Lean Hybrid Low-Alloy PM Molybdenum Steels

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Abstract
The volatility in the price of alloy additions has led to a fresh approach to alloying in ferrous PM materials. Hybrid low-alloy materials based on prealloyed powders in which molybdenum is the principal alloy addition provide flexibility in alloy design. The molybdenum content of the base powder can be adjusted to suit the hardenability requirements of the intended application. A review will be presented of the performance characteristics of hybrid low-alloy molybdenum steels in the as-sintered and the heat-treated condition. Two examples will be presented to show the flexibility of these hybrid low-alloy materials.

Introduction
Prior to the commercial introduction of a water atomized, prealloyed low-alloy steel powder with 0.85% molybdenum in 1990 [1,2], prealloyed steel powders had generally contained a combination of nickel and molybdenum. Individually, nickel and molybdenum have a limited effect on compressibility (Figure 1) [3], but when used together they increase the compacting pressure required to reach a given green density quite significantly (Figure 2).

Figure 1: Effect of alloy additions on compressibility [3].

The FL-4600 material (Figure 2) typically contains 1.8% nickel and 0.5% molybdenum. It is the least compressible of the materials shown. The FL-4200 material with less nickel (0.5%) and a similar amount of molybdenum (0.6%) is more compressible. The most compressible material is the FL-4400 with 0.85% molybdenum, and this powder is as compressible as some water atomized iron powders (F-0000). Increasing the amount of molybdenum to 1.5% (FL-4900) reduces the compressibility compared with that of the FL-4400 material. Nevertheless, the compressibility of the powder with 1.5% molybdenum is still better than either of the nickel-molybdenum prealloyed steels. One of the attributes of molybdenum as an alloy addition is its influence on hardenability (Figure 3) [4].

Soon after its introduction, the prealloyed powder with 0.85% molybdenum was in widespread use; just with a graphite addition for heat-treated parts, and with additions of nickel, or nickel and copper for parts to be used in the as-sintered condition or for heat-treated parts. These hybrid low-alloy steels (prealloyed powder base with elemental, master alloy, or ferroalloy additions) have been applied extensively [5-9] and in the 2007...
edition of MPIF Standard 35, Material Standards for PM Structural Parts, these materials were recognized as a material classification in their own right [10].

Two of the hybrid low-alloy steels, listed in the 2007 edition of the MPIF material standard, deserve special recognition. These are the hybrid analogs of the traditionally diffusion-alloyed Ni-Cu-Mo steels (FD-0205 and FD-0405). They are listed in the material standard as FLN2C-4005 and FLN4C-4005 and are based on a prealloyed steel powder with 0.5% molybdenum to which nickel and copper additions have been added during a binder-treated premixing process. These materials were originally offered commercially in 1999 [11-13]. They have greater hardenability compared with the diffusion-alloyed materials (Figure 4), and exhibit complex multi-phased microstructures in the as-sintered condition - Figure 5.

This paper will present two examples of the flexibility of hybrid low-alloy steels that are based on prealloyed powders that contain molybdenum as the principal alloy addition. While the price of molybdenum remained stable for many years, it increased significantly a few years ago and although it decreased significantly by the early part of 2009, it still remains above its original level. Prealloyed powders are now available with 0.3%, 0.5%, 0.85%, and 1.5% molybdenum. The compressibilities of the first three materials are comparable and their hardenability increases as the molybdenum content increases – Figure 6. Molybdenum levels above 1% lead to reduced compressibility.

Example 1 – Lean Versions of Ancorloy, Hybrid Low-Alloy Materials

The hybrid low-alloy steels, FLN2C-4005 and FLN4C-4005 have mechanical properties that are comparable to those of the diffusion-alloyed steels FD-0205 and FD-0405 – Figure 7 [10]. In the as-sintered condition, the tensile strength and fatigue response of the hybrid alloys exceeds that of the diffusion-alloyed materials. This is due to the greater hardenability of the hybrid alloys; because they are based on a 0.5% molybdenum prealloyed powder. In the as-sintered condition the greater hardenability results in there being more martensite and bainite in the microstructure and this leads to higher performance.

The higher heat-treated strength of the hybrid alloys was not expected. The tensile specimen cross-section is quite small and all of the materials should have a tempered martensitic microstructure. There was a difference in the temperature at which the materials were tempered (200 °C for the hybrid alloys compared with 180 °C for the diffusion-alloyed materials) and this might have had some effect.
In light of the good performance of the hybrid alloys based on a prealloyed powder with 0.5% molybdenum, it was decided to evaluate hybrid alloys with the same nickel and copper additions based on a prealloyed powder with 0.3% molybdenum. The samples were sintered at 1120 °C for 13 minutes at temperature in a nitrogen:hydrogen atmosphere (90 v/o :10 v/o). No accelerated cooling was used. The oil-quenched and tempered specimens were tempered at 200 °C for 1 h. The results are summarized in Figure 8.

