OPTIMIZING PROPERTIES OF P/M PARTS THROUGH SELECTION OF PROPER SINTER HARDENING POWDER GRADES

François Chagnon and Yves Trudel

Quebec Metal Powders Limited

ABSTRACT

Sinter hardening is a cost effective process to manufacture P/M parts exhibiting high strength and apparent hardness at lower cost than conventional heat treatment. This process is particularly attractive for parts that are difficult to quench due to their size and shape. Indeed, during the sinter hardening process, the transformation to martensite takes place during the cooling phase of the sintering cycle, thus reducing thermal stresses as compared to oil quenching.

Many powder grades have been developed for sinter hardening applications. Depending on their alloy formulation, these grades offer a wide range of compressibility and response to hardening. The objective of this paper is to discuss the effect of alloy composition on compaction behavior and response to hardening of different powder grades in order to facilitate the selection of materials, mix formulations and processing conditions to optimize the properties of sinter hardened P/M parts.

INTRODUCTION

Sinter hardening is 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. As shown in Figure 1, 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, 2]. 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. On the other hand, pre-alloying generally reduces powder compressibility due to the strengthening of the ferrite by the alloying elements. Therefore in applications where density is a key parameter, it could be preferable to select powder grades with lower hardenability but showing higher compressibility and admix elemental

1

constituents. Graphite is always added in powder mixes because carbon is the element that has the most pronounced effect on hardness of hardened materials. Some other elements such as copper and nickel can also be admixed to the base powders to further improve hardenability. However, for sintering temperatures of 1115 to 1150°C generally used with mesh belt sintering furnaces, nickel will not dissolve uniformly in the iron matrix and Ni-rich heterogeneous phases will be present in the sintered parts. These areas could result in low hardness regions.

Dimensional control is another important issue with sinter hardened parts even if better tolerances can be achieved compared to the quenched and tempered process because of the low thermal stresses involved in sinter hardening. In many P/M applications, a sizing operation can be added to correct the dimensions of P/M parts to meet tight tolerances. With sinter hardened parts, sizing is not possible because of high apparent hardness reached after sintering. Therefore, mix formulations and processing conditions must be selected to minimize dimensional variations during the sintering operation.
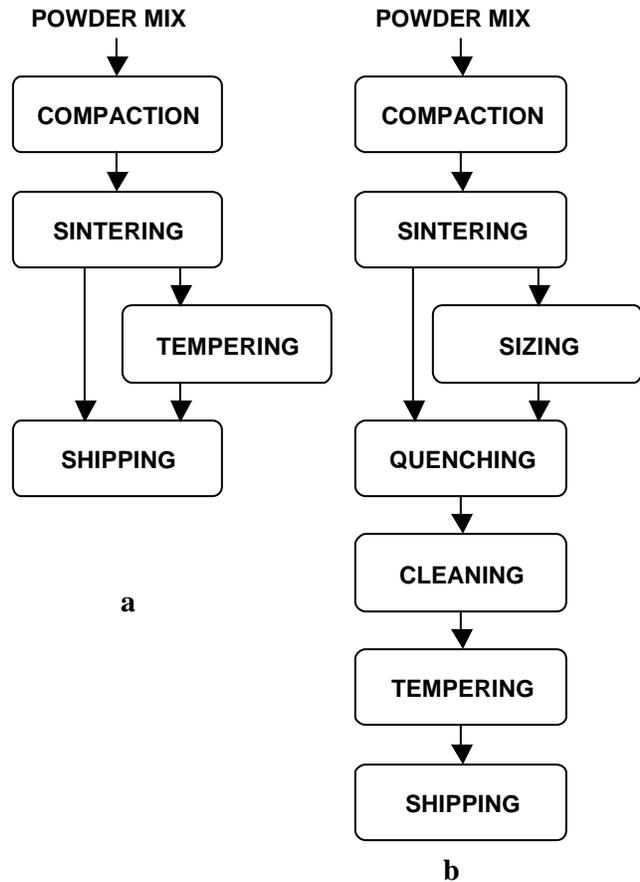
Figure 1. Comparison of the sinter hardening and quench and temper process.
a) **Sinter hardening process.**
b) **Quench and temper process.**

The objective of this study is to review the impact of alloy composition on compaction and response to sinter hardening of different powder grades used in sinter hardening applications. The impact of mix formulation and processing conditions on sinter hardened properties of P/M parts will be also discussed.

EXPERIMENTAL PROCEDURE

Four different powder grades that exhibit sinter hardening behavior were selected for this study. Their typical chemical compositions are given in Table 1. Powder compressibility was determined with mixes containing 0.5% EBS wax. Sintered properties were evaluated with dog bone specimens pressed from mixes containing various amounts of graphite, copper and nickel. Specimens were pressed to reach green densities ranging from 6.7 to 7.1 g/cm³. These were sintered 25 minutes at 1135°C in mesh belt furnaces under a 90% nitrogen/10% hydrogen atmosphere with post-sintering cooling rates of 0.6 and 1.5°C/s in a temperature range of 650 to 400°C. Sintered properties were determined in the as-sintered condition and after tempering 60 minutes at 200°C in air. The microstructure was characterized by optical microscopy.

Table 1.
Chemical composition of the four powder grades.

Identification	Grade	Mn, %	Ni, %	Mo, %	Cr, %
A	ATOMET 4901	0.15	-	1.50	-
B	ATOMET 4601	0.20	1.80	0.55	0.05
C	ATOMET 4701	0.45	0.90	1.00	0.45
D	ATOMET 4801	0.20	4.00	0.50	-

RESULTS AND DISCUSSION

Properties of sinter hardened parts are influenced by both the sintered density and the final microstructure. The selection of the base powder grade is of prime importance in designing new applications because it will affect these two characteristics.

Effect of density

Figure 2 illustrates the compressibility curves of the four base powders admixed with 0.5% EBS wax. Powder A exhibits the best compressibility while powder B is slightly more compressible than powder C and finally, powder D is the least compressible of the four powders. At a compacting pressure of 620 MPa (about 45 tsi), green densities of 7.05, 6.98, 6.95 and 6.88 g/cm³ are reached with powders A, B, C and D, respectively.

