Steel cleanness requirements for X65 to X80 electric resistance welded linepipe steels

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In Australia, a large proportion of the gas pipelines traverse rural areas of low population density with considerable distances between population centres. As these pipelines transport non-sour gas, there have been considerable economic advantages to be gained from the use of thin walled, small diameter, high strength linepipe grades. The successful development of these X65 to X80 grades has required a balance to be constantly maintained between process parameters, alloy design constraints and quality control measures. This paper considers this mixture of metallurgical and processing challenges in the context of steel cleanness. The steelmaking and casting processes are required to not only produce a low volume fraction of suitably morphology modified inclusions, but also to ensure their dispersion in cast and hot rolled structures. Critical in the achievement of these aims was found to be the order in which calcium treatment and vacuum processing of the liquid steel are carried out. As these steels are complex microalloyed grades, the clean steel concept was extended to include the composition and precipitation of the carbide and nitride species. This broad approach to steel cleanness was achieved while also maintaining a narrow range of casting temperature and chemical composition. I&S/1783

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INTRODUCTION

In Australia, a unique set of conditions have favoured the development and use of high strength, electric resistance welded (ERW) linepipe grades: X65 to X80. A large proportion of the pipelines run through low population density, rural areas with considerable distances between population centres. Also, these pipelines are for the transport of sweet or rich gas. Under these conditions, there is an economic advantage to be gained from the use of high strength, thinner wall thickness and smaller diameter pipe. As a consequence, since 1993 there has been a rapid growth in Australia in the use of X65 to X80 linepipe steels. These grades are required to have three key characteristics,[1] these are:

1. They must be weldable with cellulosic electrodes without the need for preheating.
2. They must contain a high steel cleanness for both longitudinal weld integrity and resistance to ductile fracture propagation.
3. They must contain a reduced central segregation especially for weld integrity in small diameter pipe produced from centre slit hot rolled coil.

To consistently achieve these characteristics in a tonnage-produced grade requires a balance to be constantly maintained between process parameters, alloy design constraints, and quality control measures. This paper will discuss these interactions from a steel cleanness perspective. In this context, steel cleanness will be considered to be the control of the amount, size, morphology and dispersion of oxide, sulphide, nitride and carbide particles such that performance requirements of the final pipe are met.

MANUFACTURING PROCESS

The X65 to X80 linepipe steel grades are produced at the BHP Steel Ltd, Port Kembla Plant by the process route shown in Fig. 1. The heat lot size is 270 t and cast sequences are typically three heat lots. After hot metal desulphurising in the torpedo ladle with a lime–aluminium mix to a sulphur content of less than 0·005%, the liquid iron in the transfer ladle is slag raked prior to charging into the BOS vessel. The hot metal ratio is increased and only low sulphur scrap is used. A special blowing practice and flux additions are made to the BOS vessel with inert gas bottom bubbling facilities. A slag dart is used at tap to minimise carryover furnace slag into the ladle.

The ladles are alumina lined with bottom bubbling through a porous plug. Approximately 0·22 kg/t of calcium is introduced as powdered CaSi with argon as the carrier gas through a lance into the steel in the ladle. The vacuum degassing (VDG) treatment for the fine tuning of composition and temperature is of about 18 min duration.

The casting occurs with fully protected streams: a ceramic shroud between ladle and tundish and ceramic submerged entry nozzle between tundish and mould. Flow control into the mould is by a three plate slide gate system. There is extensive use of argon shrouding at all the refractory joints. The tundish is lined with MgO and is prepared by slurry gunning. Two in-roll electromagnetic stirrers are used to control central segregation. A BHP Steel designed vibration system operating off the shroud arm is used to automatically shut the ladle slide gate when slag is detected.

A suite of computer support systems is employed including a temperature model used to achieve the target tundish temperature by specifying temperatures at each intermediate step of the steelmaking process. Other systems record casting events, the assignment of the event to affected portion of the skelp and the monitoring of key process and equipment parameters.

To augment the flowchart presentation of the process route in Fig. 1, key plant details are given in Table 1.

Typical chemical compositions of X65 to X80 linepipe grades are given in Table 2. In recent years, the trend has been to a tighter range of mechanical properties in the pipe and as a consequence tighter controls are needed on the chemical composition of the steel. Maximum sulphur specifications are now typically 0·005% with some projects involving 'rich' gas requiring a 0·003% maximum specification. These specifications are readily met by the combination of hot metal desulphurisation with lime–aluminium and by powdered CaSi injection in the steel ladle. As shown in Table 2, the pipe grade alloy design has evolved from the traditional microalloyed, Nb–V steels to the lower carbon

