SULPHIDE INCLUSIONS IN LOW MANGANESE STEELS

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ABSTRACT

The influence of Mn and S content on sulphide formation in plain carbon thick, continuously cast steel slabs has been evaluated using a combination of standard metallographic techniques and analytical electron microscopy. Steels with low Mn levels of about 0.3 wt% are characterised by a relatively uniform dispersion of spherical MnS particles throughout the entire cast slab along with an additional non-uniform dispersion of larger MnS occurring predominantly in the slower cooled mid thickness region. The finer, more uniform particles are related to the increased solubility of S while the formation of the larger sulphide inclusions is associated with the increased sulphur level in the mid thickness position which results from the strong segregation of S during casting. As the S level increases, the number of large sulphide particles increases and the formation of FeS in association with the MnS becomes evident. Simulated slab reheating had a minimal effect on the overall size distribution of sulphide particles, however, the FeS formed in the cast slab reverted to MnS. Hot rolling the cast steel to below 10mm thick strip had minimal effect on the fine spherical sulphide inherent to lower Mn steels, however, elongated sulphide inclusions were produced in the mid thickness region of the rolled steel. Microalloy additions of Ti and Nb resulted in the formation of complex alloy carbosulphide precipitates, which did not significantly influence the inherent dispersion of MnS inclusions. Chromium had little effect on the number and length of sulphide inclusions with the maximum recorded solubility of Cr in MnS being 5wt% in a steel containing 0.81wt% Cr steel, 0.3wt%Mn and 0.008wt%S.

KEY WORDS: Microalloy, Low Mn steel, Sulphide Inclusion, MnS, FeS, CuS, Carbosulphide, Inclusion Plasticity

INTRODUCTION

Fracture toughness is an important attribute of high strength steels and is often assessed in terms of Charpy upper shelf energy levels and impact transition temperature. Ferrite grain size exerts a controlling influence on the transition temperature but factors such as C content [1,2], microstructural banding, cold worked ferrite and non metallic inclusions [3] are some of the important factors influencing the upper shelf energy levels. In terms of non-metallic inclusions, the formation of MnS is well known for its detrimental effect on mechanical properties. The inherent difference in properties of the sulphide and the steel matrix results in the formation of inclusion stringers during rolling, which decreases toughness and most importantly increase anisotropy in the hot rolled strip [4].

The achievement of extremely low S levels improves toughness but it can be further improved with Ca modification of the remaining sulphides [5]. Restrictions to the level and form of S in steel involves both hot metal and ladle pre treatments and not only requires expensive consumables, but reduces valuable ladle refractory life during processing and is logistically challenging and time consuming. In response to these economic pressures BlueScope Steel has recently been exploring the potential for alternative low Mn alloy designs particularly for high strength steels [6,7]. This alternative approach recognises the benefits of reduced Mn levels on sulphide size and
deformability and additionally aims to explore the potential for other elements such as Ti, Cr and Nb to compete with Mn and form harder or less plastic sulphide inclusions.

As an alloying element in steels, manganese confers numerous benefits. It provides solid solution strengthening and importantly lowers the austenite to ferrite transformation temperature to optimize grain refinement during thermomechanical processing as commonly applied for high strength steel manufacture. A minimum level of Mn in steel (i.e. Mn/S>35) [8] is generally required to combine with S and avoid the formation of FeS, which can lead to hot shortness. However, as mentioned above, the presence of MnS stringer inclusions decrease toughness and the partitioning of Mn leads to segregation in the as-cast steel which can influence microstructural uniformity during processing and increase anisotropy in the rolled strip. During hot rolling, the extent of sulphide deformation in the mid thickness region of continuous cast slabs will be dependent on the relative properties of the sulphide and the steel matrix and to some extent the rolling conditions. There is evidence that the properties of the sulphide inclusions can be influenced by alloying elements such as Ti, Nb and Cr, which compete with Mn and so modify the sulphide properties [9,10].

This paper details some findings of an ongoing investigation into the influence of Mn, Ti, Nb, Cr and S content on the formation of sulphide inclusions through the thickness of continuously cast steel slab and the subsequent influence of reheating and hot rolling on the composition and morphology of the sulphide in the final rolled steel product.

