Vanadium in cast iron

J. V. Dawson, FIBF

Synopsis
The effects of vanadium in several types of cast iron have been investigated and the results are as follows.

In grey cast irons the marked strengthening of up to 0.5 per cent vanadium and its strong tendency to promote the formation of eutectic carbide have been confirmed. However, the carbide-forming tendency can be confined to thin sections by efficient inoculation or by modification of the base composition. The marked improvement in strength is still present in grey irons that have been annealed to a ferritic structure to facilitate machining.

Vanadium promotes the formation of eutectic carbide by:
- causing a significant increase in the metastable (carbidic) equilibrium eutectic temperature;
- causing a marked depression of the stable (graphitic) equilibrium eutectic temperature.

The addition of up to 0.5 per cent vanadium to nodular (SG) iron can produce significant increases in proof stress values and tensile strength. The most significant increases occur in irons which have been annealed to give a full ferritic matrix and the increases are accompanied by only a marginal decrease in elongation and notched impact values. It is concluded that ferritic nodular (SG) irons with vanadium could have better combinations of tensile properties, elongation and impact resistance than previously accepted.

A very fine particulate precipitate occurs in ferritic irons when vanadium is added. This is believed to be a form of vanadium carbide, and it is suggested that it contributes to the increases in strength conferred by vanadium.

In abrasion-resistant, 15 per cent chromium irons, 5 per cent vanadium content produces as-cast structures and hardness values similar to those normally obtained by high-temperature heat treatment of equivalent irons with no vanadium content. It is suggested that this effect of vanadium might be of use in complex castings that are subject to cracking during heat treatment.

Introduction
A number of authors1–100 have published information on the influence of vanadium in cast irons, but many of the more detailed publications are quite old and some of the conclusions are questionable in the light of present-day knowledge. In some cases, also, the results from different authors are contradictory, and in a number of instances the claims made for a particular effect of vanadium are not supported by any technical details.

The effects of vanadium in several types of cast iron have been investigated at BCIRA, and the present paper describes the results obtained and suggests some situations where the use of vanadium as an alloying element might be considered.

Summary of the literature
The general effects of vanadium in cast irons which could be expected, from the published data, can be summarized as follows:

Effects on general structure
Vanadium combines with the carbon present in the iron to form particles of vanadium carbide having the formula $V_2C_3$ or $VC_2$.2,13–16

Vanadium promotes the formation of eutectic iron carbide, which results in an increased tendency to form white iron structures in thinner sections.2,3,18–22,24–27,29–31

Quite small amounts of vanadium promote pearlitic rather than ferritic structures in the as-cast condition, and also make the pearlite more resistant to removal by heat treatment.2–4,19–23,28

Small quantities of vanadium give more uniformity of graphite flake size and structure, particularly in heavier sections.2–4,19,23,25,28,29

Effects on the properties of grey cast irons
Up to contents of about 0.5 per cent, vanadium increases the strength of grey iron by about 12–15 N/mm² (0.8–1.0 ton f/in²) for each 0.1 per cent vanadium.1–4,18,19,22,23,26,28–31,40–45,60,62

The tendency for vanadium to promote the formation of eutectic carbide is between one and four times that of chromium. However, much of this effect of vanadium may be offset by the addition of three to four times as much nickel or copper, or by increasing the silicon content.2,3,18–22,24–27,29–31
The hardness of grey iron increases by about 8–10 HB for each 0.1 per cent increase in vanadium content when no eutectic carbide is produced.\textsuperscript{18}

Discrete, very hard particles form when small amounts of vanadium and phosphorus are present, thus increasing the sliding-wear resistance of grey iron.\textsuperscript{53, 56, 58} This fact is made use of by some manufacturers of large diesel-engine cylinder liners and piston rings.

**Effects in nodular graphite (SG) irons**

Only a relatively small amount of information has been reported on the effects of vanadium in nodular graphite irons.\textsuperscript{4, 20, 21, 27} However, from this and by analogy with its tendency to form carbide or pearlite in grey irons it would be assumed that even traces of vanadium ought to be avoided in these irons, particularly those required to have a ferritic matrix.

**Effects in malleable irons**

As vanadium seems to increase the stability of carbide and pearlite, its presence in malleable irons should be avoided so that the annealing time required to produce a ferritic structure will not be prolonged.\textsuperscript{22–39}

**Effects in hard, abrasion-resistant irons**

Appreciable increases in wear resistance can be obtained by the addition of larger amounts (5–15 per cent) of vanadium to irons containing 5 or 15 per cent chromium.\textsuperscript{65–88, 97, 100}

**Experimental work at BCIRA**

All the melts were carried out in the BCIRA experimental foundry, and the irons examined included flake graphite, nodular graphite, malleable iron and abrasion-resistant irons, most of which contained about 15 per cent chromium. The melts were all prepared in silica-lined medium-frequency coreless induction furnaces using either steel scrap or pig iron of low residual-element content (OB pig iron), as the base materials. Vanadium was added as ferrovanadium containing either 50 or 80 per cent vanadium.

**Flake graphite (grey) iron**

A number of melts were carried out in which the influence of vanadium contents up to about 0.5 per cent was examined and also compared with those of similar amounts of molybdenum or chromium.

