Dynamic de-oxidation and inline alloying of Al in continuous casting of billets and strips

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The method of controlled stepwise de-oxidation and alloying of carbon steel melt with Al-wire has been investigated. The melt is pre-deoxidized in the ladle, the main fraction of non-metallic inclusions is removed to the ladle top slag by stirring. Final de-oxidation and alloying takes place just before solidification in the continuous casting mould. In three steps from laboratory via a pilot facility to an industrial caster the efficiency of that method was tested. No disadvantage could be found; the benefits are high amount of [Al]diss., high <Al> yield rate, better macro-cleanliness, and improved process quality by avoiding depositions and clogging. By that method, the production of Al-killed carbon steel grades should be possible also with near-net-shape casters which use in general small orifices in tundish and SEN.

KEYWORDS: continuous casting, de-oxidation, clogging, cleanliness, near-net-shape casting

INTRODUCTION

In continuous casting the liquid steel is guided through a throttle which regulates the melt flow. The narrowest point can be either in the orifices of submerged entry nozzles (SEN) in the mould or at the bottom of the tundish where a metering nozzle or valve like slide gate or stopper rod is installed [1]. At that narrowest point the melt flow velocity and also the pressure conditions are changing severely. Here, small oxidic inclusions suspending in the steel melt can come in touch with the refractory walls, and by high turbulence contact between those inclusions takes place. Heat flux from melt into refractory material changes local temperature so that in connection with change of pressure the local thermodynamic conditions in parts of the steel melt are changing. In addition, microscopic cracks in refractory material or poor clearance in the contact areas of slide gate plates or at flanges of SEN can allow pick-up air; by chemical reaction this oxygen is able to form further oxidic inclusions in the steel melt. A redox-reactions between alloyed [Al]diss. and slag, refractory or slide gate powder can increase the amount of alumina particles dispersed in steel melt [2]. Oxidic inclusions can stick to the refractory walls and form layers which are growing during the casting time. The layers are able to block the melt flow with the result of stopping the casting process; parts of the layers can break and flow into the mould where they are entrapped in solidifying steel shell and lead to poor macroscopic cleanliness. In both cases the quality of the as-cast steel will be diminished. Many steel grades require a certain aluminium content which is prescribed in technical standards. Aluminium diminishes the amount of free, dissolved oxygen in steel so that reactions of oxygen with e. g. carbon is suppressed, and the formation of (CO) bubbles which would lead to a weak strand shell or to rimming in the mould is avoided by so called total oxygen killing. Further-on, alloyed aluminium is able to control grain grows in hot rolling by (AlN) particles which are formed during hot rolling [3] by recombination of (N 2) in the later product is suppressed. In some steel grades like dual phase steel aluminium is alloyed to stabilize a certain fraction of ferritic grains in the final structure. Aluminium is a chemical element with high affinity to oxygen, and the reaction product Al2O3, called alumina, is a stable oxide with a melting point of appr. 2,050 °C. Those particles are formed by mechanisms mentioned above, and their initial diameter is about 1 µm; in terms of steel cleanliness the field of micro-cleanliness is affected. By agglomeration supported by the relatively high interfacial energy between alumina and steel melt the particles can grow rapidly by agglomeration and form macro-inclusions. When their size becomes 30 µm and more by clustering (Figure 1, [3]), those particles are degrading the steel quality in the field of macro-cleanliness, e. g. the ductility behaviour. Further-on, in the casting process those particles can block the free cross-section in the metering nozzles or the SEN; that clogging terminates the pouring duration (Figure 2, [4]). One method to overcome the clogging problem is the addition

FIG. 1 Poor macro-cleanliness by clustering of alumina particles [3].

Scarsa macro-pulizia dovuta ad agglomerati di particelle di allumina [3].

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of calcium by ladle metallurgy [5]; the formed calcium-aluminates are liquid at pouring temperature so that plating effects are avoided. Concerning macro-cleanliness that method is not the ultimate solution, but helps to prevent of clogging during casting sequences.

