EMERGING STEEL AND SPECIALTY STEEL GRADES AND PRODUCTION TECHNOLOGIES – IMPACTS ON THE SELECTION AND USE OF FERROALLOYS

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ABSTRACT

The emergence of new steel grades is largely driven by the need to produce high quality steel at a competitive price. The principal aims are to attain ultra-high purity, (especially low interstitial elements) and ultra-cleanliness (by the control of the inclusion content and size). Whereas the steel used to build the Titanic contained 650 ppm sulphur, resulting in MnS stringer-inclusions 25 mm in length, modern quality requirements for arctic pipelines would only allow 10 ppm of sulphur and inclusions in ball-bearing steels must be smaller than 5µm. Most developments are aimed at hot-metal treatment before refining and ladle treatment after decarburisation. Because ferroalloys are added during or after the refining step, it is the secondary (ladle) refining production technologies that are of specific interest to the ferroalloy producer. Through ladle treatment, hydrogen and nitrogen contents are reduced, ultra-low levels of solute impurities are attained and the shapes as well as the composition of inclusions are modified. Steelmakers are concerned about the cost effectiveness of the use of ferroalloys such as consistent product analysis and delivery, improved financing arrangements and technical support. Minimal variation in product sizing is vital because it impacts on handling problems and because particle size determines the rate of particle dissolution. The required ferroalloy product quality depends on the specific use but in general sulphur, phosphorous and nitrogen contents are of concern. Apart from the presence of trace and impurity elements, ferroalloys also contain inclusions. For example, ferromanganese may contain MnO-MnS-SiO_2 inclusions while high-carbon ferro-chrome may contain different kinds of Cr-Mn-spinels. The presence of these impurities and inclusions has a significant impact on steel production techniques and cost and hence, on the selection and use of ferroalloys. The interrelationship between ferroalloy quality and steel production technology is plant and product specific and hence, effective communication between ferroalloy suppliers and steel producers is essential.

1. INTRODUCTION

In the mid eighties, Aukrust[1] presented an excellent analysis of trends in steel developments and their impact on the ferroalloy industry, largely from a North American perspective. In similar vein, Nakamura[2], attended to quality standards of ferroalloys in his presentation at a previous Infacon Conference, giving a Japanese steelmaker's perspective of the position in the mid nineties. Both Aukrust and Nakamura emphasised the importance of close collaboration between steelmaker and ferroalloy producer if effective use of ferroalloys in the steel industry is to be realised. There is no need to repeat their perspectives and it remains to determine to what extent the development of new steel grades, improvements in steelmaking technologies and customer demands have changed the impact on the ferroalloy industry.

A highly competitive steel market requires the modern steelmaker to be sensitive to customer demands in terms of product properties, quality, price and delivery. The steel industry is confronted with high fixed costs as well as expensive and sophisticated processes, which are constrained to high production rates by efficiencies and economics of scale. Four main drivers for the steel industry have been identified: high costs; raw material shortages; environmental concerns and customer demands[3].

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The emergence of new steel grades by the use of state-of-the-art processes is largely driven by the need to produce high quality steel at a competitive price. The principal aim is to attain ultra-high purity and ultra-cleanliness. Cost reduction and environmental control have also become dominating drivers in the production of steel and traditional production techniques have been challenged by the development of new processes and alternative production technologies. We have seen the traditional ironmaking process comprising a sinter plant, coke ovens and a blast furnace being challenged by the Corex, Hismelt and Dios processes. One of the main aims of the new process technologies has been a reduction of the environmental impact of the coke ovens and sinter plant.

The traditional steelmaking route has also been challenged by a variety of processes, of which the IRSID continuous steelmaking process and the Energy Optimizing Furnace have perhaps come closest to commercial reality[4].

In reaction to these challenges, steelmakers have responded by exciting and innovative developments in traditional process technology. Most of these developments have been aimed at hot-metal treatment *before* refining and ladle treatment *after* decarburisation. The bulk removal of silicon, phosphorous and sulphur from the hot-metal product of the blast furnace prior to refining in a basic oxygen furnace has reduced tap-to-tap time, lowered cost and produced steel of much higher quality. The use of ladle refining techniques subsequent to decarburisation in the basic oxygen furnace has resulted in reduced hydrogen and nitrogen contents and reduced solute impurities. Moreover, inclusion shape and composition control has led to the achievement of much improved mechanical properties of the steel. As the impending changes in the use of ferroalloys are ultimately linked to the development of new steel grades and the implementation of specific steelmaking technologies, it is instructive to briefly refer to emerging steel grades and to attend to some of the relevant changes that have occurred in steel production technology.

2. QUALITY STEEL AND MARKET DEMANDS

Since quality is such a relative term, it is important to define what is meant by quality steel. In the present context quality refers to ultra high purity steel, especially with respect to low concentrations of interstitial elements and ultra clean steel, meaning that the inclusion content, shape and size distribution are strictly controlled.

With regard to quality it is pertinent to compare modern day market demands with that of yesteryear. For example, the steel used to build the Titanic was produced in a steel plant of note and by the best process technologies known at the time. This steel contained 650 ppm sulphur and metallographic examination revealed that MnS stringer-inclusions, up to 25 mm in length were present[5]. By contrast modern quality requirements for linepipe steels for arctic applications would require a sulphur content of less than 10 ppm while tire cord steel would be rejected by the customer if it contains inclusions greater than 10 μm in diameter[6].

Using modern steelmaking technologies, it is possible to produce steel with a total impurity content of less than 50 ppm. Alloy additions can then be made, judiciously and selectively, often in vernier quantities to attain specific mechanical properties[1]. This approach to the production of quality steel has important consequences for the ferroalloy industry because it places ever-increasing demands on the purity, homogeneity, size and size distribution as well as impurity content of the ferroalloys used to trim the chemical composition of the steel to perfection. It is quite apparent that the market demands imposed on the steelmaker will reflect on the ferroalloy producer because the steelmaker has to meet the stringent quality requirements referred to above in tonnage quantities, typically in batches of 200 tonnes, whilst the market value of his product per unit mass is less than that of bread.

3. CUSTOMER DEMANDS

In Australia, the transport of oil and gas by country pipelines has been a large consumer of steel and provided a major driving force as well as proving ground for the development of micro-alloyed steel and thermo-mechanical processing techniques. In recent times smaller diameter, electric resistance welded (ERW) pipelines have dominated the industry with several major trunklines being built over many thousands of kilometres.

Concurrent with this surge in pipeline construction, there has been a dramatic change in Australian pipeline steels with a rapid progression towards higher strength levels. The remote locations of oil and gas reserves combined with a limited number and small population centres scattered over a large area, dictate the requirement for long distance, small diameter pipelines. The economic benefits of higher strength pipelines such as reduced gas transportation costs, lower pipeline procurement and transport to site costs as well as reduced welding costs due to smaller diameter and thinner wall are critical to project viability. Examples of the chemical compositions of three different steel grades that have been developed in Australia for pipeline construction are shown in Table 1 and the corresponding mechanical properties in Table 2 [7].

Table 1. Chemical composition of selected linepipe steels.

