

EFFECT OF MOLYBDENUM CONTENT IN PM STEELS

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ABSTRACT

Molybdenum (Mo) is a highly effective alloying element in ferrous powder metallurgy (PM) alloys. It has little effect on compressibility of iron, is not oxygen sensitive, and greatly increases the hardenability of steel. As such, it gained widespread use in higher performance alloys. As a result of the increase in Mo cost, it is clearly important to use only the amount of alloy needed to obtain desired properties. Fortunately, a large range in Mo content alloys is available in the marketplace so that its use can be tailored to optimize cost and performance. This paper reviews the role of prealloyed molybdenum, from 0 to 1.5%, in ferrous PM alloys and makes recommendations on its use for various applications.

INTRODUCTION

Molybdenum is a desirable alloying element for PM steel applications for a number of reasons. The primary reason for its rapid adoption in the industry is that it has a negligible effect on compressibility. Current high density parts using an iron base could easily be converted to a Mo base iron. Mo steels are also easy to process for both the powder manufacturer and the end user with respect to oxygen content. Molybdenum oxide is not a problem in melting, atomizing or annealing, nor is it a concern during sintering of PM components.

The addition of Mo can greatly increase the mechanical properties of steel. The presence of Mo modifies the ferrite-carbide microstructure so that lamellar pearlite no longer forms, and is replaced by a divorced eutectoid structure, ie. divorced pearlite, upper bainite and/or acicular ferrite with carbide. The addition of Mo gradually increases the overall mechanical properties of the steel. More significantly, Mo greatly increases the hardenability, or the ability to form martensite, of the steel. Martensite is the hardest metallic phase in steel, and after tempering, provides an excellent combination of mechanical properties. With the advent of sinter-hardening furnaces and alloys (all of which contain Mo), hardened steel microstructures can be obtained in the as-sintered condition. Several benefits of sinter hardening exist. First is the

elimination of a processing step, namely oil quenching. The cost of this separate heat-treating step is removed and there is no issue with retained quenchant in the pores of the PM component. Retained oil can be a problem during tempering from vapor emissions, or during future secondary processing steps, such as resin impregnation, where the pores need to be free of contaminants. Another benefit of sinter hardening is the improved dimensional precision compared with oil quenching. In large parts and parts with tight tolerances, fast cooling rates can cause distortions that put components out of specification. The slower cooling rates in sintering furnaces greatly reduce these distortions.

Unfortunately, the price of Mo has increased 10 fold over the previous 5 years. Prior to this price increase, the amount of Mo present in an alloy had little effect on overall cost of a PM component. Therefore, higher than necessary Mo contents were sometimes used in applications to increase the robustness of the process. With the price increase, these priorities are being re-evaluated. In addition, lower Mo alloys, such as Ancorsteel® 30 HP with 0.3% Mo, have been introduced into the marketplace. This paper evaluates the different commercially available Mo grades, from 0% to 1.5% Mo, under different processing conditions in an effort to understand better where Mo steels should be used and the level of Mo required for different applications.

EXPERIMENTAL PROCEDURE

Five commercially available ferrous powders were selected for study, Table I. All weight % will be designated as % hereafter. To each of the Fe-Mo base irons, lubricant (0.75% EBS wax) and graphite were added. To study the effect of alloying on as-sintered properties, 2 levels of Cu (0%, 2%), two levels of nickel (0%, 2%) and a combination of 2% Ni and 1.25% Cu were added. Standard transverse rupture strength bars were pressed at 690 MPa (50 tsi) and sintered in 90% nitrogen / 10% hydrogen at 1120 °C (2050 °F) in a continuous belt furnace. Three average cooling rates were chosen for study: 0.7 °C/s (1.3 °F/s), 1.6 °C/s (2.9 °F/s) and 2.2 °C/s (4.0 °F/s). The cooling rate was measured in the sample between 650 °C (1200 °F) and 315 °C (600 °F). All samples were tempered at 205 °C (400 °F). Hardness and transverse rupture strength were measured for all conditions. All testing was performed in accordance with MPIF standards.

Table I. Nominal composition of base irons tested (in wt%).

