The Development of High Performance P/M Steels

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ABSTRACT

Ferrous powder metallurgy has continued to displace competing cast or wrought technologies in automotive applications. This required the development of materials systems with higher, more consistent performance than those available previously. However, competing technologies are not static. The paper examines the materials development and microstructural control required to meet the challenges and opportunities offered by the development of new P/M parts.

INTRODUCTION

The performance of P/M steels must increase continuously if P/M steels are to increase market share by gaining new applications at the expense of competing products and processes. Equally, the P/M process itself must become more efficient if P/M parts are to retain existing applications against other fabrication processes. This paper examines the role of materials research in developing high performance P/M steels to meet the challenges of new applications dictated by both end users and part fabricators.

REQUIREMENTS OF THE END USER

Successful introduction of P/M steels in new applications requires meeting the needs of end users for higher performance and greater efficiency than current systems. Although every application has individual requirements, there are several common themes shown in Figure 1:

Closer Tolerances
Higher Tensile Strength
Higher Yield Strength
Improved Ductility
Higher Fatigue Strength
Lower Cost

Figure 1: Market Requirements for P/M Steels

A P/M steel must demonstrate that it can meet these requirements more effectively than competing processes if it is to be adopted in a new application.

PRODUCTION AND PROPERTIES OF P/M STEELS

To a part designer the production of sintered P/M parts is often represented as a relatively simple process consisting of compaction, sintering and sizing operations, illustrated in Figure 2:

Compact Sinter Size

Figure 2: Basic P/M Production Route

The anticipated performance of some P/M steels produced by this process is given in MPIF Standard 35 1 . From the

data supplied, it is possible to see that the strength of P/M steels is a function of density (Figure 3).

Unfortunately, the strength of many sintered P/M steels produced by single compaction has been relatively Low tending towards a maximum of approximately 80,000 psi. The strength of P/M steels can be improved significantly by secondary compaction and heat treatment operations. These can increase strength towards 150,000 psi so that the properties of a high density, heat treated P/M steel are competitive with higher strength irons and some steels (Figure 4). However, in order to achieve the higher properties, the P/M production process now requires presintering, repressing and heat treatment operations (Figure 5). The addition of this double processing adds cost to the P/M process.

An aim of materials research in ferrous P/M is the development of P/M steels with properties typical of double pressed and sintered steels by single compaction. This should result in both higher performance and a simpler, more efficient process. ANCORDENSE TM1 , a newly developed material/process technology has overcome the limitation as discussed later in this paper.

AVENUES FOR P/M STEEL DEVELOPMENT

The properties of materials are determined to a large degree by the interaction of their composition and microstructure. The microstructure of a typical P/M steel, such as FC-0208 (Figure 6a), in the as-sintered condition consists of pearlite, with a wide range of pore sizes and shapes. A heat treated steel, such as FN-0205 (Figure 6b), possesses a martensitic microstructure, containing porosity and some nickel-rich areas. The data from MPIF Standard 35 and metallurgical development confirm that improving the performance of structural parts requires reduced porosity combined with a higher strength microstructure. More detailed analysis indicates that fracture stress increases if pores are "rounded" to reduce stress concentrations.

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These concepts indicate that high performance P/M steels can be produced from premixes that include a high compressibility matrix, with admixed alloying elements that diffuse rapidly or even promote sintering and do not oxidize. Prealloys, where used, should not reduce compressibility significantly, but should contribute to hardenability in the presence of carbon. These requirements indicate that the following alloying elements may be used to improve the strength of P/M steels in conjunction with conventional sintering practices.

Copper Graphite Molybdenum Nickel Phosphorus

Of these elements, only molybdenum and to a limited degree manganese and nickel, can be prealloyed without significant loss in compressibility and sintered density. Other elements, including chromium, manganese and sulphur, may be employed to meet specific requirements given controlled or high temperature sintering. The development of high performance steels using prealloyed molybdenum plus admixed alloying elements formed the basis of the development program. Application of these concepts to the development of ductile P/M steels, high performance, sinter hardening and heat treated P/M steels is illustrated below.

DUCTILE P/M STEELS

A requirement exists for ductile P/M steels with UTS of 60,000 to 80,000 psi and an elongation of three to five percent to compete with cast and ductile irons. These requirements have proven surprisingly difficult to meet. The FC-0208 composition is close to providing the mechanical strength required. However, a single compacted FC-0208 material lacks ductility. An FC-0205 composition would probably require double pressing to meet the strength and ductility requirements. Several options appear possible including improved ductility through pore rounding and matrix strengthening at lower carbon content.

