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Actual review on secondary metallurgy

Secondary metallurgy, that means the treatment of liquid steel, began in the 1950ies. Before its application the steel was finished in the applied steelmaking processes. Due to the further development and the reduced tap-to-tap times of the oxygen converters and the electric arc furnaces today these plants are only able to refine liquid hot metal, steel scrap and/or DRI to liquid crude steel. In addition to this the development of new much more high sophisticated steel grades with extreme cleanness requires especially accurate fine tuning. This is only possible with the use of the today state-of-the-art technology for secondary metallurgy *(1)*.

TASKS OF SECONDARY METALLURGY

Main target of secondary metallurgy is the conditioning of the liquid steel to achieve a homogeneous chemical composition, an exact casting temperature and a very high steel cleanness level. The tasks performed generally fall into the following categories *(2, 3)*:

- Achievement of the requested alloy analysis;
- Homogenization of the temperature and the chemical composition of the steel melt as well as control of the temperature;
- Deep decarburisation;
- Desulphurisation;
- Dephosphorization;
- Removal of trace elements;
- Degassing;
- Deoxidation;
- Spheroidisation of inclusions;
- Improvement of cleanness;
- Control of the solidification structure.

Secondary metallurgy has led to fundamental changes in the technology of steel making. These processes tailored to each specific product range are applied in all steel works today. The number of special applications and modifications is huge. Secondary metallurgy are all processes for treatment of liquid steel in the steel ladle, in the vacuum facility or in the ladle furnace, in certain cases also in the oxygen converter or electric arc furnace as well as also in the continuous caster tundish and mould. As during the development of the secondary metallurgy processes the main emphasis was set on the ladles as metallurgical reactor, today the tundish of the continuous caster gain more importance in the process steps for steel production.

The basic process stages and measures performed for secondary metallurgy are summarized in *figure 1*:

- Preventing of slag carryover in the steel production units oxygen converter (BOF) and electric arc furnace (EAF);
- Mixing and homogenizing of the steel melt in the ladle by stirring-gas treatment with porous plugs, lances or with the aid of electro-magnetic stirring systems;

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- Charging of solids like alloying elements, injection of powder by lances and the spooling-in of cored wire;
- Vacuum treatment using various techniques like the ladle degassing, the RH (Ruhrstahl Heraeus) or the DH (Dortmund-Hoerder-Hüttenunion) process, the VOD (Vacuum-Oxygen-Decarburisation) process only to mention some;
- Heating processes in the ladle furnace and the VAD (Vacuum Arc Degassing) using an electric arc;
- Stream shrouding in the steel ladle and in the continuous caster tundish;
- Electromagnetic stirring during continuous casting.

The manifold basic measures and processes of secondary metallurgy are frequently combinable, giving rise to precisely defined sequences for the production of special steel grades and for ensuring compliance with defined tolerances of the alloying elements or other additions.