Base Iron	MPIF Designation	Mo
Ancorsteel 1000B	F-0000	0
Ancorsteel 30 HP	-	0.30
Ancorsteel 50 HP	FL-4000	0.5
Ancorsteel 85 HP	FL-4400	0.85
Ancorsteel 150 HP	FL-4900	1.5

The effect of Mo on quenched hardenability was also studied. Two different sample geometries were used. The first was used to study the effect of alloy content with oil quenching. 25 mm (1 inch) diameter by 25 mm high slugs were pressed to a green density of 6.95 g/cm³ at a nominal pressure of 550 MPa (40 tsi). After sintering, using the conditions stated above, these samples were reheated to 900 °C (1650 °F) and oil quenched. The samples were tempered at 175 °C (350 °F), cross-sectioned at mid-height and mounted for microstructural analysis. In addition, microindentation hardness traverses were made from the edge to the center of the slug.

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The second technique used to evaluate quench hardenability was the Jominy end-quench test. Compositions mirroring the study with the TRS bars were used for the Jominy test. 0.6% graphite and 0.75% EBS wax were added to each alloy. In addition, 2% Cu, 2% Ni, 2% Ni + 1.25% Cu, or no admixed elemental alloys were added. Large compacts were pressed to 7.0 g/cm³ and cut into blanks. Samples were pre-sintered at 900 °C to increase strength and the Jominy test bars were machined. The samples were then sintered in a belt furnace at 1120 °C in 90% nitrogen / 10% hydrogen for nominally 15 minutes at temperature. The bars were finish machined to final size, reheated to 900 °C, and end quenched following ASTM standard A 255. After quenching, flats were ground on opposing sides and hardness profiles were measured per the standard.

RESULTS

Effect of Molybdenum Content on As-sintered Properties

The contribution of molybdenum to mechanical properties with a 0.6% graphite addition was studied with varying levels of elemental metallic additions. Figure 1 shows the effect of Mo content on both TRS and hardness at 3 cooling rates with no additional alloying elements. With the addition of 0.6% graphite, cooling rate has only a small effect on the mechanical properties of these steels. The hardenability of the Fe-Mo-C system is not great enough to cause martensite formation under these conditions. The addition of Mo does increase both the TRS and hardness. Modest gains in mechanical properties can be obtained by prealloying Mo into iron, and as a prealloy, the other powder properties such as compressibility are similar for the range of Mo grades shown.

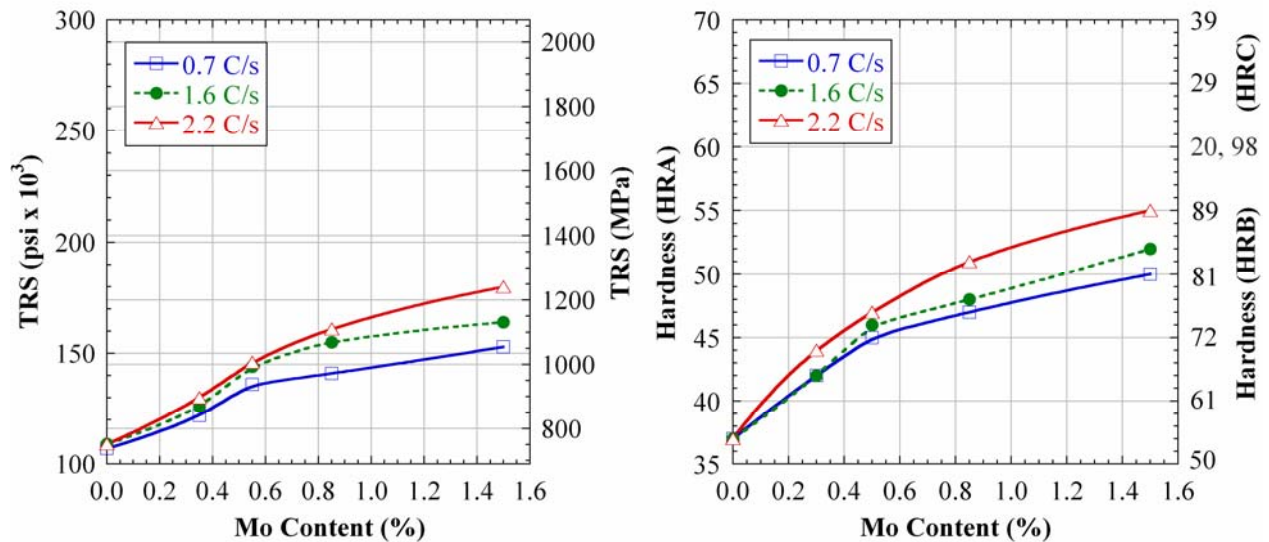


Figure 1. The effect of Mo content and cooling rate on TRS and apparent hardness in 0.6% graphite PM steels.