Particularly, small cross-sections of metering nozzles and SEN of billet or strip casters are affected by clogging problems on alumina basis. In many cases aluminium addition has to be avoided, and the oxygen in steel is killed by [Si] and [Mn]. The steel grades containing higher concentrations of aluminium cannot be produced in those cases. To overcome this problem a method of adding aluminium in several subsequent steps in the process chain has been investigated; the required dissolved aluminium content is alloyed by ‘DDA, Dynamic-Deoxidation-Alloying’ or ‘alloying on demand’.

THEORETICAL BACKGROUND

The formation of dangerous alumina particles starts spontaneously by almost homogeneous nucleation in the melt when the solubility product of the reaction

$$2 \text{[Al]} + 3 \text{[O]} \rightarrow \text{(Al}_2\text{O}_3) \quad \text{with} \quad L_{\text{Al}_2\text{O}_3} = [a_{\text{Al}}]^2 \cdot [a_{\text{O}}]$$

is reached. This temperature depending reaction is described by

$$\log_{10} K_{\text{Al}_2\text{O}_3} = -64,000/T + 20.57$$

and

$$L = 1/K$$

at 1,600 °C.

The following steps of formation of micro- or macro-inclusions on the basis of stable nuclei are [7]:

- growth by diffusion,
- Ostwald ripening,
- gradient, Brown, turbulence, or Stokes collisions.

The idea of control the particle formation is the application of aluminium to the steel in the ladle up to an amount which diminishes the oxygen concentration to about $[a_{\text{O}}]=20$ ppm (totally killed steel), remove the particles as far as possible by ladle metallurgical treatment e. g. by soft bubbling Ar stirring, and add the required dissolved aluminium by alloying in tundish, SEN, and in mould. The dynamic alloying shall be based on the result of an inline-measurement of oxygen activity e. g. using a Celox®-system. Here, not the $[O]_{\text{disc}}$ is minimized, but the $[Al]_{\text{disc}}$ to prevent of alumina formation. The following example shows the way of estimation of aluminium mass flow into the melt which is required to meet correctly the demanded final $[Al]_{\text{disc}}$ value in the steel just before solidification (Figure 3).

1) start-up oxygen content in the melt before de-oxidation, $[O]_{\text{start}}$: 100 ppm

demanded oxygen content at solidification, $[O]_{\text{final}}$: 3 ppm

demanded diss. aluminium content in the as-cast strand, $[Al]_{\text{final}}$: 400 ppm

2) Aluminium is added into the melt to diminish $[O]_{\text{disc}}$ to about 20 ppm, and the alumina is removed to the ladle top slag by stirring; $[O]_{\text{disc}}$=80 ppm; the corresponding $[Al]_{\text{disc}}$ concentration at 1,600 °C is about 0.002 wt% (resp. eq. (1) and (2)).

3) The demanded $<Al>$ is fed by Al-wire into the melt during pouring; $[Al]_{\text{demand}} = [Al]_{\text{de-ox}} - [Al]_{\text{disc}} = 400 - 20 = 380$ ppm; (3)

if there is a leakage of oxygen the unwanted oxygen flux rate of $d[O]/dt$ must be taken into account.

The mass flow of aluminium is calculated by

$$\dot{m}_{\text{Al,wire}} = \dot{m}_{\text{steel}} \cdot [\%\text{Al}]_{\text{added}}$$

(4)

$$\dot{V}_{\text{wire}} = \rho_{\text{Al}} \cdot \dot{m}_{\text{Al,wire}}$$

(5)

$$\dot{V}_{\text{wire}} = \rho_{\text{Al}} \cdot \dot{m}_{\text{Al,wire}}$$

(6)

The DDA method can be carried out by spot measurement of oxygen activity or by using a continuously working probe. For fully automated [Al]-feeding that continuous method would be preferred but there are no commercial probes available. To overcome that lack a development of probes has been started by the company Heraeus-Electronite and RWTH Aachen University where the measuring period of a Celox®-probe based on electromotive forces was extended from regularly 15 s to 2 min [3].