Figure 3 illustrates the effect of sintered density on the apparent hardness of specimens pressed from the various powders, containing 1% Cu and 0.9% combined carbon, cooled at 1.5°C/s in the temperature range of 650 to 400°C and tempered 60 minutes at 200°C. The four materials behave similarly. Indeed, apparent hardness increases linearly with density. Each increment of 0.1 g/cm³ results in an increase of about 2 HRC. It is worth mentioning that, as shown in Figure 4, the four materials also exhibit a very similar
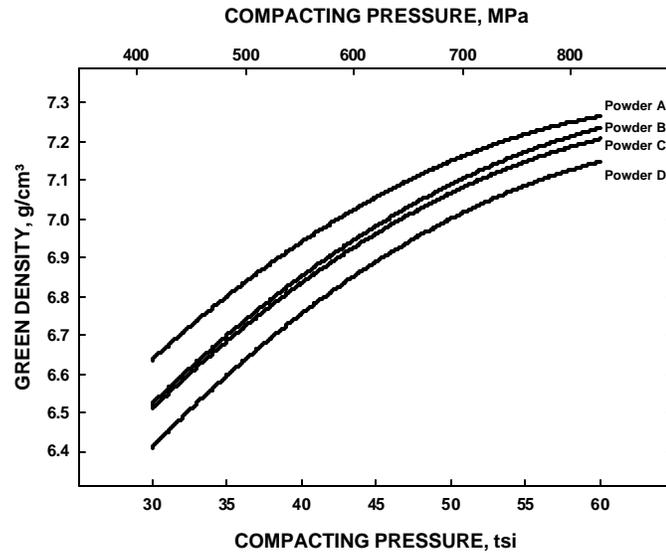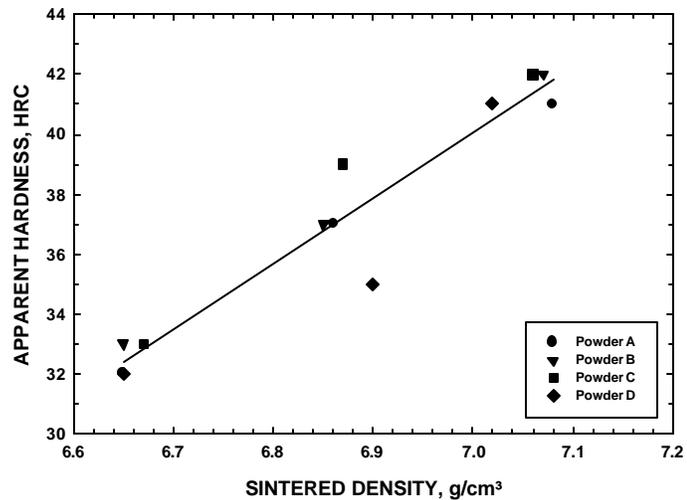

Figure 2. Compressibility of the four powders.

Figure 3. Effect of sintered density on apparent hardness of sinter hardened materials (1%Cu/0.9%C; cooled at 1.5°C/s and tempered at 200°C).

3

microstructure, which is almost fully martensitic with very few areas of bainite in material A. Powder A is in fact the powder exhibiting the lowest hardenability of the four powders evaluated.
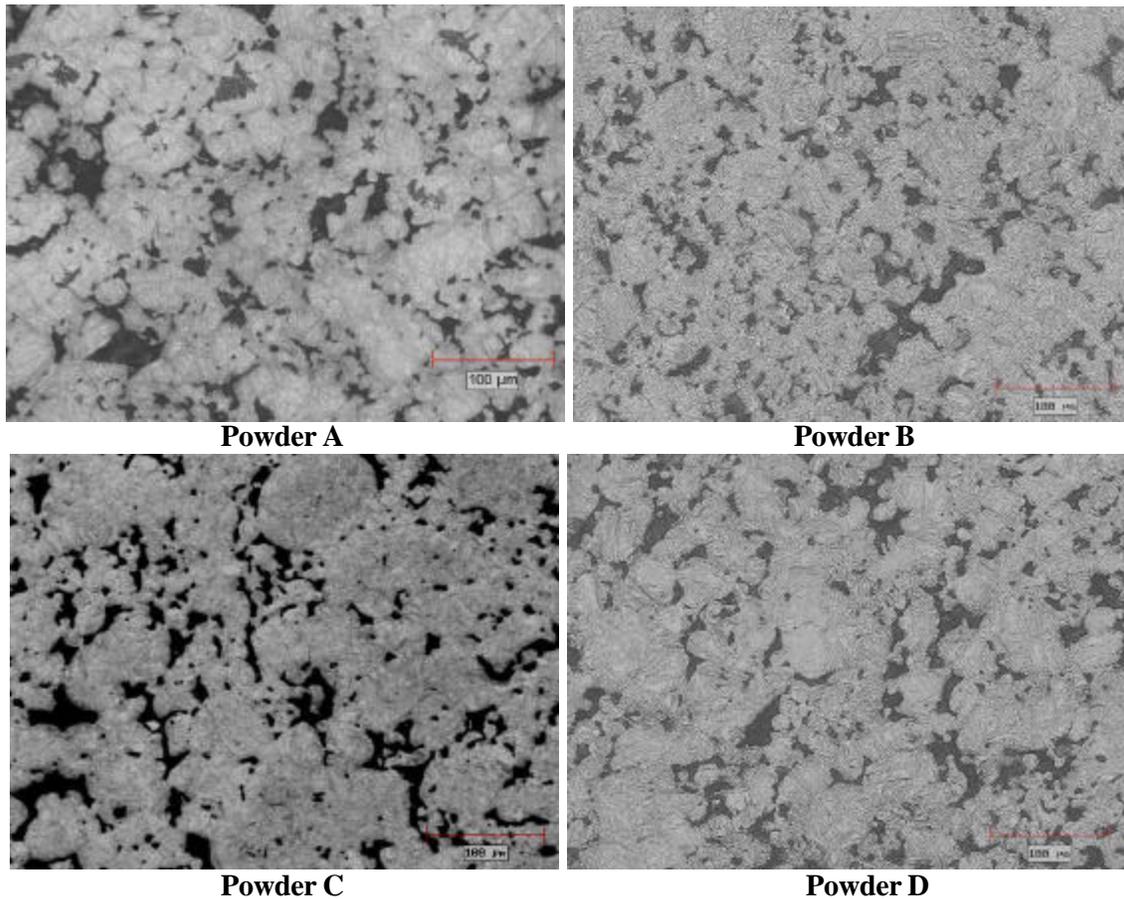

Figure 4. Microstructure of specimens prepared from the various powders (1%Cu-0.9%C, cooled at 1.5°C/s).