Steel Type	Chemical Composition, Mass %									
	C	**Mn**	**Si**	**P**	**S**	**Al**	**Nb**	**Mo**	**Ti**	**N**
X60	0.080	1.25	0.12	0.017	0.003	0.025	0.040	-	0.013	0.0050
X70	0.070	1.50	0.32	0.012	0.005	0.030	0.060	0.11	0.015	0.0050
X80	0.075	1.59	0.31	0.018	0.001	0.026	0.057	0.22	0.013	0.0060

Table 2. Typical mechanical properties of ERW high strength pipe steels.

Steel Type	Strip Thickness (mm)	Mechanical Properties		
		Tensile (Transverse)		
		LYS (Mpa)	**TS (Mpa)**	**El (%)**
X60	5.8	504	558	38
X70	5.3	605	650	31
X80	3.0	685	718	28

Central to the steel design philosophy is the application of micro-titanium additions for enhanced weldability (resistance to heat affected zone cracking) and the various combinations of niobium and vanadium for ferrite grain refinement and precipitation hardening. Where higher strengths are sought at lower carbon equivalents, molybdenum additions have been used to advantage. The added contribution of transformation hardening together with enhanced grain refinement and precipitation hardening account for the additional strength available in the Mo-Nb hot-rolled strip steels. Low sulphur contents are achieved by the desulphurisation treatment and the subsequent slag raking of the liquid iron product of a blast furnace, slag design strategies in the oxygen converter and finally, calcium silicide injection to form globular, liquid inclusions and to partially modify manganese sulphide inclusions.

Following CaSi ladle injection, alloy additions are made in a CAS facility (composition adjustment by sealed argon bubbling system) and the inclusions are ‘floated out’ during vacuum degassing without risk of oxidation or nitrogen pick-up. Vacuum degassing permit tight control of micro-alloy additions to a predictable high level of recovery and accuracy under the prevailing inert atmospheric conditions. In over 600 heats, the chemical composition control was contained within the limits +/- 0.01% C; +/- 0.015% Nb and Ti and +/- 0.001% S.

The importance of maintaining an ultra-low concentration of sulphur is illustrated in Figure 1 in which the impact toughness of steel X70 is shown as a function of sulphur content. Because there are no means of removing sulphur subsequent to vacuum degassing, it is evident that any sulphur contamination introduced through ferroalloy additions will seriously affect the toughness of the steel.

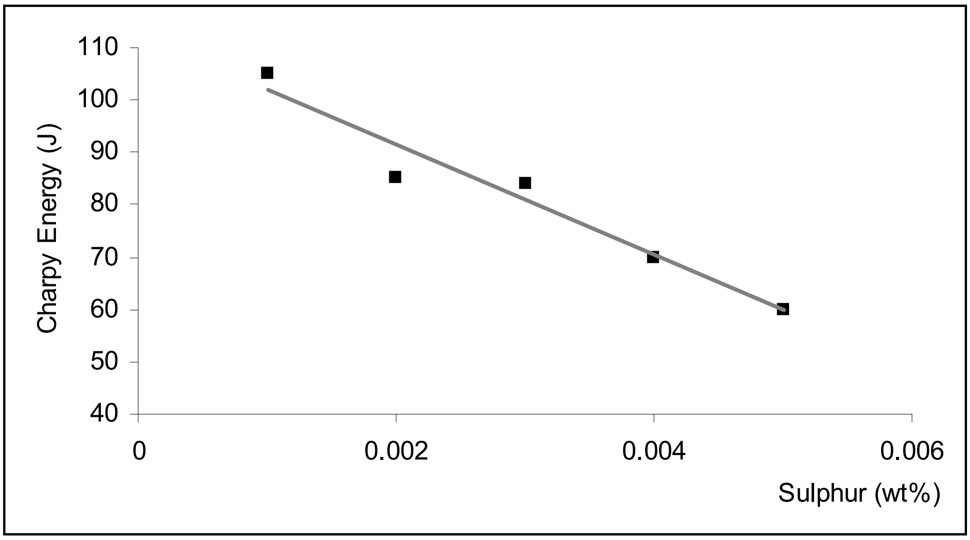

Figure 1. Effect of sulphur content of Type X70 steel on Charpy impact toughness at 10^{o}C[7].

Another example of user requirements for new steel grades may be found in the quest to develop a fuel-efficient automobile. Environmental concerns are forcing the automobile industry to reduce the production of CO_2 by reducing fuel consumption. As there is an almost linear relationship between fuel consumption and vehicle mass, considerable effort has been expended in reducing the mass of automobiles. In a collaborative effort between 35 companies in 18 countries it has been possible to achieve a 25% reduction of mass in a prototype vehicle by the judicious selection of high strength steels for body components and by using sophisticated forming and welding technologies. The range of strength of steel selected for body components in this so-called ULSAB project that was launched in 1994, are shown in Figure 2. The solid curve reflects properties of steels available prior to 1994, while the dashed curve shows the projected tensile strengths of steels that were to be developed. In response to the needs of the automobile industry, a series of new, highly formable, high-strength steels were developed[8]. The relationship between strength and ductility of these and other steels that were available for selection of body parts in the ULSAB Project are shown in Figure 3**.**

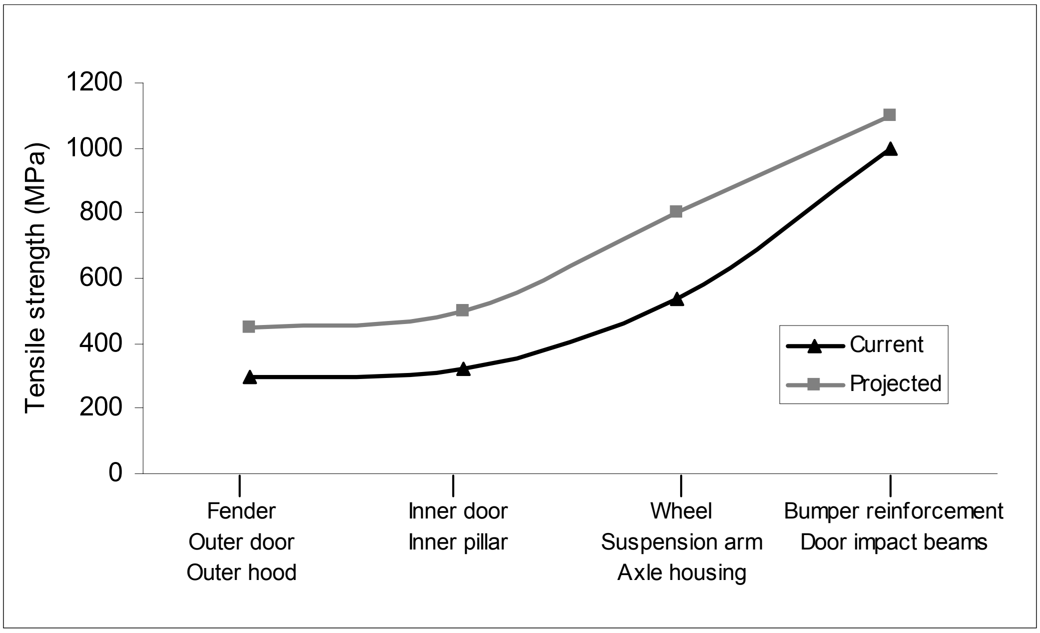

Figure 2. Tensile strength of high strength steel sheets selected for automobile body parts manufacture[8]. Current (at the time, prior to 1994) and projected values are shown.