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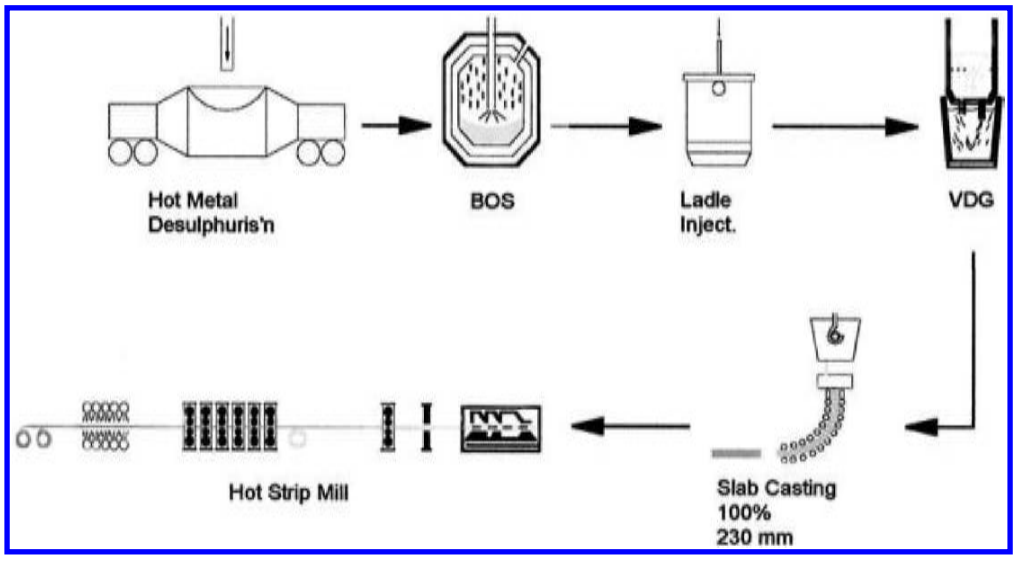


1 Process route for X65 to X80 linepipe steels

equivalent Mn–Mo–Nb–Ti steel compositions. As this chemistry requires the simultaneous tight control of a number of elements, vacuum degassing of the heat was performed after the injection step. The positioning of the vacuum degas step just prior to casting may at first seem counter intuitive to the requirement for a high level of steel cleanness, but, as will be presented in this paper, it is this very need to balance often conflicting requirements that has defined the process route in Fig. 1.

CONTROL OF OXIDES AND SULPHIDES

Clean steel practices at the BHP Steel Ltd, Flat Products plant have always been related to customers' requirements and expectations. Monitors were developed for critical cleanness grades from either in-house tests or from customer supplied data. Some of these monitors have been in existence for nearly 20 years and have successfully guided process improvements both in steelmaking and in continuous slab casting, such as ladle opening with submerged shroud, vibration ladle slag detection, argon shielding of delivery systems, weir wall design, and quick melting flux addition to the tundish on start up.

In the case of high strength ERW pipe production, there have been two key monitors from customer supplied data:

- the percentage of pipes with surface slivers
- the percentage of pipes detected with non-metallic inclusions near the weld.

The detection method used in the latter is ultrasonic inspection of the weld and surrounding area. Non-metallic inclusions near the weld typically follow the flow pattern adjacent to the weld and, depending on their position relative to the pipe surface, may cause the formation of a crack (hook crack), as shown in Fig. 2. In the case of pipe produced from

Table 1 Plant details

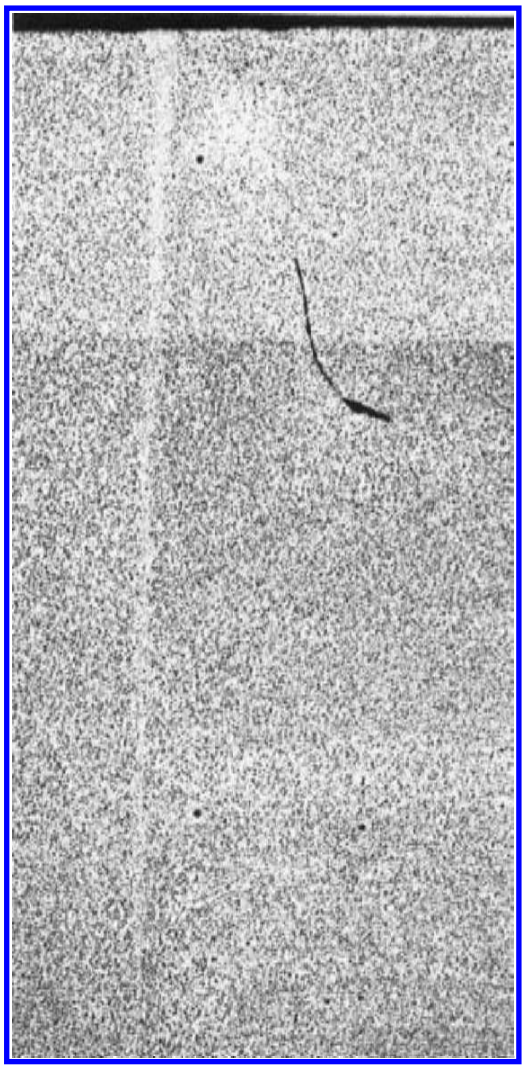
Unit (Builder)	Year*	No.	Features
BOS (NSC)	1972/1983	3	Sublance; simultaneous blowing; bottom stir (Kobe LD–OTB)
Powder injection station (Scandinavian Lancers/BHP)	1981	1	CaSi powder
RH vacuum degasser	1979	1	1996: upgrade and installation of Kawasaki KTB lance
Casters: no. 1 (Mannesmann–Demag)	1978	1, twin strand	Strands: (850–1600) × 230 mm; revamp 1999; through rollers/hydraulic nozzles; two in-roll electromagnetic stirrers; single coil eddy current auto mould level control; vibration slag detection; 45 t tundish
Casters: no. 2/3 (Schloemann Siemag)	1986	2	Twins: (850–1250) × 230 mm; single: (1400–2000) × 230/300 mm; hydraulic/air mist nozzles; revamp 1989; vibration slag detection; single coil eddy current auto mould level control; 48 t tundish
Hot strip mill	1955	1	Upgrades 1972, 1985, 1998 and 2001; walking beam furnace; reversing roughing mill with attached ingoing edger; coilbox; 6 strand finishing mill

*Year commissioned.

