MICROALLOYED PEARLITIC STEELS FOR THE WIRE INDUSTRY — MECHANISMS OF ALLOY ELEMENT REDISTRIBUTION AND STRENGTHENING PROCESSES IN CHROMIUM-VANADIUM EUTECTOID STEELS

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THE STRENGTH OF CONTINUOUSLY COOLED PEARLITIC STEEL ROD can be increased by up to 200MN/m² by small additions of chromium and vanadium. We report here a detailed investigation of the microstructure and properties of a range of such steels. In addition to conventional mechanical property and microscopical studies, the techniques of field emission STEM X-ray analysis and atom probe microanalysis have been used to examine the redistribution of alloying elements during heat treatment. Both chromium and vanadium have a strong tendency to redistribute to the cementite phase by short-circuit diffusion along the austenite-pearlite interface. Under rapid transformation conditions, however, this redistribution process is incomplete, and secondary carbide precipitation can occur within the pearlitic ferrite. An unusual feature of vanadium additions is their tendency to produce grain boundary ferrite films, even in steels of eutectoid composition. This effect is believed to be due to nucleation of vanadium carbide particles in austenite grain boundaries, prior to pearlite formation. Nucleation of pearlitic cementite is consequently inhibited, allowing a continuous ferrite film to develop. Fortunately, the presence of such films does not adversely affect subsequent cold drawing properties, which are fully comparable to those of lead patented plain carbon steels.

INTRODUCTION

Fully pearlitic steels are widely used in the manufacture of wire rod, and also for the production of rails. As ever-increasing demands are placed on the properties of these materials, efforts are being made to improve their strength by means of microalloying additions. Most work to date has been carried out on rail steels, and successful results have been obtained using additions of chromium, molybdenum, silicon, vanadium and niobium (1-7). Developments in microalloyed steels for wire and rod applications have been slower, partly because the higher transformation rates involved in wire rod production allow less flexibility in steel composition, and also because the traditional lead patenting process produces excellent mechanical properties, especially in smaller diameter rods. Increased incentive towards the use of microalloying has come from the need to produce high strengths in thick sections, for example in heavy duty pre-stressed concrete tendons. Also, the high energy costs and environmental hazards associated with lead patenting have resulted in a move towards the use of continuous forced air cooling for production of wire rod, with a consequent increase in the overall transformation temperatures for plain carbon steels. Recently some improvement in rod properties has been obtained by the use of chromium, manganese, molybdenum or silicon additions (8-15), but so far this has not permitted the complete replacement of lead patented material.

In the present work we have studied the combined effects of small additions of chromium and vanadium to eutectoid wire rod steels. The aim was to retard the kinetics of the pearlite reaction just sufficiently to obtain a fine pearlitic microstructure under continuous cooling conditions, and to develop an additional strength increment through secondary precipitate formation in the pearlitic ferrite phase. This approach closely resembles that used by Parsons et al in the development of improved rail steels, as reported in these Proceedings (7). The project was undertaken in collaboration with Templeborough Rolling Mills (T.R.M.) Ltd. of Rotherham, U.K., and Bridon Wire Ltd., of Doncaster, U.K. The present paper is mainly concerned with investigations of the physical metallurgy of the microalloyed steels, and the redistribution of the alloying elements during heat treatment; full details of
the accompanying programme of industrial trials have been reported elsewhere (16). The earlier literature on the effects of (separate) additions of chromium and vanadium on the pearlite reaction is quite extensive, and will not be reviewed in detail here. However the pioneering work on vanadium by Bain and colleagues (17), studies of secondary precipitation of vanadium carbonitrides by Dunlop et al (18) and Ridley et al (19), and recent measurements of the redistribution of chromium carried out by Al Salman (20), Chance (21) and Williams (22), are particularly relevant to the theme of the paper.

**EXPERIMENTAL**

The compositions of the steels used in this study are listed in Table I. An initial set of steels (11-14) was designed to allow investigation of the effects of chromium and vanadium additions separately and together, and to permit comparison with an equivalent plain carbon steel. These alloys were produced at the British Steel corporation (B.S.C.) in the form of 500 kg ingots, and were rolled to 11mm diameter at T.R.M. Steel P1 was used for the first large scale production trial, and was also the subject of laboratory investigation; it was produced by B.S.C. in the form of an 80 tonne cast, and was rolled to 11mm diameter rod at T.R.M. An additional set of 10kg laboratory melts was obtained (V0-V4), in which the level of vanadium was varied systematically, while the chromium level was kept constant. These steels were high purity and were prepared by vacuum melting at Sheffield University. They were received in the form of 11mm diameter extruded rod.