The bainitic and ferrite/pearlite grades in the figure refer to steel grades that were commercially available in the early nineties. The mechanical properties of dual phase steels are controlled by the amount of hard martensite dispersed in a ductile ferrite matrix while transformation-induced plasticity (TRIP) is achieved by balancing the composition of the steel such that quasi-stable austenite is retained at room temperature. This quasi-stable austenite transforms to martensite upon plastic deformation thereby rendering a high-strength, highly formable steel. The production cost of these high strength steel sheets is relatively high because of low yield and low productivity. Moreover, the higher strength is attained through the judicious selection and use of valuable alloying elements. Addition of these ferroalloys constitutes significant additional cost to the steelmaker and he would be keen to reduce the cost of alloying elements to a minimum.

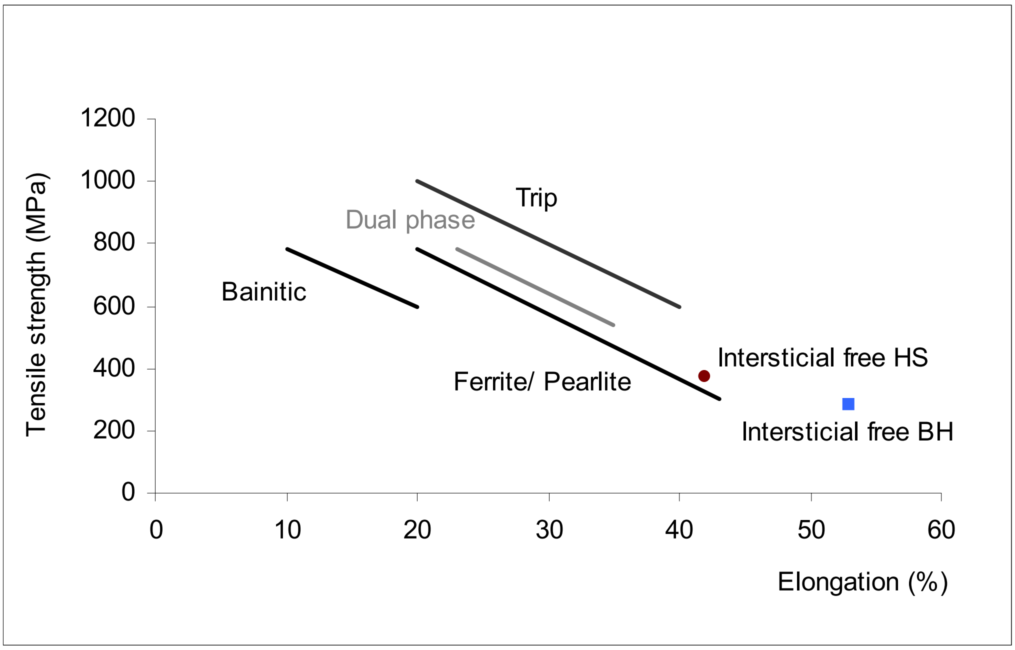

Figure 3. Strength - Ductility relationship of some high strength steel sheets that were available for selection in the ULSAB project[8].

A class of steel, which as a class probably ranks as the most important for the manufacture of automobile body parts is ‘interstitial-free’ (IF) steels. The mechanical properties of two variants of this class, bake hardenable (IF-BH) and high strength (IF-HS) are shown in Figure 3 and the production of these steels totals about 16 million tonne per annum[9].

Ultra-high strength steels with a tensile strength in excess of 1000 Mpa is required for bumper-reinforcement and door impact beams. In order to ensure sufficient formability, a very homogeneous microstructure is required and these steels are particularly susceptible to hydrogen-induced cracking. A limiting factor in the broader use of high-strength steels is their susceptibility to softening of the heat-affected zone (HAZ) of welded parts. Softening of the heat-affected zone reduces the strength and fatigue resistance and for this reason niobium and molybdenum containing high strength steels have been developed. A feature of these steels is that complex alloy carbides precipitate in the heat affected zone during welding, thereby counteracting the softening of the HAZ. Although the concomitant increased use of alloying elements will excite the ferroalloy producer, a word of caution is pertinent. Quite apart from considerations of cost, from the point of view of recycling, the steelmaker will attempt to keep the use of alloying elements to a minimum. In Japan, for example, a national project has been launched to develop high strength steel by grain refinement. By reducing the grain size from 10 μm to 1μm of a conventional steel with a tensile strength of 400 MPa, tensile strengths of 800 MPa have been exceeded[8]**.** Although the required production technology is still in its infancy and these steels are not commercially available as yet, the ferroalloy producer should take note of this and other initiatives to reduce the alloy content of steel.

4. EMERGING STEEL GRADES

Steel type X80 (tensile strength of 800 Mpa) that has been developed for use as linepipe steel, Table 1, is being considered for shipbuilding purposes and trials are currently under way. The same steel is also being considered for use on off-shore oil platforms. Linepipe steels with tensile strengths in the range 1000 MPa to 1200 Mpa are under development for 'sweet' gas and oil pipeline applications.

Buzzichelli and Anelli[10] have recently outlined new approaches for the development of these high strength steels in Europe. They have also shown that the comsumption of high strength steels in Europe is increasing and it is anticipated that 22% of the steel used in a new car will have tensile strengths in the range 500 – 800 MPa and 30% will have an ultimate tensile strength in the range 700 – 1000 MPa. It is furthermore interesting to note that a 20% reduction in the mass of the Porche 928 model has been achieved through a joint development program between VDEh and Porche by capitalising on the unique properties of Nb containing microalloyed steel.

In the metal construction industry, new markets are being developed for structures for which steel is particularly suitable. The metallurgical design is aimed at reducing the carbon content of these steels, but increasing the manganese content to increase the strength of the matrix, the introduction of aluminium and niobium to achieve grain refinement and vanadium for precipitation hardening. In these steels, the sulphur content has to be kept very low to improve toughness in the through-thickness direction[10].

New steel grades are also being developed for application in large infrastructures such as suspension bridges where ultimate tensile strengths in excess of 1800 MPa are required. New steels with nominal compositions of typically 0.8C–0.7Mn–0.25Cr or 0.8C–0.6Mn–0.2Cr–0.06V have been developed and the formation of primary cementite on grain boundaries is eliminated by slow cooling the wire rods in the temperature range 800^{o}C to 1000^{o}C or by the addition of 0.60 to 0.70% silicon to the steel[10].

Since the ULSAB Program, the catalogue of commercial steel grades available to the automobile manufacturer has grown to include new types of high strength steels, commonly known as advanced high strength steels (AHSS). These steels have become available for the prototype autobody in the advanced vehicle concept program known as the ULSAB-AVC program. The ULSAB body structure was constructed 90% of high strength steels (HSS), whereas the ULSAB-AVC body structure is 100% high strength steel, with over 80% of that total being advanced high strength steel [11]. The principal differences between HSS and AHSS are due to their microstructures. AHSS are multi-phase steels that contain martensite, bainite and/or retained austenite in such proportions as to produce unique mechanical properties. Compared to conventional micro-alloyed steels, for example Table 2, AHSS exhibit a superior combination of high strength with good formability. This combination arises primarily from their high strain hardening capacity as a result of the high tensile strength (UTS) to yield strength (YS) ratio in these steels.

