INTRODUCTION

In previous work microalloying has been shown to be an effective strategy for the development of ferrous PM alloys with enhanced properties for high-strength applications.1,2 In particular, vanadium has been shown to be effective in both the sintered and heat-treated conditions. In the sintered condition, many PM alloy steels exhibit a pearlitic microstructure. The strength of the pearlite can be increased in several ways. Since pearlite is a mixture of ferrite and iron carbide (cementite), with ferrite being the dominant phase, any alloying element that increases the hardness of the ferrite (through solid-solution strengthening) increases the strength of the pearlite and hence the strength of the alloy. Figure 1 shows the effect of various alloying elements on the hardness of ferrite. Chromium and manganese show a strong hardening effect on ferrite but generally do so at relatively high concentrations. Silicon and vanadium are more effective than those other elements at concentrations <0.80 w/o. Vanadium has a further advantage in that it combines preferentially with nitrogen to form nitrogen-rich vanadium carbonitride \( [V(C,N)] \) precipitates.

It has also been shown that factors such as the proportions of ferrite and pearlite, along with the interlamellar spacing and size of the pearlite nodules, affect the mechanical properties.4–6 Figure 2 shows that the interlamellar spacing controls the strength and hardness of wrought steels with pearlitic microstructures. Hyzak and Bernstein5 found that the yield strength and hardness were controlled primarily by the interlamellar spacing and that impact energy was dependent on the prior austenite-grain size, increasing with finer grain size, and to some extent on the pearlite-colony size.
When austenite transforms to ferrite and carbide (pearlite reaction), alloying elements can have an effect in three ways:

1. Elements are in solid solution in the ferrite.
2. Elements combine with carbon to form carbides and, at saturation, enter the ferrite.
3. Elements are in solution in the carbide phase only.

Elements such as copper, nickel, phosphorus, and silicon are in solid solution in the ferrite since their solubility in the carbide, and tendency to form alloy carbides, is low. At low concentrations elements such as chromium, manganese, molybdenum, and vanadium will enter into solution in the carbide and at higher concentrations will also go into solution in the ferrite. The partitioning of the elements during the formation of pearlite is difficult to predict, particularly in multi-alloy systems. How the elements partition between the phases and the kinetics of formation can have a significant effect on the pearlite interlamellar spacing and nodule size. Any elements or combination of elements that reduce the diffusion of carbon will decrease the pearlite spacing. Since there are many factors influencing the formation of pearlite, the present study was undertaken to examine the effects of various alloying elements on the microstructure and mechanical properties of sintered PM steels.

The ability of an alloy to transform to martensite during heat treating is affected by the various alloying elements. Hardenability is generally accepted as a qualitative measure of the ease and depth to which steel is able to transform to martensite upon cooling from the austenitizing temperature. The mechanical properties of a heat-treated steel depend primarily on its hardenability. Sokolowski et al.\textsuperscript{7} have reviewed various factors influencing the hardenability of PM steels. It has also been shown that elements such as molybdenum and nickel can have a synergistic effect leading to enhanced hardenability when alloyed together. In relation to hardenability, vanadium and silicon are not used as extensively as these elements in PM steels. Figure 3 shows the multiply factors developed by Jatczak\textsuperscript{8} for carbon contents in the range of 0.60 to 1.10 w/o and an austenitizing temperature of 926°C (1,700°F). At these higher carbon contents silicon has a hardenability factor similar to that of chromium and manganese. The role of vanadium on hardenability is more complex and is not included. Vanadium forms vanadium carbonitride [V(C,N)] precipitates and, depending on the level of nitrogen (and carbon) and the austenitizing temperature, can affect the amount of vanadium in solution. If the austenitizing temperature is high enough the precipitates will dissolve and more vanadium will be in solution prior to quenching, leading to enhanced harden-
ability. Likewise, if the composition of the precipitates (influenced by the carbon and nitrogen levels) is such that they cannot dissolve at the austenitizing temperature, less vanadium will be in solution and lower hardenability will result.

In the present study, a development program was undertaken in which silicon and vanadium were added to several ferrous systems. Mechanical properties were measured and microstructures characterized in the sintered-and-heat-treated condition to assess the role of precipitation strengthening and grain refinement during heat treatment.

**ALLOY PREPARATION AND TESTING**

Mixtures of base powders and a proprietary additive containing vanadium and silicon (patent pending) were utilized to prepare test specimens. The mean particle size (d_{50}) of the additives was 10 μm. Ancorsteel® 1000 was used for the iron-base alloy systems, and Ancorsteel 30HP was used for the iron–molybdenum alloy.