Figure 5 illustrates the effect of density on ultimate tensile strength (UTS) of sinter hardened (specimens containing 1% Cu and 0.9% combined carbon) cooled at 1.5°C/s from 650 to 400°C and tempered 60 minutes at 200°C. As for apparent hardness, UTS increases linearly with density. A gain of 3.3 ksi is observed for each 0.1 g/cm³ increment of density. A value of about 650 MPa (about 95 ksi) can be reached at a density of 6.90 g/cm³.

Therefore, from these results it can be concluded that for similar copper and carbon contents, if sinter hardened materials show similar microstructure and density, they would also exhibit similar apparent hardness and tensile strength. These observations are of prime importance in the design of new P/M components produced via the sinter hardening route because it serves to select a more compressible powder if higher densities are required. However, one must bear in mind that the cooling rate after sintering should be adjusted to achieve the adequate microstructure. In the case of parts with thick section sizes produced with a less hardenable powder a faster cooling rate will be required to achieve a thorough martensitic structure compared to those produced with more hardenable materials. This will be discussed further in the next section.

Effect of material composition

The hardenability of P/M materials can be modified by changing the alloy content in the melt and/or by adding different amount of graphite and/or other admixed elements to the ferrous powders. This is well illustrated in Figure 6. On this figure, the impact of hardenability can be visualized by measuring the apparent hardness of specimens pressed from the various powders, containing either 1 or 2% copper and about 0.5% C. The specimens were sintered at 1135°C and cooled at 1.5°C/s in the range of 650 to 400°C. Apparent hardness was measured after tempering 60 minutes at 200°C. Sintered density was similar for the various materials at about 6.83 g/cm³. Apparent hardness of specimens pressed from powders C and D is in the range of 30 to 33 HRC for both levels of copper. However, for powder B and even more for powder A, the apparent hardness increases when the concentration of admixed copper is raised from 1 to 2%. Indeed, when the copper content is increased from 1 to 2%, the apparent hardness increases respectively from 20 to 26 HRC with powder A and from 25 to 27 HRC for powder B. For powders C and D, the apparent hardness remains unchanged or is even slightly reduced when the copper concentration is raised from 1 to 2%. One possible explanation of such results could be that if a fully martensitic structure is reached at 1% Cu, a further increase to 2% would favor production of retained austenite, which has lower hardness than

Figure 5. Effect of sintered density on tensile strength of sinter hardened materials (1%Cu/0.9%C cooled at 1.5°C/s and tempered at 200°C).

Figure 6. Effect of copper content on apparent hardness of sinter hardened materials (0.5%C cooled at 1.5°C/s and tempered at 200°C).