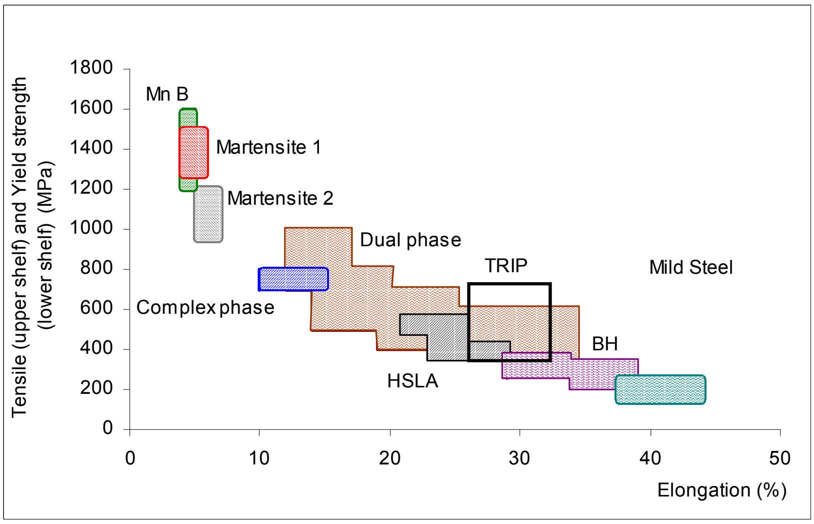

Figure 4. Tensile / Yield Strength - Ductility Relationships of steel selected in the ULSAB –AVC Auto Body Design[11]. See text.

Figure 4 shows the range of steels selected for the ULSAB-AVC body structure. The fundamental metallurgy and processing technology of conventional low and high strength steels are well understood but it is pertinent to refer briefly to these AHSS steels since the metallurgy and processing thereof are somewhat novel.

4.1 Dual Phase Steels

The microstructure of dual phase (DP) steels is composed of soft ferrite and between 20 and 70 volume percent of either bainite or martensite. The continuous soft ferrite phase provides excellent ductility but when the steel is deformed, strain is concentrated in the soft ferrite matrix, creating the unique high work hardening rate exhibited by these steels as shown in Figure 4. Carbon, silicon and phosphorus strengthen the martensite while manganese, chromium, molybdenum, vanadium and nickel are added individually or in combination to increase hardenability to the extent that martensite can be formed at practical cool rates. The alloying additions are carefully balanced to provide, in combination with selected thermo-mechanical processing, the required properties.

4.2 Transformation Induced Plasticity (TRIP) Steels

The microstructure of TRIP steels, like dual phase steels, consists of a continuous ferrite matrix dispersed with hard second phase bainite or martensite particles but in addition, these steels also contain retained austenite in excess of 5% by volume. During deformation, the dispersion of hard second phases in soft ferrite creates a high work hardening rate, as in DP steels. In addition, the retained austenite transforms progressively to martensite with increasing strain, thereby increasing the work hardening rate beyond that of DP steels. Austenite can be retained if the martensite finish temperature (Ms) of the steel is below ambient temperature. The composition of TRIP steels are similar to that of DP steels but in TRIP steels the Ms temperature is lowered through the addition of carbon, silicon and/or aluminium in concentrations higher than that of DP steels.

4.3 Complex Phase (CP) Steels

Complex Phase Steels consist of a very fine-grained ferrite microstructure containing a high fraction of hard phases that are further strengthened by fine precipitates. They use many of the same alloying elements found in DP and TRIP steels, but also contain niobium, titanium and/or vanadium to form fine alloy carbide precipitates. Under conditions of high strain rate deformation, such as in a crash, CP steels exhibit superior energy absorption compared to other AHSS and hence, candidate applications are bumper and pillar reinforcements.

4.4 Martensitic (Mart) Steels

In martensitic steels, the austenite that exists during hot-rolling and annealing, is transformed almost entirely to martensite during quenching. Carbon is added to martensitic steels to increase the hardenability of the steel and the strength of the martensite. Manganese, silicon, chromium, nickel, molybdenum, boron and vanadium are also added in various combinations to increase hardenability and hence, to obtain the desired mechanical properties.

All AHSS sheet are produced by controlling the cooling rate either on the run-out table of the hot-strip mill or in the cooling section of the continuous annealing furnace. The chemistry of these steels is carefully adjusted to produce the required properties.

Neither the linepipe industry nor the automobile industry, albeit major users of steel, are by any means the only industries that promote the development of new steels. In the present context the customer demands outlined above are merely aimed at illustrating the philosophy adopted in the development of new steel types and will serve as background to a further discussion of the impact of emerging steel grades on the ferroalloy industry. Apart from analysing the market demands for its products, the ferroalloy producer should also focus on the changing steel production technologies and how these changes will impact on his industry. It is therefore of significance to assess modern steelmaking technology from this point of view and to consider in more detail how the steelmaker, operating in a highly competitive market, responds to customer demands in terms of properties, price and quality.

5. STEEL PRODUCTION TECHNOLOGY

5.1 Background

Henry Bessemer introduced pneumatic steelmaking in 1856 and the price of steel fell from £50 per ton to £7 per ton, the steel age began and steel replaced wrought iron as engineering material. Shortly after Bessemer introduced his process, the basic open hearth was introduced and dominated steel production until the mid sixties. The top blown oxygen converter, or basic oxygen process (furnace), was developed in the mid 1950s and bottom-blowing facilities were later added. In the past 40 years, the basic open-hearth process has been almost completely replaced by various top, bottom or combination blown oxygen steelmaking processes[12]. Traditionally, liquid steel has been produced in integrated steel plants, starting with iron ore and coke, or through an electric-arc furnace route by the recycling of scrap. In integrated steelmaking, the hot-metal product from a blast furnace is refined in a basic oxygen furnace and production capacities are typically in excess of five million tonnes per annum. In the electric-arc furnace steelmaking route, scrap is recycled. Typical capacities are 0.3 to 2.5 million tonnes per annum and the capital outlay of such a facility is considerably less than that of an integrated plant.