The powders were mixed with Acrawax C lubricant and graphite. Graphite additions were 0.70 w/o (unless otherwise noted) resulting in a sintered carbon level of 0.65 w/o. Samples for transverse rupture (TR) and tensile testing were compacted uniaxially at a pressure of 690 MPa. The test pieces were sintered in a high-temperature Abbott continuous-belt furnace at a temperature of 1,260°C (2,300°F) for 30 min in an atmosphere of 90 v/o nitrogen and 10 v/o hydrogen.

For heat treatment, samples were austenitized at 900°C (1,650°F) for 60 min at temperature in 75 v/o nitrogen and 25 v/o hydrogen atmosphere prior to quenching in oil. The quenched specimens were then tempered at 200°C (~400°F) for 1 h.

Prior to mechanical testing, green and sintered density, dimensional change (DC), and apparent hardness were determined on the tensile and TR samples. Five tensile specimens and five TR specimens were evaluated for each composition. The densities of the green and sintered steels were determined in accordance with MPIF Standard 42. Tensile testing followed MPIF Standard 109 and apparent hardness measurements were made on the tensile and TR specimens, in accordance with MPIF Standard 43.

Specimens for microstructural characterization were prepared using standard metallographic procedures. Subsequently, they were examined by optical microscopy in the as-polished and etched (1 v/o nital/4 w/o picral) conditions. Etching times were closely monitored to prevent overetching the alloys containing silicon and vanadium due to the fineness of their microstructures. Also, the magnification within each figure containing photomicrographs was kept consistent to allow for a direct comparison of the details in the microstructures.

**RESULTS AND DISCUSSION**

**Sintered Alloys**

It has been shown that vanadium increases the strength of PM steels with a pearlitic microstructure by forming precipitates in the ferrite. Steel grades with a vanadium addition exhibited a 10%–15% increase in tensile strength compared with the same vanadium-free alloy. This prompted the current research to determine if the strength of these alloy systems could be increased even further by combining other ferrite strengtheners with a vanadium addition.

One of the primary reasons for the large increase in strength is refinement of the pearlite in the iron–carbon alloy containing both silicon and vanadium. The interlamellar spacing of the pearlite in the alloys with and without silicon and vanadium is shown in Figure 4. The spacing in the silicon plus vanadium-containing iron–carbon alloy is much finer than the spacing in the absence of these alloy additions. In addition, there is a reduction in the ferrite-grain size and the size of the pearlite colonies. This was also the case in the iron–nickel–carbon and iron–molybdenum–carbon
alloys cited in Table I. The iron–copper–carbon alloy was the only system that did not show a large increase in tensile strength (>10%) with the addition of silicon and vanadium. Copper is known to decrease the amount of ferrite and promote the formation of pearlite, thereby increasing the strength and hardness. In addition, copper at high levels (>2.0 w/o) may saturate the ferrite in this alloy system so that it is already at its maximum strength; hence, the addition of silicon and vanadium does not result in any further significant increase in the hardness of the ferrite.

### Heat-Treated Alloys

One of the advantages of V(C,N) precipitates is that they retard grain growth during thermomechanical processing. For PM steels, heat treatment requires austenitizing at temperatures that cause the austenite grains to grow. Since the austenitizing temperature is below the temperature at which the V(C,N) precipitates go into solution, they retard grain growth and lead to a fine microstructure after oil quenching. This grain refinement has the effect of increasing both strength and toughness. Table II shows that in the heat-treated condition

![Figure 4. Representative microstructures of iron–carbon alloys cited in Table I: (a) sintered; no silicon or vanadium, (b) sintered; additions of silicon and vanadium](image-url)
with the addition of vanadium, the general trend is to increase strength and hardness, compared with the vanadium-free alloys. Since V(C,N) precipitates refine the austenite-grain size prior to quenching, the martensite formed during quenching is finer, leading to an increase in impact energy.

The iron–carbon system is the only exception, since the strength of the vanadium-containing alloy is less than that of the vanadium-free alloy. The reason for this can be seen by examining the microstructures of the alloys. Figure 5 shows the microstructures of the three iron–carbon alloys. The iron–carbon alloy without any alloy additions transforms completely to martensite. When vanadium is added a significant amount of bainite is formed after quenching. Since vanadium is a ferrite stabilizer, further carbon additions would be necessary to fully transform this alloy. In the iron–carbon–silicon–vanadium alloy, the addition of silicon leads to a lower amount of bainite and a higher amount of martensite than in the iron–carbon–vanadium alloy, indicating that silicon aids the transformation. It can also be observed that the martensite needles in the vanadium and vanadium–silicon-containing alloys are much finer than those in the iron–carbon alloy, indicative of a finer austenite-grain size prior to quenching.