Six melts were carried out using irons with hypoeutectic low-phosphorus compositions, having tensile strengths of 220–260 N/mm\(^2\) (14–17 tonf/in\(^2\)), two of which contained 1 per cent copper. The ranges of the base compositions are shown in Table I. Additions of vanadium, chromium or molybdenum were made to the metal in the furnace before Taps 2–4, to give nominal alloy contents of 0.1, 0.25 and 0.5 per cent. All taps were inoculated with 0.25 per cent ferrosilicon one minute before pouring.

Tensile tests and hardness measurements were carried out on bars 30 mm in diameter, and the tendency to form eutectic carbide in the structure was determined by examining the depth of white iron produced in thin plates of varying thickness from 3 to 9 mm.

**Effects on mechanical properties**

The average percentage increases in tensile strength and hardness resulting from the various alloy additions to the six melts are shown in Fig. 1. Vanadium was the most effective for increasing tensile strength, and this was accompanied by the greatest increase in hardness.

The effects of similar amounts of chromium or vanadium were also compared in a lower-strength grey iron of slightly hypereutectic composition. The base composition is included in Table I. Vanadium was even more effective in raising the tensile strength in this grade of iron, 0.5 per cent vanadium content giving an increase of 110 N/mm\(^2\). For comparison, a similar content of chromium only gave an increase of 40 N/mm\(^2\).

The stress/strain properties in tension of some of the hypoeutectic iron bars containing vanadium or molybdenum were compared at room and at elevated temperatures. Typical curves obtained at room temperature and 400°C are given in Fig. 2. Both elements were effective in maintaining their influence on tensile strength at elevated temperatures.

**Effect on formation of eutectic carbide**

The increase in the tendency to form white iron in 3 mm plates, produced by vanadium is shown in Figs. 3a and b. Only a trace of white iron occurred in any of the 6 mm plates, even at 0.55 per cent vanadium content.

Very little eutectic carbide occurred in the 3 mm plates containing vanadium or chromium when 1 per cent copper was also present.

In the hypereutectic iron only a trace of white iron occurred in the 3 mm plate at the highest vanadium content, and none occurred when chromium was added. It must be emphasized that no inoculant was added in these two melts.

**Effect on structure**

The microstructures of the bars from all the grey melts consisted of flake graphite in a matrix of pearlite. The addition of vanadium caused the graphite flakes to become
Fig. 1. Effects of alloy additions on properties of Grades 220 & 260 (Grades 14 & 17) grey cast iron.

Fig. 2. Stress/strain curves at room temperature and 400°C for grey irons containing vanadium or molybdenum.

Fig. 3. Effects of up to (a) 0.5% vanadium content, and (b) 0.5% chromium content, on carbide formation in plates of 3 mm thickness.

Fig. 4. Effect of vanadium on graphite flake morphology in hypereutectic grey iron.
(a) 0.2% vanadium  (b) 0.5% vanadium
Etched in 4% picral.  x 100
more uniform in size and distribution, and this was most noticeable in the hypereutectic series. Figs. 4a & b illustrate the effect of 0.5 per cent vanadium on the microstructure of this iron, and Figs. 5a & b are scanning electron-microscope pictures of the same iron after deep etching to remove the matrix.

By comparison, chromium and molybdenum had no significant effect on the graphite structure of any of the grey irons to which they were added.

Eutectic cell counts carried out on the microspecimens indicated that the addition of 0.5 per cent vanadium produced about a threefold increase in eutectic cell number, regardless of inoculation, whereas chromium and molybdenum had no effect on the number of eutectic cells present.

As the vanadium content increased, small white inclusions appeared in more or less random distribution throughout the structures. Fig. 6a shows an optical micrograph of some of these inclusions, while Figs. 6b–d show an electron image and X-ray emission distribution for iron and vanadium for a similar inclusion. Clearly, the inclusions are rich in vanadium and they are almost certain to consist of vanadium carbide in view of the high affinity between vanadium and carbon.

**Effects in ferritic grey irons**

As all the melts described above had fully pearlite matrices, they gave no indication of the effects of vanadium on pearlite formation. A melt was therefore carried out to a composition similar to the hypereutectic iron melts but based on raw materials which avoided the traces of pearlite-promoting elements normally present in grey irons.

In the iron to which no vanadium had been added the matrix consisted of about 80–90 per cent ferrite and the tensile strength was only 145 N/mm² (9.4 tonf/in²). Raising the vanadium content to about 0.5 per cent increased the pearlite content to about 50–60 per cent and the tensile strength to 230 N/mm² (15 tonf/in²). This was accompanied by an increase in hardness of about 15 points Brinell. Typical structures are shown in Figs. 7a & b.

A duplicate set of bars from this melt were annealed by holding at 900°C for two hours and slow-cooling to below 600°C. This resulted in a fully ferritic matrix in all the bars. The tensile strength now ranged from 125 N/mm² (8 tonf/in²) with no vanadium present, to 190 N/mm² (12.3 tonf/in²) with a content of 0.5 per cent vanadium. A fine precipitate was just visible in the ferrite, in the bar with the highest vanadium content. This precipitate was similar to that observed more readily in ferritic nodular irons to be described in greater detail later.

