°C in a nitrogen based atmosphere and cooled at rates of 0.4 and 1.5°C/s respectively in the temperature range of 650 to 400°C. Tempering was carried out at 200°C for 60 minutes.

The highest amount of martensite, 91%, was obtained with specimens containing 0.55% C and 1% Cu cooled at 1.5°C/s. Raising the carbon and copper concentrations promoted the formation of retained austenite which reduces the amount of martensite in high carbon alloys. Apparent hardness increases linearly with the amount of martensite, with the largest values reached at higher carbon contents. The decrease in apparent hardness after tempering at 200°C augmented with the amount of martensite and carbon concentration. The dimensional change from die size was less sensitive to carbon variation at a copper level of 1%. This represents an interesting feature since sinter hardened parts cannot be sized after sintering. The maximum tensile strength was reached with a material containing 0.55% C and 2% Cu after tempering, with values in the range of 925 to 950 MPa for cooling rates of either 0.4 or 1.5°C/s.

INTRODUCTION

Powder metallurgy offers a significant cost advantage over conventional metallurgy to produce near net shape complex parts. In addition to the near net shape intrinsic characteristic of P/M, steel powders can be produced over a wide range of compositions by varying the concentration of alloying elements such as manganese, nickel, molybdenum and chromium added to the melt. Admixed elements are also used to tailor microstructures and mechanical properties. Finally, the sintering conditions (time, temperature and cooling rate) can be varied to modify the microstructure and the final properties of P/M parts. Sinter hardening takes advantage that, with appropriate base powders, admixed additions and sintering conditions, the martensitic transformation can be achieved during the cooling portion of the sintering cycle. This makes possible the elimination of a post-sintering heat treatment and its inherent problems such as cleaning parts before and after oil quenching [1, 2]. Also, the slower cooling rate achieved during sinter hardening compared to quenching reduces the thermal stresses and part distortion and allows a better control of dimensional tolerances [3].

Carbon is the key element in achieving high hardness in carbon steels but high carbon steels are also more susceptible to retain austenite [4] because carbon reduces the temperature at which the martensitic transformation starts, M_s. This temperature is mainly controlled by the carbon content and the concentration of alloying elements. Many studies have been performed to evaluate this temperature as a function of carbon and alloying additions and some equations are listed in reference 5. On the other hand, the temperature of the end of transformation, M_f, is not well defined but as for M_s, it is lowered as the concentration of carbon and alloying elements increases. The M_f temperature may even drop below room temperature for carbon contents as low as 0.3% depending on the concentration of other alloying elements. Once M_s is known, other equations can be used to estimate the concentration of martensite using the degree of undercooling below the M_s temperature [5]. This is useful information to estimate the amount of martensite that can be produced when the cooling rate is sufficiently fast to avoid both the pearlitic and bainitic transformation noses of the CCT (continuous cooling transformation) curve. However, such analyses are not available for P/M steels. Therefore, detailed material characterizations are required to confirm the effect of the concentrations of admixed graphite and copper and of the cooling rate on the various phases produced after sintering in order to optimize the properties of sinter hardened P/M steels.

The objective of this study is to evaluate the effect of admixed graphite and copper concentrations and of the post-sintering cooling rate on the mechanical properties of sinter hardened materials, and to correlate the results with the microstructure achieved after sintering.