Table 2 Typical compositions of X65 to X80 linepipe grades

API grade	Chemical composition, wt-% C	P	Mn	Si	S	Al	Nb	V	Mo	Ti	N*	Ca*	C_{eq}†, %
ERW pipe from full width hot rolled coil													
X65	0·08	0·014	1·45	0·12	0·003	0·025	0·038	0·042	...	0·012	50	8	0·29
X70	0·069	0·013	1·47	0·23	0·003	0·029	0·059	...	0·12	0·015	53	8	0·34
X70	0·063	0·012	1·25	0·33	0·003	0·03	0·059	...	0·1	0·014	54	8	0·29
X80	0·075	0·015	1·59	0·31	0·002	0·026	0·057	...	0·22	0·013	55	11	0·38
ERW pipe from centre slit hot rolled coil													
X65	0·065	0·014	1·10	0·32	0·003	0·032	0·049	0·06	...	0·014	48	8	0·27
X70	0·06	0·011	1·22	0·34	0·002	0·035	0·065	...	0·23	0·017	50	8	0·32

*ppm.
†Carbon equivalent (IIW).

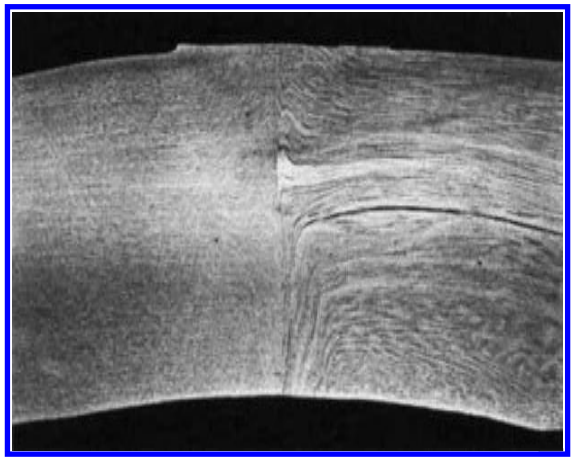


2 Example of hook crack: transverse section through pipe thickness

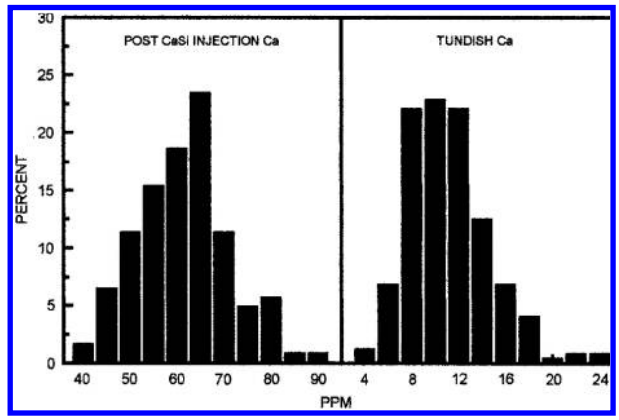
centre slit coil, (Fig. 3), if the central segregation is diverted to the pipe surface, then a crack can also occur along this segregation band or bands. These defects are also included with the hook cracks in the crack monitor.

Powder CaSi injection

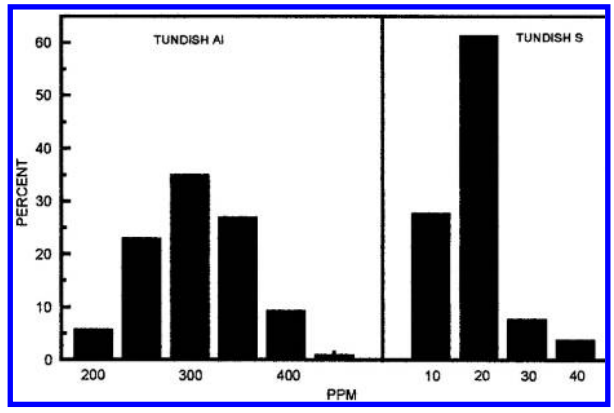
Essential to the achievement of the required oxide and sulphide species in the liquid steel is the process step of the injection of powdered CaSi. This step has two aims:



3 Weld profile in pipe formed from centre slit coil



4 Ca content of X70 grade steel after CaSi injection and in tundish

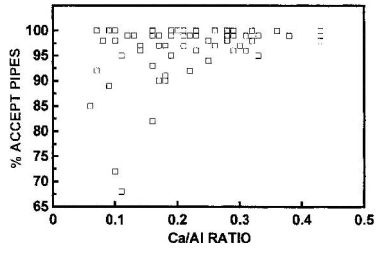


5 Al and S contents sampled in tundish

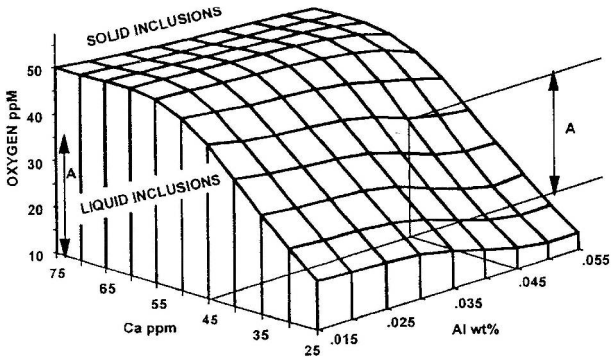
(i) to achieve the required sulphur specification
(ii) to convert the existing clusters of alumina to liquid calcium aluminates.

