CONTROL OF NON-METALLIC INCLUSIONS IN AL-KILLED STEELS[1]

Inclusion Management

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Abstract

Non-metallic inclusions are generated during deoxidation. Beyond this, additional non-metallic inclusions are formed during secondary metallurgy especially in case of Al-killed steels. Aluminium in steel reacts with oxides from refractory and top slags under formation of non-metallic inclusions. Inclusions precipitated during deoxidation modify in the course of ladle treatment. Non-metallic inclusions cause clogging and deteriorate the final product quality. Despite of that, operational experiences show that even clean steel can create clogging problems under particular conditions. In the paper the ladle metallurgy of various steel grades like ultra low carbon and low carbon steels, desulphurized and resulphurized steels is discussed. Resulting from that the given options to avoid and minimize non-metallic inclusions are shown. Steel cleanness can be controlled by tapping practice, chronology of treatment in ladle, alloying practice, soft bubbling and calcium addition. Dissolved calcium as well as inclusions modified by calcium treatment contribute to avoid clogging. Resulting from that not minimisation but optimisation of quantity and chemical composition of non-metallic inclusion is aimed at during ladle treatment.

Keywords: Clean steel; Non-metallic inclusions; Ladle treatment; Clogging.

CONTROLE DE INCLUSÕES NÃO-METÁLICAS EM AÇOS ACALMADOS AO ALUMÍNIO

Resumo

As inclusões não-metálicas no aço são formadas, principalmente, durante o processo de desoxidação. Todavia, quantidades adicionais também podem ser formadas durante a metalurgia secundária, especialmente, na produção de aços acalmados ao Alumínio. Quando em contato com refratário e escórias de panela, o alumínio do aço reage com os diversos óxidos presentes e forma inclusões não-metálicas que são precipitadas e modificadas durante a metalurgia secundária. Essas inclusões causam *clogging* e deterioram a qualidade do produto final. Por outro lado, testes industriais mostram que até mesmo aços com elevados níveis de limpeza interna podem causar *clogging* em condições particulares. Este trabalho analisa o proces-so de metalurgia de panela para diferentes tipos de aço, tais como: aços ultra-baixo carbono, aços baixo carbono, aço com baixos teores de enxofre e aços resulfurados. O nível de limpeza interna do aço pode ser controlado através das condições de vazamento do forno, sequência e procedimento de adição das ferro-ligas, condições de borbulhamento e adição de cálcio. A adição de cálcio no aço, assim como a modificação da morfologia das inclusões contribuem para evitar a formação de *clogging* durante o lingotamento. Desta forma, é almejada, como resultado final, não a minimização da formação de inclusões não-metálicas, mas a otimização do processo de sua formação com relação a quantidade e composição química.

Palavras-chave: Aço limpo; Inclusões não-metálicas; Tratamento de panela; Obstrução.

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INTRODUCTION

In the primary melting process the carbon in hot metal on its way to steel is burned off by oxygen blowing. While blowing, the oxygen content in metal increases in accordance with the Vacher-Hamiltion Equilibrium shown in Figure 1.(1) The process is maintained as long as the common analyses of carbon and oxygen follow the red arrow above the equilibrium line. At the end of blowing process the carbon content in steel usually is 0.03 %, and the corresponding oxygen content is about 700 ppm to 1000 ppm. During oxygen blowing iron and other elements like phosphorus and manganese - which can be reduced easily - oxidize and pass into the slag. Typically the content of oxidized iron ($Fe^{2+, 3+}$) in BOF or EAF slag is 15 % to 30 % depending on the process parameters. With that the initial amount of oxygen in ladle mainly depends on:

1. Oxygen content or oxygen activity respectively in steel after blowing,
2. Quantity of furnace slag carried over into ladle,
3. Iron oxide content of furnace slag.

In order to fulfill highest quality demands on steel cleanness the oxygen content in ladle and in result the final content of non-metallic inclusions in steel have to be on low level.