Both isothermal and continuous cooling transformation characteristics were investigated. Isothermal transformations were carried out in a salt bath, the extent of reaction as a function of time being estimated from subsequent metallographic examination. Continuous cooling conditions were obtained in the laboratory by using an apparatus in which lengths of 11mm diameter rod were first induction heated for austenitisation, and then force-cooled using compressed air. Temperature was measured by means of a thermocouple inserted in a blind hole drilled along the axis of the specimen, and the extent of reaction was monitored using a dilatometric method (22). A range of transformation conditions was studied as summarised in Table II. Austenitisation conditions were varied in order to maintain an approximately comparable grain size across the whole range of steels, and to ensure that the alloy elements were fully taken into solution.

Large-scale continuous cooling trials were carried out using the production facilities at T.R.M. After soaking at 1300°C, billets were hot rolled to 11mm diameter rod, which was then laid onto a conveyor, and cooled from below by a series of large fans. The maximum cooling rates attained immediately prior to transformation were approximately 5°C per second. When processing plain carbon and carbon-vanadium steels, all fans were operated. In the case of the chromium-containing steels, the fans were switched off at the point on the conveyor where transformation began. Further details are given in reference (15).

Investigations of microstructure and properties were carried out using conventional optical microscopy, scanning and transmission electron microscopy, together with microhardness and tensile strength measurements. In addition, the local redistribution of alloying elements was studied using two specialist high resolution microanalytical instruments, an atom probe field ion microscope, (AP FIN) located in Oxford (23) and an HB5 field emission scanning transmission electron microscope (STEM) fitted with non-dispersive X-ray analysis facilities, and located at M.I.T., Cambridge, Mass., U.S.A., (24). The field emission STEM work formed part of a broader study of alloy element redistribution during the pearlite reaction, details of which are to be published elsewhere (28).
Table II

Summary of Isothermal and Continuous Cooling Transformation Conditions Studied

<table>
<thead>
<tr>
<th></th>
<th>Austenitisation</th>
<th>Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal</td>
<td>950°C-1200°C,</td>
<td>680°C-430°C,</td>
</tr>
<tr>
<td>Transformation</td>
<td>(300 seconds)</td>
<td>(salt bath)</td>
</tr>
<tr>
<td>Continuous</td>
<td>850°C-1150°C</td>
<td>3°C/sec-9°C/sec</td>
</tr>
<tr>
<td>Cooling</td>
<td>(300 seconds)</td>
<td>(forced air cooling)</td>
</tr>
<tr>
<td>Transformations</td>
<td></td>
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</tr>
</tbody>
</table>

RESULTS

TRANSFORMATION BEHAVIOUR - A partial TTT diagram for the chromium-vanadium steel P1 is shown in Figure 1. The shape of the curve is broadly similar to that for an equivalent plain carbon steel. The main differences are that the temperature at the nose of the curve is raised by about 30°C, and the time to complete the reaction at the nose temperature is also increased from 5 to 10 seconds. Thus it should be possible to process a steel of this composition either by lead patenting or by continuous cooling, with only minimum change to the conditions normally used for the production of plain carbon rod. This conclusion is borne out by comparison with the CCT curves for steel I4, as shown in Figure 2. The pearlite start temperature decreases slowly with increasing cooling rate. The finish temperature shows different behaviour, in that it displays an initial gradual increase and under certain conditions it exceeds the start temperature. This is due to the exothermic nature of the pearlite reaction, and the fact that the low levels of alloying additions used are not sufficient to suppress recalcement. The fine grain size of the chromium-vanadium steel I4 meant that no martensite was produced in this material even at the highest cooling rate available in the laboratory (9°C per second).

MICROSTRUCTURES - Optical microscopy of the initial trial rods I1-I4, transformed by continuous cooling on the T.R.M. line, showed that in each case the microstructure consisted of very fine pearlite, Figure 3. The fineness of the structures was estimated by measuring the fraction of resolvable pearlite at X500 magnification. The amount of resolvable pearlite decreased in the order I1>I2>I3>I4. Subsequent examination of rods of steel P1 from the first full production trial revealed a very similar microstructure to that of I4.