martensite. As shown in Figure 7, the microstructure of the specimen pressed with powder A and admixed with 1% Cu has about 50% martensite and 50% bainite. When the copper concentration is increased from 1 to 2%, the amount of martensite increases up to about 70% but there is still about 30% bainite in the specimen. For powder B, the microstructure is fully martensitic at 2% Cu. For specimens pressed with powder C, the microstructure is almost fully martensitic at 1% Cu. Finally, for powder D, the microstructure is fully martensitic for both copper contents. Therefore, it is possible that a larger amount of retained austenite is present at 2% Cu, resulting in a slight decrease of apparent hardness. It is interesting to note that for similar microstructure, apparent hardness values are not significantly affected by the copper content at this level of combined carbon.
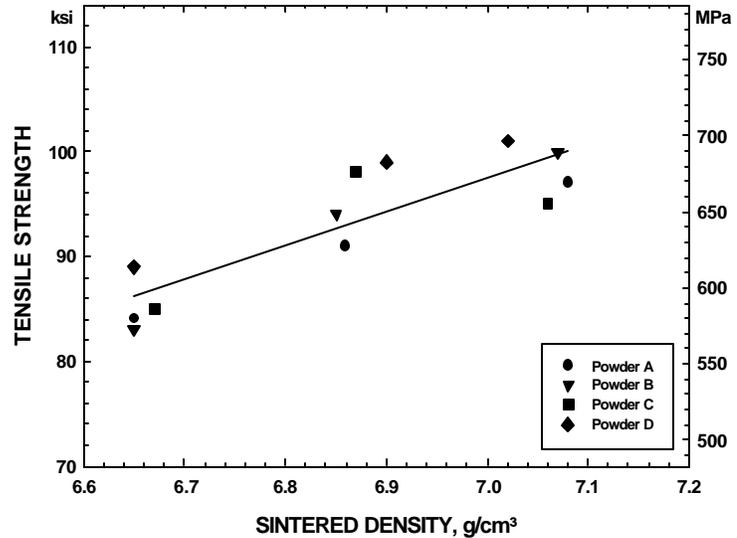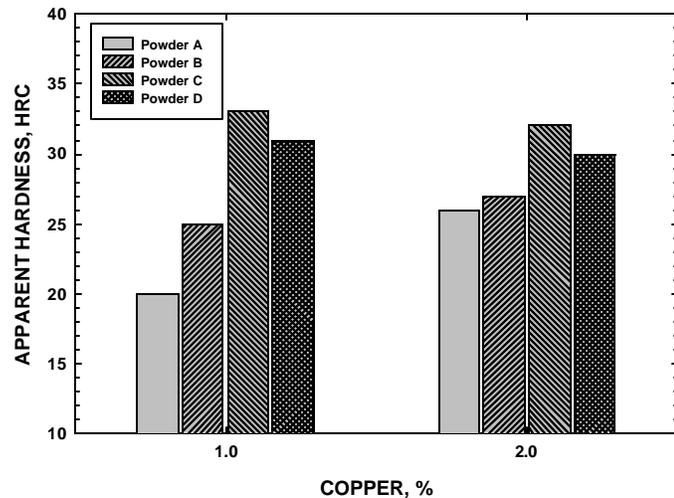
<p align="center">Powder A-1%Cu   Powder A-2%Cu</p>
<p align="center">Powder B-2%Cu   Powder C-1%Cu</p>
<p align="center">Powder D-1%Cu   Powder D-2%Cu</p>
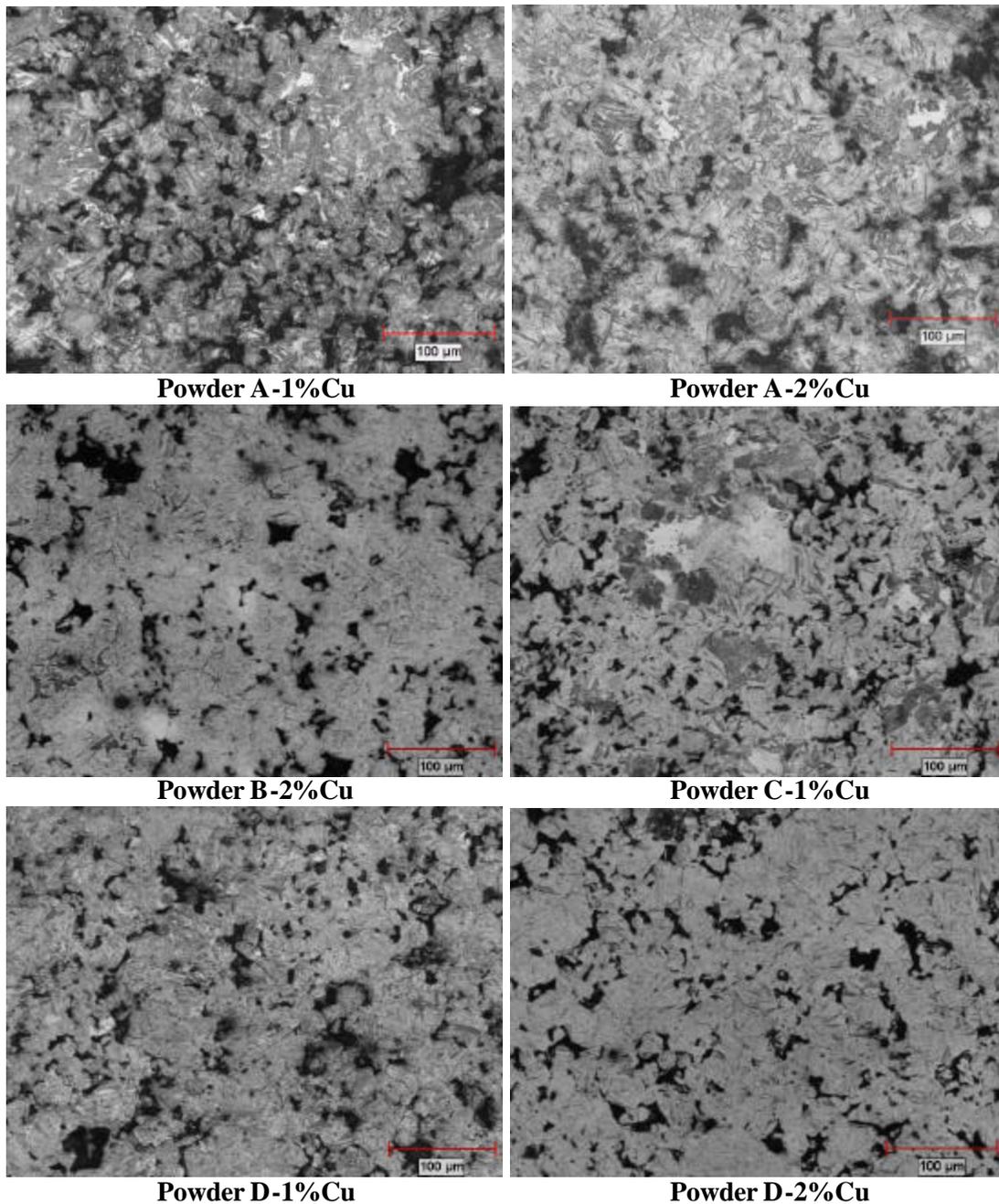
Figure 7. Microstructure of materials containing 1 or 2% copper and 0.5% combined carbon, sintered at 1135°C and cooled at 1.5°C/s.

Figure 8 illustrates the effect of admixed copper concentration at a combined carbon of 0.5% on tensile strength of specimens pressed from the various powders sintered at 1135°C, cooled at 1.5°C/s in the range of 650 to 400°C and tempered 60 minutes at 200°C. Raising the copper content from 1 to 2% improves tensile strength for the four materials but the effect is significantly more important with powder A with a gain of 30%, from 580 MPa (84 ksi) to 760 MPa (110 ksi). The latter UTS value is nevertheless lower than those achieved with the three other materials because there is less martensite.

<p align="center">6</p>

Nickel is another element that can be admixed to steel powders to increase apparent hardness and sintered strength of P/M materials. Figure 9 illustrates the effect of admixing 4% nickel on the apparent hardness of specimens pressed with powder A and containing either 1 or 2% copper and 0.7% combined carbon, sintered at 1135°C and cooled at 1.5°C/s in the range of 650 to 400°C. Results are compared to those achieved with powder D, which contains 4% pre-alloyed nickel. It should be noted that the molybdenum concentration differs in the two powders; 1.5% in powder A and 0.5% in powder D. For powder A, the addition of 4% admixed nickel slightly increases apparent hardness by about 3 HRC from 28 to 31 HRC

Figure 8. Effect of copper content on tensile strength of sinter hardened materials (0.5%C cooled at 1.5°C/s and tempered at 200°C).

