



Primary de-oxidation of Basic Oxygen Furnace steel by means of carbon

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Synopsis

The aim of this investigation was to reduce the cost of primary steel de-oxidation by substitution of aluminium primary de-oxidation with a practice that uses carbon. The cost of carbon is four times lower than that of aluminium. The application of carbon would directly result in raw material cost savings.

Investigations were conducted at Iscor's Newcastle steel plant on various steel grades. Specific production aspects were emphasized to ensure that the cost savings accrued would not create secondary expenses. These production aspects entailed:

- Yields on de-oxidation elements
- De-oxidation capabilities
- Alloying yields (Mn and Si)
- Carbon-pickup
- Nitrogen-pickup
- Temperature loss during tap
- Steel cleanliness
- Slag morphology.

This project proved that carbon de-oxidation, apart from reducing de-oxidation raw material cost due to cheaper raw materials being used and lower consumption rates, resulted in steel that is cleaner and has lower nitrogen concentrations.

Carbon primary de-oxidation has been implemented at Iscor's Newcastle plant on a large range of steel grades, ranging from ultra-high carbon (> 0.60% C) to ultra-low carbon (< 0.03% C) grades. A net saving of between R100 000 and R200 000 per month was achieved.

Introduction

Few new steelmaking technologies are developed, thus forcing steel producers such as the Iscor group to launch cost-saving campaigns. One such campaign identified raw material costs as one of the highest production expenditures.

De-oxidation of Basic Oxygen Furnace (BOF) steel is essential as it could result in steel defects such as inclusions and blowholes forming during solidification. In the past, before the carbon primary de-oxidation practice was implemented, 60 kg of aluminium was used for primary de-oxidation which was done during tapping of the first half of the Basic Oxygen Furnace steel (160 ton) from the vessel (BOF) into the casting ladle. The results

contained in this report, compares carbon de-oxidation with the original 60 kg aluminium primary de-oxidation practice.

The resulting aluminium yield (alloy concentration in the steel as a function of the mass of alloy added) was only 8 per cent due to the aluminium reacting with the oxygen in the liquid metal, forming alumina which floated out of the steel due to a lower density. Alloying was then done during the secondary de-oxidation phase while tapping the second half of the Basic oxygen furnace steel from the vessel into the casting ladle.

The aim of this study was to reduce the raw material costs of the primary de-oxidation phase, possibly improving the quality of the product and improving the yields of the alloying elements added during the secondary de-oxidation phase. The carbon primary de-oxidation process was investigated as a means of achieving the objective with tapping durations ranging from four minutes for a worn tap hole to ten minutes for a new tap hole.

The carbon de-oxidation process

When carbon is added to a bath for de-oxidation purposes, the carbon particles are heated rapidly and are subjected to a very fast oxidative pyrolysis (Morales¹) with bubbles of carbon monoxide gas forming around the particles (Figure 1).

It is assumed (Morales¹) that the pyrolysis stage lasts less than one millisecond and that during this period no reaction with the medium (liquid steel) occurs. Because conditions existing within the bubble are strongly reducing, the oxygen in the medium

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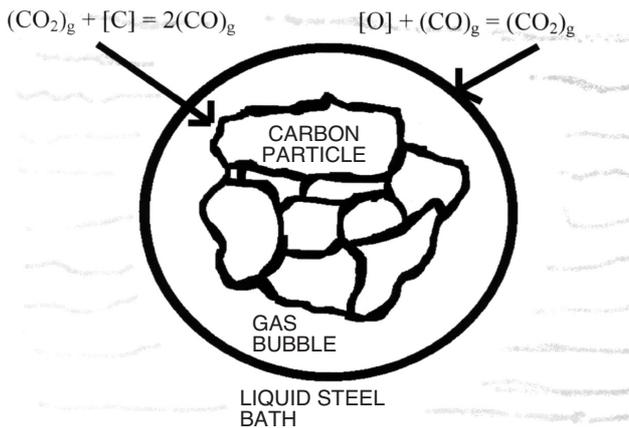
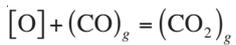
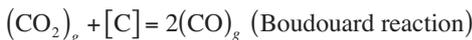


Figure 1—A gas bubble surrounding a carbon particle suspended in liquid steel that contains oxygen

is reduced by the carbon monoxide gas at the gas-carbon particle interface to regenerate carbon monoxide according to the Boudouard reaction (Deo and Boom³):



and



It is also assumed (Morales¹) that owing to the high temperatures of steelmaking, chemical kinetics at the gas-medium interface and within the bulk of the bubble (excluding the carbon particles) are so fast that local thermodynamic equilibrium prevails in that area. The controlling step of the reaction is therefore the diffusion of oxygen from the bulk of the medium to the reaction point (inner bubble surface). Every small gas bubble remains spherical and rigid in shape, constantly changing in size and with its carbon particle remaining in its centre, as it ascends through the medium.

At the steel bath surface, the CO gas surrounding the carbon particle, escapes and the carbon particle is agitated back into the steel. The process repeats itself then until the carbon particle is depleted or equilibrium is reached.

