VANADIUM AS AN ALLOYING ELEMENT IN POWDER METALLURGY STEELS

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ABSTRACT

Vanadium is a common alloying element used in wrought metallurgy to manufacture high strength low alloy (HSLA) materials. Vanadium provides improvement in strength and wear resistance through grain refinement and precipitation of vanadium carbonitrides. As PM steels typically utilize high amounts of carbon and are sintered in nitrogen containing atmospheres, potential exists to utilize the element. With small alloy additions and well controlled manufacturing conditions, it is interesting to evaluate the potential improvement in properties by the use of vanadium. In this study, prealloyed vanadium powders with differing vanadium levels were manufactured and evaluated in common ferrous PM material systems. As sintered and heat treated properties indicated the vanadium containing materials achieved identical or better mechanical properties with 50% of the total alloying content reduced.

INTRODUCTION

It is well accepted that increasing the alloying content of a powder metal (PM) steel improves the mechanical properties. Traditionally, PM steels have used copper, nickel and molybdenum as alloying additions.[1] With improvements in sintering technologies, chromium containing steels have become commonly used for a number of applications due to the unique properties these material systems can provide.[2-4] As metal price volatility is always of concern, research and development efforts have been made to explore leaner alloying compositions and new alloying elements.[5-6]

All of the materials discussed to date would be classified as low alloy steels due to the amounts of alloying present in the materials. Smaller levels of certain alloying elements have been used for over 50 years in wrought metallurgy in what are defined as microalloyed steels. Microalloyed

steels contain between 0.05 and 0.2 w/o of niobium, vanadium, or titanium. Addition of these alloying elements to steel results in an improvement in strength, hardness and toughness.[7]

Particularly in PM steels, vanadium and niobium have been investigated by numerous authors.[8-10] In these studies, the authors concluded that vanadium, in particular, was a potential candidate for PM microalloyed steels due to the improvement in mechanical properties found. Vanadium was preferred for a number of reasons, including its lower solubility temperature at high carbon levels and its preference to form vanadium carbonitride [V(C,N)] precipitates. These precipitates are responsible for the improvement in mechanical properties in the as sintered condition. However, for heat treated materials austenitized at a temperature of 900 °C, these precipitates will retard grain growth resulting in finer austenite grains prior to quenching. This improves the strength, ductility and hardness of the martensite formed.[10]

In the above mentioned studies, the addition of vanadium was completed through admixing of a fine ferrovanadium powder. Admixing of fine particles and ferroalloys is a common practice in PM today. However, there are concerns with the fine particle additions, particularly when it comes to segregation and tool wear.[11-12] Depending on the ferroalloy added, slow diffusion may necessitate the use of higher sintering temperatures to achieve the full benefit of the ferroalloy addition. These potential drawbacks could be potentially overcome through other alloying techniques.

Other alloying techniques commonly used to reduce these potential issues include diffusion alloying and prealloying. Prealloying is an alloying method where the alloying elements are added to the molten iron during the steelmaking process.[13] The result of this alloying technique is a powder particle with uniform distribution of the alloying elements added often resulting in a homogenous microstructure. The addition of alloying elements through this method does increase the hardenability of the particle. Care must be taken as certain alloying elements can have a negative impact on compressibility due to the increase in particle hardness.

In this study, vanadium was investigated as an alloying element in PM steels through the use of prealloying powder manufacturing techniques. To understand the effect of vanadium on a common PM steel, two levels of vanadium steel powders were manufactured and compared against a traditional iron powder. The properties in the as sintered and heat treated condition were evaluated for the materials investigated.

EXPERIMENTAL PROCEDURE

To understand the impact of vanadium on the mechanical properties of PM steels, two prealloyed powders were manufactured with differing levels of vanadium using an electric arc furnace and water atomization. The powders were processed under production conditions to achieve a nominal 100 mesh base powder. All of the powders produced had low non-metallic inclusion contents making them suitable for high performance applications. The chemical composition of the base powders used in this study are shown in Table I.