**Effects in heavier sections**

To examine the effects of vanadium in heavier sections, a set of four bars 150 mm in diameter were produced to the hypo-eutectic composition and having vanadium contents of 0, 0.2, 0.5 and 0.7 per cent. Test bars were cut from the mid-radius area of each bar. The tensile strengths were as follows:

<table>
<thead>
<tr>
<th>Vanadium %</th>
<th>Tensile strength, N/mm²</th>
<th>(tonf/in²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>196</td>
<td>(12.7)</td>
</tr>
<tr>
<td>0.2</td>
<td>208</td>
<td>(13.5)</td>
</tr>
<tr>
<td>0.5</td>
<td>235</td>
<td>(15.2)</td>
</tr>
<tr>
<td>0.7</td>
<td>276</td>
<td>(17.9)</td>
</tr>
</tbody>
</table>

The strengthening effect of 0.5 per cent vanadium was less apparent in the bars of heavier section. Microexamination of the structure showed that all the bars were pearlitic but that the bar with 0.7 per cent vanadium contained a discontinuous network of eutectic carbide.

The graphite flake structure again became more uniform when vanadium was added, but this effect was not so obvious as in the smaller bars.

**Mechanism of carbide promotion**

The manner in which vanadium promotes the formation of eutectic iron carbide was investigated by taking cooling-curves on bars of various sizes and determining the equilibrium temperatures for the stable (graphite) and metastable (carbide) eutectics at increasing vanadium contents. Those elements which reduce the spacing between these two temperatures promote the formation of eutectic carbide, while elements which increase the spacing reduce the carbide-forming tendency. Oldfield has shown that chromium has very little effect on the stable eutectic temperature but it causes a marked rise in the metastable temperature, thus promoting the formation of carbide in the structure.
Fig. 6a. Inclusions of vanadium carbide in grey iron. Etched 4% picral. $\times 1500$.

Fig. 6b. Electron image of vanadium carbide in grey iron. SEM $\times 5200$.

Fig. 6c. Vanadium X-ray map of inclusion shown in Fig. 6b.

Fig. 6d. Iron X-ray map of inclusion shown in Fig. 6b.

Fig. 7. Effect of vanadium on pearlite content in as-cast 'ferritic' grey iron: (a) 0.02% V.; (b) 0.5% V. Etched 4% picral. $\times 100$. 
In the present tests, contents of up to 0.9% vanadium were obtained in irons containing nominally:

3.1% C, 2.1% Si, 0.6% Mn, 0.07% S, 0.06% P.

Tests were carried out with no inoculation, and after inoculation with 0.25% ferrosilicon in the ladle. Inoculation had no effect on the stable and metastable equilibrium temperatures derived from the cooling-curves. However, with no inoculation many of the smaller bars were white at the higher vanadium contents, whereas almost all the bars were grey when the irons were inoculated.

The results obtained for vanadium are illustrated in Fig. 8, together with the previous results for chromium. Clearly, vanadium raises the metastable temperature in a similar manner to chromium, but to a lesser degree. However, the reduction in the stable eutectic temperature is quite different from the effect of chromium. The rapid reduction in the spacing between these two equilibrium temperatures due to vanadium accounts for its marked tendency to promote the formation of eutectic iron carbide.

**Influence of nitrogen**

Nitrogen contents of about 0.006–0.008 per cent and above can contribute significantly to the strength of grey irons when aluminium and titanium contents are low. Problems can arise due to the formation of the nitrogen fissures or blowholes when the nitrogen content becomes excessive, unless it is neutralized by the presence of a small amount of titanium or aluminium. These combine with the nitrogen and make it inactive, and usually result in some loss of tensile strength.

Two tests were carried out in which the nitrogen contents were raised sufficiently to cause fissure formation in bars 150 mm in diameter. Vanadium was then added, to determine whether it could be used to inhibit nitrogen fissures in a manner similar to titanium. The sections of the bars from the first test, shown in Figs. 9a–d, indicate that severe fissuring was produced by raising the nitrogen content to 0.018 per cent, and that additions of 0.08 and 0.14 per cent vanadium gave only a slight reduction in the amount of fissures present. A slightly lower nitrogen content of 0.016 per cent, and consequently less fissuring, was obtained in the bars from the second test shown in Figs. 10a–d and, in this case, no fissuring occurred when vanadium contents of 0.16 and 0.3 per cent were present. Tests carried out on bars 30 mm in diameter cast at the same time as the larger bars showed that the addition of nitrogen gave an increase in tensile strength of about 40 N/mm² (2.5 tonf/in²). However, raising vanadium content up to 0.3 per cent gave a further increase of about 40 N/mm² even though the fissuring effect of the nitrogen was suppressed.

Examination of the microstructures of the 150 mm bars showed that, as expected, the graphite flakes became heavily compacted as a result of the addition of nitrogen. The extent of compaction reduced as the vanadium content increased, but some compaction remained even at a 0.3 per cent vanadium content. No evidence of the formation of separate particles of vanadium nitride could be found in the microstructure, but it is possible that some nitrogen passed into solution in the vanadium carbide inclusions. It seems, therefore, that vanadium has only a weak affinity for nitrogen in cast iron but this might be sufficient to suppress fissure formation without reducing the beneficial effect of nitrogen on strength.