Pore Rounding

The microstructure of FC-0208 steels (Figure 6a) consists of irregular pores in a matrix of pearlite with some ferrite.

One means to improve ductility and UTS is to add a liquid phase sintering additive, such as phosphorus⁻, to the composition. This technique produces a matrix with very round dispersed porosity (Figure 7a) that possesses somewhat higher UTS and ductility than FC-0205. One advantage of the composition is that the presence of copper and phosphorus accelerates sintering such that the FC-0205 phosphorus composition develops strengths competitive with those of cast irons when sintered at relatively Low temperatures (Figure 8). P/M steels using copper, carbon and phosphorus have successfully displaced cast irons in main bearing caps³.

One possible disadvantage of compositions such as the FC-0205 phosphorus steel is high growth from die size. Since it has been shown that tolerances tend to increase as growth increases 4 , it appears desirable to develop steels of similar properties that are closer to die size when sintered. This should reduce tolerances and the need for some machining operations. Although the FC-0205 phosphorus composition competes well with some cast irons, a better combination of strength and ductility would enable P/M steels to compete with ductile irons possessing ultimate tensile strength of 80,000 psi and elongation's of five percent.

Low-Carbon Molybdenum-Phosphorus Steels

One means to improve the ductility of the phosphorus steels is to eliminate carbon. Such steels possess extremely high ductility and toughness as indicated by impact energies in excess of 80 ft-lbf 5 . However, their yield strengths and apparent hardness are lower than desired for structural P/M parts. It is possible to overcome these problems by using small additions of copper, nickel and carbon to a 0.85 w/o molybdenum prealloy. This produces a range of ductile P/M steels that possess a largely ferritic matrix with discrete, well-rounded pores (Figure 7b). This microstructure offers greater ductility than the pearlitic matrix of the FC-0205 phosphorus composition, enabling a range of P/M steels to be developed that possess ultimate tensile strength of 55,000 to 85,000 psi with elongations of 3% to 10% when compacted to 7.0 g/cm 3 (Figure 9). Depending on composition, these steels can compete with cast and some ductile irons and be closer to die size than the FC-0205 phosphorus steel.

The properties of these steels improve with increasing sintering temperature such that the optimum properties are achieved at a sintering temperature of $2250^{\circ}F$. Their properties also indicate the efficiency of carbon in increasing the yield strength of steels. Unfortunately, relatively small additions, 0.2 w/o, of carbon reduce ductility and increase growth (Figures 9 and 10).

Matrix Strengthening

An alternative to pore rounding is to increase the strength of the matrix. One means to achieve this is to alloy the molybdenum steel with an element, such as manganese, that improves hardenability significantly. Then, sinter at a temperature high enough to ensure that manganese oxides are reduced. A steel comprising Ancorstee185 HP, 1.0 w/o manganese and 0.4 w/o graphite, when sintered at 2250° F, has a microstructure of bainite and ferrite (Figure 7c) that possesses higher tensile strength (Figure 11) than the lower carbon phosphorus steels and greater ductility than the FC-0205 phosphorus. The dimensional change on sintering is approximately +0.2% and should offer improved materials.

HIGH STRENGTH SINTERED STEELS

The initial development of higher strength sintered steels concentrated upon using the high compressibility of a molybdenum prealloyed powder to achieve high sintered density, coupled with improved hardenability through the use of copper, nickel and graphite as premix additions. These alloys can all be sintered at conventional sintering temperatures. A secondary aim was to attempt to control dimensional change on sintering to a relatively Low value.

In general, these aims were achieved. The sintered molybdenum-copper-nickel steels possess microstructures described as divorced pearlite, consisting of fine carbides dispersed in alloy ferrite as shown in Figure 12.

Microstructures of this type possess significantly higher tensile strength in the as-sintered condition than compositions such as FN-0205. When compacted at pressures of 30 to 50 tsi, UTS varies from approximately 60,000 to 100,000 psi depending upon carbon content and composition (Figure 13). Generally, high hardness was

favored by increasing copper and graphite content. Increased ductility was favored by increasing nickel content at carbon contents of 0.4 and 0.6 w/o. Significantly higher strengths, approaching 130,000 psi, can be achieved at higher densities as attained by the ANCORDENSE process.

It proved possible to control dimensional change by balancing copper and nickel contents (Table I). As anticipated, copper tended to cause growth from die, nickel shrinkage. At a graphite content of $0.6~\rm w/o$, dimensional change varied from approximately -0.23% to +0.28% for the range of compositions tested.