Application of the carbon de-oxidation practice

In the carbon de-oxidation trials use was made of a 6 to 10 millimetre size fraction (chips) of a synthetic calcined pitch-enriched coke. Material finer than 6 millimetres cannot be used as the reaction will be too rapid, leading to extensive flaming (due to reaction product which is CO gas which oxidizes to CO₂) creating an unsafe working environment. Larger particles reduce the total surface area per unit mass of deoxidant added, thus reducing the reaction intensity.

The carbon is applied in batches of 10 to 20 kilograms during the primary de-oxidation phase when tapping of liquid steel commences from the Basic Oxygen Furnace into the ladle. These additions of carbon are made during the tapping of the first 50 tons of liquid steel. During tapping of the subsequent 30 tons of liquid steel, no additions of carbon are done, in order to allow for the last additions to react fully.

The addition of carbon is then followed by additions of alloying elements. These elements are also consumed during

the secondary de-oxidation phase, and will determine the final oxygen level of the bath (after tapping), as a result of a variable equilibrium state of oxygen depending on the intensity of alloying done.

There is no need for the use of high purity, but expensive carbon, as the carbon is not dissolved in the liquid steel. For example: The presence of small concentrations of nitrogen in the carbon particle will diffuse into the gas bubble that surrounds the carbon particle. The reason for nitrogen diffusing into the surrounding bubble is due to lower partial pressure of the bubble. This carbon monoxide bubble that possibly contains nitrogen escapes to the atmosphere once the bubble reaches the liquid steel bath surface.

However, small quantities of carbon for primary de-oxidation are added, thus little nitrogen is introduced into the system. Also at the time of the application of the primary de-oxidation practice the oxygen level of the steel bath is high, resulting in a lower affinity for nitrogen (oxygen is positioned interstitially in the voids in the steel leaving little space for nitrogen).

Aspects investigated

The carbon de-oxidation practice was assessed on various steel qualities, such as silicon killed, dual killed steels (combination of aluminium and silicon killed) and ultra low carbon steels. Specific aspects, such as alloying yields, nitrogen pickup and steel cleanliness were investigated on silicon and dual killed steels. For investigation of aspects such as temperature balance, carbon pickup and oxygen removal ability, the production line for ultra-low carbon steel was used. The production line of ultra-low carbon steel represents an almost pure iron system, with no additions of alloying elements that could influence the quality of the results.

After trialing the carbon primary de-oxidation practice, it was implemented and results were generated over a 6-month period. These results were compared to data generated over a one-year period, using the 60 kg aluminium primary de-oxidation practice. These results are compared in the following section.

Discussion of findings

De-oxidation efficiency

Oxygen removal abilities

Among the various ferro alloys used as deoxidants, namely aluminium, ferrosilicon, low and high carbon ferro-manganese etc., aluminium has the highest affinity for oxygen (based on the Ellingham diagram for oxides), and is therefore the most powerful deoxidant. However, the final oxygen level of the liquid bath is independent of the type of primary de-oxidation that is done, as it is a function of the equilibrium state between oxygen and the intensity of the alloying that is done during the secondary de-oxidation phase.

In Figure 2 no difference is shown between baths that are primarily deoxidized with either aluminium or carbon. Also evident in Figure 2 is the lower oxygen removal efficiencies

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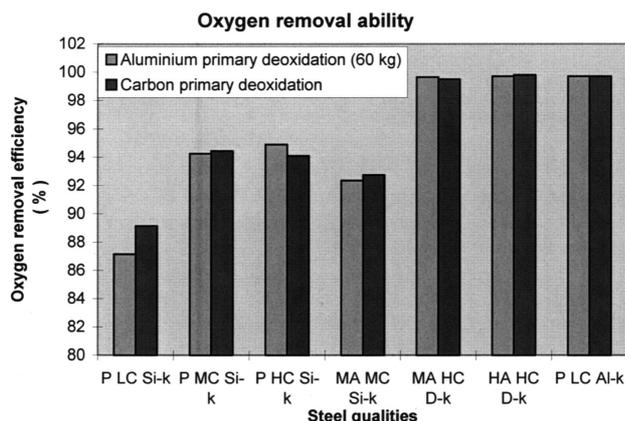


Figure 2—Comparison between oxygen levels in steel when either a carbon primary de-oxidation practice or a aluminium primary de-oxidation practice is used. (Full description of abbreviations in Table II)

of silicon killed steel qualities compared to that of dual as well as aluminium killed steel grades. The higher efficiency achieved on dual and aluminium killed steel grades is the result of aluminium alloying done at the end of tapping from the Basic Oxygen Furnace, resulting in the achievement of lower final oxygen levels.

Bulk oxygen displacement

On a basis of per mole of deoxidant added, carbon would remove more oxygen than what aluminium could do, due to the lower molecular mass fraction of oxygen in the reaction product carbon monoxide (CO), compared to that in alumina (Al₂O₃). The respective molecular mass fraction ratios of oxygen towards the reaction product in these compounds are respectively 0.57 (16/28) and 0.47 (48/102) indicating that more oxygen is consumed during the carbon monoxide reaction per mole of deoxidant added (in this case carbon). The amount of primary deoxidants that are added for various quantities of oxygen removed is depicted in Figure 3. As is evident from Figure 3, in the case of carbon de-oxidation, less de-oxidation raw materials (carbon) were used to remove the same quantities of oxygen, compared to the quantity of aluminium used for aluminium primary de-oxidation.