EXPERIMENTAL PROCEDURE

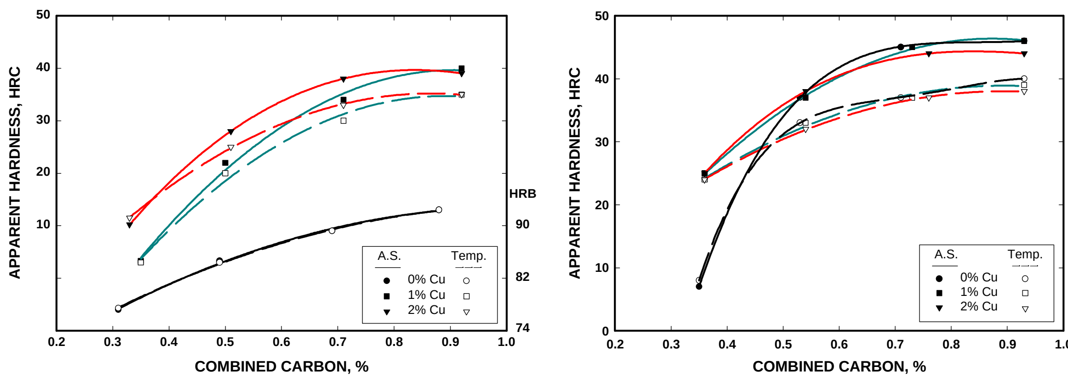
ATOMET 4701, a Fe-0.45Mn-0.45Cr-1.0Mo-0.9Ni low alloy steel powder, was used as base material for this study. Twelve mixes containing 0.75% zinc stearate were prepared with various additions of graphite and copper as reported in Table 1. Sixteen transverse rupture strength bars and sixteen dog bone specimens were pressed from each mix to a green density of 6.9g/cm³. Half of the specimens were sintered at 1120°C for 25 minutes in a 90% nitrogen based atmosphere with a post-sintering cooling rate of 0.4°C/s in the temperature range of 650 to 400°C. The other half of the specimens were sintered for 20 minutes at 1120°C in a 90% nitrogen based atmosphere in a furnace equipped with a fast cool unit in order to achieve a post-sintering cooling rate of 1.5°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 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 and image analysis. Retained austenite was determined using X-ray diffraction analysis carried out on polished rectangular bars, 1.25 X 0.5 cm², mounted in Bakelite. The X-ray scan was carried out using the Cu K_α radiation, λ of 1.540562Å, at a speed of 3 degrees per minute. The X-ray diffraction pattern of Bakelite was identified in order to eliminate its impact on the calculation of the amount of retained austenite.

Table 1
Mix Compositions Used in this Study.

Mix number	Graphite, %	Copper, %
1	0.50	0
2	0.70	1
3	0.90	2
4	1.10	0
5	0.50	1
6	0.70	2
7	0.90	0
8	1.10	1
9	0.50	2
10	0.70	0
11	0.90	1
12	1.10	2

RESULTS AND DISCUSSION

Figure 1 illustrates the effect of combined carbon and copper concentrations on apparent hardness of TRS specimens pressed to 6.9 g/cm³, sintered at 1120°C and cooled at either 0.4 or 1.5°C/s in the temperature range of 650 to 400°C, in the as-sintered condition and after tempering 60 minutes at 200°C. Apparent hardness increases with the combined carbon concentration but the rate of increase and the maximum apparent hardness vary with the cooling rate. For a cooling rate of 0.4°C/s, the addition of copper and a minimum combined carbon of 0.7% are required to achieve apparent hardness values above 30 HRC. For a combined carbon of 0.9%, raising the copper content from 1 to 2% does not contribute to further increase the apparent hardness with maximum values of about 41 HRC in the as-sintered condition. Raising the cooling rate to 1.5°C/s significantly increases the apparent hardness of the sinter hardened steel, particularly for the copper free materials. The addition of copper improves apparent hardness only for the low carbon material, i.e. 0.35%. Above 0.7% carbon, apparent hardness values tend to level off at about 46 HRC. This is related to the microstructure produced during cooling from the sintering temperature. As shown in Figure 2a, the combination of low carbon content and low cooling rate favors the formation of low hardness coarse pearlite. Raising the cooling rate and/or the combined carbon results in the formation of finer pearlite with some bainite, Figures 2b, c and e, while the microstructure is almost fully martensitic at 0.5% combined carbon for a cooling rate of 1.5°C/s, Figure 2d. It is worth noting that even with 1 or 2% admixed copper, bainite is present in the specimens cooled at 0.4°C/s, Figures 2g and i. This explains the 5 HRC difference in apparent hardness values observed at 0.4 versus 1.5°C/s. It is worth noting that retained austenite is present in a larger quantity in the high carbon materials cooled rapidly, particularly as admixed copper is increased, Figures 2f, h and j. The volume fractions of the various phases are presented in Figure 3. To obtain these curves, the volume fraction of martensite was evaluated by image analysis and each result corrected for the amount of retained austenite determined by X-ray analysis. This correction was required because the amount of retained austenite measured by image analysis was significantly lower than the value obtained by X-ray analysis. It is worth noting that such difference has also been observed with wrought steels [5]. No significant amount of martensite or retained austenite was measured in specimens cooled at 0.4°C/s in copper free alloys and at 0.33%C with 1 or 2% Cu. In alloys containing copper, the martensite content increases with the carbon content and the rate of increase is larger for the material containing 2% copper. The opposite relationship is observed for the pearlite/bainite phases. It is worth noting that within the carbon and copper concentrations used in this study, the highest martensite content for the 0.4°C/s cooling rate is about 55%. The proportion of retained austenite increases linearly with the carbon content and also with the copper concentration. The same trends are observed at a cooling rate of 1.5°C/s but a larger amount of retained austenite is produced for the same carbon and copper concentrations. On the other hand, the quantity of martensite sharply increases with the carbon and copper concentrations but a maximum is reached at about 0.55% C for copper additions of 1 or 2% and at 0.7%C for the copper free alloys. The maximum martensite proportion is observed for the 0.55%C/1%Cu alloy with a value of 91%. Higher carbon, >0.70%, and copper concentrations favor retained austenite and reduce the amount of martensite at a cooling rate of 1.5°C/s.

