

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF MICROALLOYED PM STEELS

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ABSTRACT

Microalloying is used in wrought steels to refine grain size during thermo-mechanical controlled processing (TMCP), with an attendant improvement in mechanical properties. With the exception of powder forging (PF), powder metallurgy (PM) does not utilize TMCP. In previous work by the authors, however, it has been shown that in PM steels microalloying elements such as niobium and vanadium can limit austenite grain growth during austenization prior to oil quenching and tempering. By limiting grain growth, the attendant precipitates cause a significant improvement in strength and ductility. In addition the precipitates that form during microalloying can also improve the strength of the pearlite which forms in the sintered condition. The objective of this study was to explore the use and potential benefits of microalloying elements such as vanadium and niobium in PM steels. The resulting mechanical properties and accompanying microstructure of these microalloyed PM steels are evaluated and rationalized.

INTRODUCTION

The rising cost and volatility of metals has led to the development of new alloy systems for PM steels. In particular, PM steels have utilized primarily copper, nickel and molybdenum to compete with wrought grades. Recently, due to cost constraints and availability, PM steels have also included chromium and manganese as alloying elements. These material systems are categorized as alloy steels since significant levels of these elements are required to effect changes in the mechanical properties. Microalloyed steels are defined as steels containing small amounts of niobium, vanadium, or titanium, generally at levels between 0.05 and 0.20 w/o. Notwithstanding the low alloy content, microalloying can lead to major increases in strength and toughness. This is a result of the formation of carbonitrides which lead to both precipitation strengthening and grain refinement. The contribution of these effects is dependent on thermal and mechanical processing, which are different in PM than in conventional wrought steel processing utilizing forging and rolling.

The choice of microalloying element is dependent on the solubility of the carbide or nitride that is formed. Titanium has a high propensity for forming oxides and sulphides, the lowest solubility and is generally ineffective as a precipitation strengthener in medium to high carbon steels. For this reason, niobium and vanadium were the elements studied. The strengthening produced by niobium and vanadium is due to two mechanisms: dispersion strengthening by the precipitation of fine carbonitride particles; and grain refinement during heat treatment due to the presence of precipitates. When vanadium is added, it combines preferentially with nitrogen to form nitrogen-rich vanadium carbonitride [V(C,N)] precipitates. The nitrogen determines the nucleation rate and density of the precipitates. V(C,N) is more soluble in high carbon steels and is less sensitive to carbon level compared with niobium. In niobium microalloyed steels carbon is the preferred element for precipitation and at higher carbon levels the solubility of Nb(C,N) is reduced and higher temperatures are needed to get niobium in solution. Figure 1 shows the solubility of the two systems as a function of temperature.

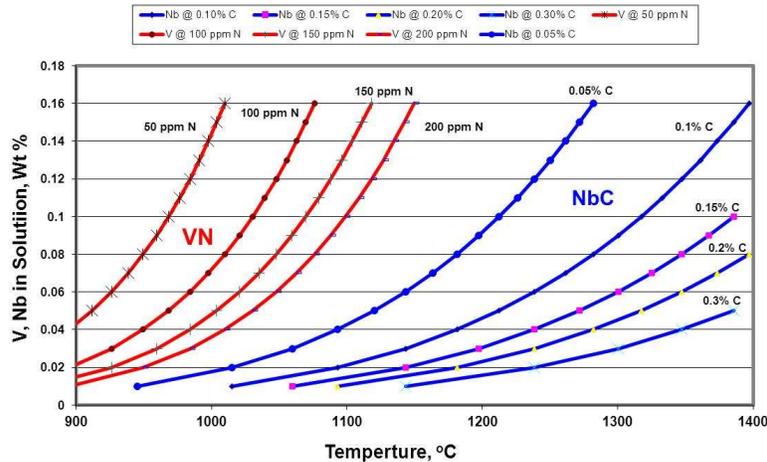


Figure 1: Effect of temperature on the maximum solubility of vanadium and niobium carbonitrides [1].

Several facts are apparent from Figure 1. First, the solubility of Nb(C,N) decreases as the carbon level increases. For most low alloy PM steels a minimum of 0.30 w/o C is necessary to achieve significant strengthening. At this carbon level sintering temperatures in excess of 1300 °C are required to completely dissolve the niobium precipitates. For vanadium, typical sintering temperatures (1120 to 1260 °C) are sufficient to get most of the V(C,N) in solution. Slow cooling from the sintering temperature will allow for the formation of fine V(C,N) precipitates which can provide strength in the sintered condition. When reheated to the austenitizing temperature (900 °C), the V(C,N) will precipitate completely and coarsen, no longer providing significant strengthening. However, these precipitates will retard grain growth, which results in finer austenite grains prior to quenching. Finer austenite grains quenched to martensite

result in higher strength, ductility and toughness. Similar results can be expected if the precipitates are Nb(C,N).