EXPERIMENTAL SET-UP

The DDA method has been tested in 3 steps:

1) In the beginning the twin roll casting process was the goal to approve castability and macro-cleanliness of carbon steel grades. The near-net-shape casting process and laboratory experimental simulations have been described in an earlier publication [8]: The furnace, the runner system and the casting tundish including the SEN of the RWTH Aachen twin roll caster at the Dept. of Metal Forming were copied for pouring experiments at the Dept. of Ferrous Metallurgy. There, a 500 kg induction furnace prepared the
carbon steel melt, and pouring experiments were carried out using the spot and continuous measurements of oxygen activity. The Al-wire with a diameter of 4 mm has been continuously added to the pouring melt with the \( \text{dmAl}/\text{dt} \)-value which was estimated by eq. (3-6) (Figure 4). Further experiments with similar set-ups and different heat sizes were carried out to confirm the results.

2) After those successful experiments the step of validation at a real twin roll caster has been done. Industrial strip casters are described in [9]. The Institute of Metal Forming (IBF) runs a Bessemer type twin roll caster in cooperation with ThyssenKrupp Steel AG. The pilot plant-size caster consists of two water cooled steel rolls, each with a nickel coated copper sleeve, resulting in an outer diameter of 590 mm and a width of 150 mm [10]. Casting duration is about 3 min limited by the furnace capacity.

In twin roll casting of steel strip, steel melt is poured into the roll nip of the counter-rotating rolls. A ‘melt pool’ is formed by the rolls and two ceramic side dams. The melt solidifies on the cold surfaces of the rolls, forming two layers of solid steel which are combined at the narrowest position by a slight force. The melt flows from the induction furnace with a capacity of 165 kg to a runner system and subsequently into the tundish; from here the melt is guided to the melt pool (Figure 5).

After melting and killing with [Si] and [Mn], a sample was taken and the oxygen activity in the melt was measured by a Celox®-system. The result was used to calculate the demanded mass of aluminium for further pre-deoxidation to \( [\text{O}]_{\text{dis.}} = 20 \text{ ppm} \). For comparison, the chemical composition of a synchronous sample from the melt was measured using a spark emission spectrometer. This procedure was repeated after 4 min to evaluate the efficiency of the pre-deoxidation. After reaching the superheat temperature of 1,700°C the furnace was tilted with a defined rate to start-up the cast. The dynamic alloying of Al-wire with diameter of 4 mm in the tundish started 25 s after the first melt-roll contact. The spooling-in was carried out manually. The feeding rate of the Al-wire was calculated as a function of steel mass flow, the content of residual dissolved oxygen and the final aimed \( [\text{Al}]_{\text{dis.}} \) concentration. The feeding rate was about 1.12 cm/s, as seen in the following calculations:

\[
\text{(7)}
\]

\[
\text{(8)}
\]

\[
\text{(9)}
\]

A cold Al-wire will freeze-up a thin layer of steel before it starts to smelt; the time of re-smelting is about 1...2 s depending on the diameter of the wire and steel superheat [11].
3) Following the twin roll casting tests the application of DDA to an industrial billet caster was done to investigate the long term reliability and metallurgical precision. The 3-strand CC machine produces carbon steel billets with 130 mm square cross section. The steel melt is prepared in an EAF and in a ladle furnace. In those trials an oil lubrication in the moulds has been applied. The metering nozzles in the tundish bottom had diameters of 18 mm. No further shrouding has been used. An aluminium wire with 2.5 mm diameter was fed into the free falling pouring jet directly above the meniscus in the mould by a commercial spooling machine which is normally used in automatic welding systems (Figure 6).

The pre-deoxidation of the melt with $[C]=0.18$ wt%, $[Si]=0.24$ wt% and $[Mn]=0.96$ wt% has been done by Si-Mn-alloying in the ladle. The steel temperature in the tundish was 1,577 °C, and the Celox measured $[O]$ diss. concentration was 36 ppm. The calculation of the wire spooling velocity which was demanded to reach the final $[Al]$ diss. concentration of 400 ppm concerns to the scheme mentioned above (eq. 7-9); the wire velocity of 63.78 m/min resp. 1.063 cm/s was adjusted at the spooling device.