In plotting a histogram (Figure 4) of the ratios of oxygen removed (in kilograms) against deoxidant added (in kilograms) the difference in the mean values between aluminium as well as carbon primary de-oxidation is evident. These practical derived ratios are on average 0.86 for aluminium primary de-oxidation and 1.22 for carbon primary de-oxidation. This is an improvement of 41.4 per cent on the ratio of oxygen removed towards deoxidant added. The theoretical ratios for aluminium primary de-oxidation (48/54) and carbon primary de-oxidation (16/12) are respectively 0.89 and 1.33. In practice there is thus a deviation of 0.03 and 0.11 respectively based on the theoretical calculation. The reason that there is a large deviation from the theory in the case of carbon primary de-oxidation are discussed in the next Section.

De-oxidation of alloying elements

The raw material yield during primary de-oxidation

The yields achieved with aluminium bars and carbon chips were respectively 97 and 86,7 per cent. These yields were calculated by deriving the amount of oxygen removed in kilograms as a function of the mass of deoxidant used (aluminium bars or chips). The lower yield with carbon chips is explained by a carbon content of only 92 per cent in the chips, compared to aluminium bars, which are almost pure metal.

Yields of alloy used for alloying

A decrease of 3,3 per cent and 2,7 per cent in the manganese and silicon yields was respectively attained (depending on manganese or silicon alloying intensity) when the aluminium primary de-oxidation practice was substituted with a carbon primary de-oxidation practice. This yield is as a result that almost all the free oxygen in the liquid bath is reduced by aluminium during the primary de-oxidation phase. The oxygen in the bath can only be reduced by carbon to a level between 100–400 parts per million, depending on the carbon content of the bath (carbon–oxygen equilibrium).

Consequently when secondary de-oxidation is done, the free oxygen that is present in the liquid bath during primary de-oxidation with aluminium is lower, resulting in lesser alloying elements that would react with oxygen during the

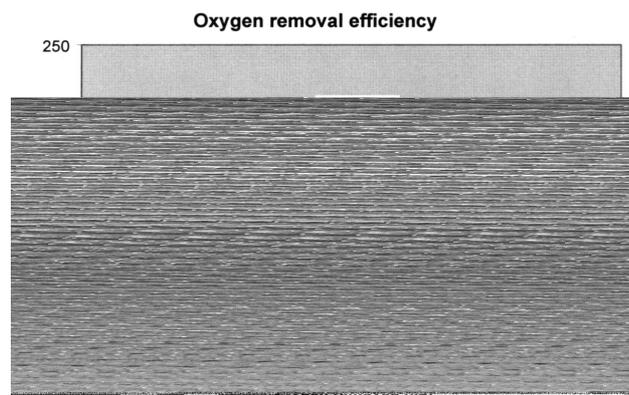


Figure 3—Quantity of oxygen removed as a function of the quantity of de-oxidation used during the production of ultra-low carbon steel

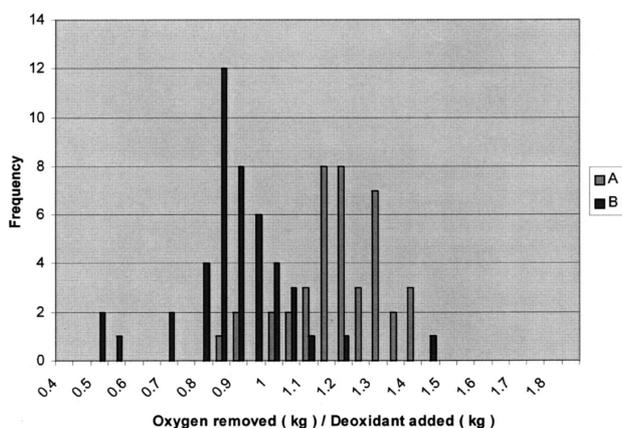


Figure 4—Amount of oxygen removed as a function of the mass of de-oxidant added. In practice A carbon is added as a primary de-oxidant. In practice B aluminium is the primary de-oxidant (60 kg)

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secondary de-oxidation phase. The yield loss in alloys that is experienced is the result of a continuous supply of free oxygen from the tapping stream during the secondary de-oxidation phase.

In Figures 5 and 6 the silicon and manganese yields that were achieved for the various steel qualities are respectively shown, illustrating the difference between silicon and dual killed steel qualities.

It is important to bear in mind that the carbon de-oxidation practice is being compared with a 60 kg aluminium primary de-oxidation practice. The results presented in Figures 5 and 6 is therefore not applicable for pure silicon and manganese killed steel. As an example, certain silicon killed steel grades have stringent steel cleanliness restrictions due to very small final product dimensions such as rope wire steels. Due to this, aluminium was never used for primary de-oxidation of rope wire steel, thus on these grades no primary de-oxidation were being done at all. Implementations of carbon primary de-oxidation on these grades resulted in improvements on all the alloy yields. Improvements of 9.13 per cent on the silicon yield (from 72 per cent to 82.13 per cent) and 1.4 per cent on manganese yield (from 94.1 to 95.5) were achieved.

It is therefore important to note that conditions vary among the different steel grades and that the alloy yield results must not be generalized.