Crucial to achievement of these aims are the total oxygen (O_{total}), calcium and aluminium contents of the steel during the injection step. Figure 4 shows the calcium distribution at two stages of the process, after calcium silicide injection and in the tundish, for the production of approximately 30 kt of X70 steel. The post-injection distribution of calcium has a mean of 62 ppm, with a standard deviation of 10 ppm; while the tundish distribution has a mean of 11 ppm with a standard deviation of 3·5 ppm. This decrease, in the main, occurs during vacuum treatment. The distributions of aluminium and sulphur compositions in the tundish are given in Fig. 5.

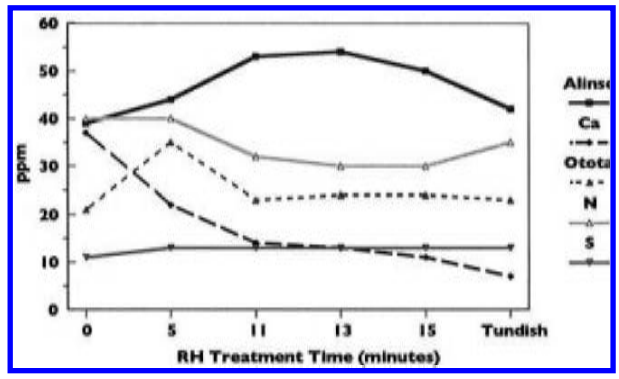
The importance of controlling the aluminium content during the injection process has been discussed previously[2,3] with respect to the formation of liquid inclusions. Early empirical studies[2] indicated low levels of hook cracks could only be achieved if the Ca/Al ratio was approximately 0·2 or greater (*see* Fig. 6). A Ca/Al ratio of 0·2 would achieve



6 Percentage accept pipes as function of ratio of post-injection Ca and Al contents for X42 (C–Mn steel) to X56 (C–Mn–Nb steel)



7 Liquid Ca aluminate formation as function of Al, O and Ca contents



8 Changes in elemental compositions during RH vacuum treatment

liquid calcium aluminates under the conditions of 50 ppm Ca, 50 ppm O_{total} and 250 ppm Al. Improvements since 1983 in ladle linings (zircon–pyrophyllite to alumina) and slag practices (such as slag dart control of furnace carryover slag) have resulted in lower O_{total} levels in the steel. Typically, total oxygen contents are now 30–40 ppm prior to the powder injection step. At these levels of O_{total}, the CSIRO multiphase equilibrium model[3] indicated that liquid calcium aluminate inclusions can be achieved with Ca/Al ratio as low as 0·11. Also, as shown in Fig. 7, liquid inclusions (A) can be achieved with aluminium contents of 0·045%, O_{total} less than 35 ppm and calcium contents of 45 ppm or greater. Above the surface, solid inclusions begin to form, such as $CaO.2(Al_2O_3)$.

Another consequence of the lower 'oxygen load' in both the liquid steel and the ladle slag is the increasing volume fraction of CaS particles in the steel. The CaS phase will be present both in solution in the liquid calcium aluminates and as separate particles. In a 0·003%S steel, up to 35 ppm of the 55 ppm total calcium content of the liquid steel after powdered CaSi injection can be present as the sulphide. Examples of the proportion of the different inclusion species after powder injection are given in Table 3.

RH vacuum treatment

The RH vacuum degassing step is crucial to the achievement of a number of aims:

(i) the required oxide and sulphide steel cleanness
(ii) the required chemical composition within a narrow carbon equivalent range
(iii) the required temperature to ensure the specified superheat target is achieved in the tundish.

The application of an RH degassing treatment to an inclusion population of mixed phases, as given in Table 3, results in a re-ordering of the inclusion phases present. There is a trend to a lower Ca/Al ratio in the oxides and a lower proportion of CaS. This is the result of two mechanisms. First, there is the continual drive to achieve equilibrium between the ladle slag and steel and also the reduction of any slag glaze build-up, principally on the snorkels of the RH degasser from previous heats. Second, there is the reduction in the soluble Ca during the vacuum degassing treatment. During the RH treatment any dissolved Ca is 'boiled off' and as a consequence there is continual replacement of Ca from the dissolution of the CaS particles. These mechanisms are explained by the following

$$CaS \Leftrightarrow (Ca) + (S)$$

$$(Ca) + (3x + 1)(O) + 2x(Al) \Leftrightarrow CaO.(Al_2O_3)_x$$

$$(Ca) \Leftrightarrow Ca_g$$

$$(Ca) \Leftrightarrow Ca_{Ar}$$

where Ca_{Ar} is calcium gas in the VDG lift gas argon bubble.