The quality of steel produced in an electric-arc furnace is restrained by the level of metallic residuals such as copper, nickel and tin in the scrap charge. However, the use of hot-briquetted iron, directly reduced iron and liquid hot metal has significantly increased the product quality range. Most modern electric-arc furnaces use a combination of oxy-free burners, pulverized coal injection and oxygen injection to supplement electrical energy input. Today, steel production in one year exceeds that of all other metals combined in ten years of production and steel is produced in integrated plants by the basic oxygen process and in mini-mills through electric-arc furnace technology. In the USA, 60% of the steel is produced by means of the oxygen converter and 40% by electric-arc furnace technology as shown in Figure 5**.**

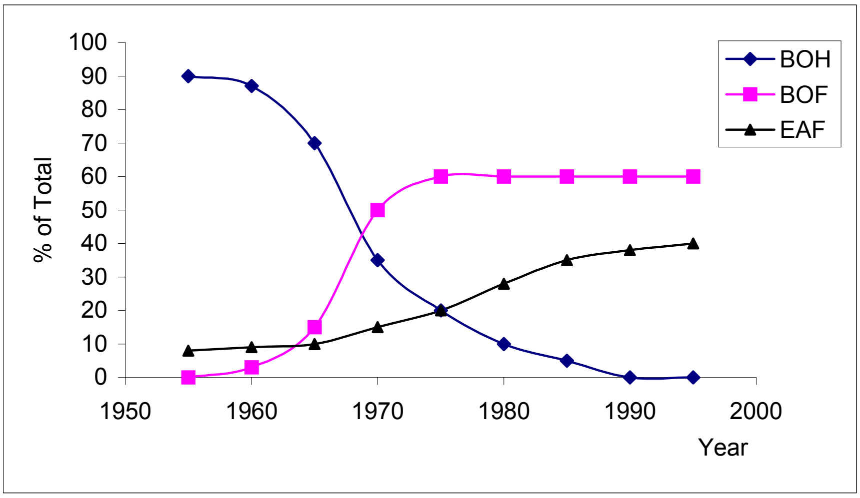

Figure 5. US Steel production 1955-1995[12]. BOH = Basic Open Hearth,
BOF = Basic Oxygen Furnace, EAF = Electric-Arc Furnace.

Traditionally the integrated mills dominated the high quality steel strip market while the mini-mills produced the standard grades. However, the introduction of thin-slab casting has broken through the boundaries that separated integrated steel producers, focusing on the flat-rolled market, from mini-mills that traditionally have made long products. Thin-slab casting effectively opens the flat-rolled market to the mini-mills because it drastically reduces capital costs by shrinking the size of the casting machine while eliminating the roughing mill**.** This revolution in steelmaking has been fuelled by equally exciting developments in twin-roll strip casting technology[13]. The potential benefits of thin-strip casting are even lower capital cost, reduced operating cost and improved quality. A large process simplification over conventional and thin-slab casting is envisaged. The high rate of heat transfer and rapid solidification that occurs in the twin-roll caster produces a microstructure unlike any steel-casting process[14]. The peak heat transfer rate is approximately 25MW/m^2 [15] and thin strip 1.5 – 2 mm thick and 1300 mm wide is produced at casting speeds up to 80 m/min [13].

The issue that is of fundamental importance to the ferroalloy producer, is that a wide range of mechanical properties can be obtained from a single chemistry through variations in casting speed, subsequent hot and cold rolling and heat treatment. Macro-segregation of impurities in strip-cast steel is significantly suppressed at the high solidification rates and hence, may lead to a greater tolerance for impurity elements, which degrades the mechanical properties of conventional processed steel products. Precise control of the mechanical properties of steel products without the stringent steel chemistry control that is currently required in the production of steel would have a revolutionary effect on the steel industry and by implication, also on the ferroalloy industry.

5.2 Modern Steelmaking Technologies

Significant improvements in steel processing technology have been made possible through a fundamental understanding of the mechanism and rate of metal/slag/gas reactions. The current trend in integrated steel plants is to remove the bulk of sulphur and phosphorous from the hot metal product of the blast furnace prior to decarburisation which occurs in a basic oxygen converter. Subsequent to decarburisation, hydrogen removal, final alloy trimming as well as inclusion removal and modification are achieved through a variety of secondary refining techniques. By these process modifications it has become possible to obtain better yields, produce cleaner steel and lower operating costs[1]. This modern trend in steelmaking is schematically shown in Figure 6, which depicts an idealised steel processing route.

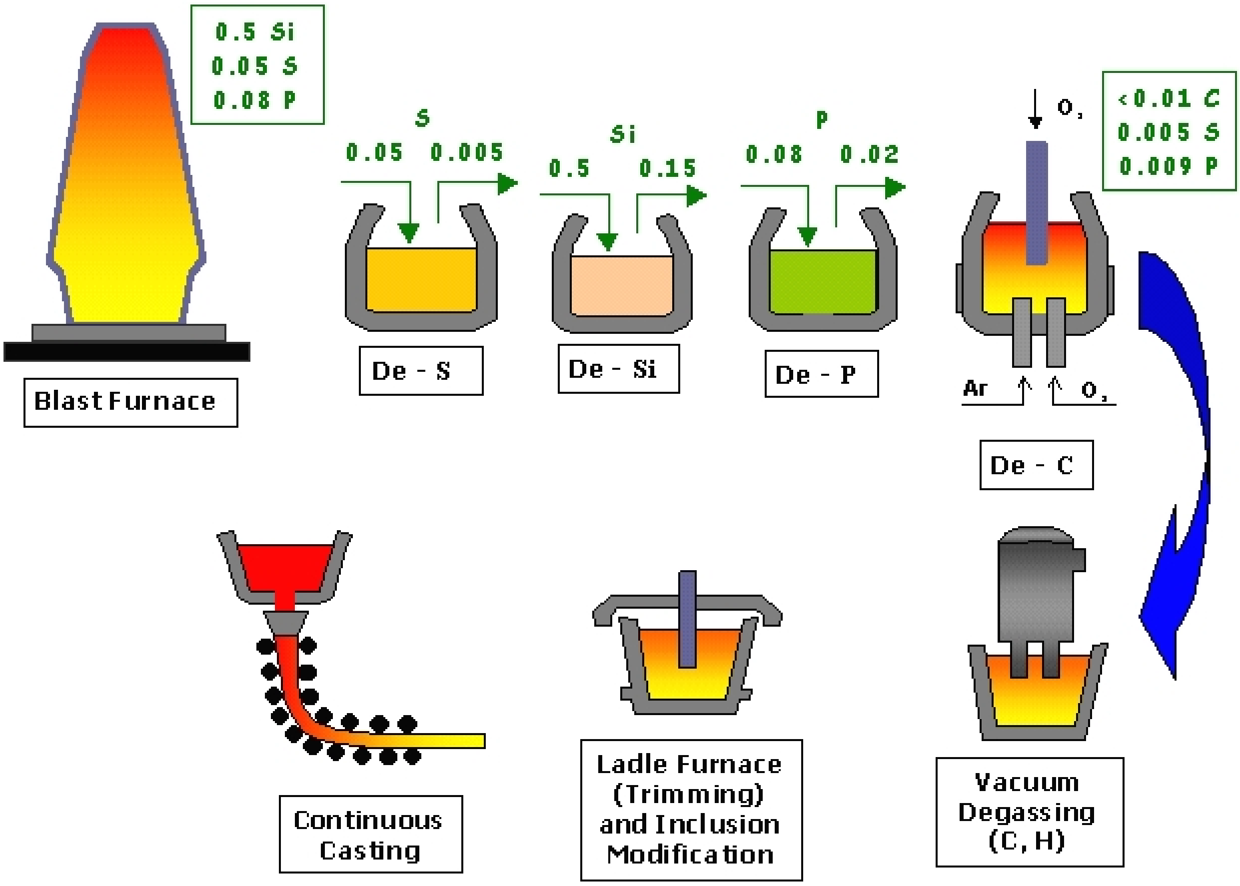

Figure 6. Idealised modern steel-making route. The decarburisation step (BOF) may be replaced by an electric-arc furnace in the EAF route of steelmaking and the processes prior to that, eliminated.

