PM MANGANESE STEELS FOR POWDER METALLURGY PARTS

W. B. James, B. Lindsley, K. S. Narasimhan

Abstract
The ferrous PM industry continues to develop and expand its use of non-traditional PM alloying elements. Price, environmental, and recyclability concerns with Mo, Ni and Cu have driven this expansion. Manganese is a relatively inexpensive, yet effective, alloying element in wrought steels. Nevertheless, oxygen sensitivity has limited the use of manganese in PM steels in the past. The current nitrogen-hydrogen sintering atmospheres with low partial pressures of oxygen now permit its use. The combination of Mn with a moderate level of Mo results in PM steel alloys with mechanical properties approaching those of FD-0405. Equally important, these alloys can be processed under typical, industrial sintering conditions. At higher carbon contents these manganese steels can be used as lean alloy, sinter-hardening grades. These materials are copper-free and nickle-free. The benefits of these ferrous PM alloys containing manganese will be discussed.

Keywords: PM manganese steels, sintering, cooling rate, microstructure, mechanical properties, industrial trials

INTRODUCTION
Manganese is an attractive alloying element for PM steels based on its cost to performance ratio. Traditional PM steel compositions that utilize high levels of Mo, Ni and Cu to achieve medium to high mechanical properties in the as-sintered condition are sensitive to the price instability that has been witnessed in the alloy market in the last decade. Prior to these price fluctuations, alloy cost was a small portion of the final component cost, so highly alloyed materials that provided robust processing windows were good choices for PM parts. Diffusion alloys FD-0205 and FD-0405, initially based on sponge iron and later with water-atomized iron, were the first alloys developed with this philosophy. Use of these alloys results in components with good strength and excellent toughness (for a PM steel), although hardness and yield strength are relatively low for the overall alloy content. These alloys are robust with respect to processing as they provide good compressibility and flexibility with respect to sintering conditions (gas composition, sintering time). Later, prealloys containing molybdenum were introduced, followed by hybrids based on the prealloys, and finally more highly alloyed sinter-hardening grades. Some of the water-atomized alloys, such as FL-4600, initially used for forgings have also been used for sinter-hardening. Most alloys were limited to Mo, Ni, Cu and low levels of Mn. Design of alloys was primarily based on the trade-off between properties and compressibility, and alloy cost was often of secondary concern.

The rapid increase in alloy cost in the 2000’s forced a re-examination of this strategy. Wrought steels have long used Mn and Cr as alloying elements to improve hardenability and mechanical properties. The adoption of low dew point, N$_2$-H$_2$ sintering atmospheres by many part producers has allowed the successful introduction of Cr-
containing PM steels into the marketplace. To date, PM steels with Mn contents \( \geq 0.5 \text{ wt\%} \) have not gained widespread use, despite extensive research into Mn-containing alloys that has been conducted [1-9]. Prealloying manganese in water atomized PM steel at levels greater than 0.5\% is impractical, as oxide mitigation becomes extremely difficult and compressibility greatly decreases. Nevertheless, manganese can be introduced by way of additives. Several additives have been evaluated, including medium and high carbon ferromanganese [1-3,5,6], Fe-Mn-Si master alloys [7], and a specially designed Fe-Mn-C alloy [8]. Upon sintering, Mn has been found to diffuse away rapidly from additives by way of gas vapor through the pore network in PM compacts [2]. This is followed by slower solid-state diffusion into the matrix of the base iron. The vapor phase occurs below 1120°C, allowing Mn steels to be processed with conventional sintering. Utilizing an Fe-Mn-C additive, demonstration oil pump parts sintered at 1120°C were found to have properties similar to that of FD-0205 [9].

The current study is an extension of earlier research [10] that showed Mn steels can be produced and sintered using conventional practices. Figures 1 and 2 show that this material system has a robust sintering response, as properties only slowly decrease with lower sintering temperature and time in a similar way to diffusion alloy FD-0405. Extended sintering times and higher temperatures were not required. The combination of Mo and Mn provides good hardenability, thereby boosting as-sintered hardness and yield strength. This paper discusses the properties of Mn steels and compares them with traditional Fe-Mo-Ni-Cu PM alloys.

![Fig.1.](image1.png)  ![Fig.2.](image2.png)

Figs. 1 and 2. The effect of sintering time and temperature on apparent hardness (Fig.1) and TRS (Fig.2) for FD-0405 and a 1.3\% Mn – 0.5\% Mo alloy [from reference 10].