A measure of the reactions with slag and ladle and snorkel glaze can be seen in the increase in O_{total} starting at 5 min into the treatment, *see* Fig. 8. The effect of the reactions involving the removal of calcium vapour plus the removal of inclusions to the slag phase can be seen in the progressive decrease in the total calcium contents throughout the RH treatment (Fig. 8). The levels of 'insoluble' aluminium content, determined by peak integration method optical emission spectrometry,[4] show the increasing alumina content of the oxides as well as their removal from the liquid steel. Throughout the RH treatment these two mechanisms result in the maintenance of liquid calcium aluminates, as shown in Fig. 9.

An example of a heat that contained CaS clusters after CaSi powder injection is shown in Fig. 10. This heat had a low total oxygen content and 0·067%Al prior to calcium treatment. After 10 min vacuum treatment at low pressure, the CaS clusters had been removed (Fig. 11).

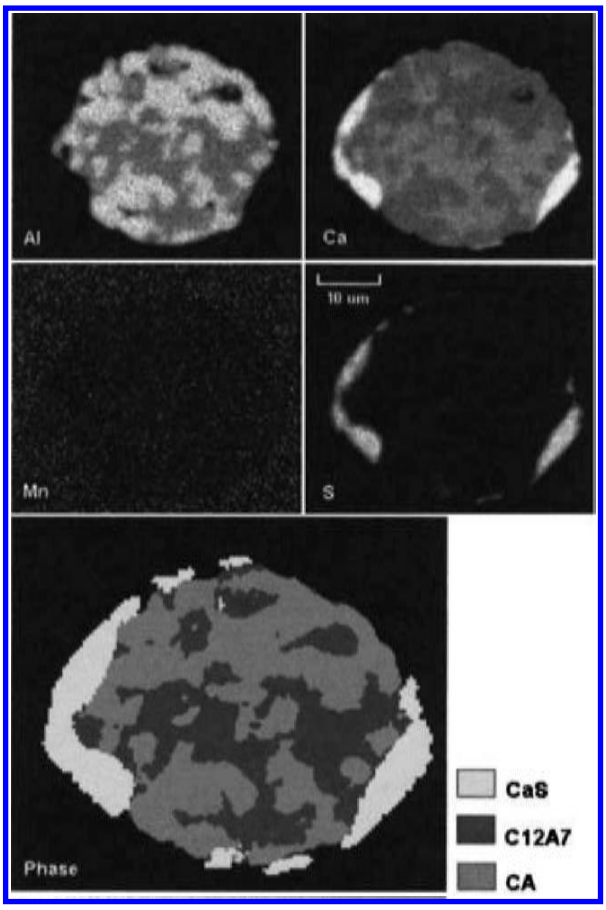
The slag–liquid metal reaction during RH vacuum treatment is also responsible for the achievement of 20–25 ppm O_{total} in the cast steel with 8–10 ppm Ca. This level of cleanness is immediately obvious in metallographic inspection of either cast slab or hot rolled strip.

The morphological consequences of these changes to the oxide and sulphide species when the steel is hot rolled to 4·8–10 mm thick strip are shown diagrammatically in Fig. 12. The decrease in the impact toughness indicated in Fig. 12 is a consequence of the formation of (Ca, Mn)S phase which, on hot rolling, will deform and form elongated inclusions. A constraint matrix study of X70 production indicated that there was a 10 to 15 J drop in transverse upper shelf energy for every 10 min of vacuum treatment.

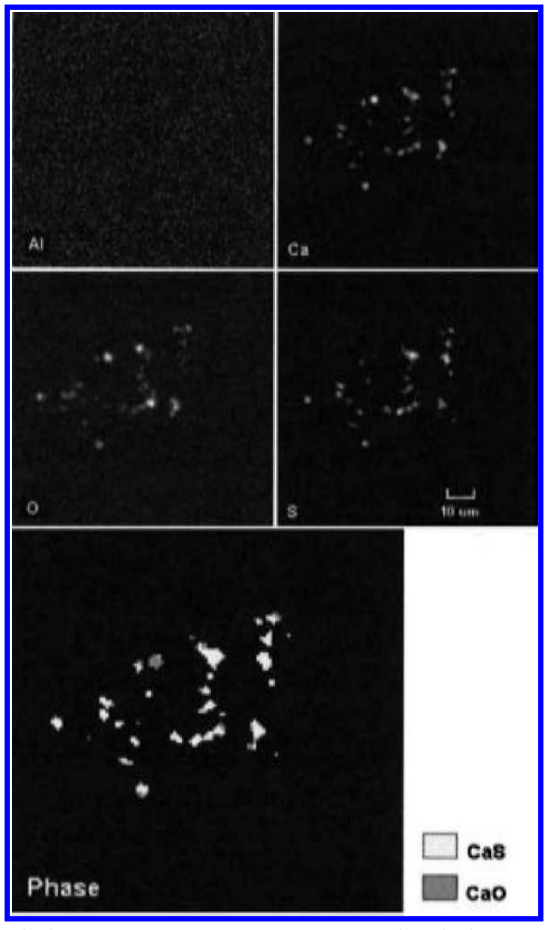
The powerful influence of the larger elongated inclusions on the transverse upper shelf energy in the Charpy impact test is shown in Fig. 13. The parameter P70[5] is the sum of the lengths of all inclusions which individually have lengths equal to or greater than 70 μm. As indicated in this figure,