**Summary of effects in grey irons**

The results of the tests on vanadium in grey cast irons indicate that, at levels up to 0.5 per cent, it is very effective for increasing the tensile strength of both pearlitic and ferritic grades. Vanadium has a greater tendency than chromium to promote the formation of eutectic carbides, but this can be controlled at acceptable levels by inoculation or by small changes in base composition. In situations where high nitrogen contents increase the risk of fissure formation the addition of vanadium might reduce this risk without suppressing the strengthening effect of the nitrogen. It is possible that the additional strength obtained from a vanadium addition would enable an iron of higher carbon equivalent to be used.

**Nodular graphite (SG) iron**

**Pearlite as-cast**

Pearlitic nodular cast iron was produced by adding small amounts of pearlite-promoting trace elements such as tin, copper and arsenic to an oxygen blown pig-iron-based melt. Additions of vanadium were made in the furnace to give nominal contents of 0.1, 0.25, and 0.5 per cent. Each tap was treated with 2.5 per cent of 5 per cent magnesium-ferrosilicon followed by inoculation with 0.5 per cent of ferrosilicon and the final base composition was approximately:

<table>
<thead>
<tr>
<th>C %</th>
<th>Si %</th>
<th>Mn %</th>
<th>Mg %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>2.5</td>
<td>0.3</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Two keel blocks 32 mm in thickness and 6 mm plates, for examining the tendency to form eutectic carbide, were poured one minute after inoculation.

**Effect on carbide formation**

Because of the similarity between a white iron fracture and the bright crystalline fracture that occurs with pearlite nodular iron, it was not possible to determine the tendency for eutectic carbide to form by measuring the 'chill' depth.
Microspecimens were therefore cut from the 6 mm plates and etched to reveal the presence of carbide. No zone completely free from graphite was present in any plate, but increasing amounts of carbide occurred as the vanadium contents increased as shown below:

<table>
<thead>
<tr>
<th>Vanadium %</th>
<th>Distance of carbide from edge, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>nil</td>
<td>0</td>
</tr>
<tr>
<td>0-12</td>
<td>6</td>
</tr>
<tr>
<td>0-24</td>
<td>13</td>
</tr>
<tr>
<td>0-51</td>
<td>&lt;13</td>
</tr>
</tbody>
</table>

Mechanical properties
The tensile properties of test bars cut from the keel blocks were examined in the as-cast condition and after annealing to a ferritic matrix. Charpy 10 mm notched-impact tests at room temperature were also carried out in both conditions.

In the as-cast condition, raising the vanadium content to 0.5 per cent gave an increase in the 0.2 per cent proof-stress value of 50 N/mm² (3.2 tonf/in²), but it had no effect on the ultimate strength. The elongation was reduced from 5 to 3 per cent and the hardness increased by 30 points Brinell. All the impact specimens failed in a brittle manner with values of only 2–3 J.

After annealing to a ferritic matrix, the addition of vanadium resulted in a significant improvement in properties — as shown in Fig. 11. The marked increase in proof stress and tensile strength was accompanied by only a slight reduction in elongation and notched-impact values.

Effect on structure
The microstructures of the bars in the as-cast condition consisted of graphite nodules in a predominantly pearlite matrix. About 5 per cent ferrite occurred around the nodules in the absence of vanadium, and this was reduced but not entirely removed by increasing the vanadium content to 0.5 per cent.

After annealing, all the bars were fully ferritic, but the ferrite grain size was reduced by the addition of vanadium as illustrated in Figs. 12a & b. At high magnification a fine precipitate was evident in the ferrite when vanadium was present, as shown in Figs. 13 & 14. These fine particles are thought to consist of vanadium carbide precipitated from the solid. However, because of the extremely small size (about 0.25 μm) it was not possible to confirm this by analysis with any instruments available. By comparison, high concentrations of vanadium were detected in the larger inclusions also visible in Fig. 14.

Ferritic as-cast
A similar iron was produced without the addition of the trace elements, thus producing predominantly ferritic matrices as-cast. The addition of vanadium produced...
Vanadium in cast iron

Fig. 10. Effects of vanadium contents up to 0.3% on nitrogen fissure formation in bars 150 mm in diameter at 0.016% nitrogen: (a) 0.006% N, 0.02% V; (b) 0.016% N, 0.02% V; (c) 0.016% N, 0.15% V; (d) 0.016% N, 0.3% V.

about 10–20 per cent pearlite in the as-cast condition.

Effects on mechanical properties
The effects of vanadium on the mechanical properties of these ferritic irons in the as-cast and annealed conditions are shown in Fig. 15. Comparison between these results and those given in Fig. 11 show that vanadium produced similar effects in these irons to those in irons annealed from an as-cast pearlite structure. The most notable difference was the severe reduction in notched-impact value, caused by the presence of some pearlite in the as-cast ferritic material containing vanadium. This pearlite was removed readily by annealing, and good impact properties similar to those shown in Fig. 11 were then obtained.