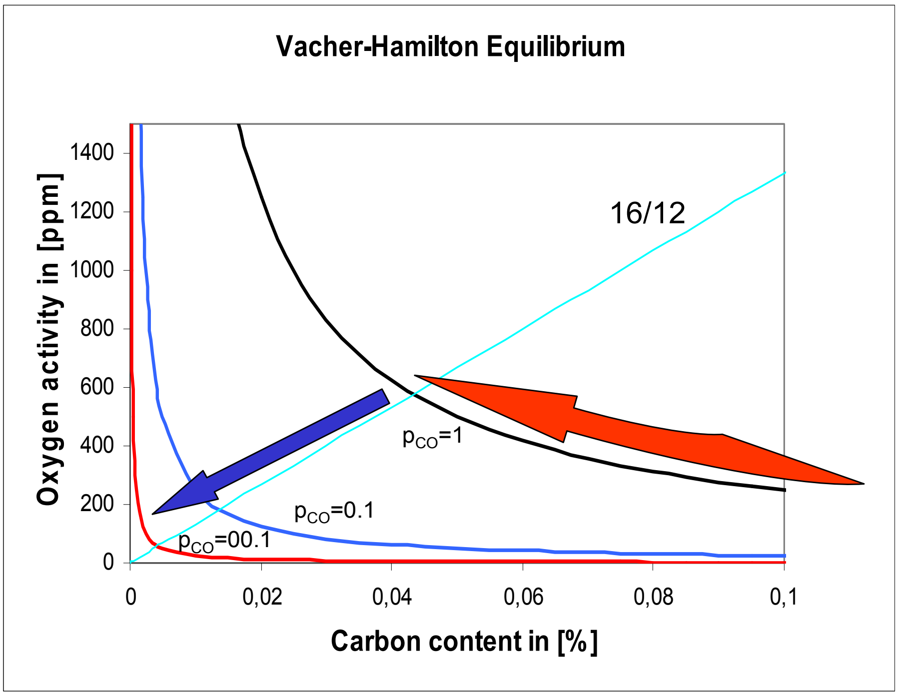

Figure 1: Carbon and Oxygen Content in Steel During Blowing   Partial Pressure in bar.

Depending on relevant steel grade, different opportunities exist to prevent the formation of additional non-metallic inclusions in steel. Regarding ladle treatment the steel grades can be classified in two main groups as shown in Figure 2: steels which have to be vacuum decarburized like ULC/IF grades and steel grades without subsequent steel decarburisation. Furthermore, the second main group roughly can be subdivided into three subgroups: the low carbon - low alloyed steels, the desulphurized alloyed steels, and the resulphurized steels.

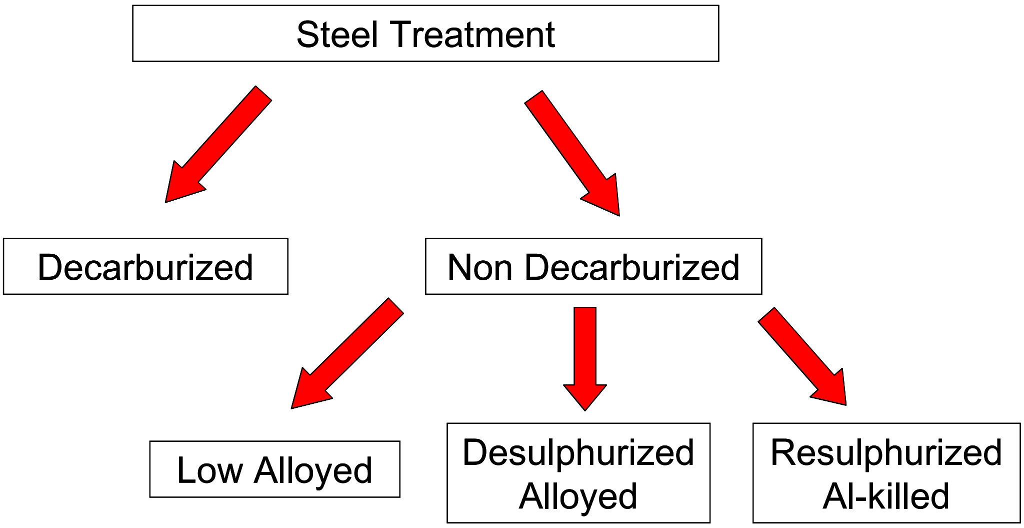

Figure 2: Subdivision of Steel Grades.

For the steel groups mentioned in Figure 2 different ways of treatment already starting from the tapping practice are required. In the following the ladle treatment regarding removal and control of oxygen is discussed individually for the different steel groups.

ULC/IF GRADES

Heats which have to be decarburized must not be deoxidized before vacuum treatment. Without any previous deoxidation the carbon burns off in direction of the blue line located close to the straight line representing the stoichiometry of CO in the ratio of 12:16 in Figure 1 during vacuum treatment.
Even without any oxygen blowing during vacuum decarburisation the actual developing of common carbon and oxygen contents in steel is smoother than to be expected from stoichiometry. The reason is furnace slag carried over into ladle during tapping.(2) Besides oxygen dissolved in steel iron oxide from furnace slag carried over into ladle participate as reactant in the vacuum decarburisation process to combust carbon under formation of carbon oxide.
During vacuum decarburization the oxygen initially dissolved in steel is to some extent removed, i.e. decarburisation is deoxidation. The initial request to remove the oxygen out of the ladle automatically is carried out during decarburisation. After vacuum decarburization the steel has to be deoxidized, i.e. the reaming dissolved oxygen in steel has to be removed by chemically compounding with elements of high oxygen affinity like aluminium, silicon and manganese under formation of metal oxide inclusions in steel.
Since the initial oxygen content in steel and the iron oxide content in ladle slag already have been decreased by vacuum decarburization the amount of elements required for deoxidation like aluminum is reduced as well. The amount of undesired non-metallic alumina inclusions in steel precipitated by Al-deoxidation according equation:(3)