Hot metal can only be dephosphorised if it contains less than 0.15% Si and for this reason it is important to desiliconise the hot metal prior to dephosphorisation. Additional advantages of the bulk removal of silicon from the hot-metal is that chemical attack on the basic oxygen refractory lining of the BOF is minimized and a minimal amount of slag-making fluxes is required, thereby maximizing process yield[16]. On the other hand, lowering the silicon content of the hot metal precludes utilization of the thermal value from silicon oxidation and hence, reduces the scrap-melting capacity of the basic oxygen converter. Because of the economic value of high scrap melting, external desiliconisation and dephosphorisation have not been adopted in the United States and many other plants[1].

In some plants, the silicon and phosphorous removal steps occur in full size oxygen converter vessels and the resulting carbon containing liquid metal is transferred, after separation of the primary process slag, into a second converter for carbon removal by oxygen blowing[16]. In this sequence, the slag from the second vessel is used as starter slag for the first step.

The heavily oxidizing environment in an oxygen converter limits the sulphur removal capability of this process. Hence the sulphur has to be removed either in the hot-metal or subsequent to the carbon blow in the converter. It is far more costly to remove sulphur from the steel and hence techniques have been developed to do bulk desulphurisation in the hot-metal. Depending on the raw materials available, the sulphur contents in hot-metal can typically vary between 0.02% and 0.2%. Through external (hot-metal) desulphurisation, the sulphur content is typically reduced to less than 0.01% before introduction into the oxygen converter[16].

The presence of a slag/metal/gas emulsion accounts for the high speed of refining in a top-blown oxygen converter. The large interfacial areas in the emulsion are conducive to effective heat transfer and rapid reaction rates. However, it also results in liquid steel containing typically 400-800 ppm oxygen and slag with 25% to 35% iron oxide. These highly oxidizing conditions contribute to the loss of valuable alloying elements, particularly manganese, by oxidation to the slag.

In bottom-blown converters, which were developed a decade after the introduction of the top-blown basic oxygen converter, oxygen is introduced through several tuyeres installed in the bottom of the vessel. Each tuyere consists of two concentric pipes with the oxygen passing through the center pipe and a hydrocarbon coolant passing through the anulus between the pipes.

A new era in pneumatic steelmaking occurred with the introduction of combination blowing. This technique that has been widely adopted for carbon steelmaking, comprises a top-blowing lance and a method of stirring from the bottom. The configurational differences in mixed blowing lie principally in the bottom tuyeres or permeable elements. In the mixed (or combined) blowing vessel, the carbon-oxygen reaction proceeds closer to equilibrium because of more effective stirring, enabling controlled production of very low carbon steels and yet the advantage of high reaction rates is not lost in combined blowing. The slag is less oxidized in this process, resulting in higher metallurgical yields and a substantially better recovery of manganese. In typical mixed blowing, a saving of 25% in manganese requirements can be made[1]. Prior to the development of the combined blowing process, this additional amount of manganese would have been charged as additional ferromanganese to the ladle. Provided the silicon, phosphorous and sulphur content of the hot-metal are significantly reduced before the hot-metal is charged to the converter, 350 tonnes of liquid steel can typically be decarburised in 10 minutes in a modern basic oxygen converter. Figure 7 shows how the blowing time has been reduced from 20 to 10 minutes over the past 25 years while the tap-to-tap time has been reduced from 40 to 20 minutes in the same period.

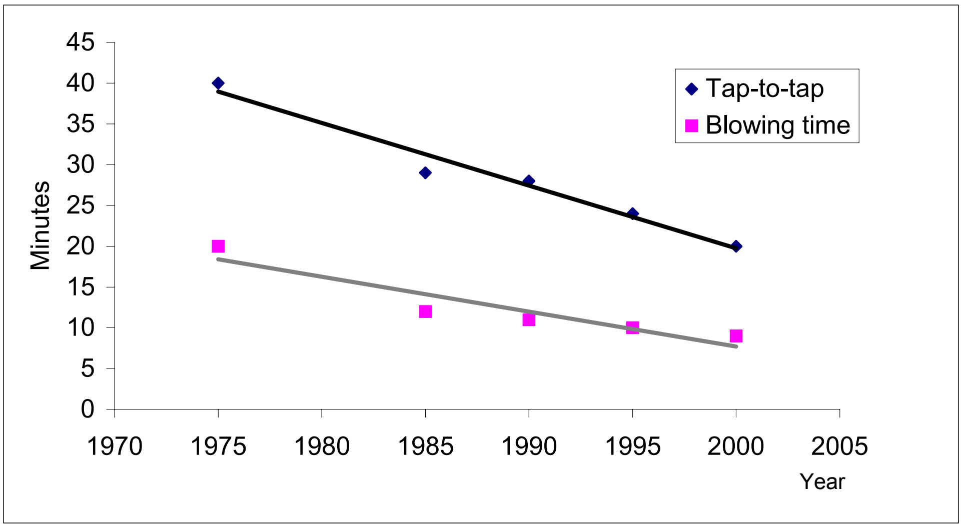

Figure 7. Reduction of tap-to-tap time and blowing time of a typical oxygen converter over the past quarter of a century.

The introduction of ladle refining, following decarburisation in an oxygen converter or electric-arc furnace, has had a pronounced effect on the steelmaking process. Moreover, the implementation of ladle refining has enabled the electric furnace steelmakers to use their furnaces as fast melters without the need to perform refining in the furnace. In addition, ladle refining and degassing make it possible for the steelmaker to exert much tighter control over the properties of the final product through improved accuracy in the composition of the final product as well as its cleanliness and by being able to control inclusion morphology[17]. A variety of ladle refining techniques, collectively known as secondary metallurgy has been developed over the years to replace, at least in part, the conventional addition of deoxidants and other alloy additions on tap from the BOF or EAF.

Key features of secondary metallurgy include:

- Temperature control of the melt by extended heating or through the provision of chemical energy.
- Final decarburisation and effective removal of hydrogen by vacuum treatment.
- Removal of sulphur and phosphorous in the ppm range through the use of synthetic slags.
- Compositional adjustments by trimming with ferroalloys.
- Deoxidation and inclusion removal by argon bubbling and slag rinsing.
- Modification of inclusion morphology by calcium treatment.

Of great significance is the very high recoveries of deoxidants and ferroalloying additions that can be ralised by the use of vacuum treatment[1].

6. IMPLICATIONS FOR THE FERROALLOY INDUSTRY

6.1 Inventory Costs and Technical Support

Although developments in steelmaking technology can affect the efficiency with which alloy additions are utilized, the actual requirements for alloying elements are determined largely by changes in the specific patterns of demand for the many different types of steel available. The actual tonnages of alloying elements can change differentially and the future requirements for the principal alloying elements cannot be related to the projected levels of overall steel production with any degree of precision[18]. Whilst Nakamura[2] has outlined the change in consumption of a number of ferroalloys in Japan between 1989 and 1993, it is extremely difficult to predict the future tonnage requirement and hence, the present analysis will be confined to technical rather than marketing aspects of the use of ferroalloys in the steel industry.