4 per cent silicon irons
The above results indicate that vanadium could possibly be of use for improving the strength of ferritic grades of nodular iron. A series of tests were therefore carried out in a nominally 4 per cent silicon nodular iron, a ferritic material which is finding increasing use for high-temperature applications. All the castings were annealed at 920°C for two hours and slowly cooled before producing the test pieces. The nominal composition was:

<table>
<thead>
<tr>
<th>C %</th>
<th>Si %</th>
<th>Mn %</th>
<th>Mg %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>3.8</td>
<td>0.2</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Fig. 11. Effects of vanadium on ferritic nodular iron annealed from pearlite as-cast.
Vanadium was added to levels of 0.25 and 0.45 per cent and a further set of castings were produced containing 0.45 per cent molybdenum. Tensile properties were measured at room temperature and at 250, 450 and 650°C. The results obtained are given in Table II. At room temperature vanadium gave a greater increase in 0.2 per cent proof-stress value and tensile strength than a similar amount of molybdenum, with less reduction in elongation. However, as the test temperature increased the difference between the effects of the two elements became less significant.
### Table II
High-temperature tensile properties of 4 per cent silicon nodular (SG) iron.

<table>
<thead>
<tr>
<th>Tap No.</th>
<th>Alloy content (%)</th>
<th>Test temp. °C</th>
<th>0.2% proof stress N/mm²</th>
<th>Tensile strength N/mm²</th>
<th>Elongation %</th>
<th>Hardness HB 10/3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Nil</td>
<td>0.24% V</td>
<td>Room</td>
<td>443</td>
<td>559</td>
<td>25</td>
<td>192</td>
</tr>
<tr>
<td>2 0.44% V</td>
<td>250</td>
<td>471</td>
<td>596</td>
<td>38.6</td>
<td>23</td>
<td>197</td>
</tr>
<tr>
<td>3 0.43% Mo</td>
<td>457</td>
<td>485</td>
<td>605</td>
<td>39.2</td>
<td>16</td>
<td>203</td>
</tr>
<tr>
<td>4 0.43% Mo</td>
<td>Room</td>
<td>457</td>
<td>563</td>
<td>26.8</td>
<td>13</td>
<td>200</td>
</tr>
<tr>
<td>1 Nil</td>
<td>0.24% V</td>
<td>360</td>
<td>23.3</td>
<td>477</td>
<td>14</td>
<td>—</td>
</tr>
<tr>
<td>2 0.44% V</td>
<td>250</td>
<td>391</td>
<td>494</td>
<td>32.0</td>
<td>11</td>
<td>—</td>
</tr>
<tr>
<td>3 0.43% Mo</td>
<td>405</td>
<td>405</td>
<td>494</td>
<td>32.0</td>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>4 0.43% Mo</td>
<td>378</td>
<td>496</td>
<td>496</td>
<td>32.1</td>
<td>11</td>
<td>—</td>
</tr>
<tr>
<td>1 Nil</td>
<td>0.24% V</td>
<td>313</td>
<td>20.3</td>
<td>352</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>2 0.44% V</td>
<td>450</td>
<td>318</td>
<td>370</td>
<td>24.0</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>3 0.44% V</td>
<td>327</td>
<td>380</td>
<td>24.6</td>
<td>4</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>4 0.43% Mo</td>
<td>323</td>
<td>381</td>
<td>24.7</td>
<td>3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1 Nil</td>
<td>0.24% V</td>
<td>60</td>
<td>3.9</td>
<td>103</td>
<td>47</td>
<td>—</td>
</tr>
<tr>
<td>2 0.44% V</td>
<td>66</td>
<td>66</td>
<td>111</td>
<td>7.2</td>
<td>52</td>
<td>—</td>
</tr>
<tr>
<td>3 0.44% V</td>
<td>73</td>
<td>73</td>
<td>119</td>
<td>7.7</td>
<td>49</td>
<td>—</td>
</tr>
<tr>
<td>4 0.43% Mo</td>
<td>74</td>
<td>74</td>
<td>130</td>
<td>8.4</td>
<td>34</td>
<td>—</td>
</tr>
</tbody>
</table>

and this is readily removed by heat treatment.

As in grey irons, the addition of vanadium to a nodular iron will increase the tendency for eutectic carbide to occur in thinner sections, but this can be removed by the annealing process.

### Malleable cast iron

A series of shaped malleable test bars were produced in a typical blackheart malleable composition, and additions of vanadium were made to give contents of 0-05, 0-10 and 0-15 per cent. Sets of bars were annealed at four commercial plants, using different types of annealing furnaces and cycles.

Tensile tests on these bars showed that 0-15 per cent vanadium gave increases of about 35 N/mm² (2.3 tonf/in²) yield stress and 60 N/mm² (4 tonf/in²) tensile strength with no significant reduction in elongation. However, the macrostructures showed that vanadium increased the tendency for traces of eutectic carbide or pearlite to be retained in the structures of those bars annealed with the shortest annealing cycles. It was therefore concluded, that although small additions of vanadium might be used to increase the strength of blackheart malleable iron, care would be required to ensure that the castings were fully annealed.

### High-chromium abrasion-resisting irons

A series of melts of 15 per cent chromium irons at different carbon contents were prepared, to which vanadium was added to give nominal contents of 0-5, 1-5, 2-5 and 5-0 per cent. Most of the melts contained about 1 per cent molybdenum to suppress pearlite formation, but some were molybdenum-free or contained nickel or copper. The silicon content was generally about 0-8 per cent, except when the influence of increasing silicon content was being investigated. Bars 30 mm in diameter were sand-cast and allowed to cool in the moulds before examination of the microstructure and measuring of the

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Fig. 16. Vanadium carbide inclusions and fine precipitate in nodular (SG) iron containing 3.7% Si and 0.5% V. Etched 4% picric/HCl. × 1000.