Nitrogen pickups

The substitution of 1 to 2 kilograms of aluminium per ton of steel with carbon for primary de-oxidation purposes will reduce the nitrogen pickup of the liquid steel by 5 to 10 parts per million (Fruehan²).

The reasons for this reduction in nitrogen pickup are twofold:

- ▶ Carbon monoxide gas as a product from the carbon de-oxidation reaction, displaces the air above the steel bath, which prevents the steel from being exposed to the nitrogen-rich atmosphere
- ▶ Carbon does not reduce the oxygen content of the steel bath to such low levels as is the case with aluminium. According to Deo and Boom³, the higher the oxygen concentration is in a liquid metal bath, the lower the nitrogen pickup would be.

According to Figure 7, which represents the nitrogen pickup during tap, it is evident that the nitrogen pickup during tapping was reduced to an average level of 5 parts per million (0,0005 weight per cent). This was achieved during all the trials with the different steel qualities, except for high-alloy steel qualities, where the pickup was approximately 15 parts per million (0,0015 weight per cent). The reasons for this higher nitrogen pickup is that large quantities of nitrogen-bearing containing alloys are added and that little time is allowed for reactions during primary de-oxidation. The little time for reaction results from large quantities of alloys that are added, thus utilizing most of the tap duration for these large amounts of alloy additions and dissolving them off.

One of the benefits of carbon primary de-oxidation is that the reaction product (that is carbon monoxide) floods the atmosphere above the bath thus preventing nitrogen pickup

from the atmosphere. With the production of high alloyed grades, the alloys added contain nitrogen that dissolves into the steel as the alloys melt. This alloy addition is why the reduction in nitrogen pickup was not very good as is the case on other grades where little alloying is done.

During the trials it was found that the reduction in nitrogen pickup of 28 per cent for plain low carbon silicon

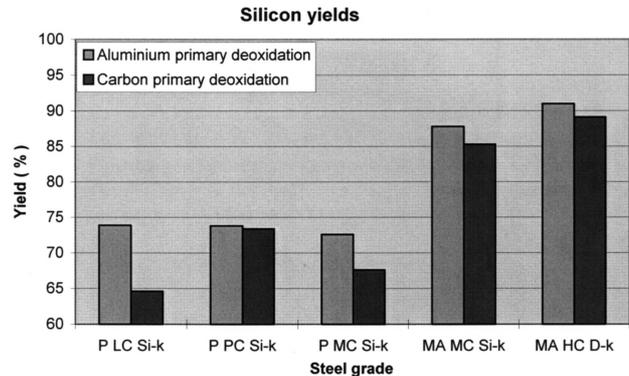


Figure 5—Silicon yields for steel baths that are primarily de-oxidized with either carbon or aluminium. (Full description on abbreviations in Table II)

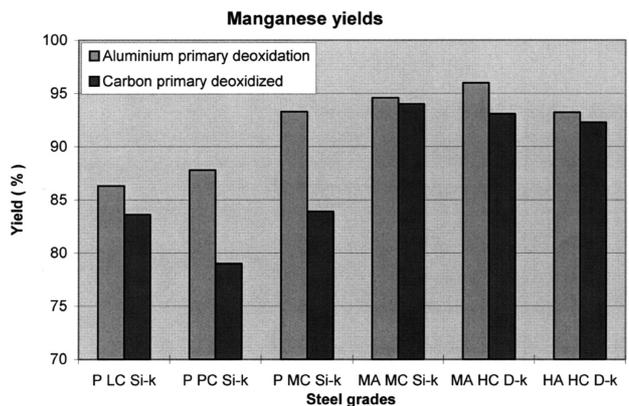


Figure 6—Manganese yields of steel baths that are primarily de-oxidized with either carbon or aluminium. (Full description on abbreviations in Table II)

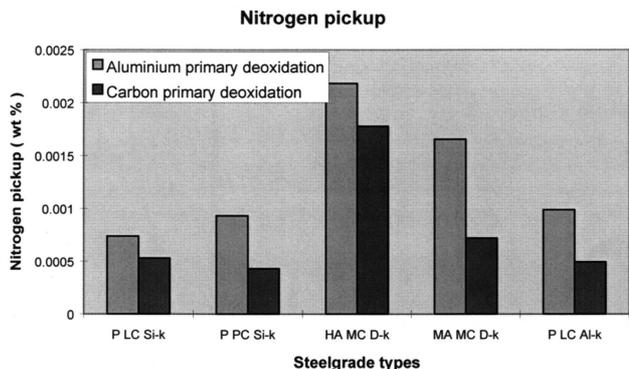


Figure 7—Nitrogen pickup of carbon and aluminium primarily de-oxidized steel baths during tapping of steel from the Basic Oxygen Furnace. (Full description on abbreviations in Table II)

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killed grades (P LC Si-K) is less than that for plain low carbon aluminium killed grades (P LC Al-K) that was 50 per cent. This is due to the aluminium killed grades being sensitive for atmospheric reoxidation due to the aluminium removing almost all the oxygen positioned interstitially in the steel matrix, leaving voids for atmospheric reoxidation. Therefore, in general, the nitrogen pickup during tap is higher for aluminium killed steel grades than for silicon killed grades, in the absence of carbon primary de-oxidation. Therefore the effect carbon primary de-oxidation has on nitrogen pickup reduction is higher on aluminium killed grades due to carbon primary de-oxidation reducing atmospheric reoxidation for which aluminium killed grades are so sensitive.