Steelmakers look towards ferroalloy producers to provide them with the most cost-effective way to utilize ferroalloys. Like all manufacturing businesses, steelmakers need to run with as low an inventory as possible and are increasingly demanding consignment stocking of ferroalloys. An example of the elimination of not only stockpiling, but also an improved delivery strategy is to be found in the Port Kembla works of BHP Steel. Calcium silicide is currently delivered to the steelmaking shop in sealed metal containers than can be directly coupled to the injection device. These containers are supplied to the steelmaking shop site on short notice, as and when required through effective communication links between user and supplier. This method of delivery has eliminated significant inventory costs as well as a huge environmental infrastructure that was required to ensure environmental compliance in the handling of the toxic CaSi dust. Also, through appropriate financial and consignment stocking arrangements, the same steel shop has reduced ferro-manganese stockpiling costs by several million dollars per annum[19].

There is a general trend in the steel industry to reduce in-house research capacity and as a consequence there is an increased expectation that ferroalloy suppliers will play a larger role in provision of technical support. In many cases such support is location and plant specific and for this reason it is vitally important that suppliers be aware of their customer’s needs, the details of their production facilities and procedures as well as the market demands imposed by the users of steel. For example, the detailed design of the ferroalloy bins used to supply alloys to the ladle at the basic oxygen furnace may be the limiting factor in the size and size distribution of alloys that can be used. A small change in the design of those feeder bins requires a significant capital investment, which the steelmaker may not wish to accept and hence, the ferroalloy supplier may have to comply with such design limitations over and above other technical considerations.

6.2 Product Quality and Homogeneity

At one stage BHP Steel had a serious problem with insufficient grain growth during annealing in the course of the production of electrical steel. The problem was tracked down to consignments of FeSi that were contaminated with titanium[1]. It was found that TiO_2 precipitation at the grain boundaries of this 2-3% Si electrical steel prevented effective grain growth.

In a recent analysis, Sjokvist et al[20] found that about 9 minutes is required to float out into the slag, MnO and MnS inclusions introduced into the liquid steel through ferroalloy additions. Hence should ferro-manganese (and by implication other ferroalloy additions) be made in the final ladle refining step in the steelmaking route and insufficient time is allowed to float MnO and MnS contaminants out, increased amounts of macro-inclusions may be found in the finally solidified steel.

When ferroalloy additions can be made economically at an early stage of the steelmaking operation, use may be made of lower-cost ferroalloys with high levels of carbon and other impurities since most of the unwanted elements are removed during subsequent refining. However, impurity elimination is less viable for additions made late in the steelmaking process and minimal for ladle additions.

Of great significance to the ferroalloy producer is the modern trend to produce essentially pure iron in large tonnage quantities as shown in Figure 6 and then to reintroduce alloying elements in precise quantities on tap, in the vacuum degasser or in any of the subsequent secondary refining steps. This is done to produce steels with narrowly defined mechanical property limits. The ferroalloys that are to be used in this new steelmaking approach must be compatible with the new steelmaking processes as well as meet the compositional constraints for the steel products.

In order to calculate the precise amount of ferroalloy which must be added to the steel to be within the narrow composition limits usually specified for each element, it is necessary that the analysis of the ferroalloys used be known accurately, the analyses must be uniform throughout a consignment and should be reproducible from one consignment to another. Such information needs to be supplied by the ferroalloy producer. Although precise control of the ferroalloy quality and homogeneity is not vital if the alloys are added on tap, the situation changes dramatically if the same ferroalloys are added in the final stages of secondary refining, often in vernier quantities. An example of the precise compositional control required to attain pre-determined mechanical properties is to be found in the production of a 0.002%C - 0.01% Ti - 0.005% Nb - 0.0004%B interstitial free steel[21]. The Ti, Nb and B additions are made in the final secondary refining step after the P and S contents have been reduced to below 50 ppm, carbon to below 20 ppm and nitrogen to below 20 ppm. In a 100 tonne ladle, these additions amount to only 10 kg of Ti, 5 kg of Nb and 400g of B. Also, a variation of 0.002% Nb and 0.0001%B makes a significant difference in the resulting mechanical properties of the steel and hence, little variation in composition of the ferroalloys can be tolerated. Ostensibly minute amounts of C, P, S or N present in ferroalloys could easily put the heat out of specification. It is also very important to ensure that sulphur be removed prior to alloying to avoid a sulphur-titanium reaction that would remove the titanium from the steel, thereby limiting or eliminating its strengthening effect on steel. Hence, if a few ppm of sulphur is introduced later in the process route through its presence in ferroalloys, the finely tuned composition balance will be upset and the required mechanical properties of the steel will not be attained.

Of course, not all steel compositions are tuned to this precision. However, the message is quite clear; much attention will have to be paid by the ferroalloy producer to the purity and homogeneity of his product. For example, traditional casting techniques will have to be revised to ensure that segregation does not cause undue variations in local composition and that oxygen or nitrogen contamination do not occur on casting. Moreover, further adsorption of oxygen and/or pickup of moisture during transportation and handling need to be eliminated. Hydrogen is effectively removed from liquid steel during vacuum treatment but it is possible to remove only about 30% of the nitrogen. For this reason, nitrogen contamination is very serious. It is furthermore of great importance to note that all hydrogen and nitrogen introduced subsequent to vacuum degassing stays in the steel. In continuous casting plants in the USA it is standard practice to qualify or eliminate suppliers of aluminium on the basis of the quality and consistency of their product[1] and we may well, in future, see this approach being extended to ferroalloy suppliers.

6.3 Size and Size Distribution

The timing of alloying additions to liquid steel depends among other on the process route, the shop logistics, the melting point of the ferroalloy, its volatility and its affinity for oxygen. Alloying additions may be made as bulk additions to the steelmaking furnace or to the ladle during tapping; by powder injection into the ladle or by wire feeding to the ladle, the tundish or even the mould. Aukrust[1], argues that bulk additions of coarse material will continue to be the first choice of the steelmaker, provided good recoveries can be achieved. The ferroalloys have to be sized such that the material can dissolve in the time of turbulent mixing generated by the tapping stream. The buoyancy effect makes bulk additions of light alloys to the ladle after tapping unattractive but a superior method of making alloy additions has been introduced. In this technique, called the composition adjustment by sealed argon bubbling system (CAS), argon gas is bubbled into the liquid steel through a porous plug or submerged lance. The rising gas/liquid plume creates an opening in the top slag cover, over which a refractory lined cylinder is lowered into the steel. Bulk alloy additions are then made in this slag-free region under an inert atmosphere. Mazumdar and Guthrie[22] have shown that buoyant additions, such as aluminium or ferrosilicon would dissolve in liquid steel, within the refractory cylinder, rather than reacting with the upper slag phase as normally encountered during conventional procedures. Therefore higher and more reproducible recovery rates of such buoyant additions can be achieved. Ferrosilicon spheres of 85 mm diameter will dissolve in less than 60 seconds. Heavier additions such as ferromanganese and ferroniobium will settle to the bottom and it is recommended that these alloys be added in finer lump form, typically 5 mm in diameter.