Table 3 Percentage by number of inclusion species in liquid steel determined by EPMA: after powdered CaSi injection

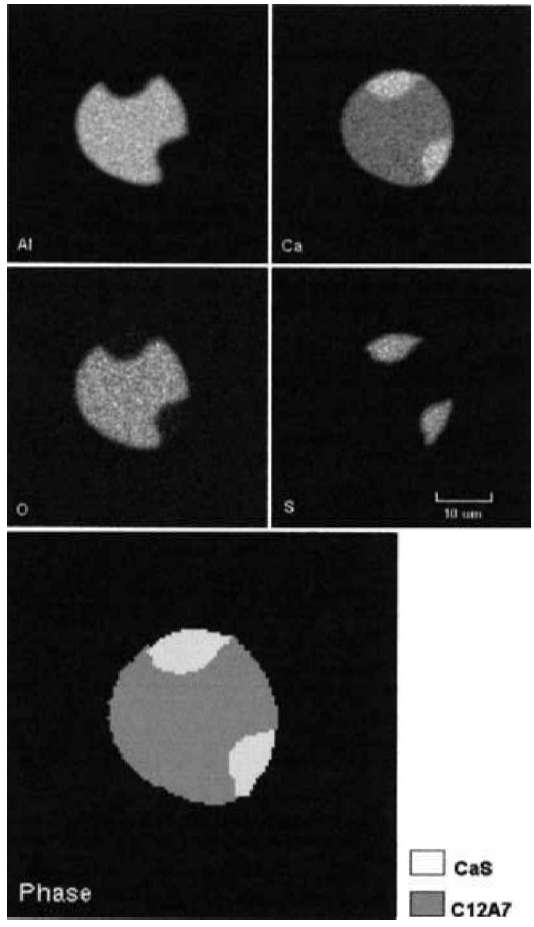
CaS	$3CaO.Al_2O_3$	$CaO_{12}.(Al_2O_3)_7$	$CaO.Al_2O_3$	$CaO.2Al_2O_3$	Elapsed degassing time, min
25–50	18–30	33–50	0–24	0	0
15	0	35	35	15	15
6	0	46–6	37–63	2–19	20–25



9 Complex oxysulphide inclusion after 16 min vacuum treatment



10 CaS cluster in 'bomb' sample taken after CaSi injection



11 Liquid Ca aluminate in 'bomb' sample after 10 min vacuum treatment

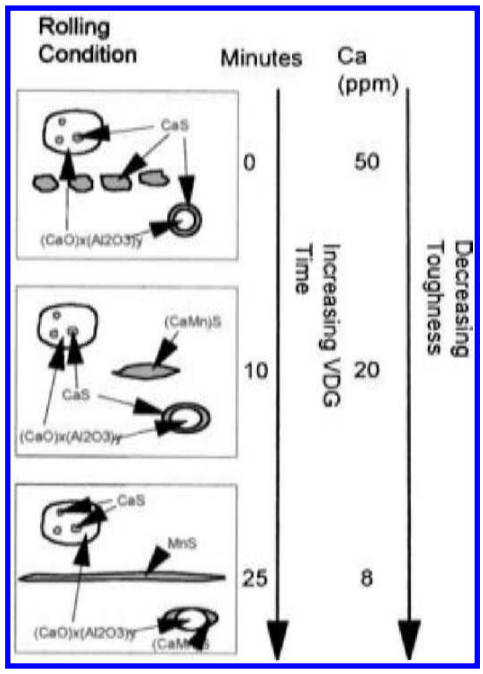
the carbon content of the steel also influences the transverse upper shelf energy. Not shown here, but also of influence, is the grain size in the hot rolled strip. In spite of this drop in ductility, for most projects the fracture toughness requirements can be adequately met in the Mn–Mo–Nb–Ti steels with a 0·005% maximum sulphur specification. The typical range of Charpy impact energies at each sulphur content is shown in Fig. 14.

Nitride and carbide control

The Mn–Mo–Nb–Ti steels achieve their higher strengths at lower carbon equivalents than the traditional micro-alloyed Nb–V steels because of the additional contributions from transformation hardening and enhanced grain refinement. Precipitation hardening is also important in the Mn–Mo–Nb–Ti steels and, in this regard, the use of vacuum degassing as the final ladle treatment step is important in the control of the nitrogen content of the liquid steel. During the powder injection step, the nitrogen content of the liquid steel can increase between 10 and 30 ppm. However, during the degassing step approximately 50% of this nitrogen pick-up will be removed, as shown in Fig. 15.

The ability to remove 50% of the nitrogen picked up during powder injection is a direct consequence of the low sulphur content achieved in the injection process. More nitrogen is removed at the lower sulphur contents because, during powder injection, more nitrogen is picked up at these lower sulphur contents. The approximate 50% removal of nitrogen during degassing thus remains independent of the sulphur content for contents less than 0·005%S.

A consequence of the vacuum degassing step is a predictable nitrogen content, which in turn allows careful control of the composition of the nitrides and carbides that form.