1. $2[Al] + 3[O] = (Al_2O_3)$

is decreased simultaneously. Beyond this additional burn off of aluminum by contact with ambient air can be reduced by wire feeding instead of addition of bars. Alumina (Al_2O_3) in steel can react with MgO from refractory or ladle slag under formation of spinel ($MgAl_2O_4$).

2. $(MgO) + (Al_2O_3) = (MgAl_2O_4)$

The extent of that reaction depends on basic conditions like extend of ladle treatment.
Non-metallic inclusions partly separate and float out and partly stay in liquid steel. Remaining non-metallic inclusions based on aluminium oxide and on magnesium oxide are detrimental for steel cleanness. Beyond this they settle down inside submerged entry nozzles and cause clogging during continuous casting.
Usually the silicon content of ULC/IF grades is limited to lowest values. For that reason these grades cannot be treated with calcium silicon to modify the solid non-metallic inclusions into liquid to prevent clogging. In operational practice oxide modification is done by application of calcium or CaFe as far as inevitably necessary only. Usually non-metallic inclusions are floated out by soft bubbling of steel at the end of ladle treatment. Clogging is avoided by argon blowing through stopper rod.

NON VACUUM DECARBURIZED STEEL GRADES

Heats without subsequent decarburisation are usually deoxidized while tapping. Without previous decarburisation under vacuum the initial amount of oxygen in ladle is higher compared to that after vacuum decarburization. So the required quantities of deoxidizing element are increased. Accordingly the amount non-metallic inclusions precipitated in steel by deoxidation is increased as well. In consequence highest attention must be drawn to the avoidance of carryover of furnace slag into ladle in case of steel grades without vacuum decarburisation.
The demand for lowest amounts of carry-over of furnace slag is the only common ground of all three subgroups.

Low carbon low alloyed steel grades

Low quantities of alloying elements require less time for addition. Often aluminium only is to be added into the ladle. The affinities of aluminium for oxygen and nitrogen are fairly strong (1). If aluminium is added at an early stage of tapping, its concentration in steel temporarily will be very high. So the steel is keen to pick up oxygen and nitrogen from ambient air. For that reason late aluminium addition is recommended. Quite the reverse, slag forming fluxes like lime should be added just after beginning of tapping. With that a liquid top slag will be formed at an early stage of ladle treatment which absorbs non-metallic inclusions.
The late addition of aluminium allows a pre-deoxidation of steel preferably with carbon. Contrary to any metallic deoxidizing elements carbon burns off to carbon oxide without leaving any trace in steel. The addition of carbon should be done permanently and smoothly while tapping to achieve an efficient pre-deoxidation. The pre-deoxidation must be stopped before any aluminium addition in order to avoid undesired carbon pick up.

By steel pre-deoxidation with carbon the required quantity of aluminium needed for deoxidation and the formation of non-metallic inclusions in steel will be reduced. Like in case of ULC/IF grades the inclusions consisting of alumina partly may modify to spinel.

The silicon content of low carbon grades often is limited by low values like that of ULC/IF-grades. For that reason no calcium silicon treatment is possible. So clogging must be avoided with argon on stopper like in case of ULC/IF grades.

Usually carry-over of furnace slag takes place at the end of tapping after pre-deoxidation has finished. For that reason the iron oxide contents in slag cannot be affected or decreased by pre-deoxidation. Therefore the carry-over of slag is more detrimental in case of low carbon grades even if they are pre-deoxidized compared to ultra low carbon grades.

Remaining iron and manganese oxides in ladle slag are a permanent source for increasing oxygen activity in steel-reoxidation. That may require late aluminium additions during ladle treatment resulting in late formation of alumina inclusions. The chance to float them out of the steel is low. That may result in serious clogging. Often the casting process can be maintained by increasing argon flow rate on stopper. The non-metallic inclusions deposited in SEN break off and settle down in the solidifying slab. Besides this, increased argon flow rates on stopper cause additional turbulence in mould. With that, drops from mould powder slag can be entrapped and remain in liquid steel in addition to the alumina and spinel inclusions from ladle treatment.