Less success in reducing the nitrogen pickup on high alloyed dual killed grades (only 19 per cent reduction) was experienced compared to the 56 per cent reduction in nitrogen pickup on micro-alloyed medium carbon dual killed grades. Due to the large amounts of additions made during the production of high alloyed medium carbon dual killed grades there is not as much time available for carbon primary de-oxidation on high alloyed medium carbon dual killed grades as for micro-alloyed medium carbon dual killed grades. This time reduction reduces the period that the carbon is effectively reacting as well as the presence of the carbon monoxide gas isolation layer above the liquid steel bath.

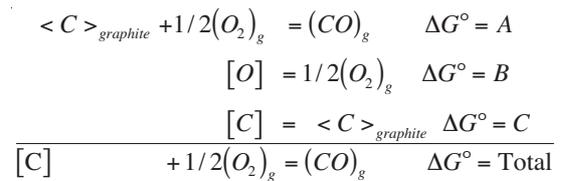
Carbon pickup

Carbon pickup by the steel bath depends on the equilibrium relations that exist between oxygen and carbon. This implies that oxygen can only be removed to levels that equal the equilibrium carbon content of the bath. After this equilibrium state is reached, carbon pickup will result with further additions of carbon.

In Figure 8 the results for ultra-low carbon steel qualities are shown illustrating a reduction of between 0 and 25 per cent in the bath carbon content of the steel when primary de-oxidation is done with aluminium. This reduction in carbon content is the result of an imbalance in the equilibrium relations between carbon and oxygen at the time of tapping, which causes these elements to react in the vessel and in the tapping stream during tap.

The use of carbon for primary de-oxidation of ultra-low carbon (ULC) steel qualities results in an average carbon pickup of 25,8 per cent by the steel. This pickup is however of little concern as this carbon, contributing approximately only 0,01 weight per cent to the total mass of these steel qualities, are utilized to achieve oxygen levels of less than 100 parts per million during vacuum degassing. It is, however, important to note that the extent of carbon pickup is a function of to what extent the equilibrium relation between carbon and oxygen is exceeded. If less or no pickup is required, for example during the production of low carbon steel qualities, less carbon must be used.

The carbon-oxygen equilibrium can be calculated through a sequence of calculations. The first step towards calculating the carbon-oxygen equilibrium is to calculate the Gibbs free energy of the reaction. It is important to take into account the various phase transformations that occur during reaction.



The equilibrium constant for the above reaction is then given by

$$\ln K_{CO} = -\Delta G^\circ / RT$$

$$\text{Or } K_{CO} = \frac{p_{CO}}{h_c h_o} = \frac{p_{CO}}{f_c [C] f_o [O]} = \chi \quad [1]$$

The values of the activity coefficients are then calculated as follows:

$$\begin{aligned} l_g f_c &= e_c [wt\%C] + e_o [wt\%O] = \\ & 0.14 [wt\%C] - 0.26 [wt\%O] \\ l_g f_o &= e_o [wt\%O] + e_c [wt\%C] = \\ & -0.20 [wt\%O] - 0.35 [wt\%C] \end{aligned}$$

Note, that this example is for a liquid bath that contains only carbon as an alloy. In practice the liquid bath contains, for example, manganese and therefore the interaction parameters of these elements (example manganese) must be included in the activity coefficient equations.

Now, doing the logarithm of Equation [1] the following equation is derived:

$$l_g K_{CO} = l_g p_{CO} - l_g f_c - l_g [wt\%C] - l_g [wt\%O] - l_g f_o \quad [2]$$

On substituting the values of $l_g f_c$ and $l_g f_o$ into Equation [2] the following is obtained:

$$\begin{aligned} l_g K_{CO} &= l_g p_{CO} - (0.14 [wt\%C] - 0.26 [wt\%O]) - \\ & l_g [wt\%C] - l_g [wt\%O] - (-0.20 [wt\%O] - 0.35 [wt\%C]) \end{aligned}$$

Solving the equation mathematically, values for carbon have to be substituted. This gives a non-linear equation that has to be solved by a suitable numerical method.

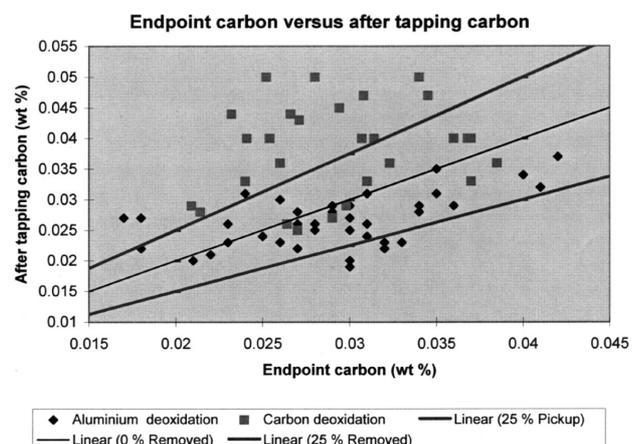


Figure 8—Change in carbon concentration during tapping of ultra-low carbon steel grades

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Temperature loss during tapping

When aluminium is used for primary de-oxidation of ultra-low carbon (ULC) steel qualities, on average a loss in heat equivalent to 37,4°C is experienced during tapping. When carbon is used, the loss amounts to 65,8°C. This loss in heat is illustrated in Figure 9.