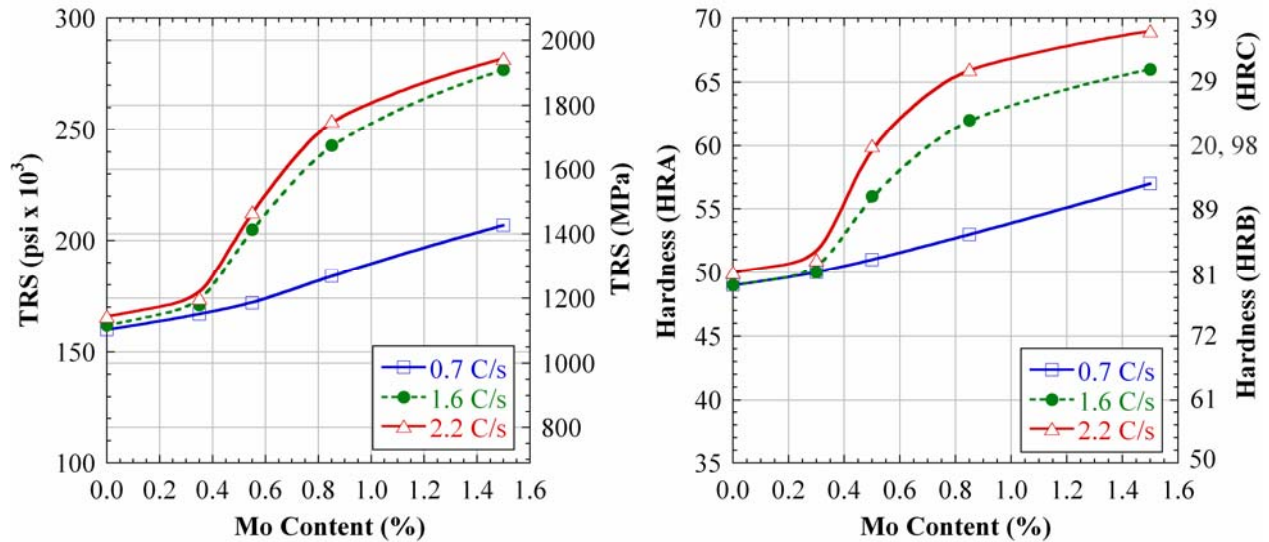


Figure 2. The effect of Mo content and cooling rate on TRS and apparent hardness in 2% Cu - 0.6% graphite PM steels.

With the addition of 2% copper, the behavior of the system changes substantially (Figure 2). First, the properties of the iron base increase dramatically with the addition of 2% Cu, hence the popularity of Fe-Cu-C alloys (FC-0205). The properties of FC-0205 shown here are equivalent to FL-4905 (1.5%Mo + graphite) shown in Figure 2. At conventional cooling rates, the properties slowly improve with the addition of Mo, again in a near linear fashion. However, the combination of Mo and Cu greatly increase the hardenability of the steel, such that the increase in cooling rate has a dramatic effect. At Mo contents of 0.5% and above, the 2% Cu – 0.6% graphite steels can be sinter-hardened at cooling rates of 1.6 and 2.2 °C/s. The hardness and transverse rupture strength abruptly increase above 0.3% Mo, with the best properties obtained at 1.5% Mo. For this reason, the alloy Ancorloy[®] DH-1 (Fe-1.5% Mo-2% Cu-0.6% graphite) or its diffusion-alloyed equivalent, became popular for certain applications. With respect to powder handling and sintering, the alloy behaves similarly to FC-0205 and it is easy to process. Enhanced cooling rates are the only modification required to increase the performance of this system greatly. There is also an associated increase in dimensional change (+0.05 to 0.07%) with sinter hardening of this and the subsequent alloy systems.