Alloyed and Desulphurized Steels

Desulphurisation of Al-killed steels in ladle usually is a reaction between steel and slag. It takes place according to following reaction equations:(4)

3. $FeS + CaO \leftrightarrow FeO + CaS$

4. $3FeO + 2Al \leftrightarrow Al_2O_3 + 3Fe$

Σ $3CaO + 3FeS + 2Al \leftrightarrow 3CaS + Al2O3 + 3Fe$

It can be taken from the above mentioned equations that two preconditions have to be met for an efficient desulphurisation process:

1. The activity of CaO in slag must be as high as possible, i.e. in ladle slag must be lime saturated as indicated in Figure 3.
2. Iron oxide content or oxygen activity in steel has to be as low as possible and correspondingly the aluminium content in steel should be as high as possible.

Beyond this, turbulent mixing of slag and metal is necessary to let the reaction go ahead. To take advantage of the turbulence during tapping synthetic slag and alloying elements including aluminium should be added at an early stage of ladle treatment. Moreover, by means of early aluminium addition the initial aluminium content in steel is fairly high. With that ideal preconditions for an efficient desulphurisation are ensured right from the beginning of ladle treatment. Moreover, by early addition a rapid and completed dissolving of all alloying elements is ensured during tapping even in case of large bulks.

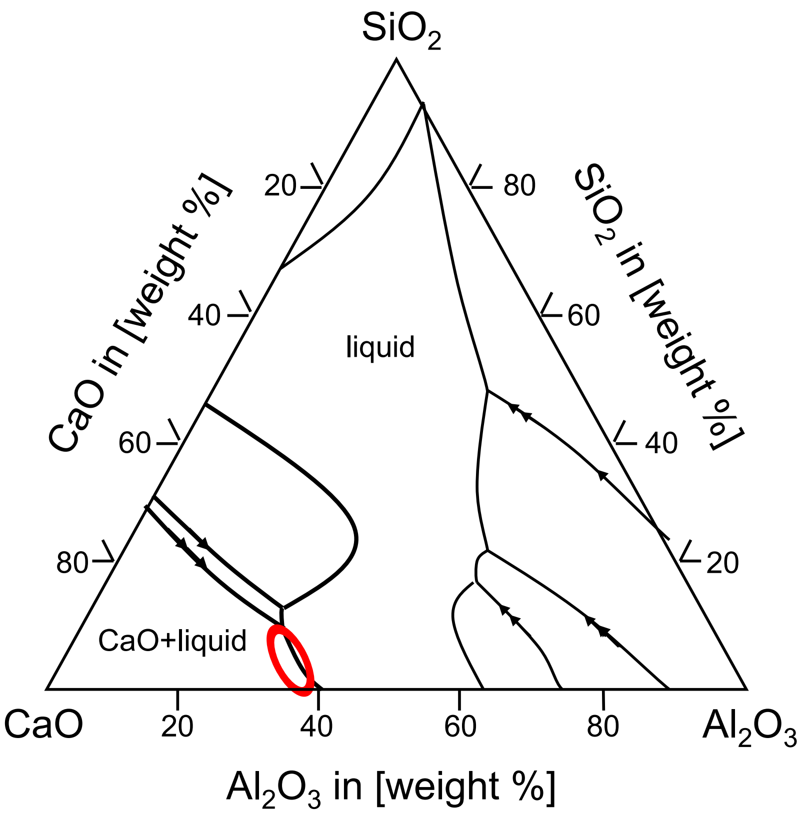

Figure 3: CaO Saturation in the Ternary System CaO- Al_2O_3-SiO_2

According the chemical reaction resulting from equations 3 and 4 alumina is formed during desulphurisation in addition to alumina precipitated while deoxidation.

The ladle treatment of desulphurized grades is more intensive than that of low carbon grades. So the amount of alumina inclusions modified to spinel inclusions is increased. Especially during vacuum treatment of Al-killed grades additionally non-metallic inclusions are formed. According to reaction equation

5. $3(MgO) + 2[Al] = (Al_2O_3) + 3\ [Mg]$

MgO from refractory and/or top slag is reduced by aluminium resulting in the formation of alumina and metallic magnesium (5). Partly magnesium vaporizes out of liquid steel and partly reacts with alumina in the steel to spinel according equation

6. $3[Mg] + 4(Al_2O_3) = 3(MgAl_2O_4) + 2[Al]$

So, especially grades with highest demands on cleanness like desulphurized and vacuum degassed sour gas pipes are charged with non-metallic inclusions from all different chemical reactions.