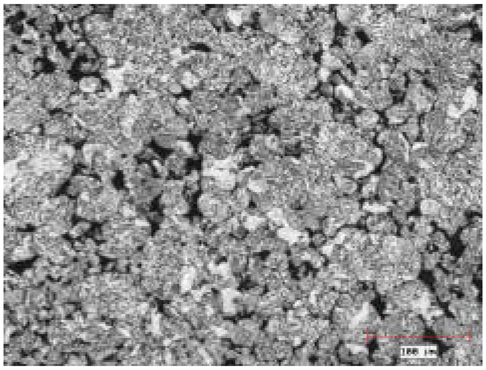


a) 0.4°C/s **b) 1.5°C/s**

Figure 1. Effect of Combined Carbon and Copper Concentrations on Apparent Hardness of Specimens Cooled at a) 0.4°C/s and b) 1.5°C/s in the Temperature Range of 650 to 400°C (Specimens Pressed to a Green Density of 6.9 g/cm³).

The effect of the amount of martensite on the apparent hardness of the test specimens is illustrated in Figure 4. The apparent hardness increases linearly with the amount of martensite for a given carbon concentration. It is worth mentioning that the large scattering of the data observed at 0% martensite is related to the different types of structure generated during cooling. In martensite free alloys, the microstructure of the specimens varied from coarse to fine pearlite and mixtures of fine pearlite and bainite with significant differences in phase hardness. Indeed, coarse pearlite may show hardness values in the order of 10-20 HRC while fine pearlite and bainite are more likely in the 40-60 HRC range [6]. Also, for a given amount of martensite, higher combined carbon concentrations result in higher apparent hardness values. As an example, when the carbon content is raised from 0.5 to 0.7%, apparent hardness increases by about 5 to 7 HRC The same behavior is observed with wrought steels with a difference of about 5 HRC between martensitic steels containing 0.5 versus 0.7%C [7].