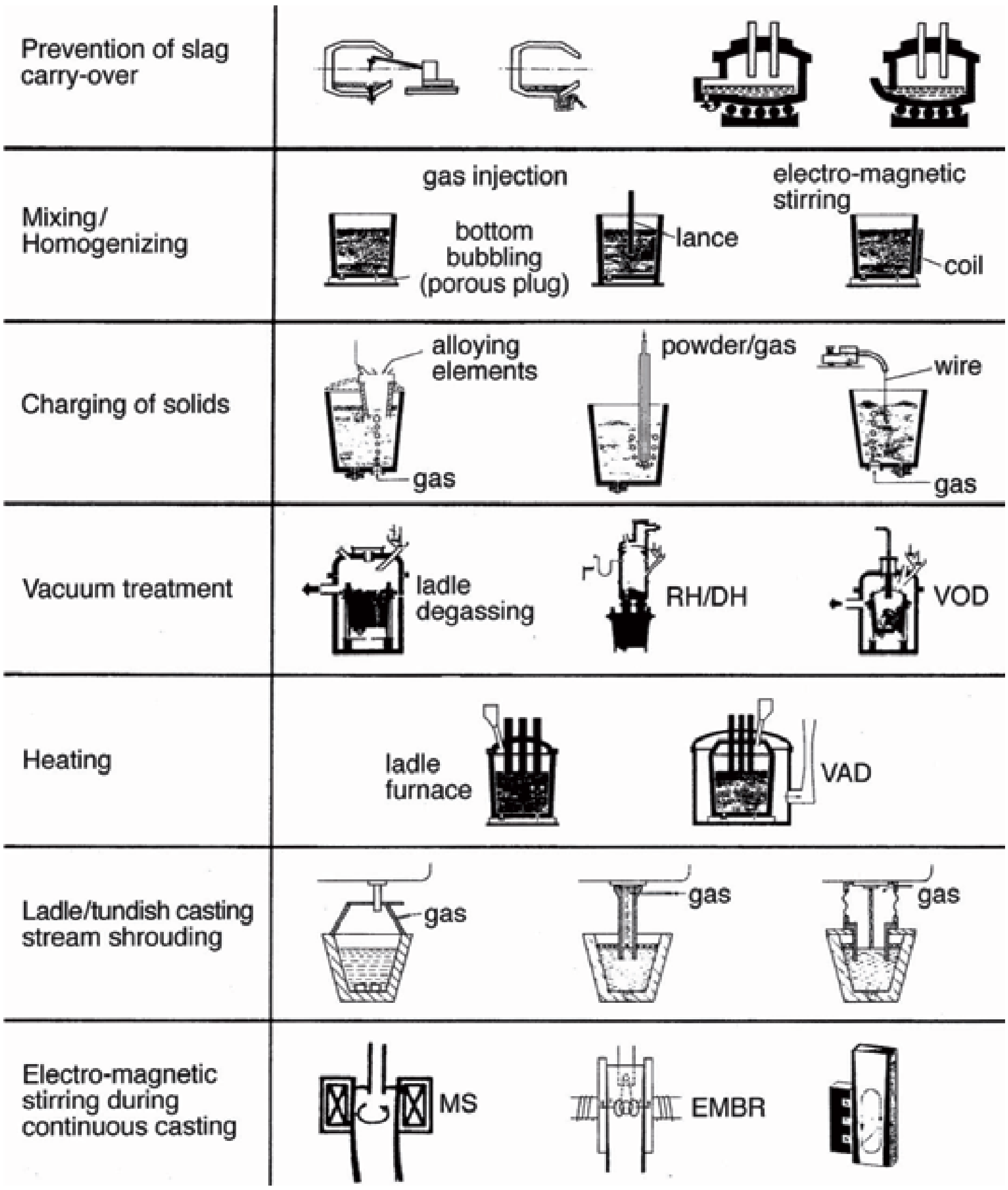

Fig. 1 - Secondary metallurgy measures *(2)*.

In the years of the developments in secondary metallurgy the efficiency of the steel treatment has been significantly improved. Table I shows typical achievable contents of undesired elements in steels *(4)*. Lower values can be reached for single elements but not for all simultaneously.

TABLE I: Achievable contents in ppm *(5)*.

Year / content	1960	1980	2000	Future
Carbon	250	150	20	10
Phosphorus	300	150	100 (50)	30
Sulfur	300	30	10	10
Nitrogen	150	70	30	20
Total Oxygen	30	30	10	10
Hydrogen	6	6	1	1
Total	1036	436	171 (121)	81

LADLE AND TUNDISH CONSTRUCTIONS

Ladles have a steel capacity of up to 400 t. A ladle consists of a steel shell and refractory materials *(fig. 2) (5)*. It should consist of a stable construction, allow high vessel temperatures, have a uniform deformation behavior, low refractory wear and a low vessel weight. The refractory lining has a wear and a permanent material as well as an insolating layer. It can be monolithic or bricked. The bricked solution uses dolomite and magnesia carbon bricks in the slag level area. Alumina oxide casting masses are used as wear lining for the monolithic solution. During the steel treatment in the ladle exothermic reactions stress the refractory materials. Chemically caused wear exists by the ladle top slag and by the reduction of the refractory materials under vacuum. Newest developments aim for an increased capacity of the ladles by reducing refractory thickness. Reducing the refractory thickness of a ladle with a capacity of 200 t by 10 mm increases the capacity by 2.5 t *(6)*.