The melting temperature of the inclusions consisting of Al_2O_3 and/or $MgAl_2O_4$ is above 2000 °C. These solid inclusions cause serious clogging when passing the submerged entry nozzle. Usually the specified silicon contents of alloyed and desulphurized grades are not restricted to lowest values. That allows application of silicon calcium for modification.

Solid alumina in steel is modified into liquid alumina by calcium treatment according to reaction equation:(6)

1. $3n[Ca] + (Al_2O_3) \leftrightarrow (1-n)(Al_2O_3)*3n(CaO) + 2n[Al]$

According to the binary diagram CaO-Al_2O_3 in Figure 4 the alumina inclusions start to become liquid as their analyses exceed the composition of CA_2 ($2CaO*Al_2O_3$) containing 21% of CaO.

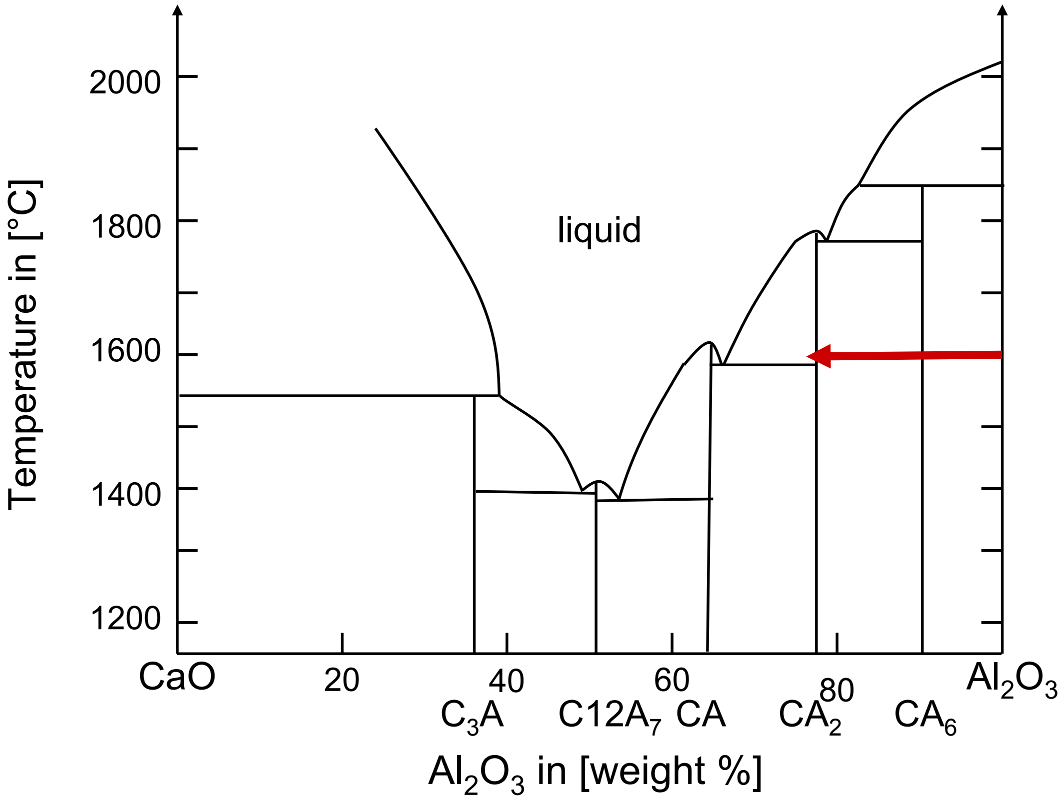

Figure 4: Binary Phase Diagram CaO-Al_2O_3.

Modification of spinel inclusions can be displayed with the help of the ternary diagram CaO-Al_2O_3-MgO shown in Figure 5.(4) The dotted line between $MgAl_2O_4$ and CaO shows the theoretical modification path of pure spinel by calcium in direction of the CaO-rich corner. In practice spinel modification by calcium treatment follows the red arrow starting from $MgAl_2O_4$ in direction to the liquid field.

The binary field of spinel and liquid is reached immediately. Contrary to that the blue arrow representing the modification of Al_2O_3 by calcium treatment stays in the solid field until it reaches the composition of CA_2 containing 21 % of Al_2O_3. To avoid clogging the inclusions do not need to be fully modified from liquid to solid. It is reported that clogging will be avoided as inclusions contain more than 50 % liquid shares. This is the case as compositions of inclusions are centrally located either in the binary field of CA_2 + liquid or in the binary field of spinel + liquid. That suggests that spinel can be modified more easy than alumina.(4)