Structure of 4 per cent silicon irons
Examination of the microstructures confirmed the ferrite grain-refining effect of vanadium, whereas molybdenum had no effect on the ferrite grain size. Relatively large inclusions of vanadium carbide were present, together with an abundance of the fine precipitate as shown in Fig. 16 for the iron containing 0-45 per cent vanadium.

Summary of effects in nodular irons
The main conclusion from the above tests on nodular cast irons is that vanadium contents up to 0-5 per cent could be useful for improving the tensile properties of annealed ferritic irons without significantly reducing the elongation and room temperature notched-impact values. Vanadium has only a weak tendency to promote pearlite formation,
hardness.

Increasing vanadium content significantly increased the hardness of the material in the as-cast condition, amounting to an increase of 200–250 HV for a 5 per cent vanadium content. This increase in hardness produced an iron of similar hardness to that achieved by heat treatment of vanadium-free 15 per cent chromium, 1 per cent molybdenum irons.

Examination of the microstructures showed that, in the absence of vanadium, the as-cast structures consisted of eutectic carbide in a predominantly austenitic matrix. Exceptions which occurred when fine pearlite was present in the structure were due to insufficient molybdenum content. A typical as-cast structure is shown in Fig. 17.

As the vanadium content was increased up to 2.5 per cent the amount of a bainitic transformation product increased, together with coarse martensite needles near to the eutectic carbide as shown in Fig. 18. The hardness was increased progressively with this change in structure.

At a vanadium content of about 5 per cent a marked change in the as-cast matrix structure took place—a fine distribution of secondary carbides was obtained, and the austenite transformed to fine martensite, accompanied by a further significant increase in hardness. A typical structure is shown in Fig. 19. The tendency to form fine

![Fig. 17. Typical structure of as-cast iron containing 15% chromium and 1% molybdenum — matrix predominantly austenite. Hardness 425 HV. Etched 4% picric/HCl. x 500.](image)

![Fig. 18. Bainitic transformation product formed in as-cast iron containing 15% Cr and 1% Mo by the addition of 2.5% vanadium. Hardness 600 HV. Etched 4% picric/HCl. x 500.](image)

![Fig. 19. As-cast structure of iron containing 15% Cr, 1% Mo and 5% V, showing matrix of secondary carbides and martensite. Hardness 730 HV. Etched 4% picric/HCl. x 1000.](image)

### Table III

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Hardness HV 30 (Average of 5 tests)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 mm diameter</td>
</tr>
<tr>
<td>Tap No.</td>
<td>As-cast</td>
</tr>
<tr>
<td>1</td>
<td>2.74</td>
</tr>
<tr>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>2.64</td>
</tr>
</tbody>
</table>
pearlite was reduced also by vanadium on those occasions when insufficient pearlite-suppressing element was present. The small areas of only partially transformed austenite, retained sometimes in the centre of the dendrites, were readily removed by tempering at 450°C. The structures and hardness of these irons closely resembled those obtained in 15 per cent chromium irons by high-temperature heat treatment when no vanadium is present.

At a vanadium content of 5 per cent large particles of a carbide having a slightly pink hue, often associated with the eutectic iron/chromium carbide, were present in the structure, as shown in Fig. 20. These were more clearly visible when examined with a scanning electron microscope, as illustrated in Figs. 21a–c, in which the high vanadium content is clearly demonstrated.

### Effect of silicon content

During the course of the investigation it became apparent that vanadium was more effective in producing high ascast hardness values when the silicon content was in the range of 1.0–1.3 per cent, which is significantly higher than normally used for the production of 15 per cent chromium irons. The most satisfactory composition range appeared to be:

<table>
<thead>
<tr>
<th>C %</th>
<th>Si %</th>
<th>V %</th>
<th>Mn %</th>
<th>S %</th>
<th>Cr %</th>
<th>Mo %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5–2.8</td>
<td>1.0–1.3</td>
<td>5–6</td>
<td>0.4</td>
<td>0.05</td>
<td>15.5–16.5</td>
<td>0.8–1.0</td>
</tr>
</tbody>
</table>

As increasing silicon content is likely to promote pearlite formation in heavier sections, tests were carried out to examine the effects of increasing silicon content in a 15 per cent chromium iron, using bars of 30 and 80 mm diameter. The compositions and hardness values in the ascast and tempered conditions for both sizes of bar are given in Table III.

Examination of the microstructures showed that about 10–20 per cent pearlite occurred in the 80 mm bars at the highest silicon content of 1.7 per cent, but no pearlite was present at any other level of silicon. The structure of the tempered 80 mm diameter bar containing 1.2 per cent silicon is shown in Fig. 22.

Vanadium contents up to 5 per cent were also examined in irons containing 25 and 30 per cent chromium, but...
these always resulted in a reduction in hardness in the as-cast condition — often to levels below 325 HV. The structures consisted of eutectic carbide in a matrix considered to be ferrite, containing particles of secondary carbide as illustrated in Fig. 23. Annealing at 930°C for two hours had no effect on the structure or hardness, thus confirming that the matrix consisted predominantly of ferrite.