To explore the practical utility of this technique in PM steels, a development program was undertaken in which niobium and vanadium were added to several material systems. Properties were measured and microstructures characterized in the sintered and heat treated conditions to assess the effects of precipitation strengthening and grain refinement during heat treatment.

ALLOY PREPARATION AND TESTING

Mixtures of base powders and ground ferroniobium (Fe-65 w/o Nb) and ferrovanadium (Fe- 78 w/o V) were utilized to prepare test specimens. The mean particle size (d_{50}) of the additives was 8 μm .

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 1120 °C for 30 min in an atmosphere of 90 v/o nitrogen and 10 v/o hydrogen.

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 10 and apparent hardness measurements were conducted on the tensile and TR specimens, in accordance with MPIF Standard 43.

Specimens for microstructural characterization were prepared using standard metallographic procedures. Then were examined by optical microscopy in the polished and etched (1 v/o nital / 4 w/o picral.) conditions.

RESULTS AND DISCUSSION

Microalloying with Niobium

Niobium results in significant strengthening via the precipitation of a hard and stable carbide, nitride or carbonitride, NbC(N). The carbide-forming tendency of niobium is stronger than that of vanadium and studies on wrought steel grades have shown that about one-half the amount of niobium is needed compared with vanadium to produce the same increment in strength. In addition, the carbonitrides of niobium are more stable at higher temperatures than those of vanadium. Niobium has a negative effect on the hardness of martensite because of its ability to effectively remove carbon from solution and is generally not used in low alloy martensitic steels.

Several investigators have examined the role of niobium in sintered PM steels [2-5]. These studies utilized carbon contents < 0.5 w/o due to the higher solubility temperature as carbon increases (Figure 1). To examine this effect a simple iron-carbon system was examined with an addition of 0.16 w/o Nb. Various carbon additions were made from 0.10 to 0.50 w/o and TR strength and apparent hardness were measured in the sintered condition (Figure 2). At low carbon levels there is an increase in the TR strength with the iron-containing niobium, presumably due to the precipitation of NbC(N). The precipitates come out of solution during cooling from the sintering temperature. As the carbon level is increased, the strength difference between the Fe-C-Nb and the Fe-C systems decreases until the influence of the niobium is completely negated at 0.50 w/o C. The apparent hardness of the two alloy systems is compared in Figure 2(b). The apparent hardness of the niobium-containing alloy is higher than that of the Nb-free system and retains hardness regardless of the carbon content. The loss in strength at the higher carbon levels is attributed to the fact that, at higher carbon levels, the precipitates are not soluble during sintering and coarsen during cooling from the sintering temperature. The increase in hardness over the range of carbon levels is likely due to the effect of niobium in solution and possibly to some refinement of the microstructure.

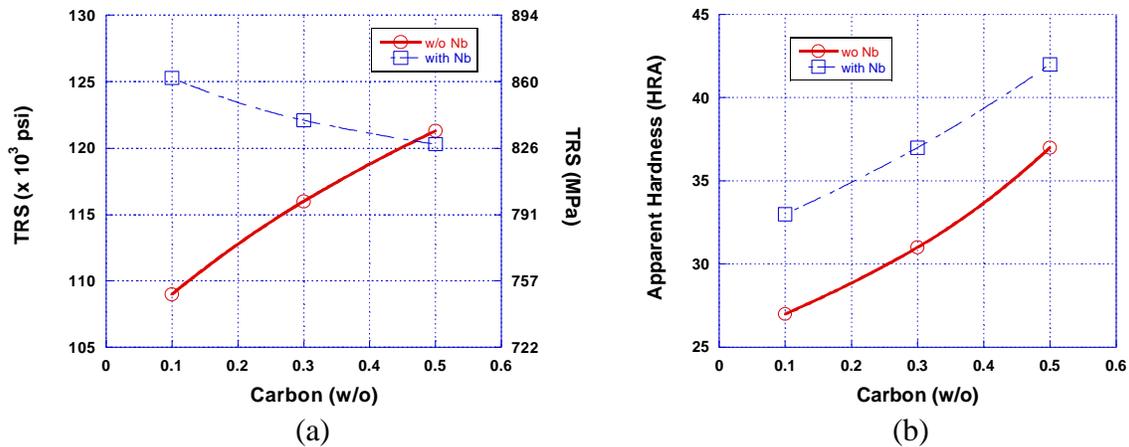


Figure 2: (a) TR strength (with and without Nb) versus carbon level, and (b) apparent hardness (with and without Nb) versus carbon level.