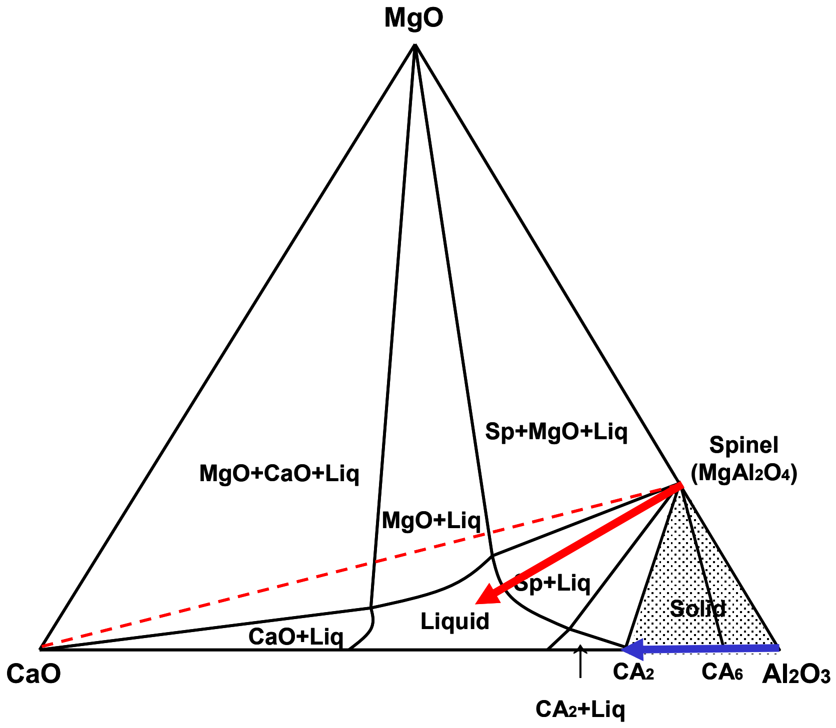

Figure 5: Oxide Modification in the Modification Ternary System CaO-Al_2O_3-SiO_2.

The ternary system Ca-Fe-Si shown in Figure 6 and the corresponding partial pressures of calcium contribute to better understanding of steel treatment with calcium-silicon. In the ternary system an extended miscibility gap exists starting from the binary system Ca-Fe (7). After feeding into liquid steel calcium-silicon containing for example 40 % of calcium initially becomes liquid. The liquid drop enriches in iron until its chemical composition reaches the miscibility gap in point **B**. Afterwards the liquid drop decomposes into an iron rich and a calcium rich phase. As indicated in the upper diagram of Figure 6 the calcium rich phase vaporizes when point **D** is reached as its calcium content exceeds 80 %. In order to suppress vaporization of calcium by ferrostatic pressure calcium-silicon must be put deeply into liquid steel either by lance injection or wire feeding. The composition of the phase corresponding to **D** is represented by point **E** close to the Fe-rich corner in the lower diagram of Figure 6. So the solubility of iron or steel for calcium is extremely low.