for a 1% copper addition. However, at 2% copper, in the alloy containing no admixed nickel, apparent hardness increases from 28 to 34 HRC, while it increases only by 1 HRC, from 28 to 29 HRC for a 4% admixed nickel addition. Figure 10 illustrates the effect of admixing 4% Ni on the UTS of specimens pressed with powder A, containing 0.7% combined carbon and either 1 or 2% copper, after sintering at 1135°C and cooled at 1.5°C/s. Again results are compared to those achieved with powder D, containing 4% pre-alloyed nickel. The addition of 4% Ni does not significantly affect UTS at either 1 or 2% Cu with values in the range of 595 to 655 MPa (86 to 95 ksi). However, raising copper content from 1 to 2% increases UTS of Ni free material from 655 to 980 MPa (86 to 142 ksi). It is also worth noting that for material D, as for apparent hardness, raising copper content from 1 to 2% slightly lowers UTS from 805 to 750 MPa (117 to 109 ksi). From these results, it appears that admixing 4% Ni is not very effective to improve both apparent hardness and sintered strength of sinter hardened materials cooled at 1.5°C/s. One reason for such a poor improvement is the modification of the microstructure.
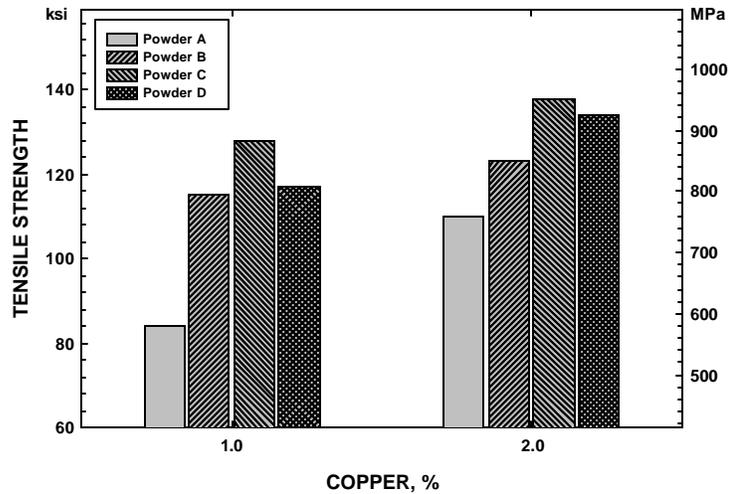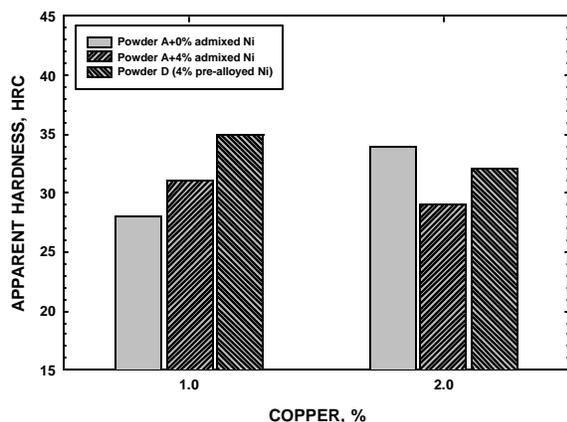
Figure 9. Effect of admixing Ni on apparent hardness of sinter hardened materials containing either 1 or 2% Cu and 0.7%C (cooled at 1.5°C/s and tempered at 200°C, 6.85 g/cm³).
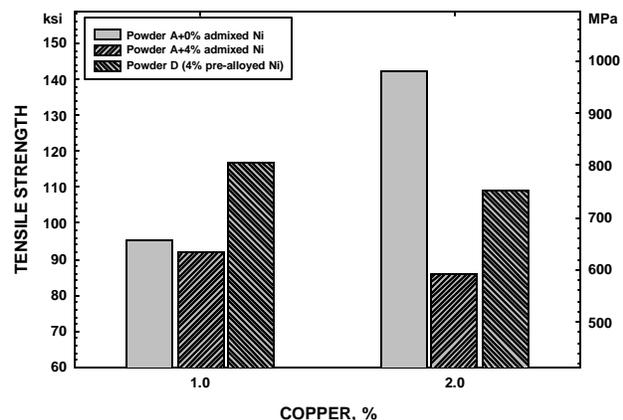
Figure 10. Effect of admixing Ni on tensile strength of sinter hardened materials containing either 1 or 2% Cu and 0.7%C (cooled at 1.5°C/s and tempered at 200°C, 6.85 g/cm³).

7

Figure 11 illustrates the microstructure of specimens pressed with powder A and containing either 0 or 4% admixed nickel and powder D containing 4% pre-alloyed Ni, with 0.7% C and 1 or 2% Cu. For powder A without admixed nickel, the microstructure is changing from an almost fully bainitic structure at 1% Cu to a 50/50 martensitic/bainitic structure at 2% Cu. When 4% Ni is admixed to the mix containing 1% Cu, the amount of bainite significantly decreases to the benefit of martensite. Ni-rich phases, the white areas, are also visible, indicating an incomplete diffusion of this element. When the copper content is raised to 2%, bainite completely disappears but the amount of white phases increases, indicating that in addition to Ni-rich phases, there is probably also a larger amount of retained austenite. Finally, with powder D, containing 4% pre-alloyed nickel, the microstructure is mainly martensitic with some retained austenite at a 1% Cu addition. At 2% Cu, the structure remains martensitic but with a larger quantity of retained austenite. The increase in retained austenite may account for the slight decrease in both apparent hardness and tensile strength.