**EXPERIMENTAL**

The chemical composition of steels evaluated is presented in Table 1. All steels were aluminium deoxidized and continuously cast as 230mm thick slab. Full width slab samples were obtained from each heat of steel and full thickness samples extracted from the quarter width position of each slab by mechanical saw cutting. Selected samples were obtained following hot rolling to a range of thicknesses. The influence of slab reheating was assessed by use of laboratory heat treatment on selected slab samples, to a peak temperature of 1250°C with a hold time of 1 hour.

Metallographic specimens were obtained from both the surface and the mid thickness region of each slab and also from the quarter width position of hot rolled plate and strip. Sample preparation involved standard metallographic techniques and care was employed to avoid removal of the fine sulphide inclusions in the final stages of polishing, particularly in the presence of large non-metallic inclusions and also porosity. The metallographic samples were sectioned parallel to the plate rolling direction (i.e. longitudinal section) to enable characterization of sulphide inclusions through the thickness of the final hot rolled steel.

<table>
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<tr>
<th>Steel code</th>
<th>C</th>
<th>P</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>Al</th>
<th>Nb</th>
<th>Ti</th>
<th>V</th>
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The chemical composition of the sulphide inclusions was evaluated using energy dispersive X-ray analysis on a transmission electron microscope (TEM) and scanning electron microscope (SEM). More detailed analyses were carried out using wavelength dispersive techniques on a Cameca SX50 electron probe microanalyzer (EPMA). Large area elemental maps revealed the presence of different elements within the sulphide inclusions and the surrounding steel matrix.

RESULTS

Low Mn Steels (Steel S1 – S3)

The subsurface region of the as-cast slab contained a uniform dispersion of light grey coloured spherical particles typically less than 0.25μm in size, which resembled MnS, Fig. 1. Also present were very fine linear particles, Fig. 2, which were identical in colour to the spherical particles. In the high S steel (S3), some larger sulphide particles were noted to have formed in a grain boundary network. Microanalysis techniques, which included energy dispersive spectrometry (EDS) in both the scanning and transmission electron microscopes, and wavelength dispersive spectrometry (WDS) in the electron probe, confirmed these particles to be rich in both Mn and S.

Transmission electron microscopy (TEM) using both EDS and selected area electron diffraction, using single stage extraction electron replicas, identified these uniformly dispersed spherical particles to be sulphide particles rich in Mn, Cu and Fe and a size range from approximately 30 – 350nm. Elemental mapping of the sulphide particles further revealed the particles to consist of an MnS core with a coating rich in Cu, Fig. 3. Individual FeS was not observed. The size and spherical nature of
these fine particles strongly suggest an origin via a solid-state precipitation reaction. Also evident in Fig. 3 is a very fine dispersion of precipitates rich in both Cu and S clustered around the Cu coated MnS particle.

The mid thickness region of the as-cast slab contained two distinct populations of inclusions. One was of a spherical morphology with particle sizes ranging from <0.2µm to approximately a few microns. The other population, as featured in Fig. 4, consisted of much coarser, irregular shaped inclusions in the sizes of up to about 30-40µm. These larger sulphide particles were observed on the free-surfaces of porosity features following what appeared to be grain boundaries or interdendritic regions emanating from the porosity. TEM investigation, using single stage extraction replicas, revealed the composition of the finer inclusions to be identical to the MnS/CuS precipitates observed in the subsurface region of the slab. The coarser, non-uniform particles were identified as a mixed sulphide containing both Mn and Cu but without evidence of CuS coatings.
Through Thickness Tensile Tests on Low Mn (Steels S1 – S3)

Through thickness tensile tests were utilized to assess the dispersion of sulphide in the mid thickness region of the as-cast slab. Fracture invariably occurred along the segregated centerline to reveal a brittle fracture with the original dendritic structure associated with pockets of porosity. Significant partitioning of S into these porosity free-surface regions had occurred during solidification with numerous sulphide particles in the valleys between the dendrite arms, which in many cases were up to many tens of microns in size Fig. 5a. In some instances the sulphide particles tended to be blocky or angular but this did not appear to be related to any particular S level or variation in other elements. The blocky morphology was only observed on the fracture faces and not in any of the metallographic sections examined. In the immediate vicinity of the porosity, in the high S steel (S3), the brittle cleavage facets contained isolated pockets of microvoid coalescence originating from a fine dispersion of spherical sulphide inclusions, Fig. 5b. The inclusions resembled that of a Type II MnS eutectic dispersion [4] and would probably correspond to the grain boundary array of MnS observed in the metallographic sections, Fig. 4.