Both reactions of respectively aluminium and carbon with oxygen are exothermic. For ultra-low carbon (ULC) steel qualities, heat equivalent to respectively 27,7°C and 8,1°C can theoretically be gained from de-oxidation with aluminium or carbon. This is calculated by firstly deriving the enthalpy for the reaction. This is done as follows:

$$\begin{aligned} <C>_{298} + \frac{1}{2}(O_2)_{298} &=<CO>_{298} \quad \Delta H_1 = A \\ <C>_{\text{work temp}} &=<C>_{298} \quad \Delta H_2 = B \\ [C]_{\text{work temp}} &=<C>_{\text{work temp}} \quad \Delta H_3 = C \\ [O]_{\text{work temp}} &= \frac{1}{2}(O_2)_{298} \quad \Delta H_4 = D \\ \frac{[C]_{\text{work temp}} + [O]_{\text{work temp}}}{[CO]_{\text{work temp}}} &=<CO>_{\text{work temp}} \quad \Delta H_T = \text{Total} \end{aligned}$$

The enthalpy for the second, third and fourth reaction needs to be calculated. This is done by integrating the heat capacity of each reaction.

$$\Delta H_{2+3} = \int_{298}^{1973} C_{p2+3} dt$$

$$\Delta H_4 = \int_{1810}^{1973} C_{p4} dt$$

The enthalpy for the reaction of primary interest is then the sum of the enthalpy's of reaction one to four.

$$\Delta H_T = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

For reaction: $C + 1/2(O_2)_g = CO$
Molecular mass: 12.011 15.99

By calculating the mass of oxygen that needs to be removed from the liquid metal, the mass of pure carbon required to react with this mass of oxygen can be calculated stoichiometrically.

$$\begin{aligned} \text{Mass } [O] \text{ to be removed} &= \text{steel tap mass (kg)} \\ & * \frac{[O]_{\text{to be removed}} (\%)}{100} \end{aligned}$$

$$\text{Mass of pure carbon required for deoxidation} = \frac{\text{Mass } [O] (\text{kg}) * C_{\text{molecular mass}}}{O_2_{\text{molecular mass}}}$$

$$\text{Thus, wt\% carbon required for deoxidation} = \frac{\text{mass_pure_carbon (kg)}}{\text{steel_tap_mass (kg)}} * 100$$

Now calculate the moles of carbon in 1 gram of liquid steel. By using the specific heat of iron constant, the reaction energy in degrees Celsius (ΔT) can be calculated with the following equation:

$$\Delta T = \frac{\text{moles carbon} * \text{liquid steel mass} * \text{enthalpy of the reaction}}{\text{molecular mass of carbon} * \text{specific heat of iron}}$$

However, with a gas as the reaction product of primary de-oxidation by means of carbon, energy is lost to the atmosphere as the gas is released. The result of this loss in energy is the approximate gain in energy from the reaction, being lost to the atmosphere. This loss of heat to the

atmosphere explains the temperature difference of 28°C as shown in Figure 9 between aluminium and carbon primary de-oxidation.

Slag morphology

In general the substitution of aluminium with carbon for primary de-oxidation results in no alumina being produced during the primary de-oxidation phase. Because alumina has a lower density than steel it would float to the surface of the steel and be dissolved by the slag. With carbon de-oxidation no alumina is produced that has to be dissolved by the slag, resulting in smaller alumina-concentrations in the slag. The slag would thus be more basic and thus less corrosive with reference to the basic refractories of ladles.

With carbon monoxide as a product of carbon primary de-oxidation, that escapes to the atmosphere as a gas, potentially less slag-forming metal oxides are produced after tapping. Consequently during de-oxidation with carbon a smaller volume of additional slag is experienced. With silicon killed steel grades where ferrosilicon acts as a deoxidant, the implementation of a carbon primary de-oxidation practice results in less silica forming. This can visually be seen in the appearance of the slag. Slag that resulted from de-oxidation with silicon is very glassy and has a transparent appearance as presented in Figure 10. By using a carbon primary de-oxidation practice, less slag is generated, resulting in the slag being lower in silica. The resulting slag has an amorphous appearance as presented by Figure 11.

Steel cleanliness

The substitution of aluminium with carbon for primary de-oxidation results in an improvement of 50 per cent (from 42 parts per million to 21 parts per million) on the concentration of aluminates in the secondary silicon killed steel directly after tapping. As no aluminium is added for de-oxidation when carbon de-oxidation is applied on silicon killed steel, it could be assumed that the 21 parts per million of aluminates that are present, originate from alumina in the fluxes that are added to the furnace (BOF) during the treatment of the steel. This origin of alumina was verified during trials, that revealed levels of 24 parts per million of insoluble aluminium