**EXPERIMENTAL PROCEDURE**

The manganese-containing alloys were compared with several MPIF standard material grades as listed in Table 1. A graphite addition of 0.6\% was made to all the materials except the FLNC-4408 which had a 0.9\% addition. An addition of 0.75\% Acrawax C lubricant was made to all of the mixes.
Tab.I. Nominal composition of the base alloys studied.

<table>
<thead>
<tr>
<th>ID</th>
<th>Fe (wt.%)</th>
<th>Mo (wt.%)</th>
<th>Ni (wt.%)</th>
<th>Cu (wt.%)</th>
<th>Mn (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANCORBOND FLM-4005</td>
<td>Bal.</td>
<td>0.5*</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>ANCORBOND FLM-4405</td>
<td>Bal.</td>
<td>0.8*</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>FLN2-4405</td>
<td>Bal.</td>
<td>0.8*</td>
<td>2</td>
<td>-</td>
<td>0.1*</td>
</tr>
<tr>
<td>FD-0405</td>
<td>Bal.</td>
<td>0.5**</td>
<td>4**</td>
<td>1.5**</td>
<td>0.1*</td>
</tr>
<tr>
<td>FLNC-4408</td>
<td>Bal.</td>
<td>0.8*</td>
<td>2</td>
<td>1.5</td>
<td>0.1*</td>
</tr>
</tbody>
</table>

* prealloyed, ** diffusion alloyed

ANCORBOND FLM-4005 = Alloy 1  
ANCORBOND FLM-4405 = Alloy 2

Standard transverse rupture strength and flat, unmachined (dogbone) tensile specimens were pressed at 415, 550, and 690 MPa and sintered in a 90% nitrogen / 10% hydrogen atmosphere in a continuous belt furnace for 15 minutes at temperature (45 minutes in the hot zone). The sintering temperature was 1120 °C with two cooling rates utilized: 0.7 °C/s, or 1.6 °C/s - measured between 650 °C and 315 °C. The samples cooled at 1.6 °C/s were tempered at 200°C for 1 hour.

In addition to standard mechanical testing, the hardenability of the Mn alloys was investigated. This was accomplished by Jominy end-quench testing. Jominy end-quench hardenability specimens were prepared using the technique described in reference 11. Bars 100 mm long and 25 mm diameter at nominally 7.0 g/cm³ were end quenched from 900°C. The hardenability of alloy FD-0405 is derived from MPIF standard 35 data and estimated for a density of 7.0 g/cm³.

Samples for metallographic examination were sectioned, mounted in a thermosetting epoxy, and ground and polished using well-established practices. The polished surface of the samples was then impregnated with epoxy to ensure accurate representation of the porosity and to seal off the porosity, thereby avoiding entrapment of polishing compound, water and etchants that can later lead to staining of the microstructure. The samples were lightly ground, re-polished and etched in a 50-50 mixture of 2% nital – 4% picral.

RESULTS

The Mn-containing alloys were compared with three standard MPIF alloys, FLN2-4405, FD-0405 and FLNC-4408. These materials were chosen as they are hybrid and diffusion alloys that provide good mechanical properties through alloying with Mo, elemental Ni additions, and in two cases, Cu additions. The compressibility of the Mn steels is ≤0.07 g/cm³ lower than the three highly compressible Mo-Ni (-Cu) alloys over a range of compaction pressures (Fig.3). Upon sintering, the Mn alloys behave similarly to Cu steels, in that they exhibit growth (Fig.4). The Ni-containing steels shrink relative to the Mn alloys, with the Cu-free FLN2-4405 having the lowest growth.
The apparent hardness values for the five alloys are shown in Fig.5. FLNC-4408, containing the higher graphite content, has the highest hardness in the as-sintered condition. Alloy 2 (FLM-4405), with the same Mo content but lower graphite and no Ni or Cu, has a similar hardness. Additionally, Alloy 1 and FD-0405, having the same Mo content, have similar hardness. The effect of Mn on hardness is clearly evident as 1.3% Mn effectively replaces 4% Ni and 1.5% Cu. The FLN2-4405 has the lowest hardness with conventional sintering. Figure 5b contains the data generated with accelerated cooling. Alloy 2 now has a higher hardness than FLNC-4408 at a lower carbon content. Alloy 1 (FLM-4005) exhibits a significant increase in hardness with accelerated cooling, reaching 30 HRC at a 7.05 g/cm³.

By adding 0.2% additional graphite, the hardness of Alloy 1 increases to that of Alloy 2. Alloy 1 with a total of 0.8% graphite is a lower cost alternative to reach high hardness, although the other mechanical properties, such as strength, elongation and impact, decrease 10 to 20% as a result. The Mo and C contents can be tailored to meet specific component requirements in the most cost-effective manner. Alloy FD-0405 shows little change in apparent hardness with accelerated cooling. This can be viewed as either FD-0405 is not an effective sinter-hardening alloy, or FD-0405 is quite stable with variations in cooling rate.