Effect of Increasing Sulphur content (Steels S1 – S3)

Increasing S level resulted in an apparent increase in the individual size of sulphide inclusions particularly in the mid thickness region of the slab. EDS of the large inclusions in the mid thickness region of the higher S bearing steels, S2 and S3, revealed the presence of a duplex FeS / MnS. The duplex nature of the inclusions is shown in Fig. 6.

Effect of Slab Reheating (Steels S1 – S3)

The influence of a simulated slab heat treatment was the change in composition of the large sulphide particles in the mid thickness region of the two higher S steels (S2 and S3). The sulphide particles were clearly a single
The FeS phase observed in the as-cast condition had been converted to MnS by the heat treatment process. Also apparent in the slab mid thickness region was a zone around the larger sulphide inclusions devoid of small MnS particles, Fig. 7a. These zones were associated with a Mn depleted region on what appeared to be prior austenite grain boundaries, as shown by large area elemental mapping, Fig. 7b.

**Effect of Hot Rolling (Steels S1 – S3)**

Fig. 8 shows an SEM image of a typical dispersion of the two different size sulphide particles present in the plain carbon 0.2wt% Mn steels hot rolled to a thickness of 6mm. EDS identified both sulphide particles as MnS however clearly evident was the effect of hot rolling deformation on the different size sulphide particles. The fine spherical sulphide particles, <0.25μm were relatively unchanged however the large sulphide particles in the mid-thickness region of the strip were elongated, some greater than 200μm in length.

**High Mn Steel (Steel M1)**

In contrast to the low Mn steels, the slab subsurface region of the high Mn (1.13%) steel, M1, contained a random distribution of spherical Mn sulphide particles in the size range of 0.5 – 1.0μm, (Fig. 9a). Also present in this steel were networks of sulphide particles, presumably on prior dendritic grain boundary networks. The slab mid thickness region contained extensive grain boundary networks of what appeared to be Type II dispersions of sulphide particles. These networks were most prominent around regions of porosity, (Fig. 9b), and contained only one phase, identified using EDS as MnS.
Microalloyed Low Mn Steel (Steel TN1)

In the Ti, Nb microalloyed steel (TN1 in Table 1), the predominant second phase particles observed on the free-surfaces of the as-cast dendritic porosity were Mn and Fe rich and in the size range 10–20μm. Isolated particles containing both Mn, Ti, Nb and S were also observed. The MnS particles predominantly existed along dendritic valleys, however, angular particles were also dispersed over the dendrite surface, Fig. 10a. Following a simulated slab heat treatment, two distinct sulphide inclusion populations existed viz, large MnS particles 10–20μm in size in the dendrite valleys and a fine dispersion of Ti, Nb and S rich particles (<1μm) on the dendrite surfaces, Fig. 10b. Hot rolling of this steel produced large MnS stringer inclusions in the mid thickness region of rolled strip which was revealed by metallographic examination of longitudinal sections, Fig. 11. Also evident in Fig. 11 were clouds of smaller particles around the large sulphide stringers. TEM examination in the mid thickness region of the rolled strip revealed MnS particles with spherical and rod shape morphologies and two different finer precipitate species rich in both Ti and Nb.

Fig. 9 MnS particles observed in the high Mn steel, M1, a) subsurface region and b) mid thickness region of the as-cast slab.

Fig. 10 SEM micrographs showing the dispersion of S rich inclusions in a) as-cast condition, MnS highlighted yellow and Ti, Nb and S rich particles highlighted red, and b) after simulated heat treatment. Note grain boundary structure on dendrite surface along with the formation of fine Ti,Nb and S rich precipitates (highlighted red).
One species of precipitates was identified by selected area electron diffraction and EDS to be (Ti,Nb)CN which ranged in size from 20 – 80nm. The other precipitate species was shown by EDS, using Al replica techniques, to contain Ti, Nb, C and S and with a (Ti + Nb)/ S ratio of approximately 2, Fig. 12. Convergent beam electron diffraction determined the crystal structure of these carbosulphide precipitates to be hexagonal with a lattice parameter a=0.326 nm and c=1.123 nm.