In wrought steel grades the level of niobium typically used is 0.02 to 0.06 w/o. In PM steels, since an additive is used, diffusion is critical. As with other PM additives, the niobium particles ($d_{50} \sim 8 \mu\text{m}$) do not diffuse completely into the iron. In this case the amount of niobium needed is higher for PM steels than for wrought steels; the effect is shown in Figure 3. In the Fe-C system the maximum strength and apparent hardness occur at niobium levels between 0.15 and 0.20 w/o. The decrease in strength at high niobium levels results from the formation of niobium precipitates at grain boundaries.

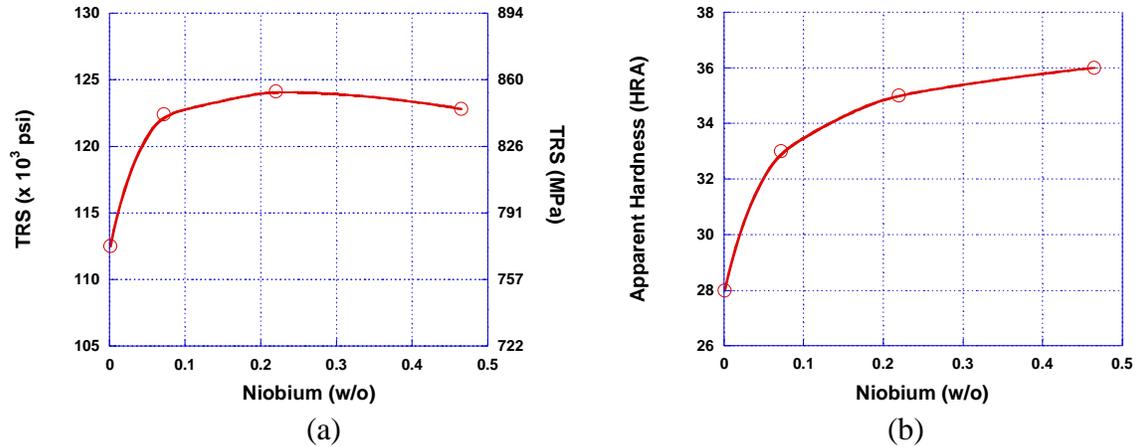


Figure 3: Effect of niobium on (a) TR strength and (b) apparent hardness.

A major benefit of microalloying is the restriction of grain growth during austenitizing. If fine precipitates exist during the austenitizing step, the growth of grains is restricted leading to a finer grain size after quenching. The fine grain size leads to an increase in strength, with a corresponding increase in toughness. To examine the role of NbC(N) precipitates in restricting grain growth during heat treatment, ferroniobium was added to a 0.30 w/o Mo alloy (ANCORSTEEL 30HP). In order to fully examine the benefits of the niobium, no carbon was added to the alloy. Tensile properties of the 0.30 w/o Mo alloy were measured with and without niobium in the sintered and heat treated conditions; the results are shown in Table I.

Table I: Mechanical Properties of 0.30 w/o Mo Alloy Sintered and Heat Treated.

Alloy	Sintered Density (g/cm ³)	Apparent Hardness (HRA)	UTS		0.20% OFFSET		Elongation (%)
			(10 ³ psi)	(MPa)	(10 ³ psi)	(MPa)	
Sintered							
0.30 Mo	7.17	16	34.1	235	18.8	129	16.27
0.30 Mo + .20 Nb	7.15	27	37.1	255	25.7	177	7.92
Heat Treated							
0.30 Mo	7.17	35	47	323	30.3	208	8.88
0.30 Mo + .20 Nb	7.15	38	49.6	341	35.1	241	6.35

Utilizing an alloy containing no carbon further highlights the role of the precipitates. In the sintered condition there is a general increase in yield strength and apparent hardness when niobium is present. On cooling from the sintering temperature, NbC(N) precipitates form and these lead to an increase in strength compared with the material without any additions of niobium. When both these materials are heat treated, the NbC(N) precipitates restrict the growth of grains during austenitizing and the finer grain size leads to an increase in the strength of the alloy containing niobium. The strength differential between the alloy with and without niobium decreases from the sintered condition to the heat treated condition. This is attributed to the fact that the austenitizing

temperature is not high enough to dissolve the existing niobium-containing precipitates and the precipitates grow and are less effective in both strengthening and restricting grain growth during heat treatment. The latter effect is supported by the microstructures of the alloys cited in Table I and shown in Figure 4.