With the addition of 2% admixed Ni, the properties again improve compared with the base plus graphite system. The properties increase in a near linear fashion with Mo content, although the slope of this increase is greater in the admixed Ni system. There is a synergistic effect with the combination of Ni and Mo on hardenability, resulting in improved properties when both are present. Even at low Mo contents (0.3%Mo), this effect is present. The admixed Ni causes alloy rich regions in the microstructure, so that accelerated cooling results in an increase in both hardness and TRS at all compositions. The sinter-hardening effect is most pronounced at the higher Mo contents. The addition of Ni also increases the toughness of PM steels, which is why an alloy such as FLN2-4405 (Fe-0.8% Mo-2% Ni-0.6% graphite) has gained widespread acceptance.

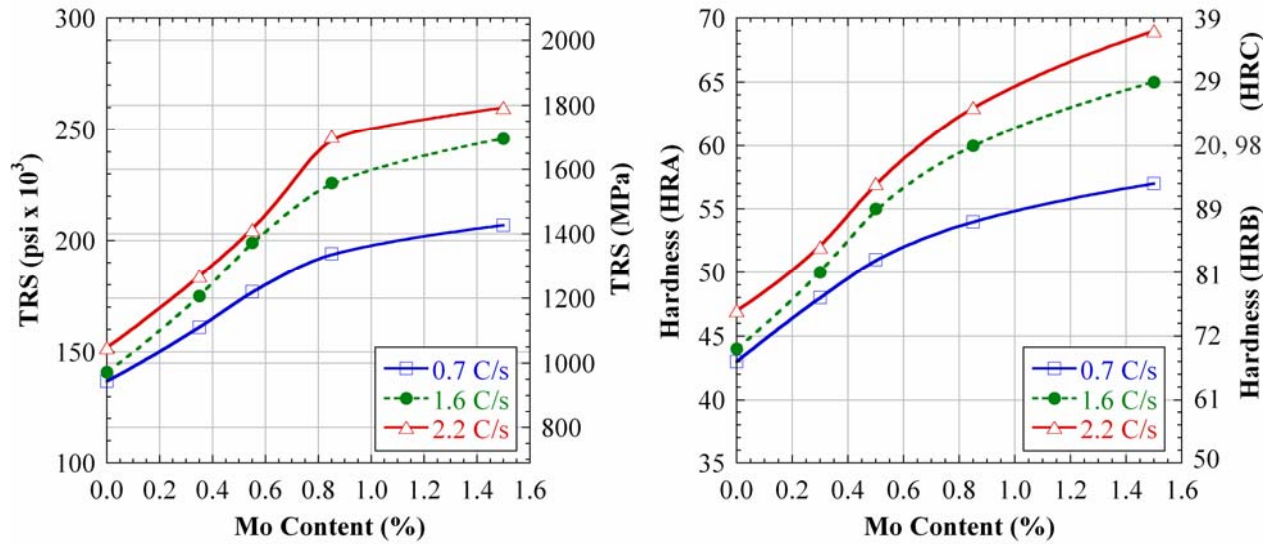


Figure 3. The effect of Mo content and cooling rate on TRS and apparent hardness in 2% Ni - 0.6% graphite PM steels.

The addition of both admixed Ni (2%) and Cu (1.25%) boosts the properties relative to the 2% Ni alloys, Figure 4. At the conventional cooling rate (0.7 °C/s), the TRS improved 140-210 MPa (20-30 x 10³ psi) and the hardness improved 4-5 HRA. With accelerated cooling, the additional hardenability of both Ni and Cu result in peak properties at 0.85% Mo, after which the properties plateau.