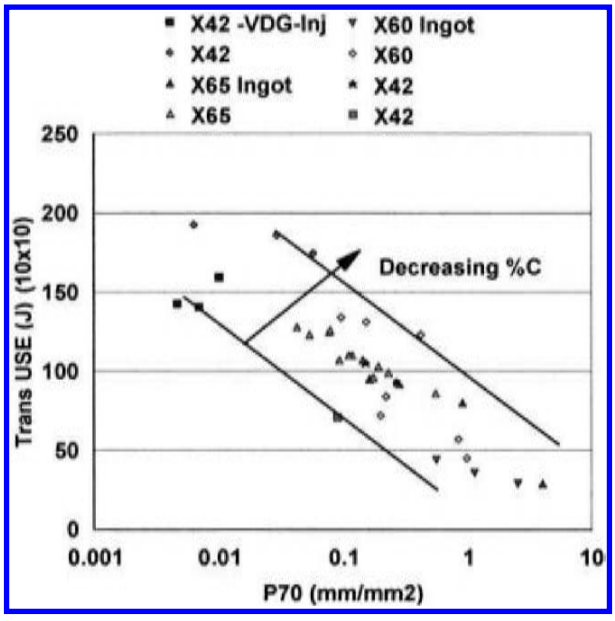
12 Changes in hot rolled morphology of inclusions as consequence of vacuum treatment

During the development of the X70 steels, the titanium content has increased from an aim of 0·015 to 0·020% in order to make use of the controlling influence titanium has on the composition of the niobium precipitates. As shown in Fig. 16, in a steel containing both titanium and niobium, initially titanium will form nitrides, removing nitrogen from solution in the steel. Thus, when niobium carbonitrides form they will be denuded in nitrogen. This denudation will be greater as the variable Ti_{free} approaches a value of zero, that is, stoichiometry between titanium and nitrogen. The variable Ti_{free} is defined as

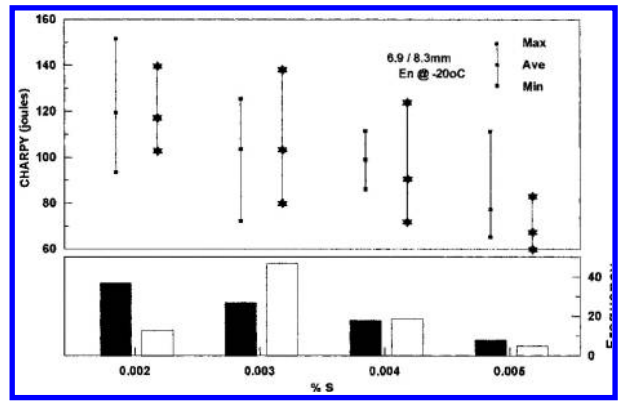
$$Ti_{free} = Ti - 3{\cdot}42(N)$$

where Ti and N are elemental contents in the liquid steel.

A consequence of the reduction of the nitrogen content of the niobium carbonitrides is an increase in the solubility of these nitrogen denuded niobium carbonitrides in austenite at



13 Effect of cumulative lengths of inclusions on transverse upper shelf energy (specimen size 10 × 10 mm)



14 Charpy impact energies as function of sulphur content for two X70 grade products (2/3 size specimens tested at −20°C)

the slab reheat temperature of 1250°C. The Mn–Mo–Nb–Ti steels thus allow the more efficient use of niobium addition, with a higher proportion of fine NbC precipitates forming on hot rolling while the TiN particles restrict grain growth. Positive values of Ti_{free} lead to the formation of a fine precipitate of TiC particles, which further enhances the strength of these steels.

SEGREGATION CONTROL

In a study of pipe produced from centre slit coil of X65 grade, Charpy impact testing was conducted on the segregated side of the ERW line. The results of this testing are presented in Table 4. The significant variables influencing the Charpy energies on the segregated side of the pipe weld (centre strip position) were found to be a mixture of casting and pipe parameters:

(i) superheat
(ii) number of segregation spots greater than 600 μm in diameter (Sum600): this measurement is obtained by mapping for manganese by EPMA of an area ±3 mm from the thickness centreline of the cast slab
(iii) distance of the Charpy notch from the weld fusion line
(iv) the size of the heat affected zone around the weld fusion line.

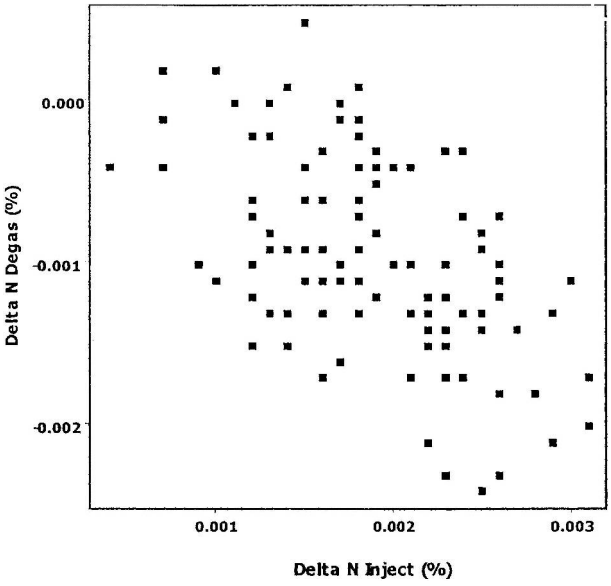
Increases in the first two parameters result in a decrease in the Charpy impact energy while, for the second two, increases in their values would result in an increase in the Charpy impact energy.