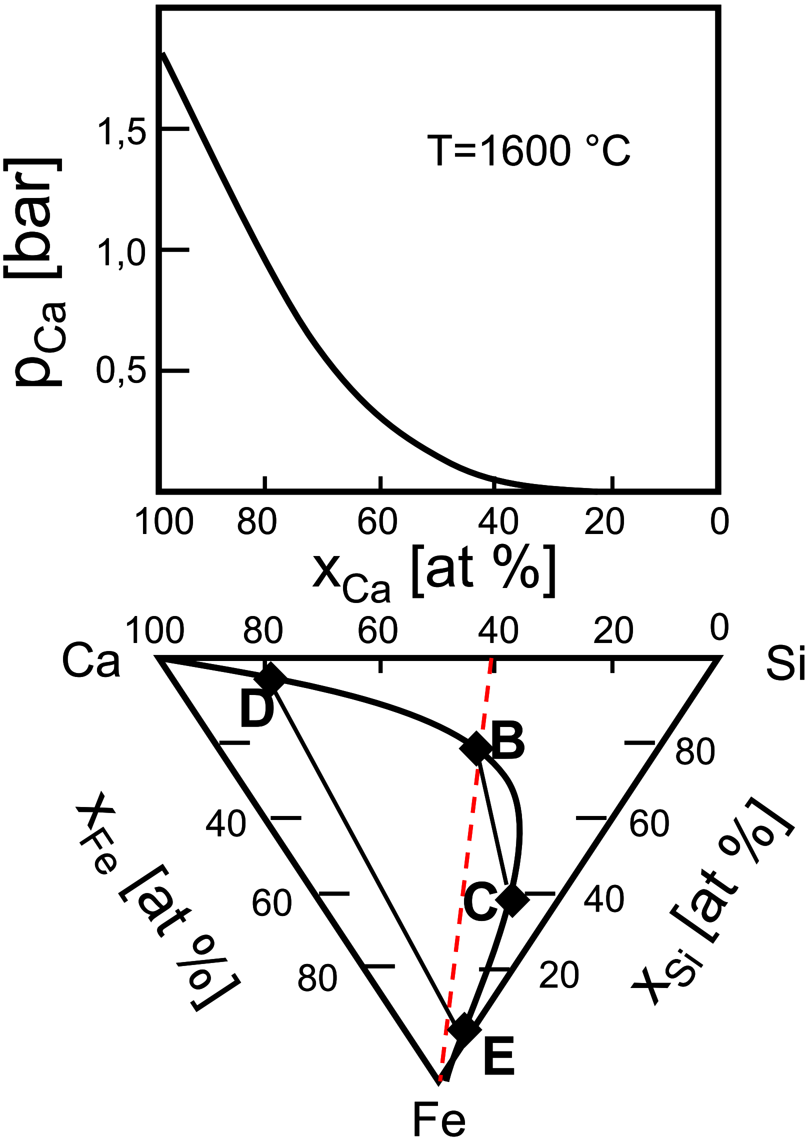

Figure 6: Dissolution, Phase Separation and Vaporization of Calcium.

The vaporisation of calcium causes turbulent flow in ladle. For that reason no additional argon stirring is required for steel homogenization. Even after Calcium treatment soft bubbling is not recommended. The argon bubbles enrich in calcium dissolved in steel. So calcium would leave the liquid steel inside the rising bubble. Indeed the argon bubbles capture the modified inclusions and float them out of the liquid steel. Under that condition the amount of non-metallic inclusions in liquid steel at the end of ladle treatment is low. Despite of that, clogging may occur especially on the background of low calcium content in steel.

Liquid steel on its way from ladle via tundish into mould cools down considerably to liquidus temperature. As indicated in Figure 7 the common solubility of steel for aluminium and oxygen declines with decreasing temperature. The inclusions formed by that so called secondary deoxidation are consisting of pure alumina. In addition non-metallic inclusions caused by ingress of air into slide gate system and connection between inner nozzle and SEN are consisting of alumina as well. As the amount of inclusions modified to liquid calcium aluminates in the steel as well as its calcium content is at the end of ladle treatment, there is no potential to modify alumina inclusions from secondary deoxidation and reoxidation. In other words: both, modified inclusions as well as small amounts of metallic calcium in steel contribute to prevention of clogging caused by secondary deoxidation and reoxidation. For that reason the strategy must be as follows: The non-metallic inclusions should be floated out to the greatest possible extend before calcium treatment by soft bubbling. After calcium treatment no soft bubbling is recommended anymore.

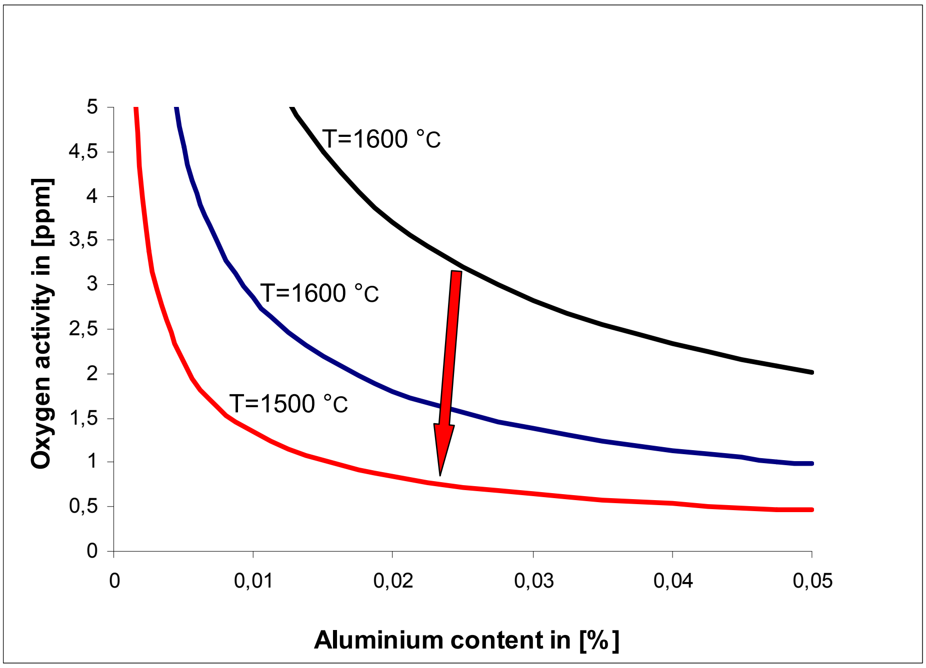

Figure 7: Solubility of Aluminium and Oxygen in Steel.