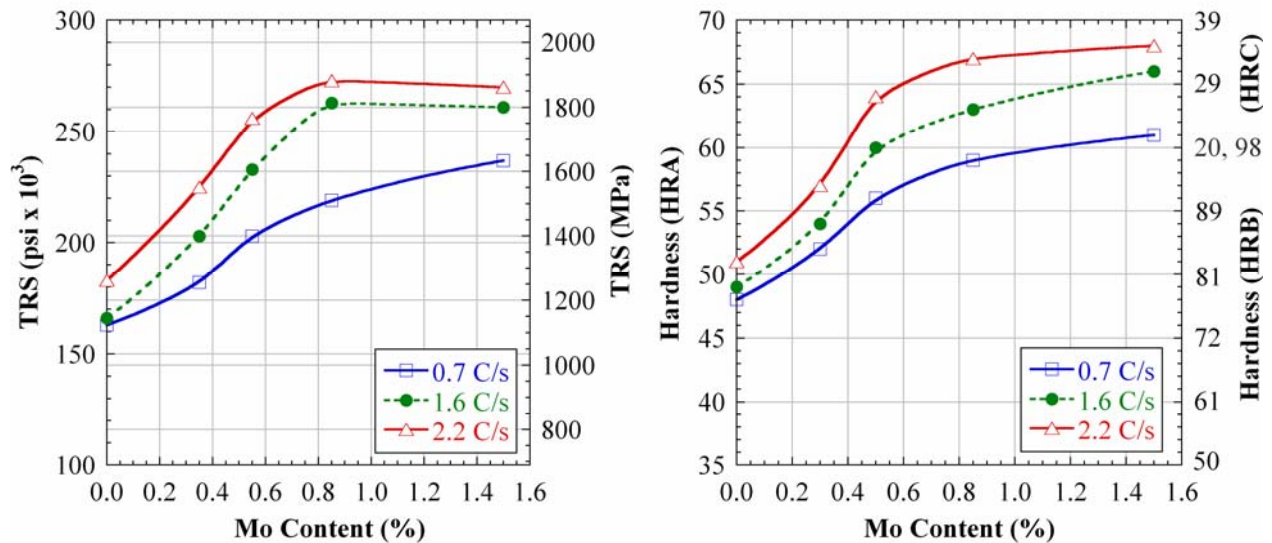


Figure 4. The effect of Mo content and cooling rate on TRS and apparent hardness in 2% Ni - 1.25% Cu - 0.6% graphite PM steels.

It is clear from the previous graphs that the addition of Mo into an alloy system improves its mechanical properties. Prior to the recent run-up in Mo price, it was logical to add high levels of Mo to obtain the best properties. However, by increasing cooling rate, lower Mo steels can be used in these hybrid-alloy systems. While high cooling rates are not always possible in larger parts, small and medium sized parts can greatly benefit. A relatively low cost modification to the sintering furnace with a convective cooling

unit could allow a 0.5% or more reduction in Mo content. For example, the Fe-1.5% Mo base alloy used in Fe-1.5% Mo-2% Cu-C sintered at slow cooling conditions could be replaced by either Fe-0.5% Mo or more conservatively Fe-0.85% Mo with accelerated cooling. At current prices for molybdenum (\$75/kg, \$34/lb), this results in a savings of \$0.75/kg (\$0.34/lb) or \$0.49/kg (\$0.22/lb) in alloy cost, respectively.

Oil Quenched Cylinders

Since molybdenum has a strong influence on hardenability, it can be wisely used in parts that require heat treatment. A small amount of Mo (0.3%) has a dramatic effect on the quench response of the 25 mm (1 inch) diameter slug. The iron and iron-copper base alloys at 0.9% graphite show a hard case to approximately 2 mm and then the hardness quickly drops off as the microstructure changes to a pearlitic morphology. The addition of 0.3% Mo to both alloys causes the samples to through harden at 0.9% graphite, Figure 5. A series of samples was made with no copper and decreasing graphite additions, and it was found that the 0.3% Mo sample through hardened at graphite levels as low as 0.6%, Figure 6. Depending on part size and microstructure requirements, this lower carbon content may be quite beneficial. Higher densities can be achieved and higher core hardness is possible compared with the iron-carbon or Fe-Cu-C system. As the carbon content decreases, the hardness of the martensite also decreases. At carbon contents lower than 0.6%, the 0.3% Mo sample no longer through hardens, leading to a hardness profile with high hardness at the surface (martensitic microstructure) and a softer core (mixed martensite / bainite / pearlite microstructure).