In the as-sintered condition, the yield strength of the hybrid alloy with 0.5% Mo exceeds that of the diffusion-alloyed material of similar chemical composition. This was expected from the data presented in Figure 7. It is interesting to note that each of the materials with 0.3% Mo has a similar yield strength to that of the comparable diffusion-alloyed material. This should be reflected in actual PM parts as the materials based on the prealloyed powder with 0.3% Mo have a hardenability that should be similar to that of the diffusion-alloyed materials.

In general, the ultimate tensile strength of the quench-hardened and tempered lower nickel content materials is better than that of the materials with 4% nickel. This is due to higher amounts of retained austenite in the material with 4% nickel. The only reason for selecting the diffusion-alloyed material with 4% nickel would be for its better hardenability. As the hardenability of the hybrid alloy with the lower nickel content is similar to that of the diffusion-alloyed material with 4% nickel, the hybrid alloy with the lower nickel content would be a more cost-effective choice.
Figure 8: As-sintered [(a) and (b)] and heat-treated [(c) and (d)] tensile properties for hybrid and diffusion-alloyed materials of the same chemical composition compared with the tensile properties of a hybrid low-alloy steel with the same nickel and copper additions but a lower prealloyed molybdenum content. All the materials had a 0.6% graphite addition and a density of 7.0 g/cm$^3$.

Example 2 – Lean Version of Chromium, Hybrid Low-Alloy Steel

Alloy additions such as chromium and manganese present difficulties when they are used in prealloyed water atomized powders due to their high affinity for oxygen. Once formed their oxides are extremely hard to reduce and if the alloy addition is not in solution it does not contribute to the hardenability of the material. A hybrid PM chromium steel alloy based on a 0.85% molybdenum prealloyed powder has been shown to have extremely good mechanical properties [14,15]. While the material may be sintered at 1120 °C in a 90 v/o : 10 v/o nitrogen:hydrogen atmosphere, a full 30 minutes are required at that temperature to develop optimum properties and it has been shown that high temperature sintering is more practical in light of the 10 to15 minutes more typically allowed at temperature during commercial sintering practice [16]. A key attribute of this PM chromium steel is the fact that it sinter hardens at conventional sintering furnace cooling rates (about 0.7 °C/s) without the need for an addition of copper; something generally needed with many sinter-hardenable materials. The absence of copper improves the robustness of the material – less sensitivity of the dimensional change of the material to density, carbon content, and cooling rate. The high cost of molybdenum in recent years led to the evaluation of hybrid PM chromium steels based on prealloyed powders with lower molybdenum contents and a lean version of the material has been developed based on a prealloyed powder that contains 0.3% molybdenum [17]. While the hardenability of the hybrid PM chromium steels is lower that that of the hybrid sinter-hardenable alloys that contain copper additions, their hardenabilities are comparable to those of other commercial products – Figure 9. The chemical composition of the hybrid PM chromium steel alloys is listed in Table 1, and the effect of cooling rate on the mechanical properties of both of the materials with a 0.6% graphite addition is summarized in Table 2 [17].
Table 1: Chemical composition of the hybrid PM chromium low-alloy steels

<table>
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<tr>
<th>Material</th>
<th>Cr (mass %)</th>
<th>Si (mass %)</th>
<th>Ni (mass %)</th>
<th>Mo (mass %)</th>
<th>Mn (mass %)</th>
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<td>0.6</td>
<td>1</td>
<td>0.3</td>
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</tbody>
</table>

Table 2: Mechanical properties of the hybrid PM chromium low-alloy steels as a function of cooling rate (cooling rate measured between 650 and 315 ºC) – graphite addition of 0.6%.

For the material that is based on a prealloyed powder with 0.85% molybdenum, increasing the cooling rate from 0.7 ºC/s to 2.2 ºC/s improved the yield strength by 42%. For the leaner alloy (0.3% Mo), the corresponding improvement in yield strength was 20% for the same change in cooling rate. The yield strength of the leaner alloy is about 80 to 90% that of the other material depending on the cooling rate. The lean alloy has significantly better tensile performance compared with a 4% nickel diffusion-alloyed material (FD-0405) over a range of sintering temperatures [17] – Figure 10.

Summary
Prealloyed PM steel powders that contain molybdenum as the principal alloy addition, provide a cost-effective and flexible base for many hybrid PM low-alloy steels. They may be used in the as-sintered or in the heat-treated condition (quench-hardened and tempered or case hardened). Some of the hybrid alloys may also be sinter hardened. The selection of the molybdenum content of the base prealloy will depend on the size of the PM part being made and the hardenability that is needed.
Figure 10: The effect of sintering temperature on the yield strength of two hybrid PM chromium steels and a diffusion-alloyed material (FD-0405) [17].

References