The yield strength of the two Mn alloys is quite good, and both meet or exceed the yield strength of the Ni-containing alloys. It can be seen in Fig.6, that the yield strength of Alloy 2 far exceeds that of the other alloys when accelerated cooling is used. The ultimate tensile strength of the Mn alloys is similar to the Ni-containing steels with conventional cooling and show a benefit with accelerated cooling, Fig.7. Given the high yield strengths, the total elongation of the Mn alloys and the sinter-hardened FLNC-4408 is lower than for the FLN2-4405 and FD-0405 – Figure 8. Impact energy is similar for all alloys except the FD-0405, as PM diffusion alloys are known for high toughness – Fig.9. These results show the potential of the Mn alloys to deliver properties greater than traditional PM steels with equivalent Mo content and no elemental Ni or Cu additions.
Fig.5. Apparent Hardness (after tempering) (a) Conventional cooling (0.7°C/s) and (b) Accelerated cooling (1.6 °C/s).

Fig.6. Yield Strength (a) Conventional cooling (0.7°C/s) and (b) Accelerated cooling (1.6°C/s).

The microstructures of all five alloys are presented in Figs.10 and 11 for conventional and accelerated cooling, respectively. The morphology of the Mn-containing steels consists of martensitic and bainitic regions. The martensitic regions etch tan-colored, whereas the bainitic regions are white and gray. With conventional cooling, the higher Mo Alloy 2 contains more lower bainite and martensite than Alloy 1. The ferrite-carbide spacing of Alloy 2 is also finer in the upper bainite / divorced pearlite morphology. All five alloys have mixed microstructures that are typical of hybrid and diffusion-alloy systems. The light-etching Ni-rich regions are clearly present in the MPIF alloys. With accelerated cooling, the amount of martensite increases with the Mn steels. The microstructures remain mixed, as limited Mn diffusion into the core of the larger base iron particles results in locally reduced hardenability. The FLN2-4405 and FLNC-4408 also show a significant increase in martensite content with accelerated cooling. Little change in microstructure was observed for the FD-0405. The microstructures correlate well with the observed mechanical
properties. The high martensite content in the Mn-containing steels results in high apparent hardness and yield strength.

Fig. 7. Ultimate Tensile Strength (a) Conventional cooling (0.7°C/s) and (b) Accelerated cooling (1.6°C/s).

Fig. 8. Total Elongation.

Fig. 9. Impact Energy.

In a separate study, the effect of high temperature sintering (HTS) was evaluated over a range of carbon contents and cooling rates for Alloys 1 and 2 at a nominal density of 7.1 g/cm³. The results for Alloy 2 are shown in Figures 12-15, and similar effects were found with Alloy 1. With conventional cooling (red data points), little change in strength was found with HTS. The drop in apparent hardness may be due to some carbon loss at high temperature. Ductility and impact resistance noticeably improved. With accelerated cooling, HTS made a significant difference in mechanical properties. While apparent hardness was unaffected, a 20% increase in strength (TRS, ultimate tensile strength) was found at select graphite additions. The high temperature sintering appeared to show the greatest improvement with higher graphite additions. Maximum yield strengths of 900 MPa and 1000 MPa were found for Alloys 1 and 2, respectively, under these conditions. Additionally, ultimate tensile strengths of 1000 MPa and 1175 MPa were obtained for
Alloys 1 and 2, respectively, at the optimum carbon contents. These results are quite impressive considering the alloys contain moderate levels of Mo, with no additions of Ni or Cu.