Figure 3 shows the construction of the continuous caster tundish *(7)*. Its particularity is that the refractory lining in addition to protect the tundish shell takes over the function to control the flow stream, the gas intake, the casting level and the casting stream shrouding.

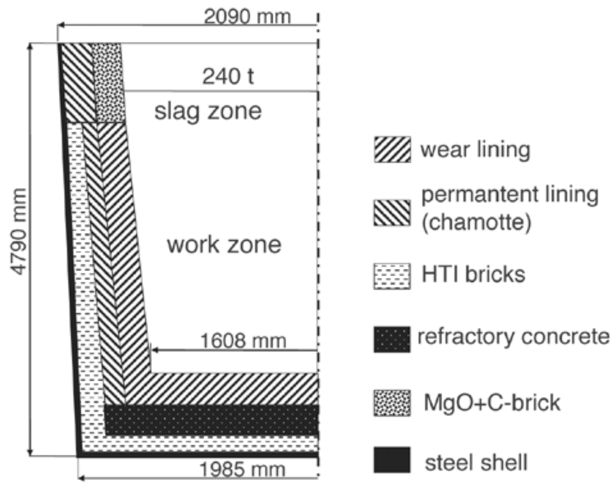

Fig. 2 - Scheme of ladle lining *(5)*.

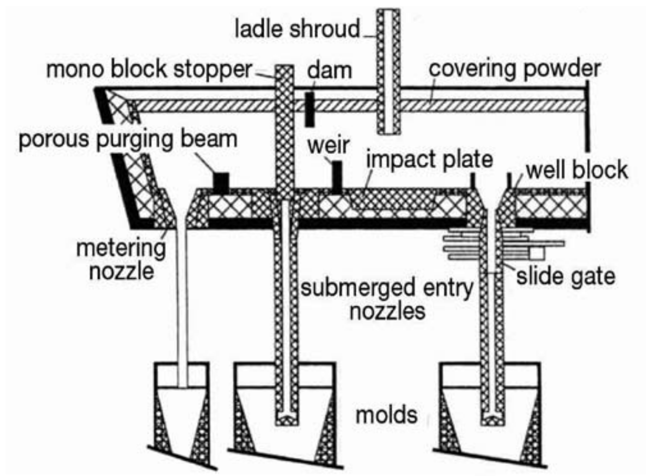

Fig. 3 - Components for tundish metallurgy *(7)*.

OVERVIEW ABOUT STEEL TREATMENT PROCESSES

Deoxidation

In steel melts without special deoxidation steps the reaction:

$$[C] + [O] = CO_{(g)}$$

takes place during solidification. The CO bubbles remain in the steel. This results in crack formation during forming of steel. In addition to this, inclusions negatively influence the properties of the steel. Therefore the special deoxidation step is one of the most important secondary metallurgy tasks for the production of high grade steels.

Deoxidation occurs by addition of special elements or via slags. The most important technical deoxidizing agents are constituents that have a specific affinity to oxygen (precipitation deoxidation), for example ferro-silicon (FeSi), aluminium (Al) and calcium/silicium (CaSi). The deoxidation products are either absorbed by the slag or remain in finely distributed and thus harmless form within the steel.

Deoxidation is increasingly performed in conjunction with other post-treatment processes. One example worthy of mention is that of deoxidation in conjunction with a vacuum treatment, or a stirring gas treatment under an absorbent slag covering. Furthermore, measures for deoxidation include calcium treatment of the melt and shrouding the flow of steel in the pouring stream during continuous casting.

The importance of complete deoxidation can be observed during the solidification of the steel. As the steel "freezes", the dissolved oxygen is largely set free and combines with the carbon to produce carbon monoxide, so doubling its initial volume. As it escapes from the melt, it causes the molten metal to "boil", with the result that the steel solidifies in its "unkilled" form (rimming steel).