RESULTS

1) Laboratory furnace: The results of the laboratory test of 500 kg-induction furnace equipped with a runner and tundish system have been reported in [8]. Laboratory tests using a copper sampler for catching steel and inclusions were performed. 95% of the rapidly solidified steel samples show inclusion diameters of less than 5 µm when the inline Al-wire application was used, in comparison to a value of 14 µm at conventional Al alloying in the furnace (Figure 7). The $[Al]$ yield increased from appr. 35 % to more than 92 %.

2) Twin roll casting: In the first trial, the dual-phase steel grade DP600 was prepared. After melting, $[O]_{\text{diss.}}$ was approx. 87 ppm. Considering the steel mass of 165 kg, the amount of $<\text{Al}>$ needed for the pre-deoxidation was calculated to 21 g, assuming a yield of 50 %. After 4 min the concentrations were $[O]_{\text{diss.}}=20.2$ ppm oxygen (by Celox) and corresponding $[Al]_{\text{diss.}}=18$ ppm at 1,600 °C. After 25 s the inline-alloying with Al-wire into the tundish was started. Strip casting speed was about 40 m/min. After the process became stable, the Al content was distributed with a mean value of 0.047 + 0.009 wt% in the as-cast strip; the yield of $[Al]_{\text{diss.}}$ in the as-cast steel could be determined at 95.8 %. The deviation is explained by the not constant Al-wire feeding rate by manual spooling. In a 2nd trial, the feeding rate of the wire was changed in a controlled way during the casting time. The dissolved $[Al]$ content was similar to the results of the first trial. The $[Al]$ concentration in the strip reacted with a small delay to changes in the feeding rate.

After the trials, the surface of the as-cast low carbon strip was inspected; no slag spots or cracks were found. No extraordinary signs of wear or skulls were observed at refractory material of tundish, side-dams, or SEN. The microstructure of the strips was observed and compared to conventionally alloyed strip with same casting conditions. The identification of size and distribution of the inclusions was carried-out by 2-dim. metallographic analysis of steel samples on determined positions in the strip length the images were interpreted by commercial image analysis software, which counts the number and size of inclusions on a defined area. Energy Dispersive X-ray Analysis confirmed that the majority of the inclusions are $\text{Al}_2\text{O}_3$ particles which have been formed in the melt.

The investigated metallographic samples indicate that the sizes of inclusions formed during the conventional alloying technique are bigger compared to the inline alloying technique [3]: The DDA method made sure that alumina particles are finer dispersed as in conventionally alloying in the furnace. Furthermore, the inclusions formed during the conventional technique tend to cluster due to collision mechanisms during the flow from furnace to the casting rolls. In both, tundish and SEN, turbulent flow patterns dominate which promote turbulent collisions between particles and result in inclusion growth by agglomeration.

By inline alloying of Al-wire into the tundish, the free residual-oxygen was killed by the spooled-in wire. Since these newly formed particles have a short residence time, and the collision events are restricted, too. Those particles flow directly through the bottom orifice of the tundish through the SEN into the pool between the rolls. The maximum inclusion size obtained by the inline alloying technique was found to be 11.4 µm (Figure 8). With the conventional technique, clusters with sizes up to 76 µm have been
detected. Inline alloying by DDA method in the tundish diminishes the total residence time in comparison to conventional alloying in the furnace, and so the agglomeration time of alumina particles. The diagram indicates that in the inline alloyed strip 90% of the inclusions are smaller than 4 µm and in contrast, 90% of the inclusions in the conventional technique are smaller than 15 µm. The slight slope of the cumulative frequency curve of conventional alloyed strip is again explained by the growth rate of the inclusions between the furnace and the roll nip. A similar observation was carried out at samples from another length position of the as-cast strip. During inline alloying, a small amount of particles, which do not flow directly through the orifice and circulate by turbulence, meet an estimated time of residence of t=22 s [12]. According to the model of Zhang and Lee [13] particles can grow in this time to a maximum size of 9.6 µm.