During the heat treatment it was noticed that the bars containing 5 per cent vanadium underwent severe oxidation, whereas equivalent bars with no vanadium content were only superficially oxidized. This is illustrated in Fig. 24. From this evidence it would clearly be unwise to consider adding large amounts of vanadium to high-chromium irons intended for use at high temperature.

Summary of effects in high-chromium irons
The results obtained suggest that, by the addition of about 5 per cent vanadium to irons containing 15 per cent chromium and about 1 per cent molybdenum, it should be possible to produce castings in the as-cast or low-temperature-tempered condition having structures and hardness similar to those normally produced by high-temperature heat treatment but with the advantage of avoiding the problems connected with high-temperature treatment.

Discussion of results
Grey cast irons
Mechanical properties
Some of the effects of vanadium in grey irons reported in the literature have been confirmed by the results of the present work. For example, the marked increase in tensile strength and the increase in the tendency to solidify with a white structure. The present results, however, show that vanadium still produces the increase in strength even when the iron is annealed to the fully ferritic condition. This could be of practical value in castings which are fully annealed to give maximum machinability, as this usually causes a marked reduction in strength — sometimes to unacceptably low levels. The addition of up to 0-5 per cent vanadium to these irons could give a considerable increase in strength in the annealed condition, while the very small increase in hardness that is also likely to occur is unlikely to have any significant adverse effect on the machinability.

The marked increase in strength produced by vanadium in grey irons could also be of value in situations where castings are used at elevated temperatures. The strength of grey iron is reduced progressively as the temperature is raised, and some reduction occurs when vanadium is present. However, much of the initial increase in strength caused by vanadium at room temperature is retained at elevated temperatures, resulting in a significant improvement in strength at these temperatures.

Effects on structure
The greater uniformity of the graphite flake size and distribution produced by vanadium has been confirmed, but the effect was less marked in heavier sections. This change in graphite distribution is similar to that resulting from efficient inoculation of grey iron, and it is likely to be the result of the increase in eutectic cell number produced by vanadium. The manner in which vanadium increases the eutectic cell number is not entirely clear.

The marked tendency for eutectic carbide to form when vanadium is added has been shown to result from an
increase in the metastable of white iron equilibrium eutectic temperature and a decrease in the stable or graphite equilibrium eutectic temperature due to the addition of vanadium. In this respect vanadium differs from chromium, which only has a significant effect on the metastable temperature. It is because of its effect on both the equilibrium temperatures that vanadium has the greater propensity to promote eutectic carbide formation.

From a practical viewpoint, the tendency for vanadium to promote eutectic carbide could be a disadvantage, particularly in thinner sections. However, the results obtained in the present work indicate that, by efficient inoculation or by adjustment to the basic composition, the formation of carbides can be confined to extremely thin sections in grey irons. In cases where the castings are annealed it is very likely that any carbides present would be removed by the annealing process.

When vanadium was added to grey irons small inclusions having a pink/white colour were formed. These were shown by analysis on the scanning electron microscope to have a very high vanadium content, and they are almost certainly the vanadium carbide inclusions described in the literature. These inclusions are relatively large, and are unlikely to have any significant effect on the mechanical properties of the iron. However, in irons that were predominantly ferritic a very fine precipitate also occurred when vanadium was added. The amount of this precipitate tended to be increased by annealing. The size of these particles was at the limit of optical microscopy, but examination on a scanning electron microscope showed them to be discrete particles of about 0.25 μm size. Owing to the extreme smallness of these particles it was not possible to analyse them. It is suggested, however, that they are vanadium carbide particles, probably precipitated from the austenite in the solid state. The presence of this precipitate is likely to contribute significantly to the increased tensile strengths obtained in the vanadium-containing irons.

Nodular (SG) Iron
Mechanical properties
In nodular iron vanadium produced the most significant increases in proof stress and tensile strength, with little loss of elongation or room-temperature notched-impact values, in annealed ferritic irons. Similar increases in tensile properties could be obtained by increasing the silicon content to above 3 per cent, but at these silicon levels the iron would be embrittled and the room-temperature notched-impact values severely reduced.

The practical implication of these results is that small additions of vanadium up to 0.5 per cent can give ferritic nodular irons with a better combination of tensile properties, ductility and impact resistance than previously recognized.

Effects on structure of nodular iron
As in grey irons, the addition of vanadium to nodular iron increased the tendency for eutectic carbide to form. The carbide can be limited to thin sections by efficient inoculation, and removed by the annealing heat treatment normally applied to produce ferritic nodular iron.

The relatively large inclusions of vanadium carbide found in grey irons were also observed in nodular irons, and it is unlikely that they had any effect on the properties of the iron.

The fine precipitate was clearly evident in the ferritic nodular irons, and undoubtedly this contributed significantly to the unusual combination of properties obtained in these irons.