This boiling process causes significant disruption during continuous casting and undesirable flow conditions which disturb strand shell formation and subsequent core solidification. It is also impossible to control the meniscus level of the molten steel in the conticasting mould. Steel continuously cast into a strand is therefore fully killed, i.e. undergoes full deoxidation.

Deoxidizing agents serve to extensively avoid the formation of carbon monoxide, so eliminating the problem of boiling and allowing the steel to "quietly" solidify. Cast killed steel does, however tend to absorb impurities and form inclusions.

Depending on the extent of the deoxidation process, a distinction is made between unkilled (rimming), semi-killed (semi-rimming), killed and specially killed steel. The choice between these various grades will depend on the application.

Deoxidation can be achieved by a various number of elements, like carbon, manganese, aluminium, silicon, calcium, zirconium or titanium. Titanium, aluminium and zirconium have a strong deoxidation effectiveness, chromium and manganese a poor *(fig. 4) (7)*.

Deoxidation elements are charged into the ladle during tapping and are quickly distributed in the melt. The deoxidation reaction in the ladle occurs in a few seconds up to the equilibrium. The remaining dissolved deoxidation elements in the steel are up to 0.3% silicon and 0.05% aluminium. Remaining oxygen contents are 100 ppm after deoxidation with silicon and less than 1 ppm after deoxidation with aluminium. Most of the deoxidation agents form solid oxides which after solidification lead to unwanted inclusions in the steel. Most of these oxides are settled out via the slag, as their density is lower than that of the steel, or via argon treatment.

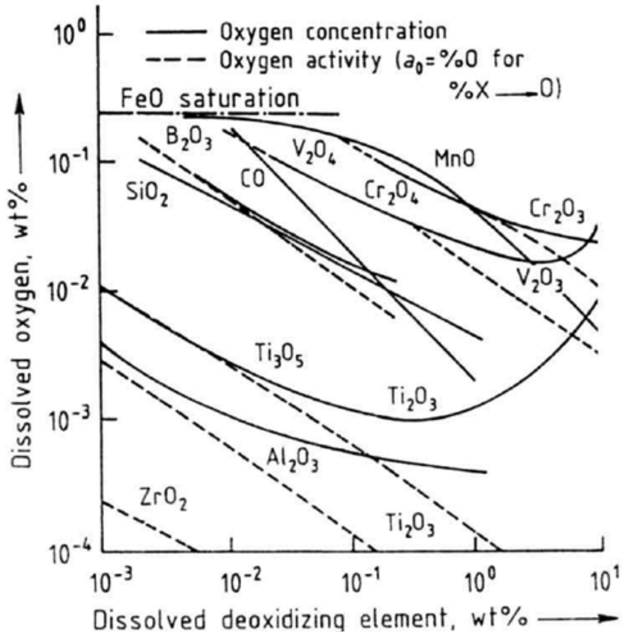

Fig. 4 - Deoxidation effect of different elements in melts of pure iron at 1600 °C *(7)*.

Desulphurization

Sulphidic inclusions harm the steel toughness even at very low contents. For this reason steel needs to be desulphurised.

In the case of the high-capacity steel production processes, sulphur reduction is only possible within certain limits. The major portion of the sulphur is already removed in the blast furnace and in a subsequent hot metal desulphurization treatment usually performed in the hot metal torpedo car. Ultra-low sulphur contents can only be achieved by a desulphurizing post-treatment of the liquid steel.

Desulphurizing post-treatments are done by a precipitation reaction using elements with a high affinity for sulphur, like soda, magnesium, lime or calcium compounds and other rare earths metals. During fine or post-treatment desulphurization geared to achieving contents <0.0002% sulphur, other impurities are likewise removed from the steel. Consequently, this process may also have the added benefit of rendering other post-treatment processes superfluous *(8)*.