As required the element titanium should be added after calcium treatment. That ensures, that steel is fully deoxidized and the amount of titanium oxide formed after addition is on lowest level. Otherwise it may happen that TiO_2 precipitated in steel is modified to perovskite ($CaTiO_3$). Since its melting point is 1970 °C perovskite in mould powder slag may lead to its malfunction.

RESULPHURIZED STEELS

Usually steels with controlled sulphur contents are aluminium killed. According to the reaction

3+4. $3CaO + 3FeS + 2Al \leftrightarrow 3CaS + Al_2O_3 + 3Fe$

alumina is formed during desulphurisation. In order to keep the amount of alumina inclusions on a low level, no desulphurisation is recommended. On the other hand it must be pointed out that during subsequent oxide modification with calcium simultaneously desulphurisation according to reaction equation

2. $Ca + FeS \leftrightarrow CaS + Fe$

may take place. Higher initial sulphur contents as well as increased amounts of calcium put into steel push the reaction ahead. Besides alumina, inclusions based on calcium sulphide may cause serious clogging as well. There is either the danger of suffering from alumina clogging in case of heats desulphurized before calcium treatment or the danger of CaS clogging without any previous desulphurization. As indicated in Figure 8 besides steel analysis and steel temperature it is important to find the right window for inclusion composition, especially in the case of resulphurized grades. Anyway adjustment of sulphur must be done after calcium treatment. Aluminium contents in steel close to the lower end of specification require low amounts of calcium addition to prevent alumina clogging. Under that condition formation of CaS is moderate.

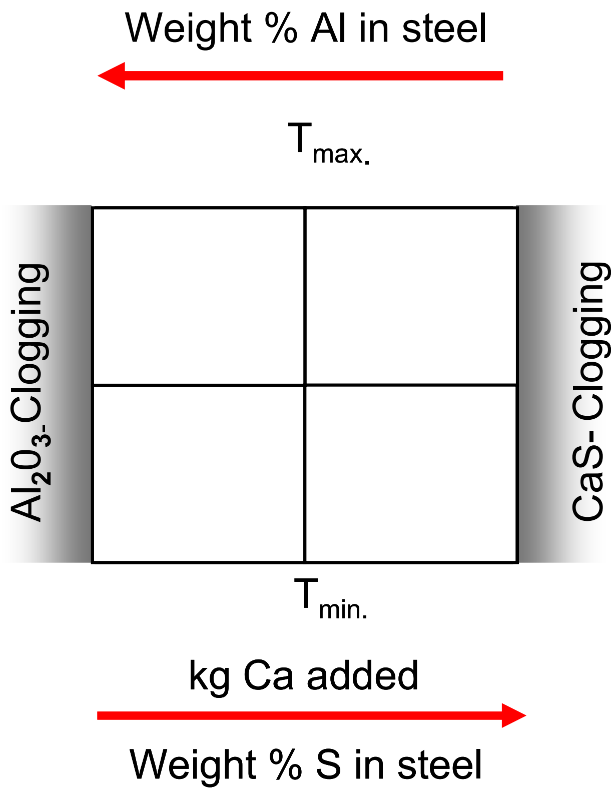

Figure 8: Conditions for Al_2O_3 and CaS clogging.

Summary

While deoxidation with aluminum, inclusions based on alumina are precipitated in steel in ladle. These non-metallic inclusions may modify to spinel during subsequent ladle treatment. Basically the quantity of aluminum required for deoxidation depends on the content of dissolved oxygen in steel and the amount of iron oxide in the furnace slag which was carried over into ladle. Until end of ladle treatment, iron oxide is a potential source for reoxidation, i.e. formation of additional non-metallic inclusions in steel.

Depending on relevant steel grade different opportunities exist to prevent formation of additional non-metallic inclusions in steel. Unavoidable inclusions must be floated out of the liquid steel to achieve maximum quality of final product and to avoid clogging in SEN. Remaining non-metallic inclusions in steel should be modified by calcium treatment to ensure smooth casting process.

Steel reasonably cools down on its way from tundish into mould. Under that condition non-metallic inclusions are formed by secondary deoxidation even though the steel was clean previously. Calcium dissolved in small quantity in steel and liquid non-metallic inclusions contribute to keeping the SEN free from alumina depositions. For

that reason the amount of non-metallic inclusions in steel should be as low as possible and floated out by soft bubbling already prior to calcium treatment.
In order to avoid undesired non-metallic inclusions some alloying elements like titanium and sulphur should be added after calcium treatment.

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