High-chromium white iron
15 per cent chromium iron
A widely used iron for abrasion-resisting applications contains 15 per cent chromium and about 1 per cent molybdenum. The as-cast structure consists predominantly of iron/chromium carbides in a matrix of austenite, but the hardness can be increased by heat treatment. This consists of holding at 900–950°C for about two hours during which secondary carbides are precipitated in the austenite, thereby reducing its carbon content. On cooling, the austenite then transforms to martensite and the structure is often referred to as a 'destabilized' structure. Any residual austenite remaining in the structure can be removed by tempering at about 450°C for two hours, and the resulting material can have hardness values up to 750 HV.

The addition of 5 per cent vanadium to irons containing 15 per cent chromium produced as-cast structures and hardness values closely similar to the destabilized structures just described. It is almost certain that the secondary carbides formed in the austenite when vanadium is present are a form of vanadium carbide, although the particles were too small for any form of analysis to be carried out. It is concluded that secondary vanadium carbide precipitates readily from austenite, and consequently the austenite is destabilized during the initial cooling of the castings.

If a casting has a simple shape it can be readily heat-treated at high temperature, and there would be little advantage in eliminating the heat treatment by alloying with vanadium. However, more complicated castings made in 15 per cent chromium irons are prone to cracking during heat treatment, and in these situations the addition of vanadium to avoid the need to heat-treat could be beneficial.

The irons containing 25–30 per cent chromium and 5 per cent vanadium had ferritic matrices even after heat treatment. It might be expected that ferritic irons of this nature could be extremely stable under conditions of cyclic heating, and indeed the heat treatment at 930°C applied to these samples had no effect on the structure. However, the extremely rapid oxidation promoted by the presence of the vanadium makes it most unlikely that these irons would be suitable for applications requiring heat resistance. This is probably an unusual manifestation of the 'oxidation catalyst' function of vanadium sometimes used in the chemical industry.

Conclusions
The main conclusions relating to the effects of vanadium on the structure and properties of the different types of iron investigated are:

1. Effects on general structure
Vanadium combines with carbon in the iron to form discrete inclusions of vanadium carbide, even at quite low levels of vanadium.

In irons having a ferritic matrix, small amounts of vanadium also produce a fine precipitate. The amount of this precipitate tends to increase during annealing and it is believed to be a form of vanadium carbide deposited from the solid.
Vanadium has a strong tendency to promote the formation of eutectic carbide but, by modification of the base composition or by efficient inoculation, it should be possible to control the carbide at acceptable levels at least up to vanadium contents of 0.5 percent.

Vanadium has only a weak tendency to promote the formation of pearlite in grey or nodular irons, and the pearlite may be removed readily by annealing.

The number of eutectic cells growing in a grey iron is markedly increased by vanadium, and this results in the formation of very uniform flake graphite structures.

2. Effects on the properties of grey cast iron

Vanadium, up to contents of about 0.5 percent, is one of the most effective elements for increasing the tensile strength of flake graphite cast iron — an increase of 0.1 percent vanadium raising the tensile strength by 15–30 N/mm² (1–2 tons/in²).

The increase in strength is still apparent when the iron is annealed to a ferritic matrix, and also at elevated temperatures.

The hardness of pearlitic grey irons is increased by about 8–10 points HB for each 0.1 percent vanadium, provided no eutectic carbide is formed. The increase is reduced to about 4–5 points when the irons are annealed to a ferritic matrix.

The tendency for nitrogen fissures to form in irons of high nitrogen content is reduced by the addition of about 0.15 percent or more of vanadium, and this is still accompanied by an increase in tensile strength.

Vanadium raises the metastable (white iron) equilibrium temperature and lowers the stable (graphite) equilibrium temperature in grey iron, thus promoting the formation of eutectic carbide.

3. Effects in nodular (SG) cast iron

The proof-stress values of all types of nodular iron are raised significantly by the addition of up to 0.5 percent vanadium, but the ultimate tensile strength is only increased in ferritic grades.

The most marked increases in proof stress and tensile strength occur in annealed ferritic nodular iron and are achieved with very little reduction in elongation or loss of ductility, as indicated by the room-temperature notch-impact value.

The increase in tensile properties still occurs in ferritic iron of high silicon content, and the improvement is maintained at elevated temperatures.

4. Effects in malleable iron

Small contents of vanadium up to about 0.15 percent can give useful increases in yield and tensile strength, with little change in elongation.

The annealability of malleable iron is retarded by small vanadium contents, and this would need to be taken into account when vanadium was added.

5. Effects in high-chromium irons

The addition of 5 percent vanadium to an iron containing 15–16 percent chromium and about 1 percent molybdenum produces as-cast hardness values and matrix structures equivalent to those produced by high-temperature heat treatment of similar irons having no vanadium addition. The most satisfactory structures are produced by vanadium at silicon contents around 1.2 percent.

The as-cast matrix structure of a 15 percent chromium iron containing 5 percent vanadium consists of secondary carbides in martensite. It is believed that the austenite is 'destabilized' by the precipitation of secondary vanadium carbide during the initial cooling.

The as-cast hardness of these irons containing 5 percent vanadium can sometimes be increased slightly by low-temperature tempering to remove any residual austenite present.

Vanadium contents up to 5 percent in irons containing 25 or 30 percent chromium produce relatively soft irons having predominantly ferritic matrices.

Extremely rapid oxidation of irons containing 25 and 30 percent chromium is likely to occur at high temperatures when they have a vanadium content of about 5 percent.

Acknowledgement

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References

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