The initial trial rods were also studied using SEM, and in general a fine regular pearlitic microstructure was found, although in some regions the rods with microalloying additions showed marginally more degenerate structures than the plain carbon steel. A typical microstructure is shown in Figure 4.

Investigations using TEM confirmed the

Figure 1. Partial TTT diagram for the Cr-V steel P1.

Figure 2. Partial CCT diagram for the Cr-V steel I4.
optical and SEM work, in that a fine pearlitic microstructure was observed in all the microalloyed rods, Figure 5. The vanadium-containing rod steels were free of any coarse carbides, in contrast to the structures of the rail steels studied by Parsons et al (7). Also, even after extensive study, no conclusive evidence of fine secondary precipitates could be found in the pearlitic ferrite by electron microscopy, in either bright or dark field, or in diffraction patterns. (Fine secondary precipitates were eventually observed by another technique, field ion microscopy, as will be described later). These differences from the case of rail steels are undoubtedly due to the much faster cooling schedules and transformation rates involved in wire rod production.

The microstructures of the series of steels of different vanadium content (V0–V4) were also examined, following isothermal transformation in the temperature range 680–430°C. As expected, the pearlite microstructures became progressively finer as the transformation temperatures were lowered, the first signs of upper bainite formation being observed at 530°C. Two additional significant effects were found in this series of experiments. Firstly, if the austenitisation temperature was 1000°C or below, some coarse carbides were observed, especially in the alloys of higher vanadium content. No particles were observed if austenitisation was carried out at 1050°C or above (consistent with the results of the previous continuous cooling trials at T.R.M., where a soaking temperature of 1300°C was employed). The second effect observed was the development of films of free ferrite along
the prior austenite grain boundaries, Figure 6. These films were completely absent in steel VO, and their abundance increased as the vanadium content was raised. The effect was also dependent on transformation temperature, increasing progressively as the temperature was lowered from 640°C to 560°C. In their study of the effects of small additions of vanadium to eutectoid steels, Bain et al (17) also observed grain boundary ferrite films. These workers found films in specimens transformed at 620°C, but not at 705°C. They suggested that the films occur because vanadium carbides precipitate selectively in the grain boundaries and deplete the surrounding regions of carbon. Therefore the formation of pearlitic cementite is inhibited and proeutectoid ferrite is allowed to develop. The almost complete absence of such films in continuously cooled rod would seem to be due to the higher temperatures at which transformation begins, this permitting the more rapid diffusion of carbon in the boundary regions.

In order to investigate the nature of the ferrite films in more detail, carbon replicas were prepared from steel V4 isothermally transformed at 560°C. TEM examination revealed the apparent presence of large isolated particles in some of the ferrite films. It was initially believed that these particles were vanadium carbides of the type reported by Bain, but STEM X-ray analysis revealed no trace of vanadium. The particles were therefore almost certainly cementite fragments arising from the transformation of the replicas. The transformation temperature involved (560°C) was much lower than that used by Bain, and so it seems likely that any vanadium carbides associated with these ferrite films were too fine to be picked up during the replication process.

MECHANICAL PROPERTIES - The tensile properties of the initial trial steels I1-I4 are summarised in Tables III and IV. The steels were hot rolled to 11.6mm diameter and transformed by continuous cooling on the T.R.M. line, and subsequently drawn to 4.22mm diameter by Bridon Wire Ltd, under standard production conditions. It is evident that additions of chromium and vanadium each produce a substantial increase in the rod tensile strength. The combined addition of both elements produces a strength increment which is approximately equal to the sum of the contributions made by the alloy elements when added separately. The increase in strength of the as-transformed rods is maintained throughout the wire drawing process. The work hardening rates of the microalloyed steels are closely similar to those of the reference plain carbon steel, and no loss of ductility in the final wires is observed as a result of the alloy additions.