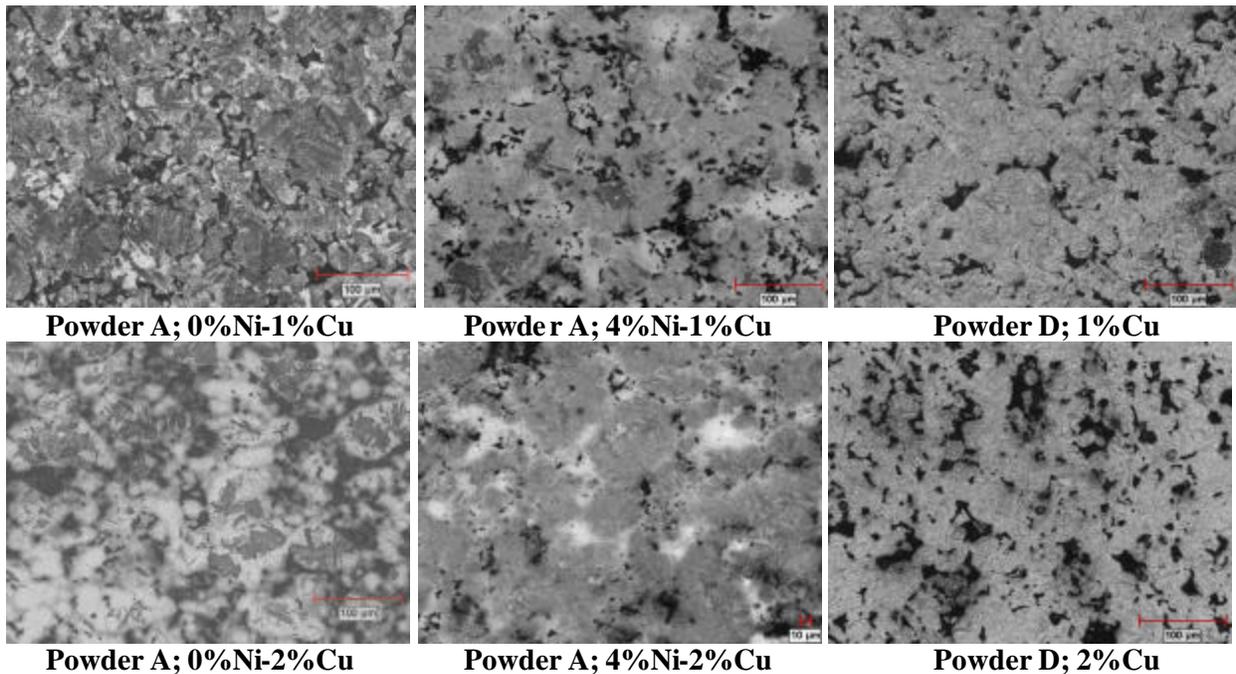| Powder A; 0%Ni-1%Cu | Powder A; 4%Ni-1%Cu | Powder D; 1%Cu |
| Powder A; 0%Ni-2%Cu | Powder A; 4%Ni-2%Cu | Powder D; 2%Cu |

Figure 11. Microstructure of specimens pressed with powder A and containing either 0 or 4% admixed Ni and from powder D containing 4% pre-alloyed Ni (1 or 2% Cu and 0.7%C, cooled at 1.5°C/s).

Effect of cooling rate

As mentioned previously, materials exhibiting lower hardenability must be cooled faster than those with higher hardenability in order to achieve adequate apparent hardness and strength. This is shown in Figure 12, which illustrates the effect of cooling rate in the range of 650 to 400°C on the apparent hardness of specimens pressed from the four powders to a density of 6.9 g/cm³, sintered at 1135°C and tempered 60 minutes at 200°C. The different materials contain 0.7% combined carbon and 2% Cu. Powders C and D exhibit apparent hardness values above 30 HRC for both cooling rates. On the other hand, materials from powder A and B must be cooled at a faster rate to attain 30 HRC. Consequently, parts made with powder C and D will be less sensitive to a variation of the cooling rate of the sintering furnace and therefore would improve the process robustness.

Figure 13 illustrates the effect of cooling rate in the range of 650 to 400°C on UTS of specimens pressed from the four powders containing 0.7% combined carbon and 2% Cu. For powder A and B, UTS increases when the cooling rate is raised from 0.6 to 1.5°C/s, while it remains unchanged for powder C and slightly decreases with powder D. For powders A and B, the gain in UTS can be related to an augmentation of martensite in sintered specimens cooled at a faster rate. For powder C, an increase of the cooling rate did not affect the microstructure, which remained almost fully martensitic. Finally, the reduction of UTS observed with powder D when the cooling rate is increased from 0.6 to 1.5°C/s could be related to a larger amount of retained austenite in this alloy containing 4% pre-alloyed nickel.
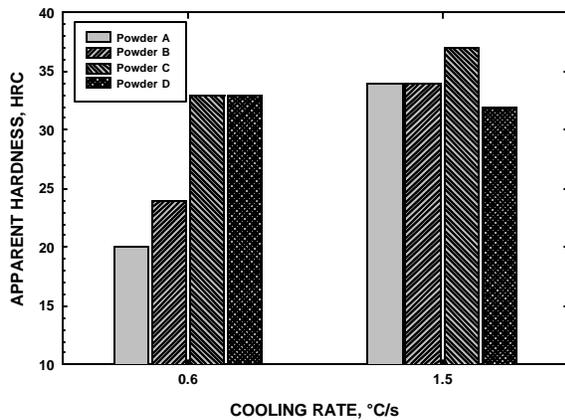

Figure 12. **Effect of cooling rate from 650 to 400°C on apparent hardness of sinter hardened materials (0.70%C-2%Cu; tempered at 200°C).**
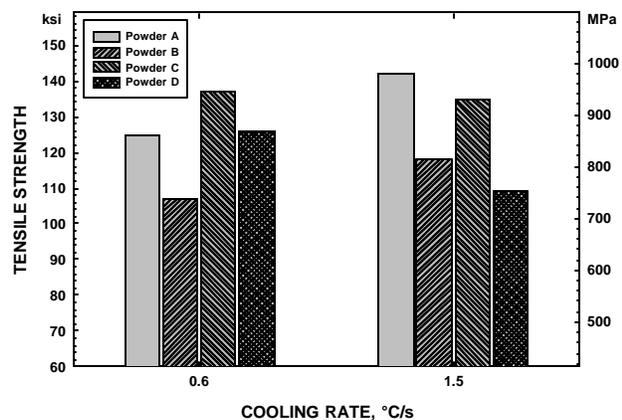
Figure 13. **Effect of cooling rate in the range of 650 to 400°C on ultimate tensile strength of sinter hardened materials (0.7%C-2%Cu; tempered at 200°C).**

Effect of tempering

Tempering is generally used to restore the mechanical properties of sinter hardened materials [3, 4]. However, tempered martensite shows lower hardness than un-tempered martensite. This is well illustrated in Figures 14 and 15, which show the effect of tempering temperature on apparent hardness and tensile strength of specimens pressed from powder C and containing 2% Cu and either 0.65 or 0.8% C, cooled at 0.6°C/s from 650 to 400°C. The highest apparent hardness is observed in the as-sintered condition with the highest carbon content. For both carbon contents, apparent hardness decreases with higher tempering temperatures to reach a minimum at about 300-400°C and then increases again to reach a secondary hardening peak at about 500°C and finally sharply drops for further increase of the tempering temperature. Secondary hardening is observed in steels containing carbide promoter elements such as molybdenum. These carbides are known to be resistant to coarsening and prevent the softening of the matrix [5]. For tensile strength, the best results are observed at the lower carbon content. However for both carbon contents, tensile strength is significantly improved by raising the tempering temperature to reach a maximum at about 200°C and then decreases with further increase of the tempering temperature.