Table I. Chemical Composition of Base Powders (w/o)

Base Powder	Mn	V	C	O_{-total}	N
ASC100.29	0.15	-	0.003	0.08	0.0010
V-1	0.15	0.07	0.005	0.10	0.0010
V-2	0.15	0.12	0.003	0.12	0.0007

Each base powder was characterized for apparent density, flow rate and compressibility in accordance with MPIF standard test methods.[14] The compressibility was determined using an admixed amide wax addition of 0.75 w/o over a compaction pressure range of 400 – 800 MPa.

As vanadium imparts an improvement in properties in pearlitic steels and also after heat treatment, a commonly heat treated PM steel was chosen for the evaluation. The mix compositions are shown in Table II.

Table II. Nickel Steel Mix Compositions Evaluated (w/o)

Mix ID	Base Powder	Nickel	Graphite	MPIF Code
1	ASC100.29	2	0.55	FN-0205
2	V-1	2	0.55	FN-0205
3	V-2	2	0.55	FN-0205

Two density levels were evaluated for each mix: 6.9 g/cm^3 and 7.3 g/cm^3. An amide wax addition of 0.75% was used for the 6.9 g/cm^3 density level. Warm die compaction using a tool temperature of 90 °C (195 °F) and 0.5% Intralube® HD was used to achieve the 7.3 g/cm^3 density. For each mix, dogbone tensile bars and impact bars were compacted according to MPIF standard test methods. To evaluate the heat treated tensile properties, impact bars were machined into round specimens using the procedures outlined in MPIF Standard 10.[14]

All bars were sintered in a mesh belt furnace for 30 minutes at a temperature of 1121 °C (2050 °F) in a 90/10 N_2 / H_2 atmosphere. Heat treatment was conducted by Advanced Heat Treatment (St. Mary's, Pennsylvania) using an austenitizing temperature of 900 °C (1650 °F) with a carbon potential of 0.8% for one hour. After quenching in warm oil, the bars were tempered for one hour at 204 °C (400 °F). The heat treatment was conducted on the bars at a density of 6.9 g/cm^3.

The tensile specimens were tested for tensile properties according to ASTM E8.[15] The impact bars were tested for impact energy according to ASTM E23.[16] The impact bars were also utilized to evaluate for sintered density, sintered carbon and nitrogen, and microstructure. Carbon and nitrogen were determined in accordance with ASTM E1019.[17]

As the results of the initial testing were favourable, decreased nickel powder additions were also evaluated using the prealloyed vanadium base irons. The same testing and processing utilized for the initial mix compositions was also utilized for the additional mix compositions.

RESULTS

Base Powder Properties
The results of the base powder property testing are shown in Table III.

Table III. Base Powder Property Testing

Base Powder	Apparent Density (g/cm^3)	Hall Flow Rate (s/50g)
ASC100.29	2.98	24.4
V-1	2.97	25.6
V-2	2.97	24.6

The compressibility curve for each material is shown in Figure 1.