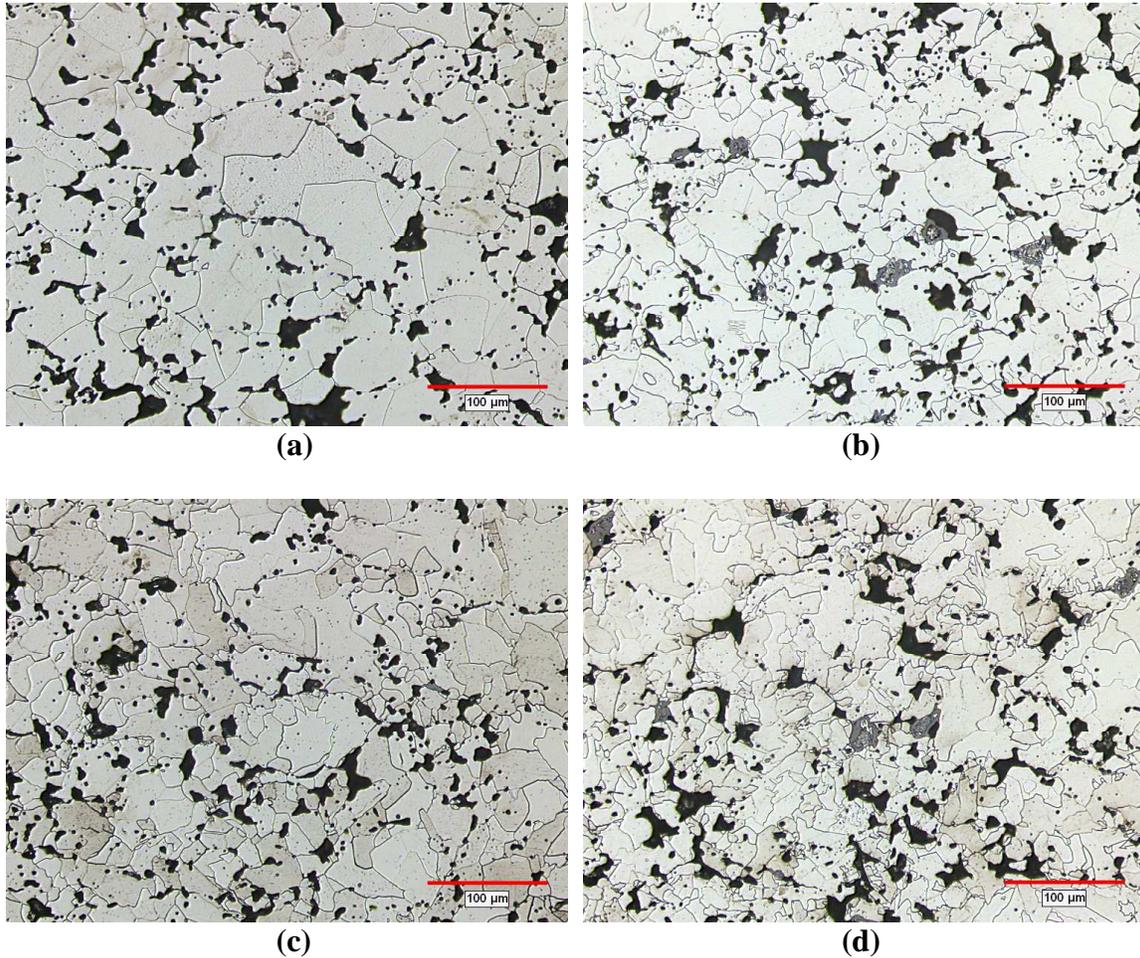


Figure 4: Representative microstructures of alloys from Table I: (a) sintered without niobium, (b) sintered with niobium, (c) heat treated without niobium, (d) heat treated with niobium.