Tempering at 200°C reduces the apparent hardness of sinter hardened specimens as seen in Figure 1. The difference of hardness before and after tempering is related to the amount of martensite and to the combined carbon in the material. As illustrated in Figure 5, the reduction in apparent hardness after tempering at 200°C varies linearly with the martensite content and with the combined carbon up to 0.7%. When the martensite fraction is less than 20%, the reduction in hardness after tempering is less than 2 HRC. The reduction is increased up to 8 HRC at 85% martensite. It is interesting to note that at 0.92% C, the hardness loss after tempering is inferior to that observed at 0.72% C. This is probably related to a larger precipitation of transition carbide particles during tempering the high carbon alloys which counteracts the softening effect of the tempering [8]. Such precipitation has been observed in these materials using TEM (transmission electron microscopy) [9].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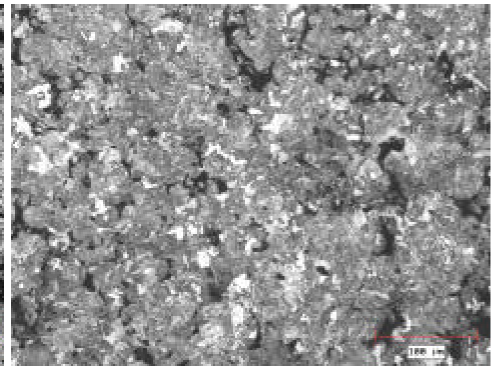
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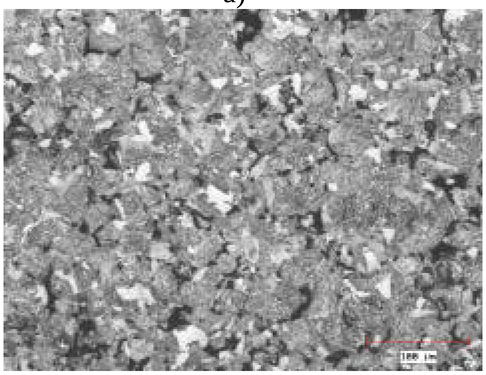
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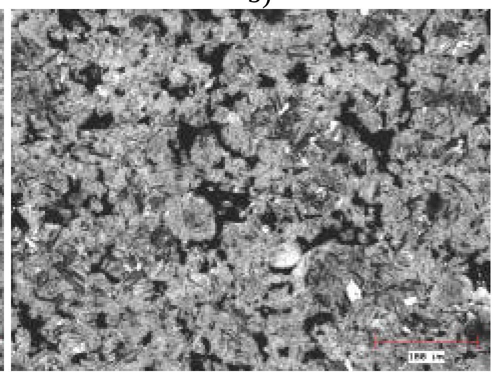
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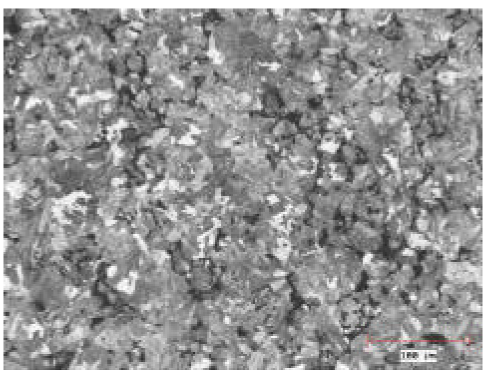
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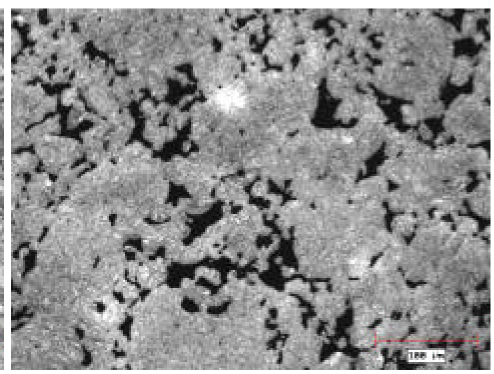
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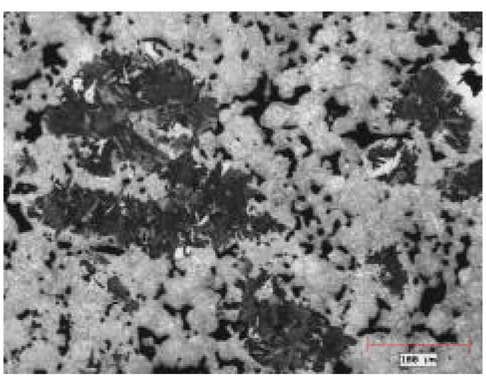
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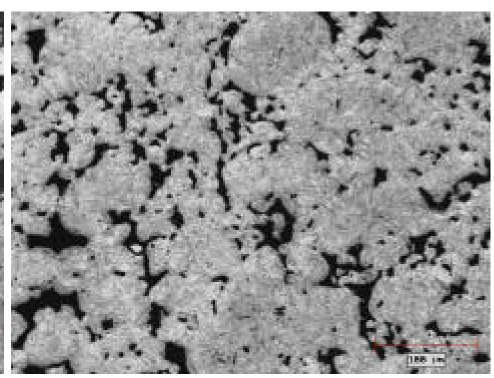
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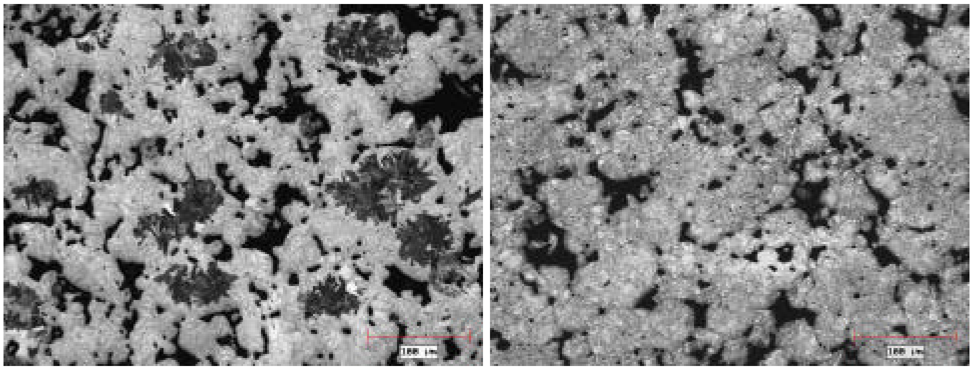
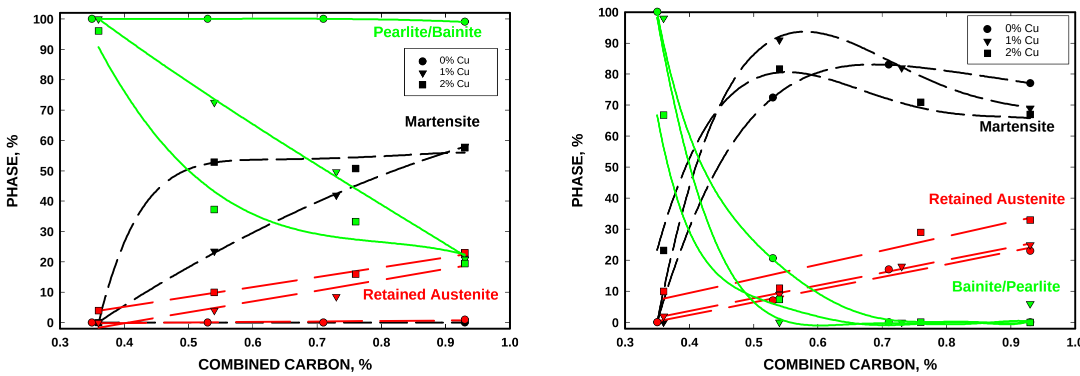