The excellent mechanical properties obtained from the initial trial steels were maintained when a first production cast of the chromium-vanadium steel Pl was tested. In this case the tensile strength obtained for 11mm continuously cooled rod was 1246±15MN/m² (average of 77 coils of rod). This compares favourably with the strength of 1236±15MN/m² obtained for an equivalent lead patented plain carbon steel. Drawing of steel Pl to 4.22mm diameter wires produced a final tensile strength of 2001±52

| Table III |
| --- | --- | --- | --- |
| **Mechanical Properties of Initial Trial Steels I1-I4 (11mm continuously cooled rod)** |
| | I1 | I2 | I3 | I4 |
| Tensile Strength (MN/m²) | 1070 | 1127 | 1234 | 1274 |
| Reduction in area (%) | 30 | 36 | 32 | 38 |
| Elongation (% 50mm) | 15 | 16 | 15 | 15 |

| Table IV |
| --- | --- | --- | --- |
| **Mechanical Properties of Initial Trial Steels I1-I4 (4.22mm cold drawn wires)** |
| | I1 | I2 | I3 | I4 |
| Tensile Strength (MN/m²) | 1746 | 1847 | 1903 | 1956 |
| Reduction in area (%) | 45 | 48 | 43 | 45 |
| Elongation (% 50mm) | 5 | 5 | 5 | 4 |
MN/m², compared to 2048±60 MN/m² for wires drawn from an equivalent patented plain carbon steel. Thus the controlled cooled microalloyed rod is capable of being used as a direct replacement for lead patented feedstock.

In order to assess the role of the vanadium additions in more detail, a series of isothermal transformation studies was carried out using the experimental steels V0-V4. Microhardness measurements were made on specimens austenitised over a range of temperatures and isothermally transformed at a fixed temperature of 560°C. The results are summarised in Figure 7. It is apparent that the hardness increases with increasing vanadium content for all the austenitising conditions. This suggests that at least some vanadium is going into solution even at the lowest austenitising temperatures used. Steel V0 shows a decrease in microhardness with increasing austenitising temperatures, steel V2 is approximately constant, and steel V4, after an initial increase in microhardness, levels off above 1050/1100°C. Thus the bulk of the vanadium in steel V4 must be in solution at approximately 1050°C (see note, reference 33).

A series of microhardness measurements was also made on the steels austenitised under fixed conditions (300s at 1050°C) and subsequently transformed at a range of different temperatures. These results are depicted in Figure 8. The general trend in the results is consistent with the microstructural observations, in that there is an increase in microhardness as the pearlite becomes finer and a substantial decrease when upper bainite is formed. In the temperature range in which pearlite is formed, progressive increases in vanadium content produce progressively greater increments in strength. Interestingly, however, in the bainite temperature range vanadium additions do not appear to raise the strength significantly.

INTERLAMELLAR SPACING MEASUREMENTS - In order to assess the influence of each microalloying addition on the pearlite interlamellar spacing, this parameter was measured for continuously cooled samples of I1-I4, from the T.R.M. line. Obviously, any value of interlamellar spacing quoted for continuously cooled rod will only be approximate, because there will be variations caused by the transformation temperature not being constant in all regions of the rod. Minimum spacings were measured (near the surface of the rod) for 20 areas of each steel, using SEM micrographs recorded at X10,000 magnification. The data are summarised in Table V. Each microalloyed steel had a smaller interlamellar spacing than the reference plain carbon steel, the actual spacings decreased in the order I1>I3>I2>I4. This result is particularly significant in view of the fact that the later fans on the line were turned off when processing the chromium-containing steels I2 and I4, thus reducing their cooling rates compared to the plain carbon and carbon-vanadium steels.

Table V
Average minimum interlamellar spacings for steels I1-I4 transformed by continuous cooling. (SEM measurements)

<table>
<thead>
<tr>
<th>STEEL</th>
<th>Interlamellar spacing (nm)</th>
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<tbody>
<tr>
<td>I1</td>
<td>139±13</td>
</tr>
<tr>
<td>I2</td>
<td>126±10</td>
</tr>
<tr>
<td>I3</td>
<td>129±8</td>
</tr>
<tr>
<td>I4</td>
<td>118±9</td>
</tr>
</tbody>
</table>
Table VI

<table>
<thead>
<tr>
<th>STEEL</th>
<th>V0</th>
<th>V4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average spacing (nm)</td>
<td>149</td>
<td>166</td>
</tr>
<tr>
<td>Standard Deviation (nm)</td>
<td>±18</td>
<td>±15</td>
</tr>
<tr>
<td>Overall Range of Spacings observed (nm)</td>
<td>118-190</td>
<td>138-188</td>
</tr>
</tbody>
</table>