Desulphurization, mostly conducted in the ladle, is performed by injecting or otherwise introducing calcium, calcium alloys or synthetic slags based on calcium oxides/alumina/calcium fluorides. Both types of processes require intensive bath agitation which can be promoted by additional stirring with inert gases and elevating the bath temperature. Following the desulphurization process, the sulphur compounds remaining in the melt take on a spheroidal shape which has no negative influence on the subsequent forming process. Desulphurization can also be performed in the vacuum ladle furnace with an electric arc and argon stirring.

Decarburisation

The reduction in the carbon content can largely be effected during the combined blowing process with inert gases injected through the bottom of the oxygen steel converter. Ultra-low carbon contents are achieved by a down-stream vacuum degassing process. Vacuum refining can also result in very low levels of carbon. The decarburisation is achieved in two steps: forming of CO gas bubbles in the melt and CO flushing out of the melt by the argon bubbles. In the vacuum decarburisation process the pressure dependency of the carbon oxygen equilibrium is used:

$[C] + [O] = [CO]$

The equilibrium formula:

$K = P_{CO}/([\%C] \times [\%O])$

is shown for different CO partial pressures in the iron rich edge of the ternary system Fe-C-O *(fig. 5) (9)*. In the area I, which is the light treatment area, most of the oxygen is removed under vacuum at a relatively low decarburisation. In area II a decarburisation is achieved under vacuum to deepest levels without oxygen addition from outside. Area II is the working field of the vacuum decarburisation *(9)*.

The most common processes for the vacuum decarburisation are the vacuum decarburisation (VD) process, the vacuum oxygen decarburisation (VOD) process, the RH oxygen blowing (RH-OB) process and the argon oxygen decarburisation (AOD) process.

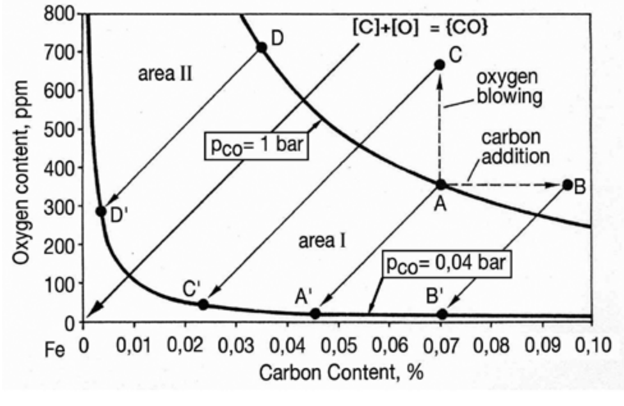

Fig. 5 - Carbon and oxygen consumption in melt during vacuum treatment *(9)*.

Dephosphorisation

The dephosphorization should largely be completed at the end of the steel melting process in the converter. In the ladle or ladle furnace, lower contents of phosphorus can be obtained with the aid of synthetic slag combined with intensive mixing (stirring gas). When pouring the molten steel from the melting vessels, retention of the slag is imperative in order to prevent rephosphorization *(10)*.

Nitrogen removal

As nitrogen is introduced into the melt whenever it comes into contact with the air, nitrogen entrainment must be avoided during both (combined) blowing and tapping of the liquid steel. The ladle treatment for removing nitrogen is performed under a protective layer of slag. Nitrogen can also be removed under vacuum (vacuum refining or other vacuum treatment) with additional argon stirring *(10, 11)*.

Hydrogen removal

Low hydrogen contents are achieved by a vacuum treatment involving intensive stirring.

Removal of tramp elements

Copper, tin, arsenic and antimony cannot be removed using the normal methods of secondary metallurgy. Careful selection of the scrap, the main source of these trace elements in the melt, constitutes the only possibility of minimizing the content of these usually deleterious minerals in the steel.

Vacuum treatment

The "vacuum treatment" of steel is a process of prime importance owing to its versatility and the special advantages it brings. The associated techniques involve post-treatment of the molten steel under significantly reduced pressures (i.e. partial vacuum only), so giving rise to the general, if slightly inaccurate, category nomenclature *(fig. 6) (3)*.