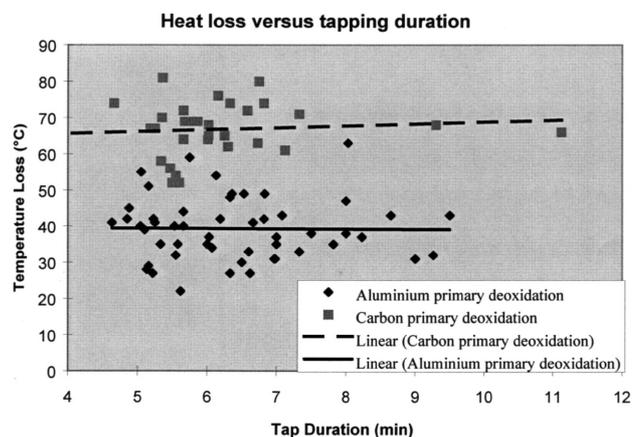


Figure 9—Heat loss versus duration of tapping of ultra-low carbon steel grades when either carbon or aluminium are used as deoxidants

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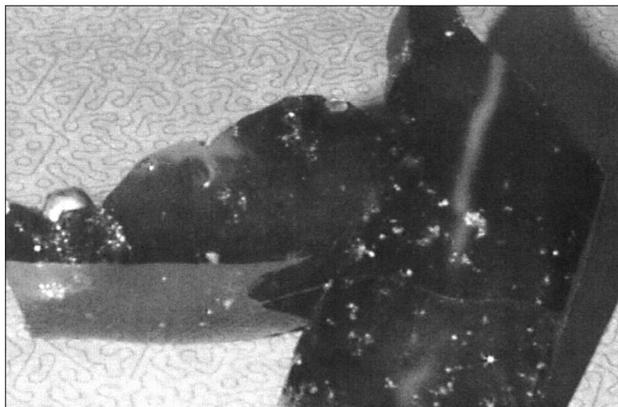


Figure 10—Slag sample of silicon killed steel grade that was not primary de-oxidized

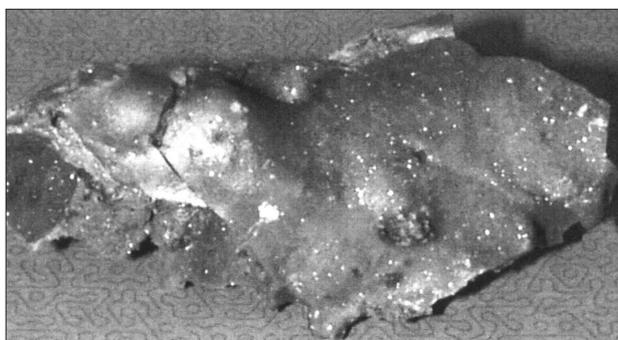


Figure 11— Slag sample from a silicon killed steel grade that was primary de-oxidized with the high carbon de-oxidation practice

Table I

Difference in content of insoluble alumina between baths primarily de-oxidized with either aluminium or carbon (the 41 sample is directly after tapping and the 61 sample is just before casting)

Carbon de-oxidation applied	No	No	Yes	Yes
Sample number	41	61	41	61
Plain low carbon aluminium killed steel	189		162	
Plain low carbon silicon killed steel	42	22	21	16
Plain medium carbon silicon killed steel	24	18	16	15
Plain ultra-high carbon silicon killed steel	27	20	20	18
Micro-alloyed medium carbon dual killed steel	131	54	129	51
High-alloyed high carbon silicon killed steel	27		28	

Table II

Description of abbreviation used in the Figures

Abbreviation	Description
P LC Si-k	Plain low carbon silicon killed steel grade
P PC Si-k	Plain peritectic carbon silicon killed steel grade
P MC Si-k	Plain medium carbon silicon killed steel grade
P HC Si-k	Plain high carbon silicon killed steel grade
P UHC Si-k	Plain low carbon silicon killed steel grade
MA MC Si-k	Micro-alloyed medium carbon silicon killed steel grade
MA HC D-k	Micro-alloyed high carbon dual killed steel grade
HA HC D-k	High-alloyed high carbon dual killed steel grade
P LC Al-k	Plain low carbon aluminium killed steel grade

immediately before tapping into the ladle. In Table I the insoluble aluminium levels are shown for various steel qualities that were primarily deoxidized with carbon and those that were not. For certain steel qualities, for example the high-alloy, high-carbon silicon killed steel, no improvement on aluminium insolubles were achieved. This lack of improvement in insoluble aluminium was a result of little available time for primary de-oxidation by means of carbon to take place, attributed to large quantities of alloys that are added. The result is a very short carbon de-oxidation practice.

The substitution of aluminium with carbon for primary de-oxidation produced steel with improved cleanliness in terms of inclusion counts. No steel defects, as a result of the primary de-oxidation practice, was observed for carbon primary deoxidized steel qualities.

Conclusions

From the results of this study on the different de-oxidation practices, the following conclusions can be made regarding the advantages of the carbon primary de-oxidation practice.