An optimum composition appears to consist of FL-4400 plus 3 w/o nickel and 0.75 w/o copper. This offers dimensional change close to die size and high tensile strength. Subsequent testing confirmed that an alloy of this composition possesses an ultimate tensile strength of approximately 105,000 psi (Figure 14).

Both yield strength and ultimate tensile strength could be increased further by increasing the hardenability of the matrix through the use of the 1.5 w/o molybdenum prealloy. The tensile properties of this composition then exceeded those of double pressed and sintered compositions, such as FN-0405.

High Temperature Sintering

Although the as-sintered properties of the molybdenum-copper-nickel steels exceeded those of more conventional double pressed and sintered steels, customer demand indicated a requirement for further improvements of strength, ductility and, if possible, impact energy. A development program was initiated in cooperation with a parts producer to assess whether high temperature sintering could improve properties by a combination of pore rounding and enhanced diffusion of alloying elements into the iron matrix⁶. In this case, control of dimensional change to die size was less critical. Indeed, it was anticipated that shrinkage during sintering would increase density and performance.

The experiments proved very successful, in that the copper molybdenum nickel steels attain densities of 7.0 to 7.45 g/cm³ following compaction at pressures of 30 to 50 tsi and sintering at 2400°F. The alloys possessed yield strengths of 90,000 to 140,000 psi and ultimate tensile strength of 100,000 to 195,000 psi depending on composition and sintered density (Figure 15).

High temperature sintering produced relatively round pores in a matrix consisting of divorced pearlite, bainite and martensite (Figure 12b). High temperature sintering improved solution of alloying elements and improved hardenability as indicated by martensite formation. Due to the presence of martensite, elongation was slightly less than anticipated, varying from 1.5 to 2.8%, depending upon density and composition. However, the combination of properties achieved by single compaction and high temperature sintering exceeded those published for double pressed and sintered steels and approach those of some wrought steels.

DIFFUSION ALLOYING

The P/M molybdenum-copper-nickel steels possess high ultimate tensile strengths. However, some applications require a better combination of toughness and ultimate tensile strength than can be developed in the prealloyed molybdenum steels. In these applications, it may be desirable to consider a P/M steel that is partially alloyed by diffusion annealing. After sintering, the diffusion alloying process produces a heterogeneous microstructure consisting of martensite and nickel-martensite distributed in ferrite and pearlite. This multi-phase structure provides greater toughness and work hardening than the molybdenum steels. The softer regions are able to deform plastically and absorb energy under applied stresses. Thus, crack growth is more difficult and the impact energy increases relative to more conventional P/M steels. These advantages in toughness have been observed in both sintered and hardened conditions.

SINTER-HARDENING P/M STEELS

Although the as-sintered properties of the FL-4400 alloys exceeded those of double pressed and sintered steels, they were still inferior to those of the heat treated P/M nickel steels. However, the increased hardenability of the molybdenum prealloy suggested that it should be possible to form martensite by sinter-hardening, that is rapidly cooling the steels from the sintering temperature. Ideally, the sinter-hardened parts would then possess ultimate

tensile strength and hardness equivalent to those of heat treated P/M steels produced by double pressing and sintering. This was confirmed by a test program conducted jointly with a parts fabricator⁹.

By changing cooling conditions, P/M copper-molybdenum-nickel steels were produced with martensite contents of 50 to 80% as illustrated in Figures 12a-12d. The high martensite contents produce high hardness and strength. Apparent hardness increases from approximately 22 HRC at 6.8 g/cm^3 to 32 HRC at a density of 7.2 g/cm^3 (Figure 16).

Ultimate tensile strength increases from 110,000 psi to 160,000 psi over the same density range (Figure 17). Both apparent hardness and ultimate tensile strength appear to be determined by martensite content (Figure 18).

At a density of 7.1 g/cm³, apparent hardness increases from 18 to 30 HRC as martensite content increases from 45 to 80% (Figure 16). Ultimate tensile strength increased from 120,000 to 150,000 psi with a similar increase in martensite content. The properties were relatively predictable in terms of cooling rate and composition. Increasing hardenability by increasing the molybdenum content of the matrix from 0.65 to 1.5 w/o increased martensite formation and strength. Increasing nickel content from 2 w/o to 4 w/o offered little improvement in properties under the conditions employed. Most significantly, the properties of the sinter-hardened molybdenum-copper-nickel steels produced by single compaction exceeded those of the double pressed, double sintered and heat treated FNO405HT. Thus, where part design permits, the sinter-hardening of molybdenum prealloyed steels offers a significant reduction in process costs over alternative routes.