The fundamental principle underlying all vacuum treatments is the realization that dissolved gases can only partially escape as the solidification of steel progresses. This can impair the technological properties of the steel.

If the external pressure is reduced, the gases dissolved in the metal will escape much more readily, like the carbon dioxide escaping when opening a bottle of mineral water. This is the principle applied in all vacuum treatment processes. The application of these vacuum processes became feasible once it was possible to generate very low pressures (0.1- 0.5 mbar) economically on a large scale.

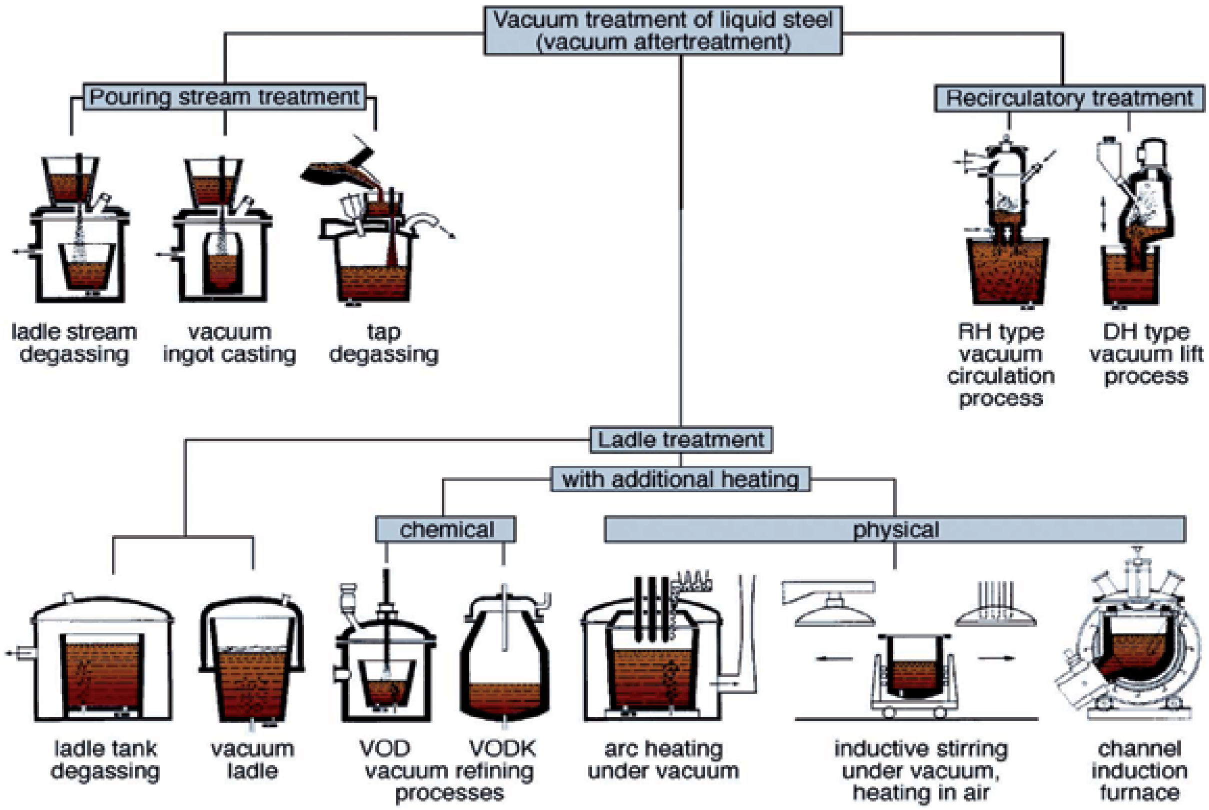

Fig. 6 - Overview of the most common vacuum treatment processes for steelmaking and casting production *(3)*.