Therefore, in the design of a new sinter hardened component, if apparent hardness is the only key parameter, tempering could be omitted and the combined carbon raised to maximize this property. However, if high UTS values are required, tempering at 200°C is recommended to maximize mechanical properties. Also, the combined carbon should be lowered to about 0.6% for a further gain in UTS. On the other hand, if both apparent hardness and sintered strength are required, the combined carbon and the tempering conditions could be selected to optimize these properties.
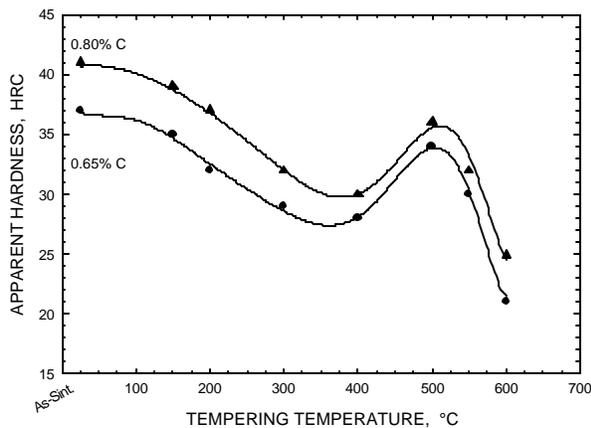
Figure 14. Effect of tempering temperature on apparent hardness of specimens pressed from powder C with 2% Cu and various amounts of combined carbon [4] (7.0g/cm³, 0.6°C/s in the range of 650 to 400°C).
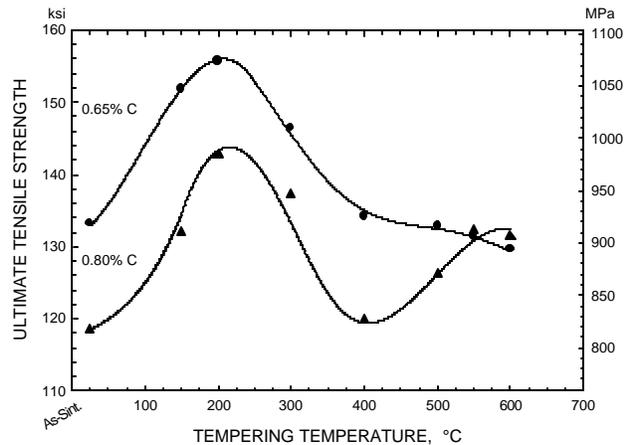

Figure 15. Effect of tempering temperature on tensile strength of s pecimens pressed from powder C with 2% Cu and various amounts of combined carbon [4] (7.0g/cm³, 0.6°C/s in the range of 650 to 400°C).

Dimensional control

Sinter hardened parts cannot be sized after sintering due to their high hardness. Therefore, good control of dimensional change during sintering is required to reduce size variation. In addition to good control of powder production parameters, dimensional control can be improved by proper selection of the mix formulation. Indeed, as illustrated in Figure 16, the four powders behave similarly to a change in carbon and copper concentrations. In the copper free materials, dimensional change increases with the carbon content. At 1% Cu, dimensional change is less sensitive to carbon content variations while at 2% Cu, a slight variation of the combined carbon in the range of 0.6 to 0.9% has a significant impact on dimensional change. These results can be explained by different diffusion mechanisms occurring during sintering when carbon and copper are present [6, 7]. These are of interest since it can allow the selection of base powders and mix formulation that could minimize dimensional variation during sintering. Indeed, formulations with 1% Cu are recommended to better control size change variation. However, the base powder must also be carefully selected to achieve adequate microstructure after sintering. Because of the slightly lower hardenability, resulting from the reduction of copper content from 2 to 1%, less hardenable powders will require a faster cooling rate to achieve a martensitic structure after sintering.