These measured lattice parameters are between that of Ti₂CS (a= 0.321 nm c=1.12 nm [11]) and Nb₂C₁₋ₓS (a=0.328 nm c=1.15 nm [12]) are therefore assumed to be (TiNb)₂CS. Recent research has confirmed that (Mn, Fe)S co-exist with (Fe,Ti)S in the macro-segregated regions at the centerline of 0.3wt%Mn slab cast steel microalloyed with Ti [13,14,15]. Heat treatment transforms the (Fe,Mn)S to MnS while the (Fe, Ti)S transforms to a finely dispersed complex carbosulphide.

**Chromium Bearing Low Mn Steels (Steels C1 - 3)**

Examination of the low Mn, Cr bearing steels (C1, C2) revealed a large number of fine spherical particles in the sub surface region of the plate. The particles were similar to those observed in the low Mn plain carbon steels (S1 – S3) and were again identified by TEM as MnS, some revealing a shell rich in Cu, presumably CuS. In the mid thickness region of the hot rolled plate, elongated sulphide stringers were observed. These inclusions varied in length with Cr, Mn and S content and also hot rolled plate thickness. The influence of hot rolling on the morphology of the sulphide inclusions in these Cr bearing steels was evaluated in plate ranging in thickness from 40 to 8mm by quantitative metallographic assessment of the length of sulphide inclusions at both the quarter and...
mid thickness position of the rolled plate. As numerous sulphide inclusions were in close proximity to each other, an interacting length of in-line clustered inclusions was also determined. Individual inclusions were assumed to be interacting if the separation distance was less than half the length of the longest inclusion. As mechanical properties, and in particular toughness, is influenced by the total length of stringer inclusions \[16\] the average of the 20 longest inclusions was also determined.

In both the 8 and 20mm thick low S steel, C1, the majority of inclusions were spherical inclusions less than 15μm in diameter, typical of calcium aluminate multiphase particles. Isolated stringer sulphide inclusions were observed in the 20mm thick low S C1 plate but the number of particles was very low. The absence of any observable elongated sulphide inclusions in the 8mm thick C1 sample may be related to the very low number present and the distance between such particles after the additional rolling reduction. The presence of spherical multiphase particles was also a characteristic feature of the conventional high Mn steel, C3, however, in that case, isolated elongated sulphide inclusions were also observed.

In the high S steel, C2, numerous elongated stringer inclusions were observed in all 3 plate thicknesses. As shown in Fig. 13, the average length of interacting sulphide inclusions increased with reduction in thickness. Large area elemental mapping carried out on selected elongated sulphide particles in the 20mm thick high S plate revealed the particles to be rich in Mn. On the surface of the sulphide stringers were precipitates rich in Ti, V and N, which are assumed to be either carbonitride and/or mixed carbosulphides produced as a solid-state precipitation reaction on cooling following hot rolling similar to that observed in the low Mn microalloyed steel TN1. The role of alloying elements on the composition of sulphide inclusions in these high Cr steels was further evaluated using EPMA by wavelength dispersive microanalysis. The compositional mapping involved analysis of inclusions and the surrounding matrix in the mid thickness region of a high Cr steel in the as-cast condition. Although segregation of alloying elements is known to occur in this region of the steel, microanalysis conditions were selected to optimize compositional resolution along with quantitative ZAF correction factors to ensure accurate inclusion analyses \[17\].

The analysis revealed that the maximum Cr content detected in the MnS inclusions was less than 5wt%, although close microscopic examination suggests that separate sulphide phases could be present, Fig. 14. This is in agreement with other published data \[9\], which suggests that a significant level of Cr in the steel is required to increase the Cr/Mn ratio in the sulphide. At a Cr level of 0.21wt%, steel C3 did not reveal any evidence of Cr partitioning to the MnS inclusions.

**DISCUSSION**

The results of this investigation have provided information on the role of Mn Ti, Nb and Cr in the formation of sulphide inclusions in steels containing a range of S contents. In the solidification of conventional high Mn steels, the segregation of S and Mn along with the high driving force for MnS formation results in significant partitioning of these elements ahead of the solid/liquid interface. MnS inclusions progressively form from the liquid throughout the slab thickness with the largest occurring in the mid thickness region of the cast slab. The presence of a finer dispersion of 0.5-
1.0µm MnS particles in these steels (Fig. 9a) suggests the possibility of being precipitated from the solid at high temperature.