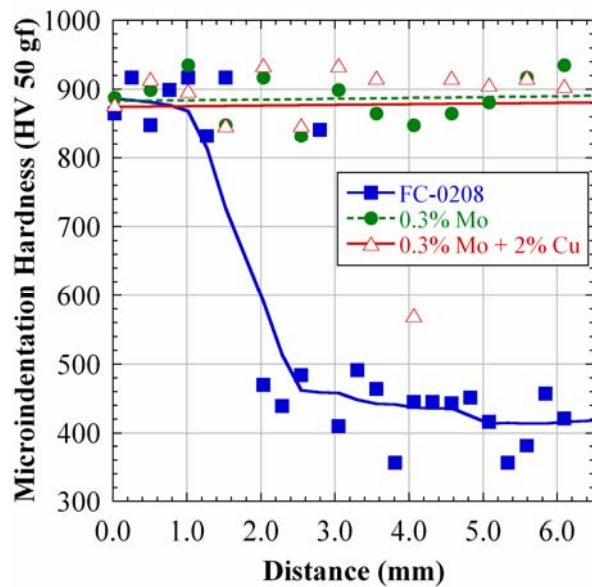


Figure 5

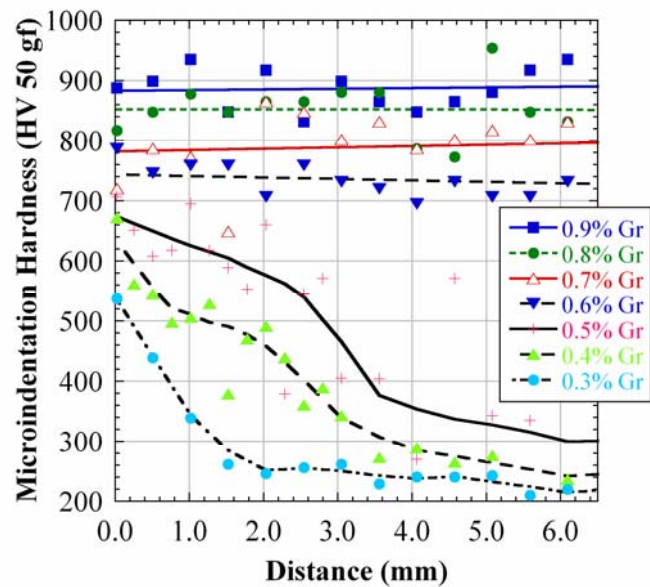


Figure 6

Figure 5. Microindentation hardness profiles from the edge (distance = 0) toward the center of oil quenched 25 mm diameter slugs with 0.9% graphite.

Figure 6. Microindentation hardness profiles of oil quenched 25 mm diameter slugs with 0.3% molybdenum and different carbon contents.

As Mo content is increased, the carbon content required for through hardening is reduced, Figure 7. The required carbon content drops in a nearly linear fashion as Mo content is increased from 0.3% to 1.5%. The 1.5% Mo alloy required only 0.2% graphite addition to through harden. The average microindentation hardness for each Mo-graphite combination is stated on the graph. The decrease in hardness with carbon content is apparent. The 0% Mo data point did not through harden at 0.9% graphite, so the hardness of the case is given.