QUENCHED AND TEMPERED P/M STEELS

The properties of the sinter-hardened P/M steels increased with increasing martensite content. For maximum strength and hardness, particularly where part design dictates machining, heat treatment to develop a fully martensitic microstructure may be the preferred or only production route. Testing confirmed that the molybdenum-copper-nickel steels processed under industrial conditions possess a martensitic microstructure (Figure 12d) with very high strength and hardness. The data show that following single compaction, the heat treated steels possess hardnesses of 30 to 45 HRC (Figure 19) and strengths of 120,000 to 200,000 psi (Figure 20). Both strength and hardness of the P/M steels can be controlled by changes to alloy composition and graphite content. Maximum strength tends to occur at sintered carbon contents of approximately 0.5 w/o and maximum hardness at sintered carbon contents of about 0.75 w/o. The properties of the heat treated steels produced by single compaction exceed those of a quench-hardened double pressed and sintered FN-0405HT.

FATIGUE STRENGTH OF HIGH PERFORMANCE P/M STEELS

Many applications for P/M steels require improved fatigue strength. The data indicate that the fatigue strength, i.e. stress that causes 50% survival to 107cycles, of the high performance steels improved as the pores were rounded and matrix strength increased 7 . When fatigue strength is plotted against ultimate tensile strength for steels compacted to 7.0 to 7.1 g/cm 3 , it can be seen that for many materials, fatigue strength is proportional to ultimate tensile strength as indicated in MPIF Standard 35 (Figure 21).

However, inspection of the data suggests that the trend is closest for steels composed of a mixed microstructure (pearlite, bainite and martensite). The P/M steels that possess the more rounded pores, resulting from liquid phase sintering, have higher fatigue strengths than indicated by the trend line. In both the phosphorus-bearing FC-0205 and ferritic FL-4400 plus Cu-Ni-P steels, fatigue strength can approach 45 to 50% of ultimate tensile strength.

Surprisingly, the fatigue strengths of the high temperature sintered copper-nickel steels are lower than anticipated from the trend line although they possess rounded pores. The microstructure of these steels possess some copper and nickel-rich areas, plus some relatively large pores. It is possible that these combine to present a preferred path for fracture. The data show that the fatigue strengths of the sinter-hardened and heat treated steels increase with ultimate tensile strength and martensite content.

Carbonitriding

The data show that fatigue strength increases with strength and martensite content. It may be possible to improve fatigue strength further by using a carbonitriding treatment to increase surface hardness and introduce residual compressive stresses that suppress crack initiation. Normally, it is considered that P/M steels cannot be "case-hardened" due to their porosity. However, the fatigue data show that it is possible to develop case-hardening P/M steels through alloy design. When carbonitrided, low carbon, 0.25 w/o, derivatives of both the 0.85 w/o molybdenum, 2 w/o nickel and Ancorsteel 41AB' possess an ultimate tensile strength of approximately 125,000 psi at a density of 7.0 g/cm^3 . However, they possess a median fatigue strength of approximately 70,000 psi (Figure 22). These values are higher than those of quenched and tempered P/M steels of higher ultimate tensile strength.

ANCORDENSE

All of the data indicate that the properties of the high performance P/M steels increase with density. The ANCORDENSE process technology 12,13 offers a means to increase the density of single compacted P/M steels to those typical of double pressed and sintered steels. The ANCORDENSE approach has been applied successfully to the molybdenum-nickel steels to produce densities and strengths of the same order as these steels possess when processed by double pressing and sintering (Figure 23). Thus, the application of ANCORDENSE technology and the principles of high performance P/M steels offer a quantum increase over the properties of conventionally processed P/M steels.

CONCLUSIONS

The aim of the programs was to develop, by single compaction processing, P/M steels with properties typical of double pressed and sintered steels, ideally, the materials would have dimensional change close to die size. The test data indicate that this was achieved.

The sintered properties of the single compacted high performance steels exceed those of double pressed and sintered steels significantly (Figure 24). For the data in MPIF Standard 35, densities of 7.0 g/cm^3 or higher were achieved by double pressing and double sintering.

The sinter-hardened and quenched and tempered strengths of the molybdenum-copper-nickel steels exceed those of double pressed and sintered steel (Figure 25).

The fatigue strength of the molybdenum-copper-nickel steels increases with increasing ultimate tensile strength. There is no simple relationship between fatigue strength and ultimate tensile strength between materials of different microstructures.

The improvement in properties, achieved by matrix strengthening and pore rounding, should enable P/M to compete more efficiently with alternative processes.