In 0.2wt% Mn steels, the driving force for MnS formation from the liquid is much lower than for high Mn steels because of the increased solubility of S as demonstrated by solubility product data for both austenite [18] and delta ferrite [19]. The presence of a relatively uniform distribution of fine spherical MnS particles, generally less than 0.5µm and typically around 0.25µm, dispersed throughout the low Mn as-cast slab suggests that the reduction in Mn has delayed precipitation of these sulphide particles to lower temperatures most likely in the solid state. This conclusion is supported by the observation of the fine linear particles of MnS, observed in steels S1 to S3, and also the very fine CuS precipitates and the coatings of CuS on spherical MnS particles observed by TEM in the subsurface regions of the as-cast slab. The activity of S in the solid state appears to have been significantly increased by the reduction in Mn so as to enhance the formation of an alternative dispersion and species of fine sulphide precipitates. The effect of an increased S solubility in both delta ferrite and austenite would be to reduce the amount of S partitioning ahead of the advancing solid/liquid interface during solidification and thus minimize the deleterious effects of S segregation in the final stages of solidification in the mid thickness region of the slab.

The formation of large interdendritic sulphide inclusions in the mid thickness region of as-cast low Mn slabs, Steels S1-S3, was evident for all S levels (0.008-0.017wt%S). However, after hot rolling it was apparent that the resultant stringer inclusions progressively reduced in size (and length) with reducing S levels. The very low level of stringer inclusions observed in steel C1 containing only 0.002wt%S points to the value of both low Mn and low S levels on inclusion size in the mid thickness region of slabs. A schematic model summarizing the above observations regarding the dispersion of sulphide particles and inclusions formed through the thickness of a cast slab as a function of Mn and S content is presented in Fig. 15.

The present work has shown that, in low Mn Steels S2 and S3, (i.e. containing ≥ 0.011wt%S), only MnS inclusions were produced in the subsurface regions of the as-cast slab but in the mid thickness region, both MnS and FeS were formed. It thus appears that in 0.2wt% Mn steels and at these higher S levels, local equilibrium conditions were not achieved in the final stages of solidification leading to the formation of FeS in preference to MnS [20]. A slab reheat treatment at 1250°C resulted in the conversion of this FeS back to the stable MnS phase. Despite the change in sulphide composition, the heat treatment process did not significantly change the overall size distribution of the sulphide particles in both the subsurface and mid thickness regions of the slab. The slab mid thickness region, however, showed evidence of a sulphide denuded zone around the large MnS particles. It is estimated that sulphide particles not much greater than a micron would have been dissolved and re-precipitated on the more stable larger particles, consistent with an Oswald ripening process. The maximum distance over which the denuded zone was observed around “larger” sulphide inclusions was less than 10µm in size. The change in composition of the FeS and the associated Mn depletion along grain boundaries, as reported by Salmon-Cox and Charles [21], demonstrates the activity of Mn and the high driving force for MnS formation.
Hot rolling clearly deformed the large sulphide particles formed in the mid thickness region of the slab leading to elongated MnS stringer inclusions. However, the fine spherical particles in the subsurface regions of the as-cast steel were relatively unaffected by hot rolling. Although the low S steels (C1 and C3) contained sulphide inclusions in the mid thickness region of hot rolled plate, the number and total length were much reduced compared to that of the high S steel. It is known that in high Mn steels (without Ca sulphide shape control), long stringer sulphides are still evident in the centreline region of steels at levels of 0.002%S. The absence of such stringers in Steel C1 at this S level suggests that further modification of remaining sulphide inclusions (e.g. via Ca treatment) may eventually be unnecessary for low Mn steels when S levels are sufficiently low. This would be of advantage in instances where complete sulphide shape control is being sought such as for high toughness levels or HIC resistance in pipeline steels [7].

Microalloying additions of Ti and Nb, in the levels investigated, resulted in the generation of complex alloy carbosulphides, (TiNb)₂CS, which were formed by a solid-state precipitation reaction generally on the surface of larger more stable MnS particles on cooling from hot rolling. These carbosulphide particles are in addition to the (Ti,Nb)CN particles traditionally employed for grain refinement and precipitation strengthening of thermomechanically processed steels.