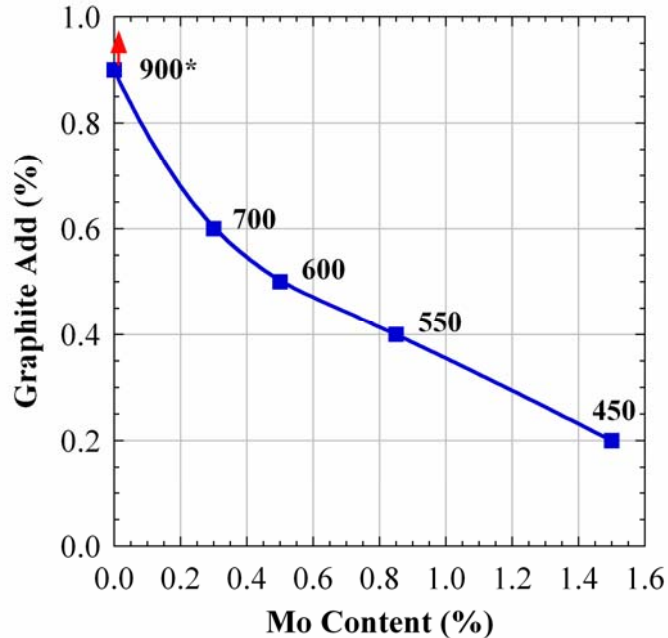


Figure 7. Minimum graphite contents for different Mo alloys required for through hardening of an oil quenched 25 mm diameter cylinder. The average microindentation hardness (HV 50 gf) is given for each Mo-graphite condition. * Note that the 0% Mo did not through harden at 0.9% graphite and the microindentation hardness value was taken in the surface hardened case.

The higher Mo alloys are ideally suited for applications such as gears, where the samples are often carburized. The desired microstructure is often a carburized case and a lower carbon martensitic core, which provides good toughness and strength. The carbon differential between the case and core is responsible for the high compressive stresses in the case, imparting good fatigue resistance. The low graphite content required to form a martensitic core and the good compressibility of the higher Mo powders allows for high green densities. Finally, a low carbon content would facilitate surface densification prior to heat treatment. All of these attributes are beneficial to gearing applications.

Part size should be kept in mind when determining an alloy composition. The samples in this study were 25 mm in diameter. Smaller parts would not require the same level of Mo to achieve a through-hardened microstructure at a given carbon content, so less expensive alloys can be used with smaller parts. Given the part requirements, carbon content can also be increased slightly, allowing a reduction in Mo content as well.

Jominy End Quench

The effect of molybdenum on hardenability is again apparent in the Jominy end-quench data. Recall that samples were made using the 5 base alloys and 0.6% graphite, 2% Cu plus 0.6% graphite and 2% Ni plus 0.6% graphite. The hardness profiles for all 15 alloys are shown in Figure 8. Increasing the Mo content increases both the hardness at slow cooling rates and the depth of hardness above 65 HRA (30 HRC). Jominy hardenability is often rated by the depth at which the sample reaches 65 HRA. The addition of Cu increases the hardness at slow cooling rates so that little difference is found between 0%, 0.3% and 0.5% Mo. This is consistent with the data shown in Figure 2. The presence of Cu greatly increases the hardenability for both 0.85% and 1.5% Mo and flattens out the hardness profile. Nickel has a similar effect as copper, with two notable exceptions. The 0% Mo alloy does not benefit nearly as much from Ni content as compared with Cu at distances greater than 6 mm (0.25 inch). Second, the 0.85% Mo plus Ni alloy has a similar hardenability response as the 1.5% Mo plus Ni alloy. This response was not seen in the hardness of the TRS bars (Figure 3), where the 1.5% Mo was consistently harder than the 0.85% Mo alloy.