ACKNOWLEDGMENTS

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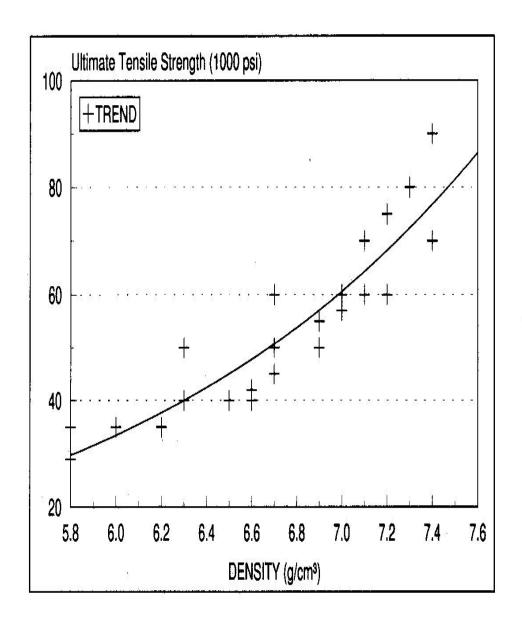


Figure 3: Ultimate Tensile Strength vs Sintered Density for P/M Steels

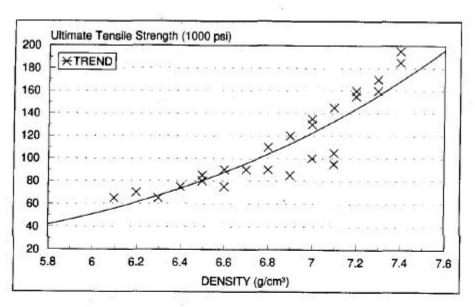


Figure 4: Ultimate Tensile Strength vs Density of Q&T P/M Steels

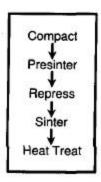


Figure 5: Production Process for High Strength P/M Steels

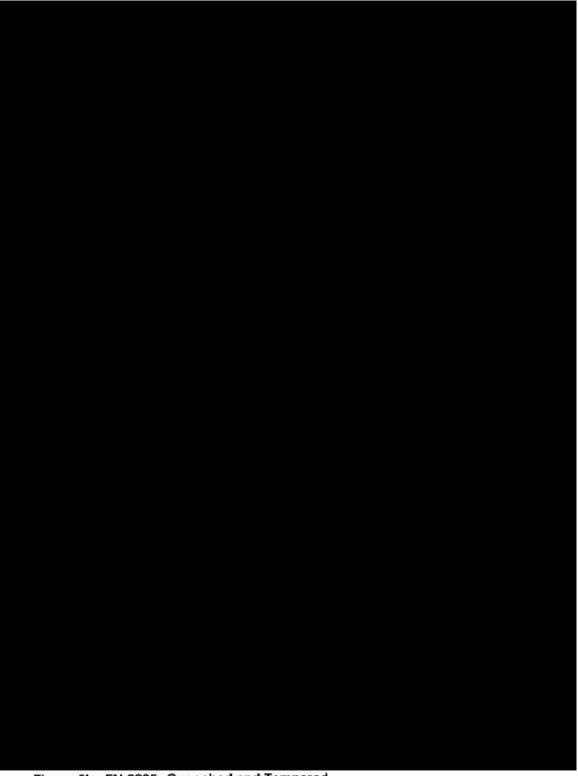


Figure 6b: FN-0205--Quenched and Tempered

Figure 6: Microstructures of P/M Steels. 500X Magnification. Etched nital/picral.

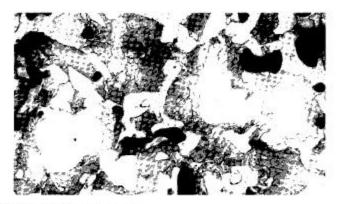


Figure 7a: FC-0205 + 0.5 w/o Phosphorus



Figure 7b: FL-4400 + 0.5 w/o Cu + 0.5 w/o Ni + 0.6 w/o P

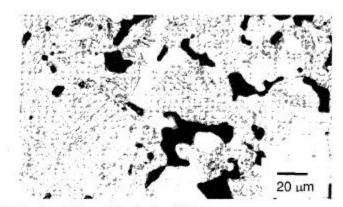


Figure 7c: FL-4400 + 1 w/o Mn + 0.4 w/o Graphite

Figure 7: Microstructures of Ductile P/M Steels. 500X Magnification. Etched nital/picral.