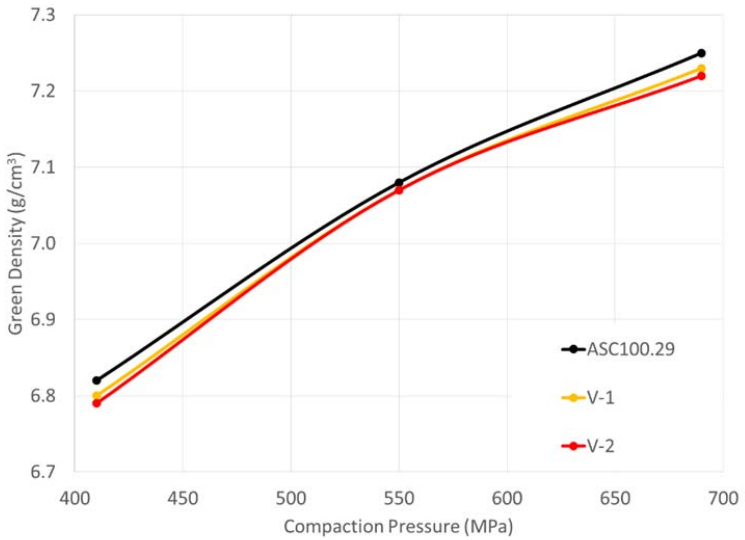


Figure 1. Compressibility curves for base powders evaluated using 0.75% amide wax addition for lubrication

Little difference was observed between the base powders for apparent density, flow rate and compressibility. The vanadium addition did not have a major impact on the compressibility and is in line with a conventional iron powder.

As Sintered Properties
After sintering, all of the materials measured a sintered carbon level of 0.5%. The as sintered tensile data for the FN-0205 compositions are shown in Figure 2.

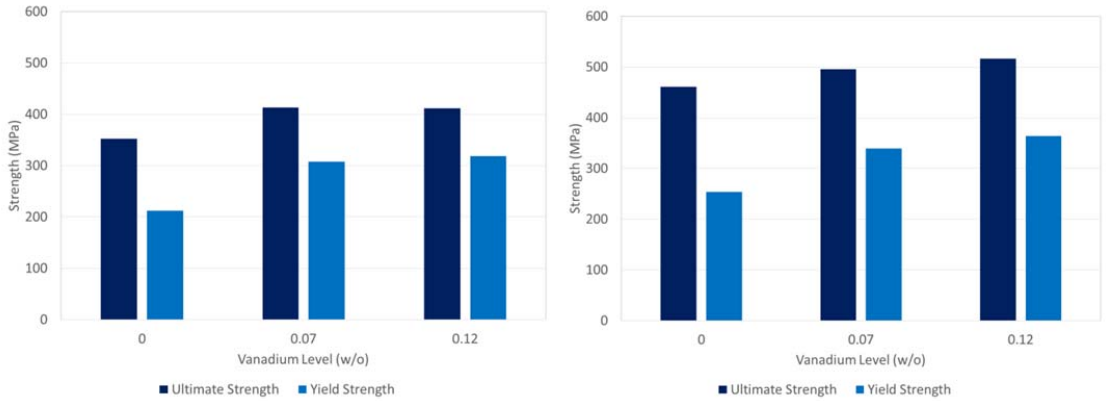


Figure 2. Tensile properties of FN-0205 compositions (Left: 6.9 g/cm^3 density, Right: 7.3 g/cm^3 density).

An improvement in tensile strength was observed for the vanadium prealloyed powders. The tensile strength improved by 17% at the 6.9 g/cm^3 density level and by 12% at the 7.3 g/cm^3 density level. A larger improvement was found for the yield strength. At the 6.9 g/cm^3 density level, the yield strength was improved by 45-50%. While the yield strength improvement was not as high at the 7.3 g/cm^3 density level, an impressive 25-30% was achieved using prealloyed vanadium. The impact energy of the materials is shown in Figure 3.