i) j)

Figure 2. Microstructures of As-Sintered Specimens;

a) 0.31% C; 0.4°C/s
b) 0.35%C; 1.5°C/s
c) 0.49%C; 0.4°C/s
d) 0.53%C; 1.5°C/s
e) 0.88%C; 0.4°C/s
f) 0.93%C; 1.5°C/s
g) 0.92%C; 1% Cu; 0.4°C/s
h) 0.92%C; 1% Cu; 1.5°C/s
i) 0.92% C; 2% Cu; 0.4°C/s
j) 0.93% C; 2% Cu; 1.5°C/s



a) 0.4°C/s **b) 1.5°C/s**

Figure 3. Variation of the Relative Amount of Martensite, Retained Austenite and Pearlite/Bainite as a Function of Combined Carbon and Copper Concentrations for Cooling Rates of a) 0.4°C/s and b) 1.5°C/s in the Temperature Range of 650 to 400°C (Specimens Pressed to a Green Density of 6.9 g/cm³).

Figure 6 illustrates the effect of combined carbon and copper concentrations on dimensional change from die size of TRS specimens pressed to 6.9 g/cm³, sintered at 1120°C and cooled at either 0.4 or 1.5°C/s in the temperature range of 650 to 400°C, in the as-sintered condition and after tempering 60 minutes at 200°C. Very similar trends are observed for both cooling rates. At a low combined carbon content of 0.3%, increasing the copper content favors specimen growth. Raising the combined carbon concentration reduces growth for materials containing 2% admixed copper and increases it for materials without copper. Dimensional change of specimens with 1% copper is less sensitive to carbon variations. This is an interesting behavior, since sinter hardened parts cannot be sized after sintering to meet tighter dimensional tolerances. At 0.7% C, the dimensional change of the specimens from die size is similar for the three copper levels. Above 0.7% C, larger growth values are observed with the copper free specimens while lower values are seen with a 2% Cu addition.

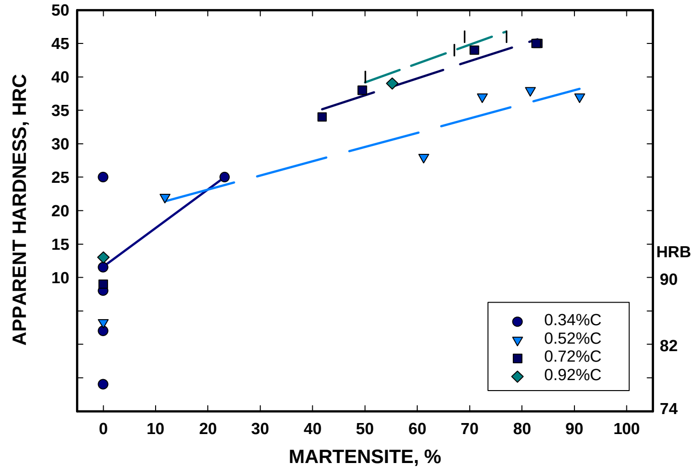


Figure 4. Variation of Apparent Hardness with the Amount of Martensite and Combined Carbon in Sinter Hardened P/M Steels (Specimens Pressed to a Green Density of 6.9 g/cm³).