Finally, it is interesting to note that the tempering treatment causes shrinkage, particularly when a larger amount of martensite is produced, i.e. with higher combined carbon and copper contents and with more hardenable powders. This is in fact related to a change in the lattice structure, from BCT (body-centered tetragonal) to hexagonal, when the specimens are tempered at 200°C[5, 8].
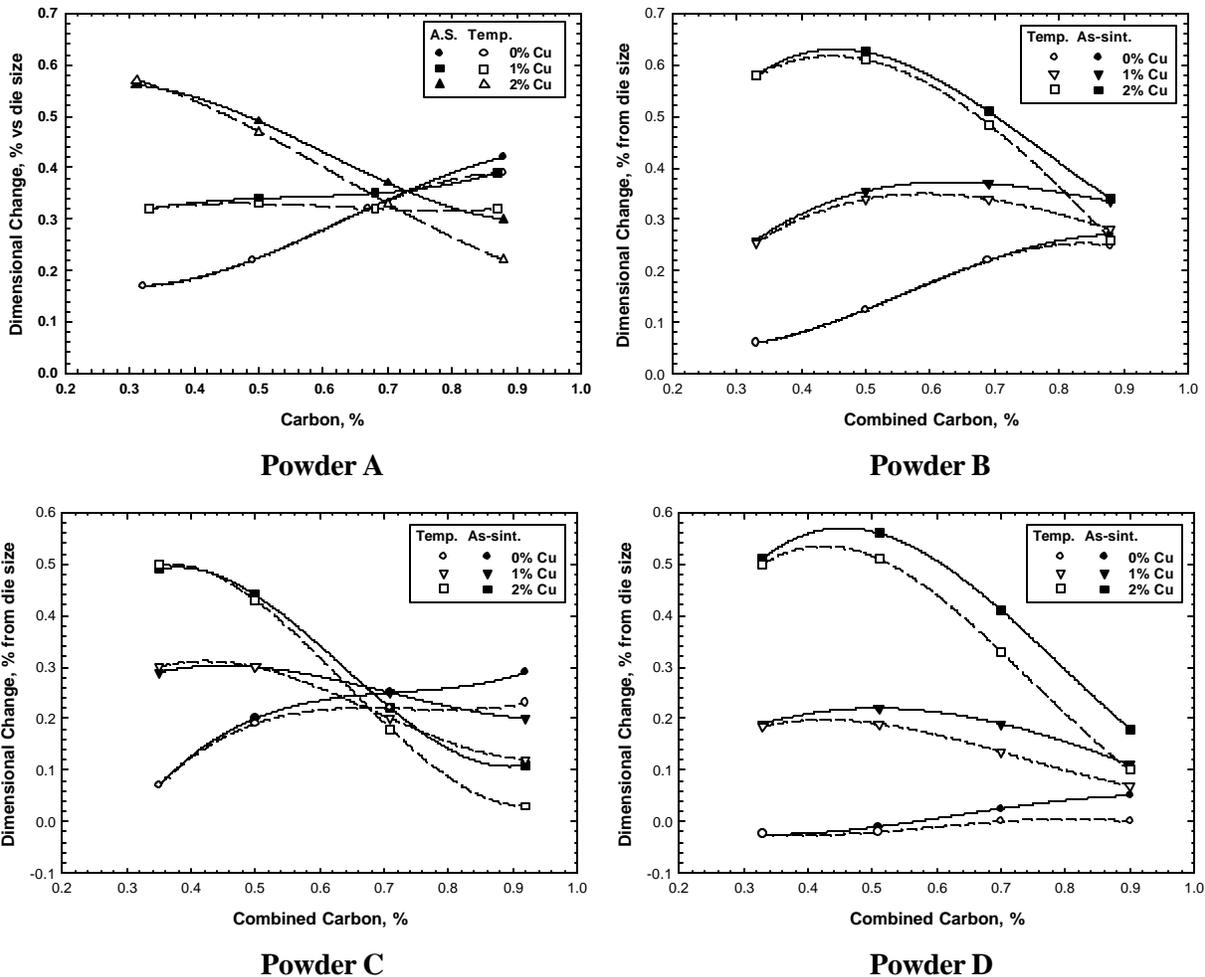
10

Figure 16. Effect of carbon and copper concentrations and tempering at 200°C on dimensional change of specimens pressed at 6.9 g/cm³ with the four powders, sintered at 1135°C and cooled at 1.5°C/s in the range of 650 to 400°C.

CONCLUSIONS

Many powders have been developed for sinter hardening applications. The choice of the base powder must be driven by the application requirements together with the processing conditions. From the observations made in this study, the following conclusions can be made:

- Powders exhibiting good compressibility also generally show lower hardenability. These powders require a higher copper and/or carbon content or faster cooling rate to achieve a fully martensitic structure.

- For similar mix formulations and microstructure, apparent hardness and ultimate tensile strength of specimens pressed from the various powders increase linearly with sintered density.

- Admixing 4% nickel is not effective to improve hardenability or mechanical properties of a 1.5% Mo pre-alloyed steel cooled at 1.5°C/s. The presence of Ni-rich phases and probably also the presence of retained austenite, which shows lower hardness than martensite could be the cause of such behavior.

11

- Both apparent hardness and tensile strength can be increased by raising post-sintering cooling rate of specimens produced with less hardenable powders. On the other hand, the use of a fast cooling rate with materials exhibiting high hardenability can result in a deterioration of the sintered properties likely due to the presence of a larger amount of retained austenite.

- The application requirement drives the choice of the mix formulation and processing conditions. If high apparent hardness is required, carbon content of about 0.8% without tempering is recommended. If high UTS is required, a reduction of the combined carbon to about 0.6% and tempering at 200°C would maximize this property. If both apparent hardness and UTS are required, both the mix formulation and tempering temperature must be adjusted to optimize properties.

- Mix formulation with 1% Cu is recommended to minimize dimensional change variation during sintering due to a change of combined carbon.

- A slight shrinkage is observed when sinter hardened specimens are tempered. The degree of shrinkage increases with the amount of martensite due to a modification of the lattice structure. This must be taken into account in the design of a new component.

REFERENCES

1. E. Ilia, S. Krise, R. Frawley, F. Chagnon and J.A. Danaher; "Cost Reduction Processes for Transfer Case Sprockets. Part 2: Processing Variables", SAE 2000 World Congress, SAE International, Warrendale, PA, paper 2000-01-1001.

2. F. Chagnon, J.A. Danaher E. Ilia and S. Krise,; "Cost Reduction Processes for Transfer Case Sprockets. Part 1: Metallurgical Aspects", SAE 2000 World Congress, SAE International, Warrendale, PA, paper 2000-01-1000

3. F. Chagnon and D. Barrow; "Effect of tempering temperature on Sintered Properties of Sinter Hardened PM Steels", Advances in Structural PM Components Porduction, European Powder Netallurgy Association, Shrewsbury, UK, 1997, p. 273

4. F. Chagnon and M. Gagné, "Effect of Tempering Temperature on Mechanical Porperties of Sinter Hardened Materials", Advances in Powder Metallurgy & Particulate Materials, Vol. 2, Metal Powder Industries Federation, Princeton, NJ, 1999, pp 7-205 to 7-216.

5. G. Krauss, "Steels: Heat Treatment and Processing Principles", ASM, Materials Park, OH, 1990, p. 205-261.

6. F. Chagnon and M. Gagné, "Dimensional Control of Sinter Hardened P/M Components", Advances in Powder Metallurgy and Particulate Materials, Vol. 5, Metal Powder Industries Federation, Princeton, NJ, 2001, pp 5-31 to 5-42.

7. F. Chagnon, G. Olschewski and S. St-Laurent, "Effects of Product and Process Parameters on Dimensional Stability of Sinter Hardened Materials", EURO PM2001, Vol. 4, EPMA, Shrewsbury, 2001, pp 230-235.

8. G. Krauss, "Steels: Heat Treatment and Processing Principles", ASM, Materials Park, OH, 1990, p. 43-106.