Fig. 10. Microstructures of the five materials after conventional cooling (0.7°C/s).
The results indicate that carbon content and processing conditions should be optimized for the specific properties required. The relationship between carbon content, cooling rate and apparent hardness is straightforward, as seen in Fig.12. Additional graphite (0.1% to 0.2%) can be added to Alloy 1 (0.5% Mo, 1.3%Mn) to obtain the same apparent hardness as Alloy 2. This did not hold true for the other properties, as optimum strength levels were found between 0.5% and 0.7% graphite additions for both alloys. Given these results, it is recommended that Alloy 1 be used for smaller components where faster cooling rates can be obtained, whereas the improved hardenability of Alloy 2 allows it to be used in slightly larger parts. This assumes that maximum properties are needed. Alloy 1 can also be used in larger parts where the property requirements are less demanding.
The presence of Mn and Mo increases alloy hardenability greatly in both wrought and PM steels. Given that both are present in Alloys 1 and 2, these Mo-Mn alloys should have good hardenability. Evidence of this was observed in the mechanical properties and microstructures. To quantify the hardenability of the Mn-Mo alloys, Jominy end-quench tests were performed. Figure 16 shows the results, where a greater distance from the quenched end ($J_{65}$ depth) indicates greater hardenability. The iron-based diffusion alloy has poor hardenability, as evidenced by the short $J_{65}$ depth. Alloy 1 and FLN2-4405 exhibit better hardenability than the more highly alloyed FD-0405, with $J_{65}$ depths of 16 and 14 mm respectively. A significant improvement in hardenability was found with FLNC-4408, as an increase in graphite content and the addition of Cu boosted hardenability above that of the related alloy FLN2-4405 from a $J_{65}$ depth of 14 mm to 33 mm. Alloy 2 has the highest
hardenability of the alloys studied, with a depth of 38 mm. The addition of 1.3% Mn to a 0.8% Mo base is clearly superior to an addition of 2% Ni and 1.5% Cu, with respect to hardenability. The hardenability of these Mn alloys allows a predominantly martensitic microstructure to be produced at intermediate carbon contents and with accelerated cooling. These lean alloy systems do not, however, provide the hardenability of traditional sinter-hardening steels, where $J_{65}$ depths of 90 mm and greater have been reported, and as such, should not be used when uniformly martensitic microstructures are required.

![Figure 16](image)

**Fig. 16.** Jominy end-quench hardenability for the five alloys at a 7.0 g/cm$^3$ density. $J_{65}$ represents the distance from the water quenched end of the Jominy bar where the apparent hardness fell to 65 HRA.

**CONCLUSIONS**

1. Mn-containing alloys have been developed that provide good sinterability under conventional sintering conditions. High temperatures are not required, although the combination of high temperature sintering and accelerated cooling results in very good properties for a lean-alloy system.
2. Nitrogen-hydrogen atmospheres with low dew points and low oxygen contents are required with these alloys. Endothermic gas should not be used due to oxidation of the manganese.
3. The mechanical properties of the Mn-Mo steels met or exceed that of several Mo-Ni-Cu PM steels. Strength and hardness were higher than for FD-0405, FLN2-4405 and FLNC-4408. Ductility and impact resistance was similar to that of FLNC-4408.
4. These lean alloys are appropriate for sinter hardening of small to medium sized parts.

**INDUSTRIAL TRIALS**

Several industrial trials were conducted to ensure that the new alloys are robust under commercial processing conditions.
In one trial a sprocket was made from the ANCORBOND FLM-4008 that had an addition of 0.8% graphite. The sprockets were compacted to 7.0 g/cm$^3$ and sintered at 1120°C in a 90:10 (nitrogen:hydrogen) atmosphere and accelerated cooling was used. The sprockets had an apparent hardness after tempering of 69 HRA (39 HRC). The sprocket and the microstructure obtained are shown in Fig.17.

![Sprocket and Microstructure](image1.png)

**Fig.17.** Sprocket (a) and etched microstructure (b).

For the second trial a mechanical diode was made to a sintered density of 6.8 g/cm$^3$. An apparent hardness of 30 HRC was achieved on the part surface. A similar part and the microstructure obtained are shown in Fig.18. The part met all the requirements for the application including the tight dimensional tolerances specified.

![Mechanical Diode and Microstructure](image2.png)

**Fig.18.** Mechanical diode and its microstructure.

A third industrial trial was conducted to see whether the manganese steels could be induction hardened [12]. The part selected for the trial was the sprocket shown in Fig.19.
In the trial, the two PM manganese steels, ANCORBONDFLM-4005, and ANCORBOND FLM-4405 were compared with the material currently used to make the induction hardened sprocket, FLN2-4405. The microstructures of the as-sintered hub section of the sprocket for all three materials are illustrated in Fig. 20.

The teeth of the as-sintered sprockets were induction hardened by heating for 3 s on a 60 kW, 450 kHz induction unit followed by quenching in oil at 60°C. The parts were then tempered at 200°C for 1 h.

The induction-hardened sprocket teeth are shown in Fig. 21 and an unetched view of the surface of the teeth is presented in Fig. 22 and it can be seen that there is no indication
of preferential oxidation of the sprocket made from the PM manganese steel compared with the sprocket made from FLN2-4405.

The desired microstructure was obtained in the induction-hardened sprockets and the sprockets made from the manganese steel matched the performance of the sprockets made from FLN2-4405.

Fig.21. Etched microstructure of the induction hardened sprocket teeth for all three materials.
Fig. 22. Oxide thickness on the surface of the induction-hardened sprocket teeth FLN2-4405 and (b) FLM-4005.

References