In the sintered condition, the niobium-containing alloy clearly has a finer grain size than the niobium-free alloy; however in the heat treated condition the difference in grain size is less evident although the grains in the alloy with niobium are smaller.

In summary, although niobium is effective as a microalloying element in PM systems, the high solubility temperature, together with the fact that as carbon increases the solubility decreases (Figure 1), restricts the use of this element to systems which have low carbon levels. In turn, this limits the use of niobium to specialized PM materials.

Microalloying with Vanadium

Compared with the Fe-C-Nb system, V(C,N) is more easily dissolved in medium and high carbon steels and the solubility is less sensitive to carbon than niobium [6]. The solubility temperatures for vanadium (Figure 1) are in the range of typical sintering temperatures (1120 to 1260 °C) and these temperatures are capable of dissolving all the vanadium carbonitrides compositions. Another advantage of vanadium versus niobium is the fact the vanadium combines readily with nitrogen to form V(C,N) precipitates which are primarily nitrides (V(0.2 w/o C-0.8 w/o N)). This is a distinct advantage in PM steels, since they are sintered in nitrogen-containing atmospheres and generally contain higher levels of nitrogen than wrought materials. In this context, strength is an increasing function of the vanadium and nitrogen levels [7].

Additions of vanadium to medium carbon alloys effectively increase the strength of the pearlite. Strengthening is accomplished by the precipitation of fine vanadium carbonitride particles in the ferrite of the pearlite microstructures [8]. Because of the low solution temperatures for vanadium, they are dissolved and in solution during sintering. Upon cooling from the sintering temperature, V(C,N) precipitates form in the ferrite of the pearlite and increase the strength. Table II shows the results for several material systems which form pearlite in the sintered condition.

Table II: Mechanical Properties of Material Systems With and Without Vanadium.

Alloy	Sintered Density (g/cm ³)	Impact Energy		Apparent Hardness (HRA)	UTS		0.20% OFFSET		Elongation (%)
		(J)	(ft.lbf)		(10 ³ psi)	(MPa)	(10 ³ psi)	(MPa)	
Fe-C									
No Vanadium	7.13	22	16	41	60.4	416	38.2	263	4.8
0.16 w/o Vanadium	7.11	16	12	47	72.1	496	53.8	370	3.4
Fe-2Ni-C									
No Vanadium	7.18	27	20	48	80.0	550	46.6	321	4.2
0.16 w/o Vanadium	7.16	22	16	51	93.9	646	64.3	442	3.8
Fe-2Cu-C									
No Vanadium	7.12	19	14	52	92.9	639	70.6	486	2.7
0.16 w/o Vanadium	7.10	16	12	53	91.5	630	73.5	506	2.4
Fe-.30Mo-C									
No Vanadium	7.13	20	15	46	71.7	493	51.0	351	3.8
0.16 w/o Vanadium	7.11	16	12	48	83.2	572	64.0	440	3.1

Except for the Fe-Cu-C system, the addition of vanadium led to an increase in both the ultimate tensile and yield strength of the systems in the sintered condition. This is attributed to the precipitation of V(C,N) during cooling from the sintering temperature. Additional solution strengthening may occur due to the high solubility of vanadium in ferrite, and this is one reason it is commonly used as a pearlite strengthener. The lack of increase in strength in the copper system is likely due to the fact that copper, although limited in solubility in ferrite, does provide solution strengthening and this may be the dominant effect. The copper system exhibits the highest strength, even when no vanadium is present.

The most dramatic effect of vanadium on the microstructure is found in the molybdenum-containing alloys. Molybdenum is known to change the morphology of the microstructure in as-sintered steel from lamellar pearlite to a dual upper bainite-divorced pearlite microstructure. While molybdenum additions strengthen steel, this change in microstructure reduces the benefit at lower molybdenum levels. Additions of vanadium to molybdenum-containing steels were found to change the microstructure back to a lamellar pearlitic morphology, thereby boosting the mechanical properties significantly. Figure 5 shows the microstructure of Fe-0.3 w/o Mo-C and Fe-0.3 w/o Mo-C-V alloys. The addition of vanadium clearly changes the microstructure from bainitic-divorced pearlite to conventional ferrite + lamellar pearlite. This change in microstructure increases the as-sintered strength of molybdenum-containing PM steels, as shown in Table II.