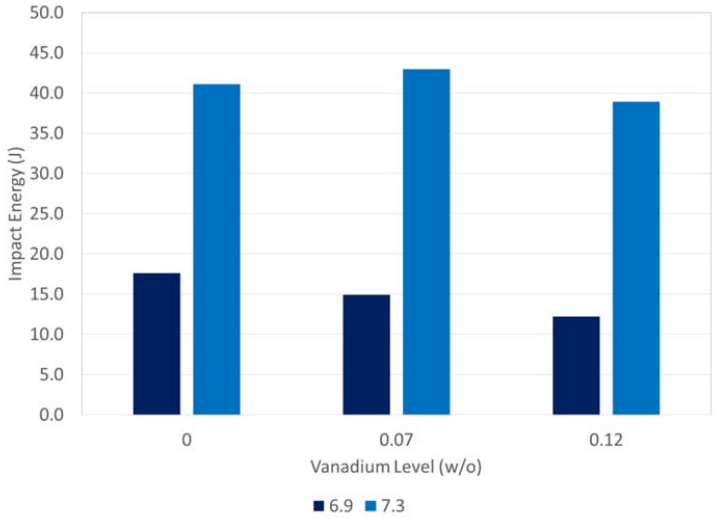


Figure 3. Impact Energy for FN-0205

The vanadium additions resulted in a slight decrease in impact energy at the lower density level. At the higher density level, the 0.07 w/o material obtained a slight improvement in impact energy. The apparent hardness measurements are shown in Figure 4.

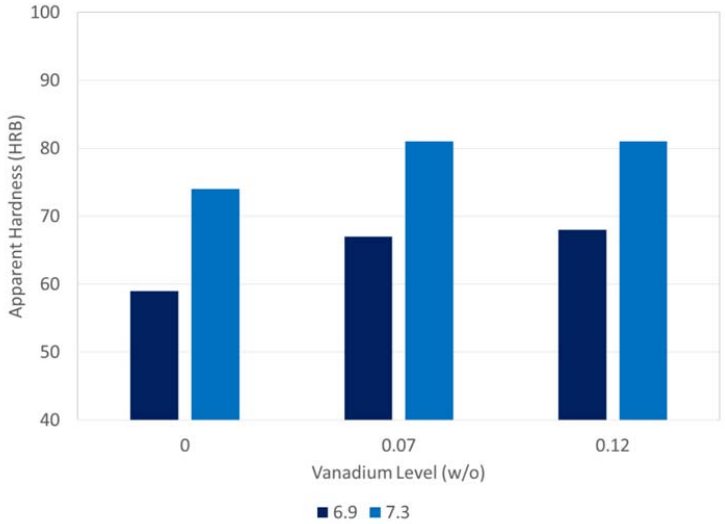


Figure 4. Apparent hardness for FN-0205

A large increase in apparent hardness was observed for the vanadium containing materials. The apparent hardness increased by 7- 9 HRB.

Overall, the results of the vanadium containing materials were similar. The increased level of vanadium alloying in the V-2 base iron did not result in an appreciable improvement in mechanical properties. Similar tensile and hardness properties were found for both of the vanadium containing materials. In regards to the impact energy, the higher level of vanadium had a negative effect.

The microstructures of the as sintered FN-0205 material using the traditional iron powder is presented in Figure 5.

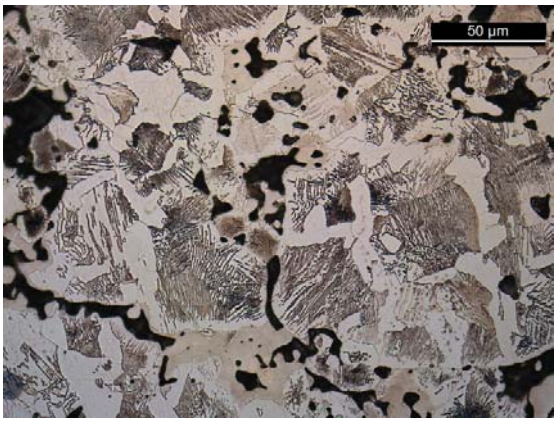


Figure 5. Sintered microstructure of the FN-0205 material

The structure for the traditional material consisted of pearlite, ferrite and nickel rich austenite. The pearlite spacing was a mixture of coarse and fine pearlite.

The microstructures of the FN-0205 materials based on the prealloyed vanadium powders are shown in Figure 6.