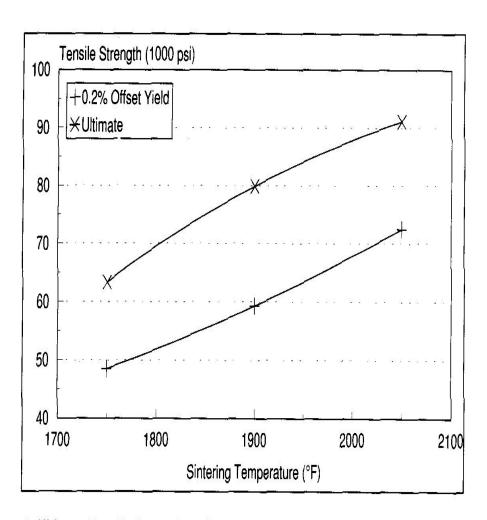


Figure 8: Ultimate Tensile Strength vs Temperature for FC-0205 plus 0.5 w/o Phosphorus

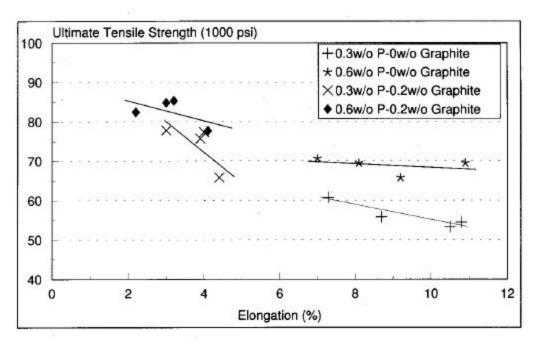


Figure 9: Ultimate Tensile Strength vs Elongation of Mo-Cu-Ni-P-Graphite Ductile P/M Steels at a Density of 7.0 g/cm³

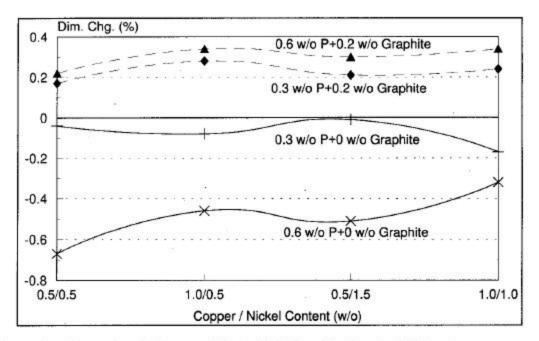


Figure 10: Dimensional Change of Mo-Cu-Ni-P-Graphite Ductile P/M Steels at a Density of 7.0 g/cm³

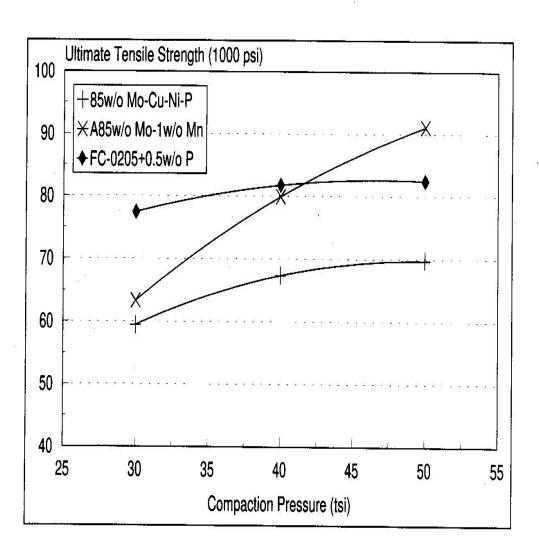


Figure 11: Ultimate Tensile Strength of Ductile P/M Steels

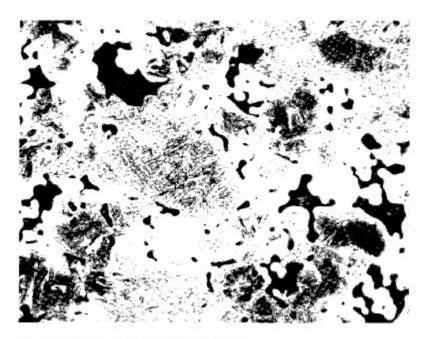


Figure 12a: FL-4405 + 4 w/o Ni, Sintered 2050°F.