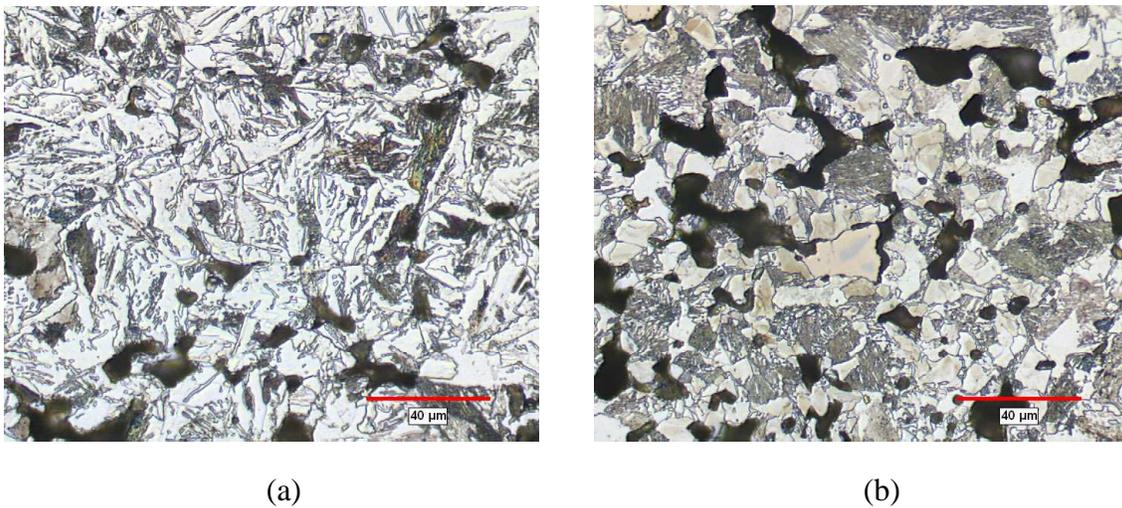


Figure 5. Sintered microstructures of: (a) Fe-0.3w/o Mo-C and (b) Fe-0.3 w/o Mo-C-V.

One of the major reasons for microalloying is to retard grain growth during thermo-mechanical processing. For PM alloys, heat treatment requires austenitizing at temperatures which will 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 finer microstructure after oil quenching. This grain refinement has the effect of increasing both strength and toughness. Table III cites the mechanical properties of the alloy systems in the heat treated condition. In all the systems except the Fe-C, the addition of vanadium leads to an increase in ultimate tensile strength of approximately 10 to 15 percent. Corresponding to this increase in strength is an increase in the impact toughness due to the refined grain size. If a further increase in strength is required, some degree of toughness can be sacrificed by adding more carbon. Examination of the microstructures of the Fe-C alloy revealed that this system contains non-martensitic regions and it is obvious that this system did not have an adequate hardenability to fully transform to martensite.

Table III: Mechanical Properties of Alloys With and Without Vanadium in Heat Treated Condition.

Alloy	Sintered Density (g/cm ³)	Impact Energy		Apparent Hardness (HRA)	UTS		0.20% OFFSET		Elongation (%)
		(J)	(ft.lbf)		(10 ³ psi)	(MPa)	(10 ³ psi)	(MPa)	
Fe-C									
No Vanadium	7.13	11	8	73	138.7	954	121.0	832	0.9
0.16 w/o Vanadium	7.12	13	10	65	120.0	826	109.3	752	1.2
Fe-2Ni-C									
No Vanadium	7.18	15	11	72	132.8	914	108.2	744	0.8
0.16 w/o Vanadium	7.16	16	12	71	140.1	964	108.0	743	0.9
Fe-2Cu-C									
No Vanadium	7.11	11	8	70	122.2	841	98.1	675	0.7
0.16 w/o Vanadium	7.09	12	9	71	138.8	955	120.8	831	0.9
Fe-.30Mo-C									
No Vanadium	7.12	11	8	71	147.2	1013	115.5	795	0.9
0.16 w/o Vanadium	7.11	13	10	71	163.5	1125	142.1	978	1.1

Figure 6 shows the heat treated microstructure of the Fe-Mo and Fe-Mo-V systems cited in Table III. The martensite needles in the heat treated condition are much finer in the alloy with vanadium than in the vanadium-free alloy, indicative of a finer austenite grain size prior to quenching. The finer grain size is believed to lead to a higher ultimate tensile strengths with enhanced ductility and impact energy, as noted in Table III.