- There is no decrease towards the extent that oxygen is removed from the steel, as this is determined by the final de-oxidation of the steel as well as through alloying.
- There is on average a 41,8 per cent reduction in the consumption of raw materials used for primary de-oxidation.
- There is on average a 6 parts per million decrease in nitrogen pickup during tapping.
- Lesser quantities of acidic metal oxides are introduced into the slag.
- Since the de-oxidation product is a gas, lesser quantities of slag are produced in the ladle.
- There is 20 per cent less insoluble aluminium in silicon killed steel grades, and 14,3 per cent in aluminium killed steel grades.
- No insoluble aluminium is produced during the primary de-oxidation phase.
- A 9,3 per cent silicon and 1,4 per cent manganese yield improvement is experienced on silicon killed grades that were not primary deoxidized before due to their stringent cleanliness restrictions (rope wire steel grades).
- There is a 25,8 per cent (0,01 weight per cent) carbon pickup in ultra-low carbon steel qualities, that is effectively utilized to achieve low oxygen concentrations during vacuum degassing.

With regard to the disadvantages of the carbon primary de-oxidation, the following conclusions can be made.

- A reduction of 2,7 per cent and 3,3 per cent respectively in silicon and manganese yields when aluminium primary de-oxidation (60 kg aluminium) is substituted with carbon primary de-oxidation.
- The heat gained from the exothermic reaction is lost due to loss in energy with the gas escaping to the atmosphere (an increased heat loss is therefore experienced during primary de-oxidation).

Primary de-oxidation of Basic Oxygen Furnace steel by means of carbon

References

1. MORALES, R.D., ROMERO, J.A., RODRIGUEZ, H.H., LULE, R., and CAMACHO, J. Reduction of FeO and foaming properties of steelmaking slags. Department of Metallurgy, Apolo Mexico, —15th PTD Conference Proceedings, 1995. pp. 405–408.
2. FRUEHAN, R.J., BOF and EAF Steelmaking and clean Steel Production. Conference proceedings, Iscor Club Vanderbijlpark. South African Institute of Mining and Metallurgy. 1994.
3. DEO, B. and BOOM, R. *Fundamentals of Steelmaking Metallurgy*. Published by Prentice Hall International (UK) Limited, 1993, pp. 4–8, 86–94, 141 239–242. ◆

Mintek produces first commercial-sized copper cathodes using proprietary bioleaching technology*

Mintek, Johannesburg, 2 October, 2001—Mintek and its partners Industrias Peñoles SA de CV of Mexico (Peñoles) and BacTech Enviromet Corporation of Canada (BacTech), today announced they have produced the first commercial-sized copper cathodes from copper concentrate using their proprietary bioleach process technology.

Procesos Biometalúrgicos SA de CV (PBM), a joint venture company representing all three partners, has produced several tonnes of cathode at its demonstration plant in Monterrey, Mexico, using an integrated bioleach, solvent extraction and electrowinning circuit, with design capacity for 500 kg/day of copper.

'The production of commercial-sized cathodes is a clear demonstration that the Mintek-BacTech proprietary bioleach process technology is able to recover copper from sulphide concentrates,' said Dr Tony Pinches, Manager of the Biotechnology Division, Mintek. 'Given the environmental, capital and operating cost advantages that the technology offers over traditional treatment processes, it is only a matter of time before bioleaching combined with solvent extraction and electrowinning becomes the process of choice in the US\$7 billion smelting industry and for other base metal projects.'

The production of the copper cathodes also represents a significant step towards the completion of a feasibility study being conducted by PBM to evaluate the viability of building, owning and operating a commercial plant for toll treatment of concentrates and for projects in which PBM owns an equity interest. The feasibility study, based on the performance of the demonstration plant, is expected to be completed by the end of February 2002.

The Mintek-BacTech proprietary bioleach process technology uses naturally occurring bacteria to oxidize sulphides, liberating valuable metals from refractory sulphide ores and concentrates. Historically, the bulk of the world's base metal supply has come from sulphidic ores. Typically, these ores have been milled and floated to produce a concentrate of higher metal grades. This concentrate is then treated by roasting or smelting and refining to produce metal.

'The problem with this traditional method is that the

roasting and smelting process generates large quantities of sulphur dioxide gases,' Dr Pinches said. 'In many cases, so-called 'dirty concentrates' can also release toxic elements (such as arsenic) which are increasingly becoming environmentally unacceptable.

'The Mintek-BacTech proprietary process provides mining companies with the ideal solution—an environmentally friendly technology that keeps them on the right side of the environmental debate and allows the production of metal from previously uneconomic ore or concentrate', Dr Pinches said. 'Peñoles, through their belief in the technology and financial commitment to PBM have played a pivotal role in the development of the process to recover copper from sulphide concentrates.

'Mintek-BacTech and PBM are also continuing to review a number of other base and precious metals project opportunities that we believe may be amenable to our proprietary process technology', said Dr Pinches. 'This breakthrough on copper presents a tremendous opportunity for all partners of PBM to create substantial shareholder value through the acquisition of interests in such projects.'

Mintek's patented technology and processes use naturally occurring bacteria to liberate valuable metals from refractory sulphide ores and concentrates. Mintek's commercially proven, cost-effective, proprietary-process technology is an environmentally benign alternative to the traditional smelting process. Mintek's business strategy is to demonstrate the technology and to acquire equity interests or sell rights for cash and royalties where the technology can add significant value in mining ventures in southern Africa and world-wide.

For further information, please contact: Mintek, South Africa, Tony Pinches, Tel: +27 11 709-4397. Please note: Photographics are available in electronic format—please e-mail: antony@mintek.co.za for these or phone him on +27 (0)11 709-4319. ◆

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