In all cases, no clogging occurred during the casting period of 3 min. The yield of [Al] diss. could be increased by the prevention of re-oxidation due to inline alloying from appr. 52 % to more than 92 %.

3) Industrial billet caster: The DDA method was applied to one mould for the duration of 6 min. No casting problems occurred. The Al-wire was spooled exactly into the free falling melt jet to prevent of asymmetric enrichment of [Al] in the solidifying shell. For metallographic investigations the corresponding as-cast billet with a length of 11.3 m was investigated; three cross section samples with 10 mm thickness from positions ‘head’, ‘middle’, and ‘tail’ have been taken.

The chemical analysis was carried out by emission spectroscopy as well as by chemical analysis. The concentration of [Al] diss. was 0.0366 wt%+6 ppm versus length and +4…6 ppm in the cross sections; compared to the aimed value of 0.040 wt% of [Al] had the ratio of [Al] diss./[Al] tot. was 366/400 *100 %=91.5 %. Those results show that the pre-calculated wire feeding rate and the application had been adjusted correctly.

The metallographic analysis resulted in fine disperse alumina which were identified by EDX-analysis in a scanning electron microscope in addition; in some cases particles containing Si and Mn have been found. No cluster formation could be observed. The distribution of the non-metallic particles is similar to results of the laboratory and strip caster experiments. The size of the alumina inclusions were almost between 1 and 2 µm, 90% of the particles are smaller than 4 µm (Figure 9). A single bigger inclusion reached the size of 15 µm. This result is representative for all 3 investigated cross section samples in the billet.

CONCLUSIONS

The dynamic de-oxidation alloying (DDA method) allows the final de-oxidation and the alloying of carbon steel melt with aluminium on the point, that means with high yield of added aluminium, and with small deviations of [Al] diss. from the required concentrations. By this method, big particles influencing the macro-cleanliness of the steel can be avoided since the duration of agglomeration controlled growth is decreased significantly. Excess oxygen after pre-deoxidation and entrapped oxygen from leakage in the shrouding systems is bound by alloyed aluminium just before solidification so that the Al₂O₃ particles stay small, al-

FIG. 8 Cumulative frequency of alumina grain sizes: comparison of ‘inline alloyed’ (DDA) and conventionally de-oxidized and alloyed samples. Left: steel grade ‘Dual Phase DP 600’. Right: steel grade ‘Low Carbon’.

Frequenza cumulativa delle dimensioni dei grani di allumina: confronto fra provini con alligazione in linea (DDA) e con disossidazione e alligazione convenzionale. Sinistra: acciaio tipo bifasico DP600; Destra: acciaio tipo a basso carbonio.

FIG. 9 Cumulative frequency of alumina grain sizes: Results of 3 different billet cross section samples.

Frequenza cumulativa delle dimensioni dei grani di allumina: risultati di provini relativi a 3 billette con diverse sezioni trasversali.
most less than 4 µm, influencing only the degree of micro-cle-
anliness. The biggest particles have a diameter of about 15 µm by short-time-agglomeration.

During the 3 min cast with small SEN at the twin roll caster nei-
ther clogging nor deposition of alumina could be noticed; this behaviour is also expected for long term castings. With conti-
uous casting of billets no clogging could occur because the <Al-
alloying took place just above the meniscus. The feeding rate of Al-wire can pre-calculated at high accuracy and by automatic feeding control the recent casting speed can be taken into ac-
count. The feeding point must be adapted in a proper way to avoid super-saturation in the billet cross-section to prevent break-outs by weak shell. The distribution of [Al] in strip and billet was sufficient in all cases. Smelting of Al-wire and solution of liquid [Al] in the steel melt flow worked without any problem. Good results of DDA method application are also expected at other CC processes using relatively small SEN like Thin Slab Ca-
sting [14], or Single Belt Casting [15].

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