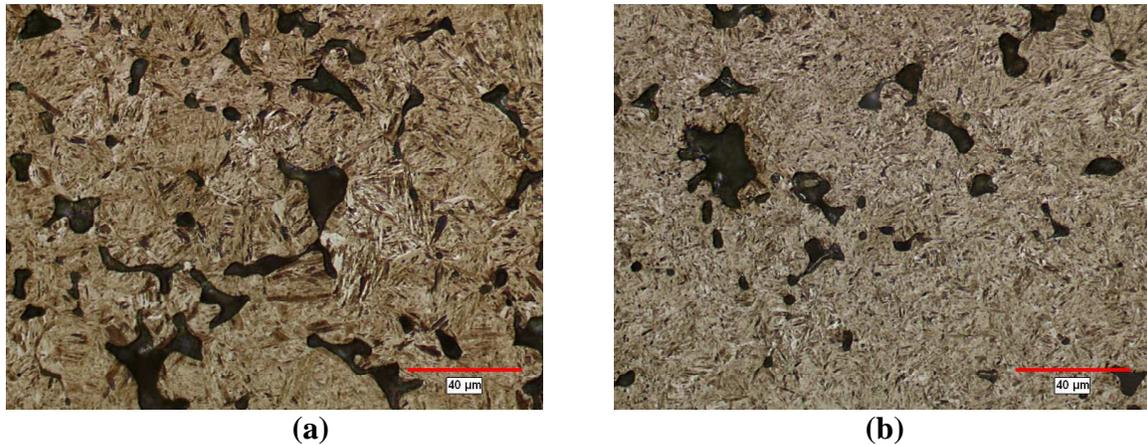


Figure 6. Heat treated microstructures of: (a) Fe-0.3 w/o Mo-C and (b) Fe-0.3 w/o Mo-C-V.

The data in Table III suggest that vanadium has an influence on hardenability. However, the level of hardenability in vanadium steels is complicated by the fact that some of the vanadium can be in solution while some can be tied up as carbonitrides; thus the austenitizing temperature is of paramount importance [9]. If the austenitizing temperature is high enough for all the vanadium to go into solution then a true effect of vanadium on hardenability is unambiguous. However it must be remembered that the higher the

temperature, the larger the grain size. This increase in grain size will increase hardenability. At lower austenitizing temperatures undissolved carbonitride particles will exist retarding grain growth and also reducing the amount of dissolved carbon; both of which lead to lower hardenability. Therefore in relation to other alloys, with the standard Jominy end quench test, hardenability varies as a function of austenitizing temperature. Since vanadium can have a strong influence on hardenability, it is difficult to compare an alloy containing vanadium with other alloys using the Jominy end quench test.

Therefore a test which compares the effect of alloy content in the heat treated condition, similar to the actual production route was used as a comparison. The effect of Mo on quenched hardenability was also studied using this test. A 25 mm (1 in) dia x 25 mm high slugs were pressed to a green density of 6.95 g/cm³. After sintering using the conditions cited previously, these samples were reheated to 900 °C, oil quenched and tempered at 175 °C. These samples were cross-sectioned at the mid-height and mounted for microstructural characterization. In addition, microindentation hardness measurements were made from the edge to the center of the slug. Figure 7 gives the microindentation hardness profiles of several alloy systems.

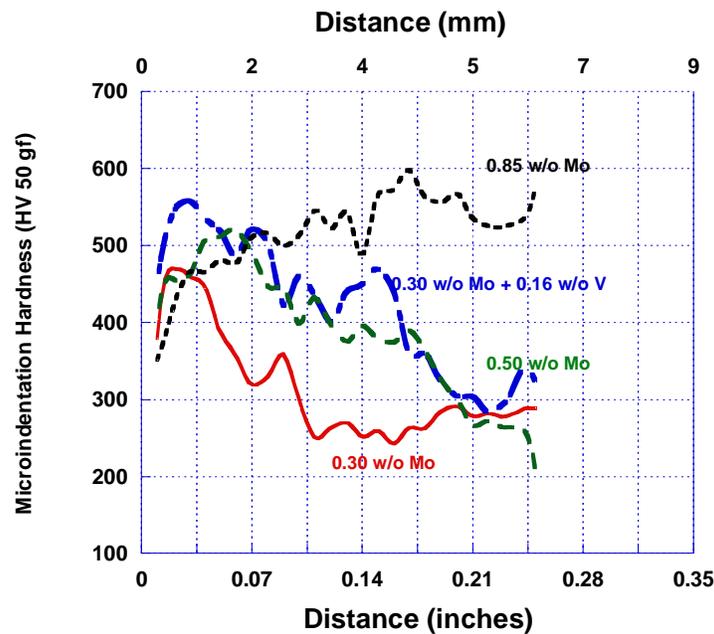


Figure 7: Microindentation hardness profiles from the edge (distance = 0) toward the center of oil quenched slugs with 0.4 w/o graphite for various molybdenum contents.