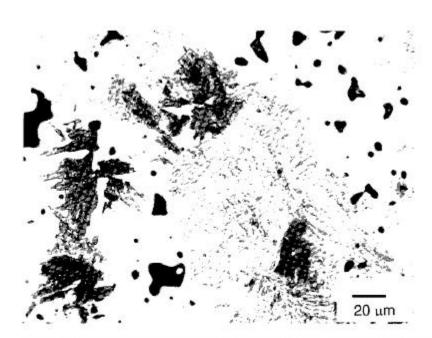


Figure 12b: FL-4405 + 6 w/o Ni + 1 w/o Cu, Sintered 2400°F. 500X Magnification.

Figure 12: Microstructure of P/M Mo-Cu-Ni Steels. 500X Magnification. Etched nital/picral.

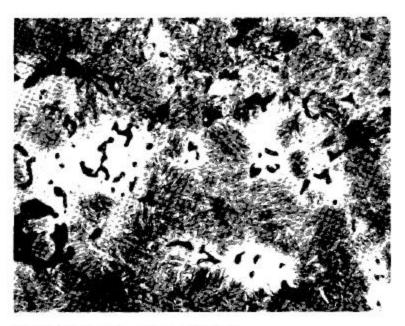
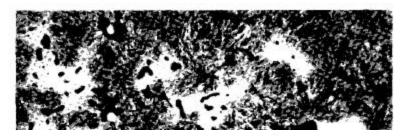
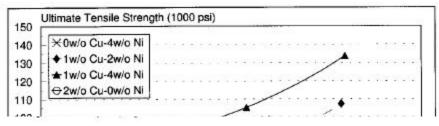
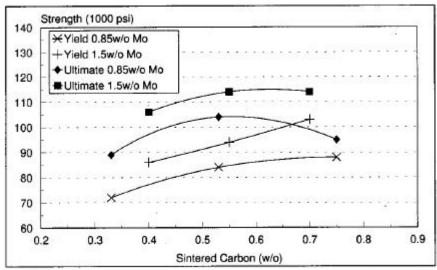


Figure 12c: FL-4405 + 4 w/o Ni, Sinter-Hardened







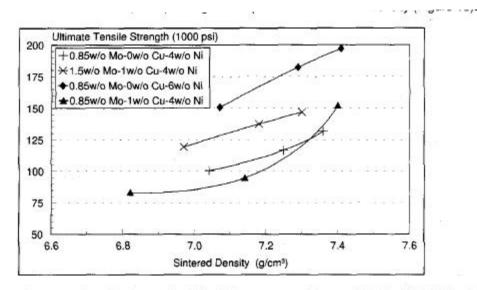
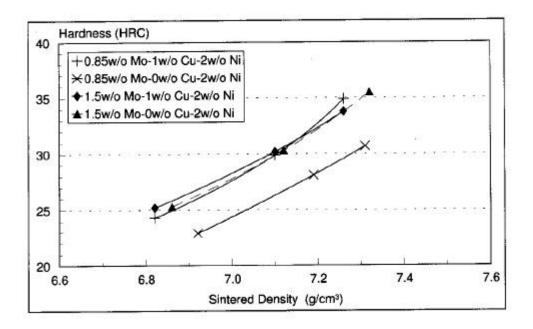


Figure 15: Ultimate Tensile Strength of High Temperature Sintered Mo-Cu-Ni P/M Steels



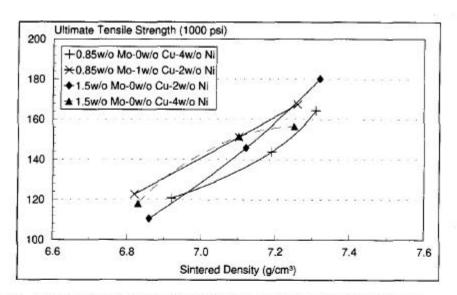


Figure 17: Ultimate Tensile Strength of Sinter-Hardened Mo-Cu-Ni P/M Steels

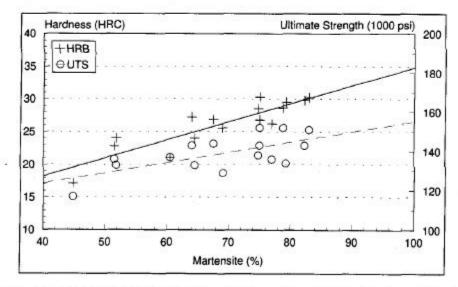


Figure 18: Effect of Martensite Content upon Properties of Sinter-Hardened Mo-Cu-Ni P/M Steels