In order to obtain a more quantitative estimate of the influence of vanadium additions on interlamellar spacing, some additional measurements were performed on specimens of steels V0 and V4, isothermally transformed at 640°C. A TEM method was used to measure the spacings, in order to remove the problems associated with the analysis of oblique sections on bulk samples. Five thin foil specimens of each steel were examined. Each foil was tilted until one of the pearlite colonies was aligned exactly parallel to the electron beam, a micrograph was recorded, and then the procedure was repeated for other colonies. Latex spheres, deposited on the surface of each foil, provided a magnification calibration. For each colony, measurements were made over 15-20 interlamellar spacings, to an accuracy of ±1%. The results, which are summarised in Table VI, reveal two main features of interest. Firstly, the average spacings of the isothermally transformed high-vanadium pearlite (V4) is slightly larger than that of the very low-vanadium pearlite (V0). The difference is more significant when it is remembered that vanadium raises the eutectoid temperature, and thus increases the undercooling at a given transformation temperature. The magnitude of this effect is not well documented, but it can be deduced from the work of Bain et al (17) that an addition of 0.21%V will increase the eutectoid temperature by approximately 20°C. Thus a significant refinement in spacing would be expected in the high vanadium steel, other things being equal, which is the opposite of what is actually observed under isothermal transformation conditions. The small reduction in spacing which was observed under continuous cooling conditions is therefore probably due to a slight lowering of the average transformation temperature by the vanadium addition.

The second effect of interest is that both the vanadium-containing and vanadium-free steels exhibit a substantial spread of true interlamellar spacings, even when transformed under strictly isothermal conditions. It has previously been inferred that a variation of this kind may exist (25), but we believe that this is the first occasion in which it has been demonstrated directly.

ATOM PROBE FIELD ION MICROSCOPY - The AP FIM was used (a) to search for and measure the size, distribution and composition of any ultra-fine secondary precipitates present in vanadium-containing steels, and (b) to investigate the overall distribution of chromium and vanadium in the cementite and ferrite phases. Two steels were examined using this instrument, the vanadium steel I3 and the chromium-vanadium steel PI.

The experiments were successful in observing secondary precipitates in the pearlitic ferrite of both steels. These appear bright in the FIM images as illustrated in the photomicrographs of steel I3 shown in Figure 9. These were recorded at a voltage lower than best-image voltage in order to increase the precipitate/ferrite contrast. The precipitates are typically 3-4nm in diameter. The interparticle distance is difficult to quantify with a limited field of view, but at an imaging voltage of 10kV (approximately 100mm across the image), both steels displayed a maximum of 4 particles per image. Precipitate free zones were observed when a cementite plate was present in the imaging region. This is consistent with previous TEM observations of coarser vanadium-containing pearlettes carried out by Dunlop et al, (18), Ridley (19) and Parsons and co-workers (7).

An atom probe mass spectrum accumulated from analysis of three secondary precipitates in steel I3 as shown in Figure 10. Peaks due to vanadium, chromium, carbon and nitrogen are evident. The large iron mass peaks are believed to be due to ions captured from the ferrite matrix surrounding the small particles. Atom probe data for a series of precipitates analysed in steels I3 and PI are summarised in

![Brightly Imaging Particles in the Ferrite matrix of a Fully Pearlitic Steel. (All at 86Kv)](image_url)
Figure 10. Atom probe mass spectrum from secondary precipitates in steel I3.

Figure 11. Atom probe composition profile across ferrite-cementite interface in steel I3.

Table VII (excluding the contribution from iron peaks). The particles are essentially mixed carbnitrides with compositions typical of vanadium rich precipitates, M<sub>g</sub>(C,N), to M(C,N). The level of chromium in the particles is noticeable, even when this element is present at only residual levels in the steel, and is quite substantial in the mixed chromium-vanadium alloy (Pl). The proportion of carbon to nitrogen varies with the nitrogen content of the steel, the particles from the first vanadium steel (I3) containing substantially more nitrogen than the production trial steel Pl (see note, ref. 34).