Figure 3 also indicates that silicon has a hardenability factor similar to that of chromium at concentrations <1.0 w/o. Although extensive data on the hardenability of PM steels containing silicon do not exist, Table II shows that the addition of silicon leads to an increase in the heat-treated mechanical properties (yield strength and ultimate tensile strength), without a significant decrease in impact energy compared with the vanadium and vanadium-free alloys. The one exception is the iron–molybdenum–carbon alloy system, which does not show a dramatic increase in these properties compared with the alloy containing vanadium. Since the thickness of the specimens is small and molybdenum has a high hardenability factor, an extreme change is not expected. It has been shown previously that molybdenum (~0.35 w/o) can be effective in through hardening thin-section PM parts.\(^{10}\)

**Hardenability**

The heat-treated microstructures in the preceding section indicated that silicon may contribute to the hardenability of some of the alloys cited in Table II. Jatczak's work (Figure 3) indicated that at the higher carbon levels typically used in PM, silicon would be as effective as chromium and manganese in terms of hardening. Additionally, Jatczak found that certain elements, when present together, exhibited a higher hardenability than would be predicted by the individual hardenability factors. Silicon was noted to have this effect when used in molybdenum-base alloys. Silicon

<table>
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<th>Alloy</th>
<th>Sintered Density (g/cm(^3))</th>
<th>Impact Energy (ft.·lbf)</th>
<th>Apparent Hardness (HRA)</th>
<th>UTS (10(^3) psi) (MPa)</th>
<th>0.20% OFFSET (10(^3) psi) (MPa)</th>
<th>Elongation (%)</th>
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<tr>
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<td>73</td>
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\[^{10}\] Volume 48, Issue 6, 2012
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increased the amount of carbon and carbide-forming elements in solution at the austenitizing temperature, leading to a higher concentration of carbon in the martensite upon transformation. However, since molybdenum is a strong carbide former, its effect is strongly dependent on the austenitizing temperature; a temperature of 927°C (1,700°F) was found to be optimum for hardenability in the molybdenum–silicon-containing alloys. The hardenability of the alloys in this study is also affected by the addition of vanadium that can go into solution and alter the prior austenite-grain size by the formation of precipitates.

**Suppression of Carbides**

Research on wrought steels used for rails and wire has shown that when vanadium and silicon are added to high-carbon steels (>0.8 w/o) they reduce the formation of grain-boundary carbides. The cost effectiveness of carbon has been exploited in PM steels for years with levels of carbon typically higher than those in wrought steels. However, above 0.80 w/o C a continuous film of carbides tends to form on the grain boundaries in PM steels leading to embrittlement and to a decrease in mechanical properties. It has been found that in wrought steels, vanadium fragments the grain-boundary cementite by combining with the carbon. Silicon has been found to slow the diffusion of carbon to the cementite, thereby suppressing the formation of the grain-boundary cementite. These two effects have resulted in wrought steels with carbon levels between 0.90 w/o C and 1.10 w/o C, with excellent mechanical properties.

To examine this phenomenon in a PM steel, an iron–carbon alloy with carbons ranging from 0.70 w/o to 1.30 w/o C was evaluated. The results of

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**Figure 5.** Representative microstructures of sintered and heat-treated PM steels: (a) iron–carbon; (b) iron–carbon–vanadium, and (c) iron–carbon–silicon–vanadium
the yield-strength and impact-energy measurements are shown in Figure 6. In the iron–carbon alloy with no silicon and vanadium, the impact energy decreases with the carbon level and drops significantly at carbon levels >1.0 w/o. Notwithstanding the much higher strength level in the alloy containing silicon and vanadium, the impact energy does not dramatically decrease with carbon additions >1.0 w/o.

Examination of the microstructure of the two alloys containing 1.3 w/o C shows the reason for the differences in the behavior of impact energy (Figure 7). The iron–carbon alloy with no addition of silicon or vanadium shows a thick, nearly continuous network of grain-boundary carbides while the iron–carbon alloy with silicon and vanadium added does not exhibit these carbide networks, and hence suffers no significant decrease in impact energy at 1.10 w/o C with a strength increase of ~30% over that of the 0.70 w/o C-containing alloy. When carbon was added to the alloy systems (Table I), the same results were found, namely, silicon–vanadium additions reduced the level of grain-boundary carbides and led to increased strength with acceptable toughness at higher levels of carbon. The optimum level was between 1.00 w/o and 1.10 w/o C.

CONCLUSIONS
• Silicon in solid solution in ferrite in pearlitic PM steels results in strengthening.
• Vanadium increases the strength of pearlite through solid-solution strengthening and precipitation hardening in the ferrite.
• Silicon and vanadium can be used in combination to significantly increase the strength of PM steels exhibiting pearlitic microstructures.
• Silicon and vanadium can be used to improve strength in heat-treated PM steels. Vanadium precipitates restrict grain growth of the austenite during heat treatment and this leads to higher strength and toughness. Silicon increases the hardenability of PM steels.
• A combination of silicon and vanadium allows for the use of higher carbon levels in PM steel by reducing the formation of carbides at the grain boundaries.
REFERENCES