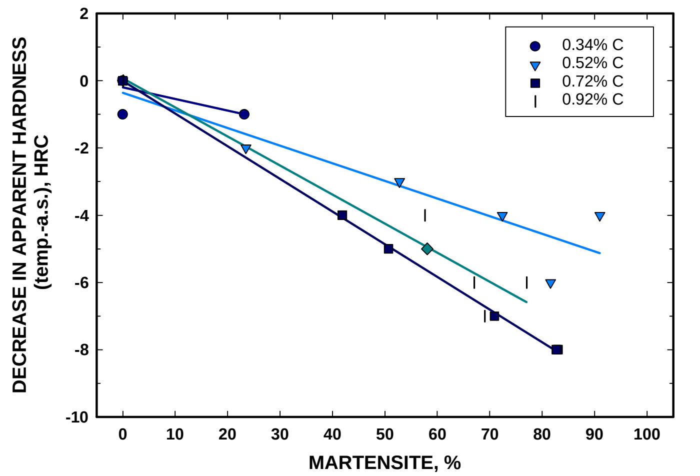
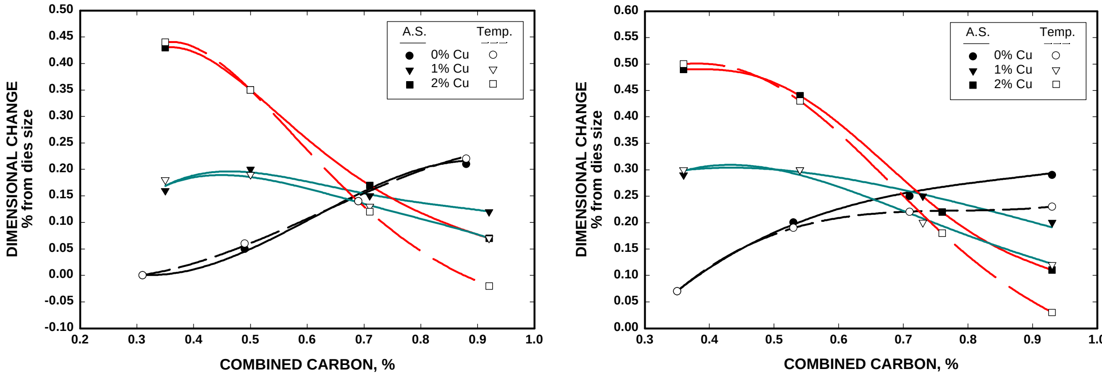


Figure 5. Loss in Apparent Hardness After Tempering at 200°C as a Function of Martensite and Combined Carbon in Sinter Hardened P/M Steels (Specimens Pressed to a Green Density of 6.9 g/cm³).

At low martensite content, the dimensional change of the specimens is not affected by tempering at 200°C. However, as the carbon and copper concentrations in the specimens increase, the formation of martensite is promoted. When the tempering treatment is carried out at 200°C, martensite looses its BCT (body-centered tetragonal) structure due to the precipitation of transition carbides. This is accompanied by a modification of the BCT to a hexagonal structure which accounts for the size change [5]. As illustrated in Figure 7, the relaxation is enlarged with increased martensite content, particularly for carbon concentrations above 0.5% with differences as high as 0.09% between the as-sintered and tempered conditions.



a) 0.4°C/s **b) 1.5°C/s**

Figure 6. Evolution of Dimensional Change from Die Size as a Function of the Combined Carbon and Copper Concentrations for Cooling Rates of a) 0.4°C/s and b) 1.5°C/s in the Temperature Range of 650 to 400°C (Specimens Pressed to a Green Density of 6.9 g/cm³).