The composition of the ferrite matrix in the central region of a lamella is summarised in Table VIII. There is some carbon, chromium and vanadium present, but as expected the levels are very low. Composition profiles were obtained across a cementite plate in the vanadium steel I3, as shown in Figure 11. There is substantial enrichment of chromium and vanadium in the cementite phase, whilst silicon is depleted. The situation in the adjacent ferrite is reversed. The chromium and silicon results are in agreement with previous atom probe work by Williams (22,23) The total amount of vanadium in solution in the cementite can now be calculated. If this quantity is added to the amount dissolved in the ferrite, the amount of vanadium remaining to form secondary precipitates can be estimated. Assuming that 1/7 of the structure is cementite, and that vanadium is only in solution appreciably in the central 50% of the ferrite, the interesting result obtained is that only 1/6 of the vanadium present in the steel is used to form secondary precipitates. If this vanadium forms VC precipitates which are spherical, 3nm across, and form only in the central 50% of the ferrite, then the interparticle spacing calculated is

Table VII

<table>
<thead>
<tr>
<th>STEEL</th>
<th>I3</th>
<th>Pl</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>171</td>
<td>301</td>
</tr>
<tr>
<td>N</td>
<td>55</td>
<td>17</td>
</tr>
<tr>
<td>Cr</td>
<td>25</td>
<td>91</td>
</tr>
<tr>
<td>V</td>
<td>226</td>
<td>294</td>
</tr>
<tr>
<td>Average V&lt;sub&gt;g&lt;/sub&gt;Cr C&lt;sub&gt;g&lt;/sub&gt;N&lt;sub&gt;g&lt;/sub&gt;</td>
<td>V&lt;sub&gt;g&lt;/sub&gt;Cr&lt;sub&gt;g&lt;/sub&gt;N&lt;sub&gt;g&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>Precipitate Composition</td>
<td>Composition</td>
<td></td>
</tr>
<tr>
<td>(V,Cr)(C,N)&lt;sub&gt;g&lt;/sub&gt;</td>
<td>(V,Cr)(C,N)&lt;sub&gt;g&lt;/sub&gt;</td>
<td></td>
</tr>
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</table>

Table VIII

<table>
<thead>
<tr>
<th>STEEL</th>
<th>I3</th>
<th>Pl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.65</td>
<td>1.00</td>
</tr>
<tr>
<td>Cr</td>
<td>0.01</td>
<td>0.13</td>
</tr>
<tr>
<td>V</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Total number of ions collected</td>
<td>14,229</td>
<td>17,097</td>
</tr>
</tbody>
</table>
approximately 20nm. This is of the same order on that observed.

STEM MICROANALYSIS - The STEM was used to confirm and extend the atom probe studies of the redistribution of alloy elements during the pearlite transformation. In particular, it was found useful for investigating the migration processes occurring in the vicinity of the pearlite growth interface. Small disc specimens of steel P1 (3mm diameter x 0.5mm thick) were partially isothermally transformed at 630°C, and were then rapidly quenched to freeze the pearlite reaction, and to convert the remaining untransformed austenite to martensite. Thin foils were prepared from these discs by a combination of jet polishing and ion milling techniques. An electron micrograph showing the pearlite growth interface is illustrated in Figure 12. An X-ray microanalysis composition profile across the martensite-cementite interface is shown in Figure 13. It is clear that there is a step-function increase in the concentration of chromium manganese and vanadium on going from the martensite to the cementite phase, indicating that all three elements redistribute rapidly in the growth interface. A corresponding decrease in alloy element concentration is observed across the martensite-ferrite interface, but in this case the overall composition profile is complicated by the presence of a local solute concentration peak at the actual transformation front. This peak is particularly marked in the case of chromium, Figure 14. The peak is apparently due to partial local equilibration of solute across the growth interface, and is of importance in understanding the mechanism by which alloy elements retard the rate of transformation (see reference 28).

POST TRANSFORMATION AGEING TREATMENTS - In view of the AP FIM results of Table VIII, which showed that a small amount of vanadium was retained in solid solution in the ferrite phase immediately after the pearlite transformation, a series of soaking experiments was designed, to see whether a further increment of strength could be obtained. Samples of steels V0, V2 and V4 were austenitised for 300 seconds at 1050°C. They were then soaked for periods of up to one hour at 560°C and 640°C. The resulting changes in hardness with time are shown in Figure 15. A significant effect is observed, especially in the steel with the highest vanadium content (V4). The hardening is quite rapid, occurring within about three minutes of ageing. Therefore if a controlled cooled or lead patented vanadium steel is held briefly at temperature following transformation, an additional strength increment of several per cent may be obtained. This could be achieved with only minimum changes to standard production conditions.
Figure 15. Effect on microhardness of post transformation ageing treatments of steels V0, V2 and V4 at (a) 560°C and (b) 640°C

DISCUSSION

The results presented above show that small additions of chromium and vanadium to pearlitic wire rod steels produce substantial strength increases. In the continuously cooled condition, the strength increment may be as much as 200MN/m², without any deleterious side effects appearing in subsequent wire drawing properties. The material thus provides a very satisfactory replacement for lead patented feedstock. The laboratory investigations have led to an improved understanding of the influence of the alloying additions, and provide the basis for optimisation of the production process.