RH process

The RH (Ruhrstahl-Heraeus) degassing process was developed in the 1950s to lower the hydrogen content of forging steel. Several degassing facilities have been developed and the most widespread of these is the RH or re-circulation degasser. In this process the two legs of the degasser vessel are immersed in the steel ladle. A powerful pumping system reduces the pressure inside the chamber. The steel circulates up one leg and down the other leg by injecting argon gas into the upleg. This continuously exposes fresh steel to the vacuum. The reduced pressure results for example in lower solubility of hydrogen in the steel. Hydrogen is diffused out and pumped away. In the RH process the slag is separated from the steel and this results in an extreme low slag metal mixing.

Aside from degassing, additional metallurgical reactions are performed under vacuum, e.g. fine decarburization, alloying, deoxidation and inclusions removal to improve the cleanness of the steel. For this reason, it is more appropriate to speak of "vacuum metallurgy" rather than "vacuum degassing". The essential benefits derived from the vacuum treatment of liquid steel lie in the high level of cleanness, low gas contents and close alloying tolerances achieved. Thanks to these advantages, the preceding refining process can thus also be effectively simplified and shortened.

Ladle degassing

Aside from decreasing hydrogen and nitrogen contents in the melt, ladle degassing includes the possibility to obtain lowest sulphur contents. Today it is mostly used for production of steels for heavy plates and pipeline steels *(3)*. In terms of plant engineering, ladle degassing processes are relatively easy to perform. Following tapping, the ladle containing the melt is placed in a vacuum container so that the dissolved gases can escape. The contents of the ladle may be additionally heated and stirred with argon. In ladle degassing, the entire slag/bath interface in the ladle participates in the vacuum treatment process.