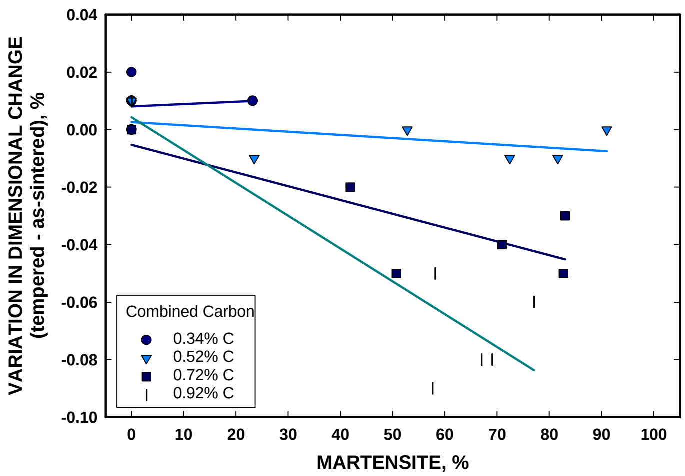
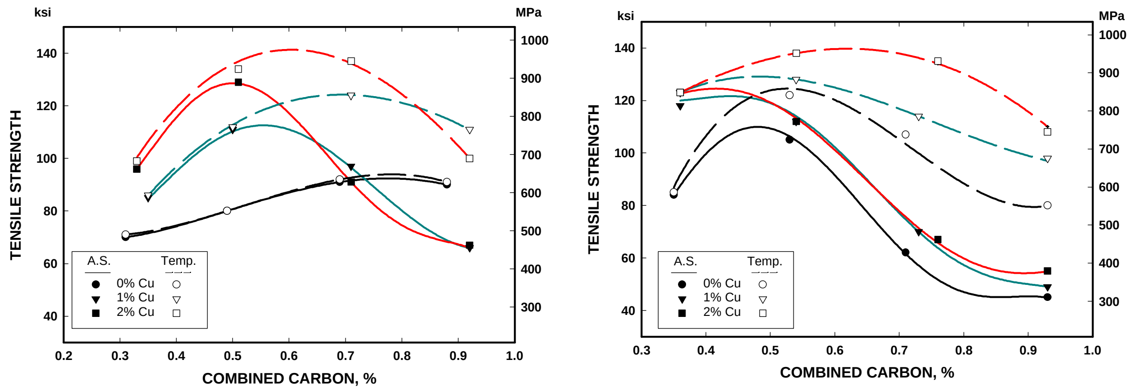


Figure 7. Difference in Dimensional Change Between the As-Sintered and Tempered Conditions of Sinter Hardened Specimens as a Function of the Martensite and Combined Carbon Concentration (Specimens Pressed to a Green Density of 6.9 g/cm³).

Figure 8 illustrates the effect of combined carbon and copper concentrations on tensile strength of specimens pressed to 6.9 g/cm³, sintered at 1120°C and cooled at either 0.4 or 1.5°C/s in the temperature range of 650 to 400°C, in the as-sintered condition and after tempering 60 minutes at 200°C. In the as-sintered condition, the tensile strength reaches a maximum which is shifted to lower carbon concentrations as the copper content and/or the cooling rates are raised. This maximum is obtained at about 0.85% C in the copper free specimens cooled at 0.4°C/s and at about 0.4% C with specimens containing 1 or 2% Cu and cooled at 1.5°C/s. This is probably related the amount of martensite in the test specimens because there was no martensite in the former and about 45 to 55% in the latter as estimated from Figure 3.

The highest tensile strength values are in the range of 850-890 MPa and are reached at 0.5% C and 2% Cu for a cooling rate of 0.4°C/s and at 0.4%C and either 1 or 2% Cu for a cooling rate of 1.5°C/s. It is worth noting that the martensite content in these conditions varies in the range of 45 to 60%. Also, at 1.5°C/s, raising the copper content from 1 to 2 % does not significantly affect the tensile strength for the different concentrations of combined carbon.

Tempering significantly raises tensile strength and slightly shifts the maximum tensile strength values reached for the different copper concentrations and cooling rates to higher combined carbon contents. The highest tensile strength values (925 to 950 MPa) after tempering at 200°C are obtained at 2% copper with a carbon content of about 0.55%.

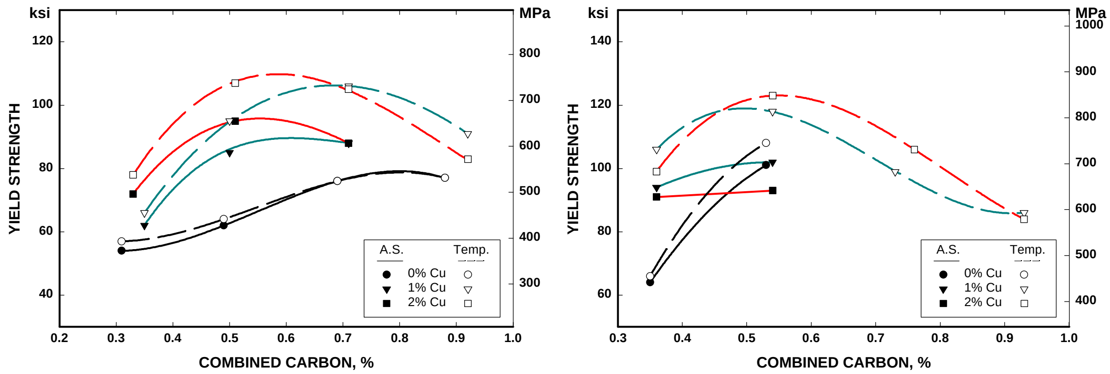


a) 0.4°C/s **b) 1.5°C/s**

Figure 8. Evolution of Tensile Strength as a Function of the Combined Carbon and Copper Concentrations for Cooling rates of a) 0.4°C/s and b) 1.5°C/s in the Temperature Range of 650 to 400°C (Specimens Pressed to a Green Density of 6.9 g/cm³).