QUANTITATIVE RELATIONS BETWEEN MICROSTRUCTURE AND STRENGTH - There are clearly two main contributions to the increased strength of the microalloyed rod, one from the refinement of pearlite interlamellar spacing, and the other from secondary precipitation hardening. In attempting to assess the relative contributions of these two mechanisms, it is instructive to compare the yield strengths obtained from the steels II-I4 in the present work with the results of Ridley et al (19) for steels with a range of vanadium contents. In Figure 16, data from both sets of work is plotted as different functions of interlamellar spacing, for each vanadium content. When the yield strengths are plotted as a Hall-Petch type function of the reciprocal square root of the interlamellar spacing, Figure 16a, it is found that extrapolation back to infinite spacing gives large negative values for the friction stress. However, when the data is plotted as a

Figure 16. Graphs of proof strength as a function of interlamellar spacing for steels II-I4, with comparative results from the work of Ridley et al (19) (a) Plotted versus \( S^{-1} \) (b) Plotted versus \( S^{-1} \).
simple reciprocal of spacing, Figure 16b, a more sensible positive value is obtained for this parameter. This agrees with the conclusions of Marder and Bramfitt (29), who studied a wide range of plain carbon eutectoid steels, and is also in accordance with results from a wide range of lamellar eutectoid alloys, reviewed by Chadwick (30). The explanation appears to be that yielding is governed by the presence of faults and defects within the lamellar microstructure, and that a simple Hall-Petch type relationship is unlikely to be obeyed in this case.

Referring to Figure 16b, the data from the present work appear to lie on two distinct lines, each with a similar slope. The displacement between the two lines is evidently due to the differences in the content of vanadium, which increases the strength by precipitation hardening. From the Figure, it is possible to estimate that the difference in interlamellar spacing between the chromium-vanadium steel (I4) and the plain carbon steel (II) is responsible for a strength increment of approximately 100MN/m², or about half the total strength increase observed. It follows that precipitation processes are responsible for a strength increment of similar magnitude in steels I3 and I4.

Using the data obtained from the AP FIM experiments, it is possible to carry out an independent first-principles calculation to estimate the strength contribution due to secondary precipitation. Values of (f), the volume fraction of precipitates, and (X), the mean effective diameter of the precipitates, can be substituted into the following equation given by Ashby (31) for the yield strength (σ) of a dispersion hardened iron alloy:

$$\sigma (\mathrm{MN/m}^2) = \frac{5.9/\varepsilon}{x} \ln \left( \frac{x}{2.5 \times 10^{-4}} \right)$$

Taking X as 3 x 10⁻⁴m, and calculating f from

$$f = \frac{4}{\pi} \left( \frac{X}{r} \right)^{1/3}$$

$$3 \left( \frac{2}{D} \right)^{1/3}$$

where D is the mean interparticle spacing, in this case 2 x 10⁻⁴m, we obtain a value for σ of 200MN/m². This predicted increment of strength only applies to the centre regions of the ferrite, because precipitate free zones exist adjacent to the cementite lamellae. Thus the calculation appears broadly consistent with the empirical estimate of 100MN/m² made above.

From the studies of the hardness of steels of varying vanadium content (V0-V4), it is clear that the strength increment due to precipitation hardening could be increased above the level of 100MN/m² if desired. However the increased constraints placed upon austenitisation conditions, and the more extensive formation of grain boundary ferrite films at higher vanadium levels, would not appear to favour this course.