The low S, Cr bearing steels, C1 and C3 primarily contained a fine dispersion of spherical multiphase calcium aluminate particles produced by the CaSi injection process during steelmaking. In the high S steel, C2, the average interacting sulphide length ranged from 43μm in the 40mm plate up to 96μm in the 8mm thick plate. The low S steel, C1, did not contain a statistically significant number of stringer inclusions to permit a valid estimation of inclusion length. This further suggests that in low Mn steels a lower S level (perhaps below about 0.004-0.005%S) will eventually be reached where the sulphide size and shape can be effectively controlled and resist deformation during rolling without the need for Ca modification.
The properties of MnS are believed to be influenced by the presence of alloying elements in solid solution [9]. The present investigation has demonstrated that in a 0.81wt% Cr steel with high S (0.008wt%), the maximum solubility of Cr in the sulphide phase, after conventional steel processing, was determined to be less than 5wt% Cr. According to Kiessling and Lange [9], this would relate to a significant increase in hardness of the MnS inclusion. The observed presence of elongated sulphide inclusions in steel C2, which increased in length with rolling reduction (particularly below 20mm plate thickness) suggests that the influence of 5wt%Cr in MnS was insufficient to reduce the sulphide plasticity during hot rolling at that high level of S content. The current results tend to support the comments by Portevin and Castro [22] that these levels of Cr in MnS would not significantly change the properties of MnS. The level of Cr required to influence properties of the MnS may need to be significantly higher (or alternately, the S level may need to be lower) in order to induce a beneficial effect on sulphide morphology. Clearly in steels with relatively high S levels and a Cr content <0.81wt%, MnS remains the dominant sulphide species. Further work is required to understand whether higher levels of Cr substitution may occur in MnS of low Mn steels when S levels are below about 0.005%S. Similar research is needed to clarify the potential for Ti and Nb to also beneficially assist in forming less plastic sulphide inclusions at hot rolling temperatures in low Mn steels at these reduced S levels. The resistance to deformation of sulphide inclusions in low Mn steels is likely to be controlled by a combination of reduced inclusion size and possible hardening effects conferred through the activation of these other sulphide forming elements. Both of these mechanisms would ultimately derive from the inherently reduced activity of Mn for sulphide formation in low Mn steels.

CONCLUSIONS

The influence of Mn, Cr and S contents on the formation and deformation of sulphide inclusions has been investigated and the following conclusions may be drawn.

1. A reduction in Mn level to about 0.3wt% results in the formation of a uniform dispersion of fine MnS inclusions, less than 0.5μm in size, throughout the thickness of the product. These inclusions are thought to form in the solid state as a result of increased solubility of S in both delta ferrite and austenite.

2. The mid thickness region of 230mm thick cast slab, contains an additional non-uniform dispersion of larger MnS particles as a result of the strong segregation of S during solidification. The size and number of MnS increase with Mn and S content.

3. The composition of the sulphide particles in the mid thickness region of low Mn, high S cast slabs were duplex in nature consisting of both MnS and FeS.

4. Slab reheating had no significant influence on the size distribution of the as-cast sulphide particles. In terms of sulphide composition, the FeS present in the cast slab was converted to MnS and produced both a sulphide denuded zone <10μm around the large sulphide inclusions and Mn depletion along prior austenite grain boundaries.

5. Hot rolling had minimal effect on the morphology of the fine spherical MnS inclusions, however the larger MnS in the slab mid thickness region was elongated into stringer inclusions.

6. Microalloy additions of Ti and Nb resulted in the formation of complex alloy carbosulphide precipitates associated with the dispersion of MnS inclusions.

7. A maximum of 5wt%Cr in MnS was recorded in 0.3wt% Mn steel containing 0.81wt% Cr which at least in the case of higher S levels appears to have minimal effect on the plasticity of the sulphide during conventional hot rolling processes.

8. The investigation has pointed to the potential for achieving control of sulphide size in low Mn steels at less restrictive S contents that would apply for high Mn steels. More work is required to better understand the ability of other sulphide formers such as Ti, Cr and Nb to harden sulphide inclusions in low Mn steels at S levels below about 0.005wt%.
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