More generally, materials that are more dense than iron can be added as lumps, whereas lower density materials require either plunging methods or injection of powders in a gas stream. The uniformity with which these alloys are incorporated in the steel then depends on the melting points of the additions, on the sizes of the lumps and the degree of ladle stirring. Argyropoulos and Guthrie[23] studied the dissolution kinetics of ferroalloys systematically and defined two categories of ferroalloys: Class I with melting points below the temperature of liquid steel and Class II with melting points higher than that of the liquid steel temperature. Their results on dissolution kinetics were supported by the later work of Lee et al[24]. When a ferroalloy is added to liquid steel, a solidified shell of steel forms around the alloy particle as a result of local chilling. As time progresses, the shell melts away while the ferroalloy inside the shell is heated to its melting point. The complete dissolution is governed by convective heat transfer processes in the bath, as well as the size of the ferroalloy added[17]. Compacted powder mixtures of ferroalloys such as Fe-V, Fe-W, Fe-Mo dissolve faster than solid pieces of similar size. Lee et al[24] have shown that the time required to melt back the initially solidified shell around the submerged pieces of ferroalloys accounts for most of the dissolution time in the steel melt. The dissolution time for ferroalloys with a lower melting point than that of steel is approximated by the melting-back time of the initially formed shell, suggesting that the dissolution kinetics for such alloys is controlled by heat transfer. On the other hand, the dissolution time for ferroalloys with a higher melting point than that of steel is longer than the melting-back time of the steel shell predicted from heat transfer considerations. Hence, the dissolution kinetics for these ferroalloys is controlled not only by melting-back of the chilled shell, but also by the mass transfer process after the initially formed shell melts back completely.

Wire feeding of alloys by means of cored-wire techniques is practiced for adding alloying elements that are less dense than steel or have limited solubility, high vapour pressure and high affinity for oxygen. The cored-wire technique permits the quantity of alloy being fed into the steel to be adjusted with high precision and to trim the composition of the steel to within narrow limits. Submerged powder injection into the steel bath has inherently good heat and mass transfer characteristics and can be used effectively for the additon of most alloying elements.

The choice of optimum size and size distributions of ferroalloy additions clearly depends on the specific alloy to be added, its density, its melting point, available plant equipment such as feeder systems, plant logistics and the timing of addition. Hence, although a uniform size and narrow size distribution would generally be preferred, the actual particle size should be chosen to satisfy individual plant requirements and effective consultation between user and supplier is of the essence.

6.4 Inclusion Modification and Sulphide Shape Control

Calcium treatment of steel is common practice in most steelmaking shops in which deoxidation with aluminium is practiced and is aimed at modifying alumina inclusions so as to prevent nozzle clogging during continuous casting operations. During this treatment, commonly known as inclusion modification, alumina and silica inclusions are converted to liquid calcium aluminates or calcium silicates. These liquid inclusions are globular in shape because of surface tension effects. In addition, in calcium-treated, low sulphur steels, the grain boundary precipitation of MnS during solidification is suppressed as a result of the precipitation of sulphur as a Ca(Mn)S complex on the calcium aluminate inclusions. The extent to which sulphide shape control can be achieved in calcium-treated steel, depends on the total oxygen, sulphur and calcium content of the steel[17]. Important consequences of inclusion modification and sulphide shape control are amongst other improved castability and the minimization of the susceptibility of high-strength , low alloy line pipe steel to hydrogen induced cracking in sour gas or oil environments.

Of specific relevance to the ferroalloy producer is the fact that sulphur (and phosphorous) is removed from the liquid steel, either by the treatment of hot-metal or by the subsequent, and more costly, treatment with synthetic slag in the ladle, before calcium treatment. Therefore, should ferroalloy additions containing sulphur be introduced subsequent to calcium treatment, sulphide shape control will not be possible.

7. DISCUSSION AND CONCLUSIONS

Traditional ironmaking techniques have been challenged by the development of new processes, primarily aimed at reducing capital cost. Hismelt recently announced that a 800 ktonne/annum commercial plant will be built in Kwinana, Western Australia. The American Iron and Steel Institute (AISI) process, the Direct Iron Ore Smelting (DIOS) process and the ROMELT process have progressed to the stage where a demonstration or commercial plant is the next step[25]. In these processes, higher sulphur and phosphorous contents than in the hot-metal product of the blast furnace is anticipated. However, because the modern trend is to remove bulk sulphur and phosphorous from the iron by slag treatment before refining in the basic oxygen furnace, implementation of these new technologies should have little impact on the ferroalloy producer.

Fruehan and Nassaralla[4] have argued that economic and strategic consideration with regard to steelmaking have changed in the past decade and will continue to change. They have shown that the IRSID continuous steelmaking process or the Energy Optimising Furnace (EOF) may be viable alternatives to the traditional basic oxygen furnace (BOF) and Electric-Arc Furnace (EAF) techniques of steelmaking, essentially because of lower capital costs. There are few indications that these new processes will replace the BOF and EAF in the foreseeable future but even if they do, the impact on the ferroalloy producer will be minimal.

New continuous casting techniques will have a more significant impact on the ferroalloy supplier. Thin slab casters are more chemistry sensitive than conventional casting machines. The steel composition has to be controlled within narrow bands to ensure castability and product quality[10] and ferroalloys introduced during secondary refining will have to comply with strict quality requirements with respect to homogeneity and impurity content. On the other hand, microsegregation during solidification is suppressed in the strip-casting process and, as a result, stringent steel chemistry requirements are somewhat diminished. Through a combination of the unique microstructure of strip-cast steel and thermo-mechanical processing techniques, the required mechanical properties may be achieved without the need to add alloying elements to the same extent as through traditional continuous casting routes.

The modern trend in the production of quality steel is to remove silicon, phosphorous and sulphur in the hot-metal prior to refining the steel and to add alloying elements late in the secondary processing route. This practice has important implications for the ferroalloy producer. With the trend towards the production of cleaner steel, the foremost consideration is higher grade ferroalloys with lower contamination of sulphur, phosphorous, nitrogen, oxygen and hydrogen. Uniform size distributions are also important. In modern steelmaking alloying is done in such a way that the active alloying elements are not lost by reoxidation or reactions with sulphur or nitrogen. With the low level of impurities present in the liquid steel after ladle refining, the purity and homogeneity of the ferroalloys used might well be the limiting factor with regard to the cleanliness of the steel being produced. The nitrogen, sulphur, phosphorous and hydrogen control of the ferroalloys warrant particular attention.

Central to the development of new steel grades is strict control of mechanical properties within narrow bands. This objective is usually achieved by fine tuning of alloying additions. Because these additions are usually made late in the secondary refining chain of events, high purity and homogeneous ferroalloys are required. For flat-rolled products, consistency over large tonnages, even for minor elements, poses an increasing challenge. Alloying with small vernier additions, of the order of grams per tonne of steel has been identified as a need[27] and small additions can quite possibly only be made by the use of wire feeding techniques.

Close collaboration between ferroalloy producers and the steel plants that they serve is required to provide alloys specifically suited to fit special plant practices. McQuiston[26] argues that in today's business environment, customers have higher expectations of their suppliers than ever before. He suggests that a four tier approach towards a total solution will enhance effective interaction: the physical performance of the product; fast and efficient delivery of the product; effective customer support and lastly, having a corporate mission of putting the needs of the customer first. Ferroalloy requirements of the steel producer are plant, process and steel product specific and it is of the utmost importance that the ferroalloy supplier develops a deep and fundamental understanding of the process and product requirements of steelmakers and works in close collaboration with them towards specific solutions.

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