REDISTRIBUTION OF ALLOY ELEMENTS - The overall pattern of redistribution of alloy elements in these microalloyed steels is quite complex. Several different processes are occurring in parallel with one another. The redistribution of chromium has been studied in detail by Al Salman et al (20), Chance (21) and Williams (22,26). The mathematical analysis presented by Williams showed unambiguously that chromium must diffuse to the cementite phase via a short circuit diffusion path in the transformation interface. According to Al Salman (32), the redistribution of silicon to the ferrite regions occurs by a combination of bulk and interface diffusion. The results of the STEM analysis carried out during the present work indicate that manganese and vanadium must redistribute by interface diffusion. An earlier report by Ricks et al (27) concluded that vanadium migration probably occurred by bulk diffusion in the ferrite phase behind the transformation front. Their concentration profiles appear inconsistent with ours, and may have been due to an artifact associated with their use of extraction replicas, rather than thin foils, for chemical analysis purposes. Our interpretation of the vanadium redistribution process is shown schematically in Figure 17. Diffusion of vanadium to the cementite phase occurs by lateral migration in the transformation front. This leads to the development of concentration gradients of this element from the centre to the edges of the ferrite regions. Secondary precipitation of vanadium-rich carbonitrides is
a competing process which will occur preferentially where the local vanadium (and carbon) contents are highest, i.e. in the central areas of the ferrite. Precipitate free zones will exist adjacent to the cementite lamellae, where the vanadium content is lowest.

OPTIMISATION OF PROCESSING ROUTE – A number of different parameters have to be controlled in order to optimise the properties obtained from these microalloyed steels. Austenitisation temperatures should be sufficient to dissolve the vanadium-rich carbides, but excessive grain coarsening must be avoided. Cooling rates prior to transformation should be as rapid as possible, to minimise coarse alloy carbide precipitation, transformation temperatures should be kept low, and transformation times should be adjusted to maximise the strength increments from spacing refinement and secondary precipitation processes. In actual practice, the operating environment of a wire rod mill is well suited to the task of obtaining maximum benefit from the alloying additions. High austenitisation temperatures are possible, the hot rolling schedule prevents grain coarsening, and rapid cooling is possible to the transformation temperature range. The outlook for the future exploitation of these steels in the wire industry is therefore extremely promising.

CONCLUSIONS

1. Additions of chromium and vanadium to plain carbon pearlitic wire rod steels produce strength increments of up to 200MN/m², under continuous cooling transformation conditions.

2. The resultant steels show excellent wire drawing behaviour, their properties being fully equivalent to those of lead patented plain carbon steels.

3. The observed strength increment is due to two effects, refinement of pearlite interlamellar spacing, and secondary precipitation strengthening of the ferrite phase. The respective contributions of these two effects are approximately equal.

4. A complex pattern of alloy element redistribution between ferrite and cementite is observed during the transformation of these steels. Chromium, manganese and vanadium partition preferentially to cementite via a short-circuit diffusion path in the transformation interface. Silicon partitions preferentially to the ferrite.

5. Fine secondary precipitates form in the central regions of the ferrite and have been identified by atom probe analysis as chromium-vanadium carbonitrides. The concentration of nitrogen in the precipitates is substantial, and varies with the overall nitrogen level in the steel. A precipitate free zone exists adjacent to the cementite lamellae.

6. At higher vanadium levels a grain boundary ferrite phase forms at the prior austenite grain boundaries, especially under isothermal transformation conditions. The formation of these films is believed to be due to preferential nucleation of vanadium carbides at the boundary, which denude the boundary region of carbon, and inhibit cementite nucleation. Fortunately the presence of these films is not detrimental to wire drawing properties.

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REFERENCES


3. S. Marich and P. Curzio, ibid. pp 167-211.


stages of cooling. This effect would be enhanced at higher vanadium contents.

34. Note that the tensile strength obtained for continuously cooled samples of the chromium-vanadium steel I4, which contained 0.011\% nitrogen, was 28MN/m² higher than that for the closely similar steel P1, for which the nitrogen content was <0.007\%. This is consistent with the results of Parsons et al (7) who also report higher strengths for steels having higher nitrogen nitrogen levels. A possible explanation would be that there is competition between the two processes involved in vanadium redistribution (i.e. interface diffusion to the cementite phase, and secondary precipitation). It is well known that the carbonitride of vanadium is thermodynamically more stable than pure carbide, and so the addition of nitrogen to the steel may enhance the precipitation reaction at the expense of partitioning to the cementite.

33. Note that in the present work, no saturation effect is observed in the strength increment as the vanadium content is raised. This contrasts with the results of Parsons et al for rail steels (7). The most likely explanation for the difference in behaviour is that the slower cooling rates involved in rail production result in the precipitation of relatively coarse vanadium carbonitrides directly from austenite during the first