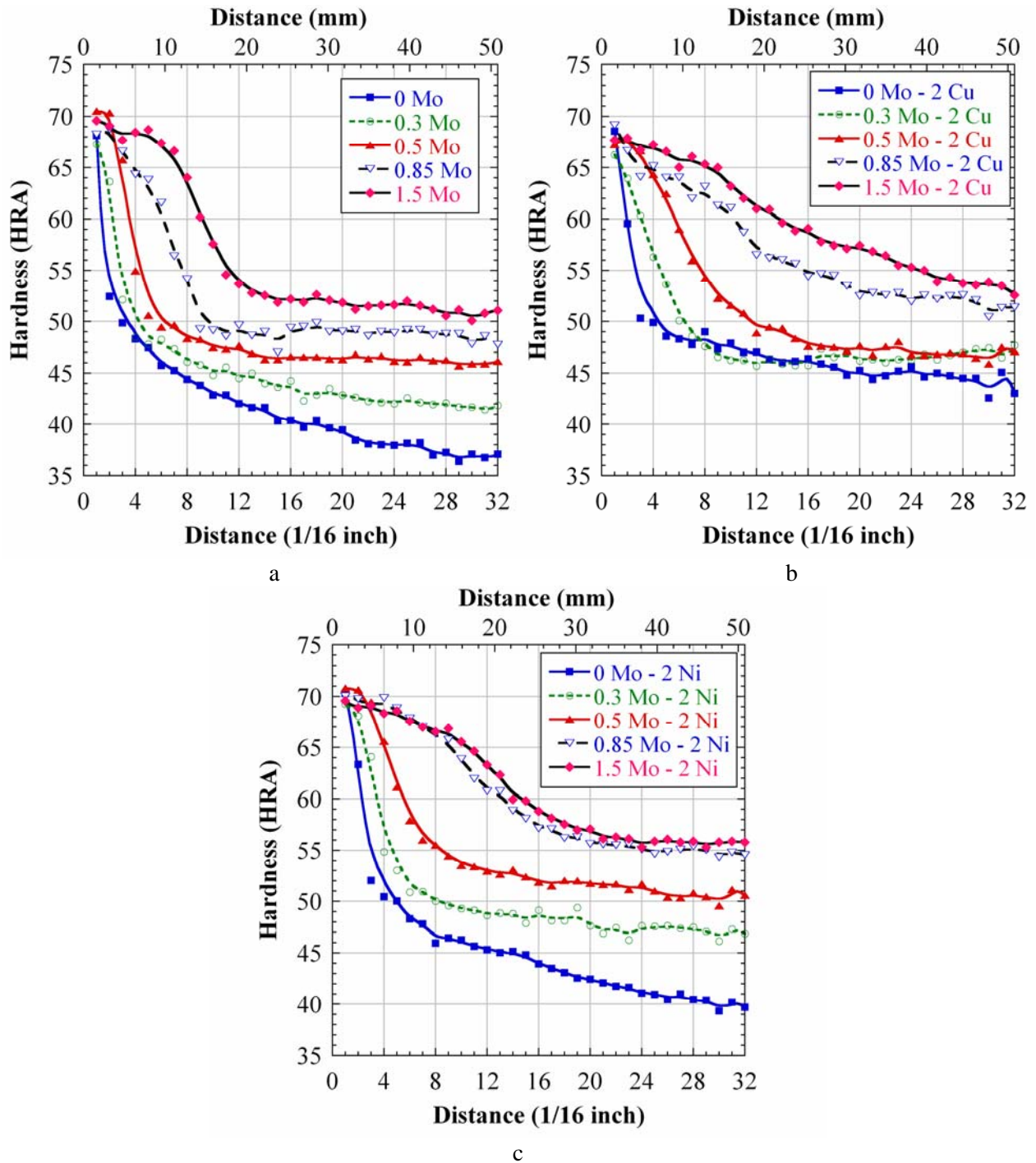


Figure 8. The effect of Mo content on Jominy end-quench hardness profiles for (a) carbon, (b) Cu-C and (c) Ni-C alloys. All mixes contained 0.6% graphite.

However, the Jominy curves may provide some explanation as to why the 1.5% Mo base is preferred in Cu-containing steels (FLC2-4905), whereas the 0.85% Mo base is preferred in Ni-containing steels (FLN2-4405).

The large benefit of a 0.3% Mo addition to iron with respect to the oil quench response is not clearly apparent in the Jominy data. While a small increase in hardenability is present, it does not appear

significant in these tests. Recall that 0.6% was the lowest graphite addition for through hardening of the oil quench slugs. As carbon content increases, so does the effect of the added Mo. A larger difference in the Jominy hardness profile between the 0% and 0.3% Mo alloys would likely be seen at higher graphite contents.

CONCLUSIONS

The addition of molybdenum to ferrous PM alloys increases strength and hardenability. The use of molybdenum should be properly tailored for each application to gain the best combination of properties and cost. For sinter hardening, a minimum Mo content of 0.85% is recommended with Ni and/or Cu additions, although sinter hardening of 0.5% Mo alloys is possible with both Ni and Cu additions. For heat-treated parts, as little as 0.3% Mo can greatly improve the heat treatment response of the alloy. With an alloy cost similar to FC-020X alloys, the 0.3% prealloyed Mo alloys should provide not only better heat-treat response, but should also improve dimensional precision. Higher molybdenum and lower carbon contents are well suited for carburizing, allowing the development of a high carbon martensite case and a low carbon martensitic core.

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