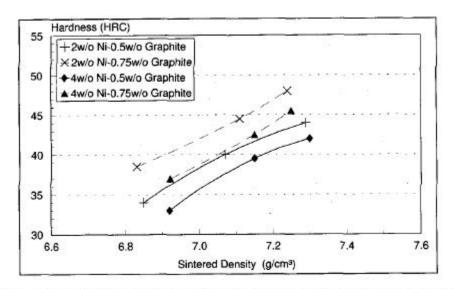


Figure 19: Apparent Hardness of Quenched and Tempered, 0.85 w/o Mo-Ni P/M Steels

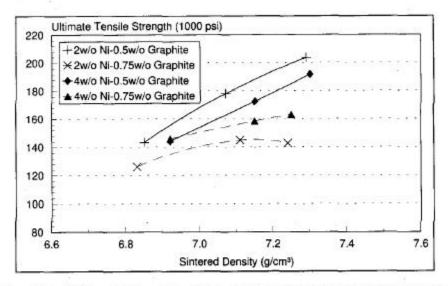


Figure 20: Ultimate Tensile Strength of Quenched and Tempered 0.85 w/o Mo-Ni P/M Steels

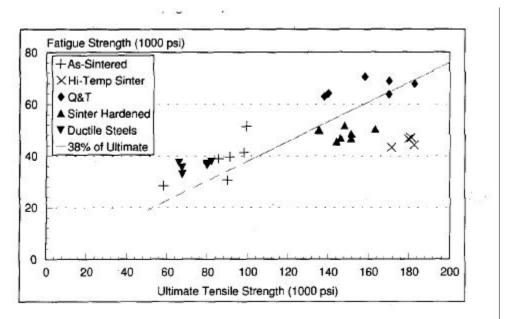


Figure 21: Fatigue Strength of Mo-Cu-Ni P/M Steels

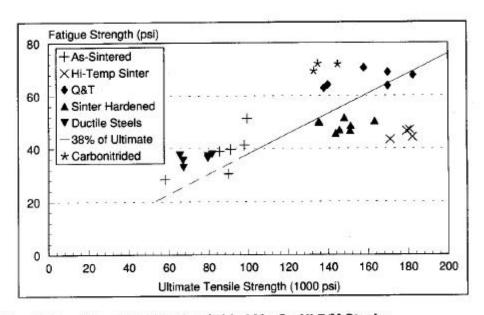


Figure 22: Fatigue Strength of Carbonitrided Mo-Cu-Ni P/M Steels

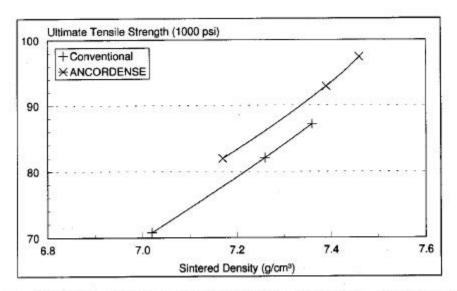


Figure 23: Ultimate Tensile Strength of ANCORDENSE 0.85 w/o Mo, + 2 w/o Ni, + 0.4 w/o Graphite P/M Steels

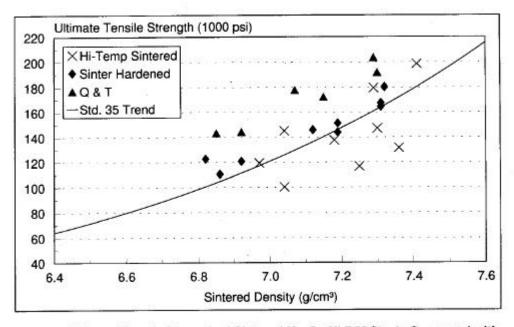


Figure 25: Ultimate Tensile Strength of Sintered Mo-Cu-Ni P/M Steels Compared with MPIF Standard 35 for Quenched and Tempered

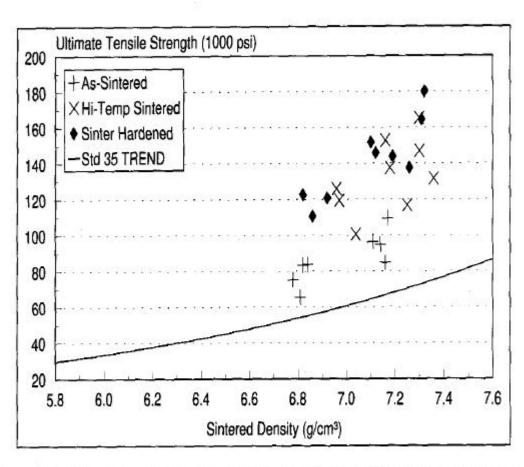


Figure 24: Ultimate Tensile Strength of Sintered Mo-Cu-Ni P/M Steels Compared with MPIF Standard 35