The results indicate that an alloy containing 0.30 w/o Mo and 0.16 w/o V has the same through hardening capability as a 0.50 w/o Mo alloy, and a much higher hardening capacity than the 0.30 w/o Mo alloy without vanadium.

In recent years, the cost of alloying elements has been influenced by a number of factors ranging from availability and economic, to societal and political. Therefore it is difficult to assess the full economic benefit of microalloying over a continuous period of time. Rather, it is more useful to provide a technical comparison in which, for a given processing route, the level of alloying needed to reach a certain property requirement is established. Figure 8 plots the level of alloying elements needed to attain mechanical properties in the sintered condition for two different alloy systems.

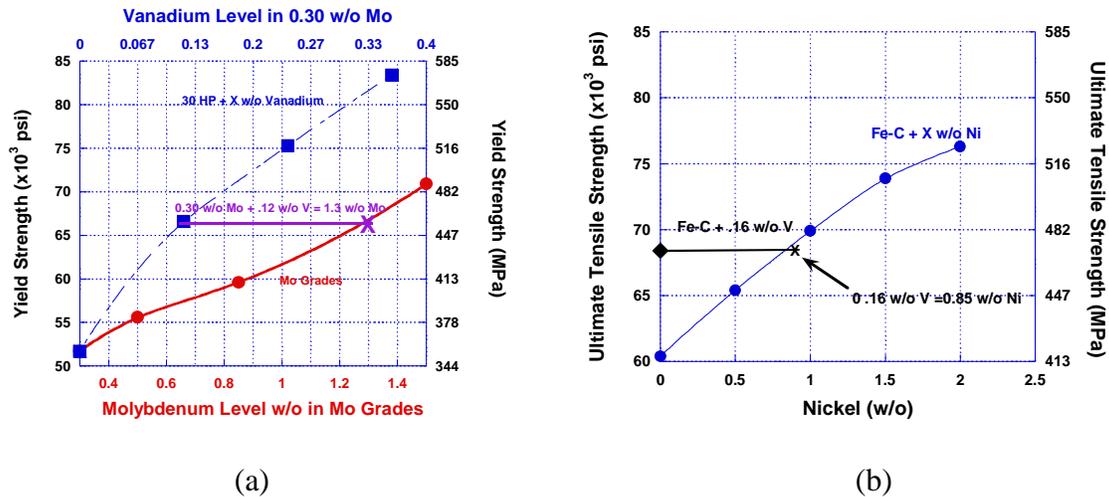


Figure 8: Plots showing the level of vanadium to replace various amounts of (a) molybdenum (sintered condition) and (b) nickel (sintered condition) with 0.70 w/o graphite.

Figure 8(a) illustrates that a 0.30 w/o Mo alloy with 0.12 w/o V can achieve the same sintered yield strength as an alloy with 1.3 w/o Mo (equivalent carbon additions). In this respect, 0.12 w/o V can replace 1.0 w/o Mo for these processing conditions. In Figure 8(b), a similar plot shows that 0.16 w/o V addition in the Fe-C system can achieve the equivalent ultimate tensile strength of a Fe-Ni alloy containing ~ 0.8 w/o Ni. Thus, in order to calculate the cost savings, the cost of 0.07 kg (0.16 lb) of vanadium should be compared with 0.36 kg (0.80 lbs) of nickel.

CONCLUSIONS

- Microalloying with niobium is more effective at lower carbon levels and requires high temperature sintering to get the niobium in solution.
- Microalloying with vanadium is effective at higher carbon levels and, because of the lower solubility temperature, is more effective in increasing mechanical properties.

- Vanadium is effective in increasing the tensile properties of sintered PM steels with pearlitic microstructures.
- Both niobium and vanadium inhibit grain growth during the autenitizing step leading to enhanced strength and impact toughness.
- Vanadium increases the hardenability of a molybdenum-containing alloy, as measured in oil quenched slug.
- Vanadium can be used to replace other elements such as nickel and molybdenum as cost dictates.

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