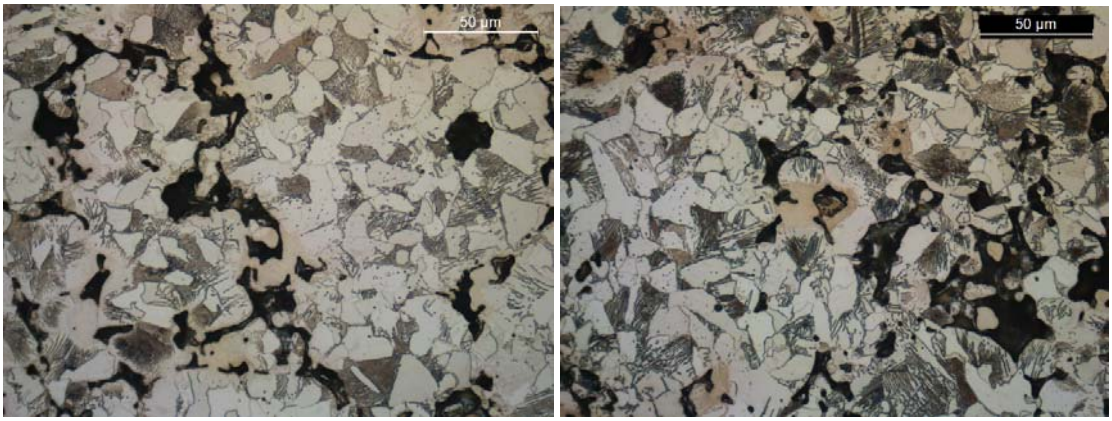


Figure 6. Sintered microstructures of FN-0205 materials (Left: FN-0205 + 0.07%V, Right: FN-0205 + 0.12%V)

For the vanadium containing materials, a refinement of the microstructure was observed. The pearlite spacing contained finer pearlite and the ferrite grains were noticeably smaller than the traditional FN-0205. Microindentation hardness measurements were determined in the pearlite for all three materials. The results are shown in Table III.

Table III. Microindentation hardness measurements of pearlite phase

Mix ID	V content (w/o)	$HV_{0.1}$
1	0	220
2	0.07	246
3	0.12	250

An increased in the microindentation hardness was found for the materials containing vanadium.

Heat Treated Properties
The heat treated tensile properties are shown in Table IV.

Table IV. Heat Treated properties of FN-0205

Property	Mix 1	Mix 2	Mix 3
Vanadium (w/o)	0	0.07	0.12
Carbon (w/o)	0.6	0.6	0.6
Density (g/cm^3)	6.9	6.9	6.9
Hardness (HRC)	31	33	33
Ultimate Tensile Strength (MPa)	952	1014	966
Yield Strength (MPa)	849	862	859
Impact Energy (J)	6	8	8

Improvement was also observed for the heat treated properties when using vanadium as an alloying element. The microstructure photographs of the traditional and 0.07 w/o vanadium material are shown in Figure 7. All of the materials were martensitic. However, the martensite was coarser in the material that did not contain vanadium compared to the two materials which did.

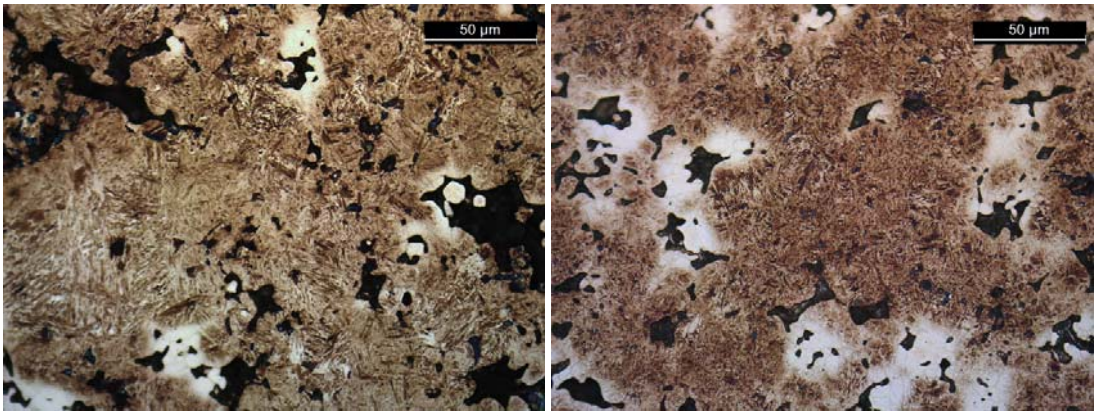


Figure 7. Heat treated microstructures (Left: FN-0205, Right: FN-0205 + 0.07% V)