Figure 9 illustrates the effect of combined carbon and copper concentrations on the yield strength of specimens pressed to 6.9 g/cm³, sintered at 1120°C and cooled at either 0.4 or 1.5°C/s in the temperature range of 650 to 400°C, in the as-sintered condition and after tempering 60 minutes at 200°C. In the as-sintered condition, no yield has been measured for specimens containing 0.9% C and either 1 or 2% Cu cooled at a rate of 0.4°C/s and for specimens containing more than 0.55% C for the three copper levels, cooled at a rate of 1.5°C/s. As for the tensile strength, the yield strength reaches maximum values towards lower carbon content as the copper concentration and/or the cooling rates are raised. It is worth noting, that for the fast cooling rate, raising the copper content from 1 to 2% and the combined carbon from 0.35 to 0.55% do not significantly affect the yield strength as also observed for the tensile strength.

Tempering at 200°C significantly improves yield strength when martensite is present. Also, with the exception of materials containing 0.75 and 0.9% C without copper addition for the fast cooling rate condition, yield points are observed for materials with the different concentrations of copper and carbon. The maximum yield strength values are reached towards the lower combined carbon content as the copper concentration and/or the cooling rates are raised. The highest yield strength values are reached with a cooling rate of 1.5°C/s with a combined carbon of about 0.55% with either 1 or 2% Cu with values ranging from 815 to 850 MPa.



a) 0.4°C/s **b) 1.5°C/s**

Figure 9. Evolution of Yield Strength as a Function of the Combined Carbon and Copper Concentrations for Cooling Rates of 0.4 and 1.5°C/s in the Temperature Range of 650 to 400°C (Specimens Pressed to a Green Density of 6.9 g/cm³).

CONCLUSIONS

1. The largest amount of martensite, 91%, was obtained with specimens containing 0.55% C and 1% Cu cooled at a rate of 1.5°C/s in the range of 650 to 400°C. Higher combined carbon and copper concentrations favor the formation of retained austenite while a slower cooling rate and lower combined carbon promote a pearlitic and/or bainitic microstructure.

2. Apparent hardness increases linearly with the martensite content and the combined carbon concentration. Apparent hardness levels off at about 0.7% C for the specimens cooled at 1.5°C/s with a maximum apparent hardness of 46 HRC at 6.9 g/cm³. Further increases of the combined carbon and/or copper concentrations did not affect hardness due to the reduction in martensite content caused by the increase of retained austenite.

3. Retained austenite increases linearly with the combined carbon and a larger amount is observed with copper additions and faster cooling rates. Values up to 33% were reached in specimens containing 0.93% C and 2% Cu, cooled at 1.5°C/s.

4. The difference in apparent hardness before and after tempering at 200°C increases linearly with the martensite fraction. The largest difference in hardness before and after tempering, 8 HRC, was observed at 0.7% C and a martensite proportion of 83%.

5. Raising the carbon content favors growth in copper free specimens while reducing it in specimens containing 2% Cu. At 1% Cu, the sinter hardened P/M steel shows a more stable dimensional change with variations of carbon content. This is an interesting feature to maintain good dimensional tolerances in sinter hardened parts.

6. In specimens with low martensite content, the dimensional change was not affected by tempering at 200°C. However, as the martensite content exceeds 20%, the difference in the dimensions before and after tempering increases linearly with the proportion of martensite due to the change in crystal lattice from BCT martensite to hexagonal tempered martensite. Larger differences were observed at higher combined carbon concentrations.

7. The maximum tensile values achieved at 0, 1 and 2% Cu are shifted to lower carbon concentrations as the cooling rate increases due to the formation of a larger proportion of martensite. In the as-sintered condition, this maximum was reached at a combined carbon of about 0.85% C in martensite free

specimens without copper and at 0.4% C with 1 or 2% Cu at levels of 45 to 50% martensite. Similar trends were observed after tempering at 200°C but the maximum tensile strength values are slightly shifted to higher combined carbon concentrations.

8. The highest tensile strength was reached at 0.55% C and 2% Cu for cooling rates of either 0.4 or 1.5°C/s with values in the range of 925 to 950 MPa. For yield strength, the highest values were also reached at 0.55% C but with either 1 or 2% Cu and a cooling rate of 1.5°C/s with values ranging from 815 to 850 MPa.

ACKNOWLEDGMENTS

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