The parameter Sum600 is a compound measure of the effects of elongated sulphides and carbonitride clusters and elemental segregation, which can occur together as semi-macrosegregation. The lower carbon and manganese contents of the Mn–Mo–Nb–Ti steels reduce the volume fraction and peak elemental concentrations in the semimacrosegregation spots that form in the central regions of the cast slab. The elemental contribution to Sum600 is presented in Fig. 17. Steels with manganese contents less than 1·4% reduce the chance of forming semimacrosegregation spots with manganese contents greater than or equal to 2%. This level of manganese content was found in previous studies to promote the formation of martensite in these segregation spots.[6]

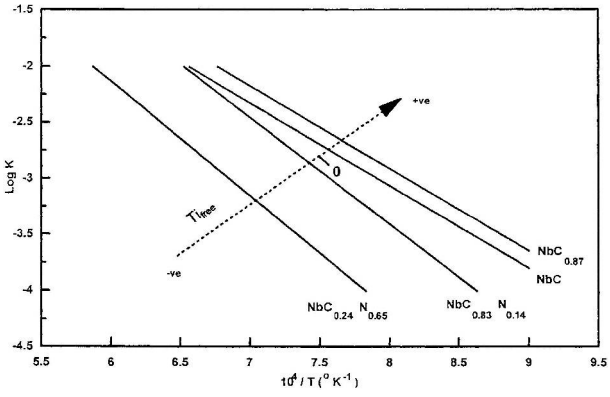
Table 4 Charpy impact testing of pipe from centre slit coil (half size specimens tested at 0°C), J

	Mean	Std	Min.	Max.	n*
Non-segregated side	82	25	23	130	407
Segregated side	56	24	10	120	409

*Number of specimens tested.



15 Change in N content during vacuum treatment as function of N increase during powder injection

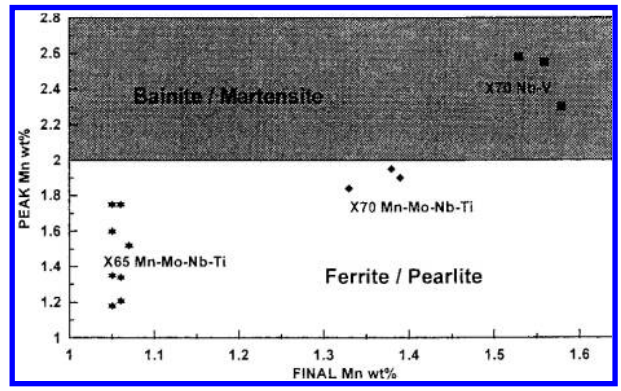


16 Solubility products for Nb carbonitrides

The phosphorus segregation in the semimacrosegregation spots can also contribute to flattened ring test failures, even in X42 grade pipe produced from centre slit coil. These phosphorus rich bands can provide an easy crack path and so contribute to a lowering of ductility. Previous experience with flattened ring tests of ERW pipe was that splitting could occur at peak phosphorus levels of 0·32% and segregation ratios of 15 times. Table 5 lists the results for nine heats of the X65 grade chemistry for centre slit product given in Table 2. These results indicate that if the phosphorus content of the steel is below 0·020%, the segregation levels of phosphorus in the bands are on average well below these values. The upper extremes of the distribution of segregation values may just meet these warning values. The effect of superheat over a 20°C range on phosphorus segregation can also be seen in Table 5.

Table 5 Centre segregation band P segregation values (9 casts)

	Superheat, °C	Mean P, %	Peak P, %	Mean ratio	Peak ratio
Mean	25·5	0·045	0·066	2·86	4·13
Std	7·1	0·019	0·048	1·08	2·62
Min.	14	0·013	0·013	1	1
Max.	34	0·079	0·175	4·67	8·67
No. of slabs	13	12	13	12	13



17 Peak Mn content of semimacrosegregation spots in cast slab as function of Mn content

Overall, the centre segregation of phosphorus in the semimacrosegregation spots can be considered to be very well controlled by the casting process and the maintenance of casting machine alignment.

It is of interest to note that in this study the segregation (weld) upset angle did not significantly influence the Charpy energy values. This study, however, only involved tests 1 mm from the weld. If only results within 0·5 mm from the weld are considered, then a trend existed between Charpy impact energy and the weld upset angle.

CONCLUSIONS

The development and economic production of X65 to X80 ERW linepipe grades for non-sour gas applications has set the steelmaker an interesting mixture of metallurgical and processing challenges. The control of the steel cleanness in these grades extends beyond the modification of clustered alumina inclusions to the more desirable round morphology of the liquid calcium aluminates. It even extends beyond controls on the volume fraction of the oxide and sulphide species and their dispersion and segregation in the cast steel. As presented in this paper, the steelmaking process must satisfy all these needs as well as controlling the composition and precipitation characteristics of the carbide and nitride species. This holistic approach requires the continual attention of the steelmaker to the levels and interactions of the anionic elements, oxygen, sulphur and nitrogen, as well as their reactants, aluminium, calcium, manganese, titanium and niobium. This paper documents how the in-ladle liquid steel processing steps of powdered CaSi injection followed by RH vacuum degassing, when carried out in that order, can readily meet the often conflicting metallurgical requirements of this holistic approach to steel cleanness, while at the same time achieving a narrow range of casting temperature and chemical composition.

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