The microindentation hardness values of the heat treated material are shown in Table V.

Table V. Microindentation hardness of heat treated FN-0205

Mix ID	V content (w/o)	$HV_{0.1}$
1	0	642
2	0.07	676
3	0.12	658

An increase in martensite hardness was observed for the prealloyed vanadium containing materials.

DISCUSSION

A clear improvement in mechanical properties was observed when using prealloyed vanadium base powders in a nickel steel. Vanadium is known to strengthen pearlite through the formation of fine V(C,N) precipitates during slow cooling. To verify this is the strengthening mechanism resulting in improved mechanical properties in the as sintered condition, nitrogen measurements were conducted on the tensile test specimens. The results of the nitrogen measurements are shown in Table VI.

Table VI. Nitrogen content of the as sintered tensile specimens, w/o

Base Powder	Nitrogen
ASC100.29	0.0099
V-1	0.0177
V-2	0.0137

All of the mixes manufactured using a prealloyed vanadium base powder contained increased amounts of nitrogen after sintering. The vanadium increased the nitrogen content by 40-80% depending on the level of vanadium in the base powder. This nitrogen would result in the formation of vanadium carbonitrides which would strengthen the pearlite.

As another confirmation to the improvement in mechanical properties resulting from nitrogen alloying with the vanadium during sintering, each of the base powders were sintered under the same conditions as the nickel steels. Only lubricant was added to the base powders to enable compaction. After sintering, the test bars were evaluated for apparent hardness, transverse rupture strength, nitrogen level and microstructure. The results are shown in Table VII.

Table VII. As sintered properties of base materials at 6.9 g/cm^3

Property	ASC100.29	V-1	V-2
Apparent Hardness (HRF)	49	54	55
TRS (MPa)	400	421	417
Nitrogen (%)	0.0039	0.0081	0.0075
Carbon (%)	0.005	0.004	0.005

Again, an increase in the mechanical properties and nitrogen content is observed for the vanadium containing materials. The increase found was not as significant compared to when there was a carbon addition to the material. The ferrite grain size is also refined in the microstructure and is shown in Figure 6.

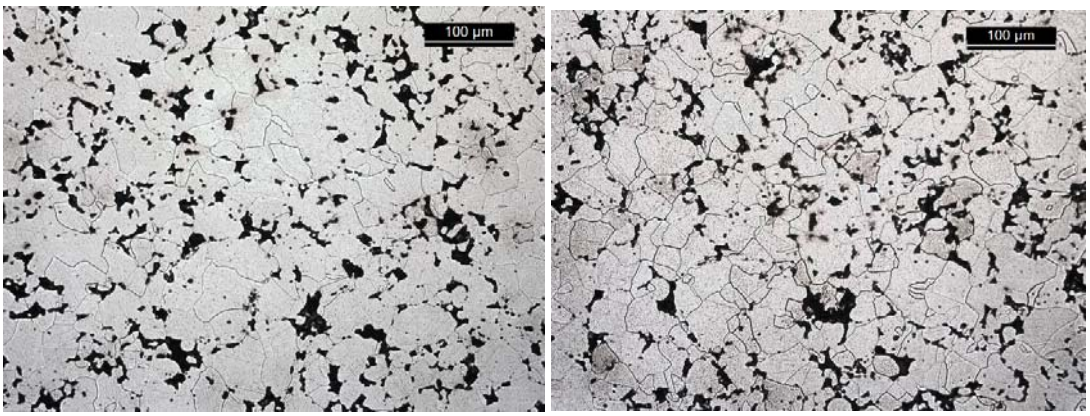


Figure 6. Sintered microstructure of ASC100.29 (left) and V-1 (right)

In wrought metallurgy, numerous prediction models indicate increased performance by using higher vanadium levels and higher nitrogen contents than were used in this study.[7] In both the nickel containing mixes and the pure base powders, higher nitrogen values were measured for the lower vanadium containing base powder. A potential theory to this observation is that the amount of vanadium available in the iron powder for alloying with the nitrogen may be not be the same for the two vanadium levels studied. The oxygen level of the base powder with the 0.12 w/o vanadium was slightly higher than the 0.07 w/o powder. Vanadium is known to have an affinity for oxygen. It is possible, through water atomization, the higher vanadium material formed stable vanadium oxides which were not reduced during reduction annealing, leaving a portion of the vanadium unable to alloy with the nitrogen during sintering. Further study of this is required to confirm the mechanism.

In an effort to understand the ability to substitute vanadium for nickel additions, additional mixes were made using the V-1 material with reduced nickel levels (1.5 w/o and 1.0 w/o). The V-1 material was chosen as there was no apparent benefit to using an increased amount of vanadium in the base material according to the previous testing. The mixes were compacted to a green density of 6.9 g/cm^3 and sintered under the same conditions used previously. The bars were tested for tensile and impact performance. The results of the testing are shown in Table VIII.

Table VIII. Mechanical properties of reduced nickel additions to vanadium prealloyed powder

Property	Mix 1	1.0% Ni	1.5% Ni	Mix 2
Green Density (g/cm^3)	6.90	6.90	6.90	6.90
Vanadium (w/o)	0	0.07	0.07	0.07
Sintered carbon (w/o)	0.49	0.47	0.45	0.48
UTS (MPa)	353	378	392	413
Yield Strength (MPa)	212	288	300	308
HRB	59	61	64	67
Impact Energy (J)	17.6	13.6	14.1	15.0

Using the prealloyed vanadium base powder allows for the reduction in nickel without sacrificing strength and hardness levels. Even at the lowest nickel addition, a 7% improvement in tensile strength and a 36% increase in yield strength were achieved. The impact energy saw a decrease compared to Mix 1 and 2, both of which contained 2% nickel. The reduction of nickel in this case has more of an effect on toughness compared to the benefit from the vanadium. However, if toughness is not a concern, then the reduced nickel materials with vanadium could potentially be cost effective options. Unfortunately, the heat treated data for these materials was not completed in time for publication.

CONCLUSIONS

Based on this study, the following conclusions can be drawn:

1. Prealloying of vanadium had limited effect on the base powder properties. The compressibility and oxygen levels were similar to a traditional base iron powder.
2. Using vanadium resulted in an improvement in the as sintered and heat treated mechanical properties. In the as sintered condition, an improvement in tensile strength of 10-20% was observed. In the heat treated condition, the improvement in tensile strength was 6% with a 30% improvement in impact energy.

3. A large improvement in the yield strength was observed for the vanadium containing materials. An increase of 25-50% over the traditional iron powder was achieved when using the prealloyed vanadium powders.
4. Comparing the two vanadium levels, increasing the vanadium from 0.07 w/o to 0.12 w/o did not have an appreciable effect on the mechanical properties. In some cases, the benefit was greater for the lower addition level.
5. The strengthening method for vanadium used the nitrogen available from the sintering atmosphere to form vanadium carbonitrides. The nitrogen content of the as sintered materials was found to be 40-80% higher than the traditional iron powder.
6. Potential exists to reduce the nickel content through the use of prealloyed vanadium and maintain strength properties in the as sintered condition if toughness is not a concern. A slight decrease in toughness was observed.

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