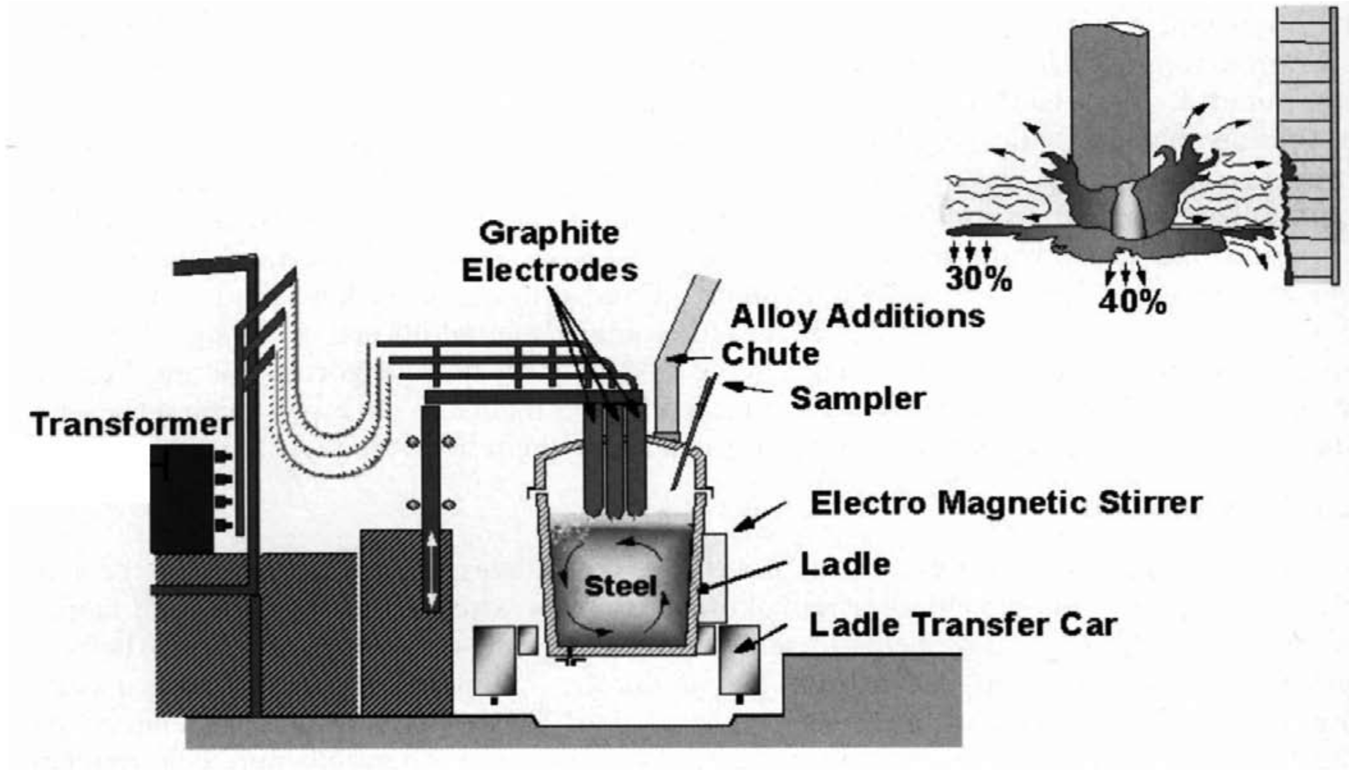

Fig. 7 - Ladle furnace *(13)*.

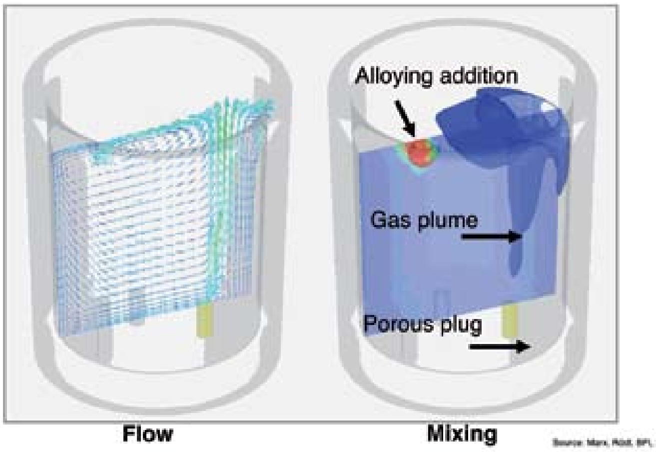

Fig. 8 - Simulation of alloy addition and mixing for addition of FeMn in a ladle.

Ladle furnace

In the ladle furnace *(fig. 7)*, the steel can be electrically reheated up to 4.5 °C per minute using graphite electrodes which are introduced through a water cooled roof. The reheating allows more time for secondary steel making treatments without the need for high tapping temperature. The strong stirring in the ladle is essential to dissipate the heat in the slag, ensure efficient thermal transfer between the slag and the steel and minimize refractory wear *(13)*. The stirring can be reached via porous plugs in the ladle bottom and by the injection of inert gas through a vertical top lance. Another way is the use of an electromagnetic stirrer. Alloying element can be added through holes in the roof or powder and wire injection. Ladle furnace slags can be chemically active and have a high desulphurising effect. They can reduce inclusions to produce very clean steel.

TRENDS IN SECONDARY METALLURGY RESEARCH IN GERMANY

Advanced steels need advanced methods for optimization of secondary metallurgy. Today, CFD (Computational Fluid Dynamics) is a powerful tool to develop e.g. suitable alloying strategies for specific steels grades, for example high manganese steels. It helps to optimize the secondary metallurgical treatment process in ladles, e.g. such process simulations are performed by the Betriebsforschungsinstitut (BFI), Düsseldorf, taking into account time-dependent multiphase flow conditions, steel melt, alloying agents and stirring gas. Especially the dynamic behaviour of e.g. different lumpy alloying agents considering also their specific melting and dissolution is simulated.

Figure 8 (14) shows numerical computations from the BFI for addition of FeMn in a ladle with the active plug and the position of alloying addition. The left side of the figure shows the velocity field, the right side the concentration of manganese which was added as lumpy material. Such results are in very good accordance with results from operational trials *(14)*. Using CFD models, the influence of parameters like number and position of porous plugs as well as stirring gas flow rate can be optimized with regard to reduced treatment time, saving of energy and material resources by achieving reliably the targeted melt composition.

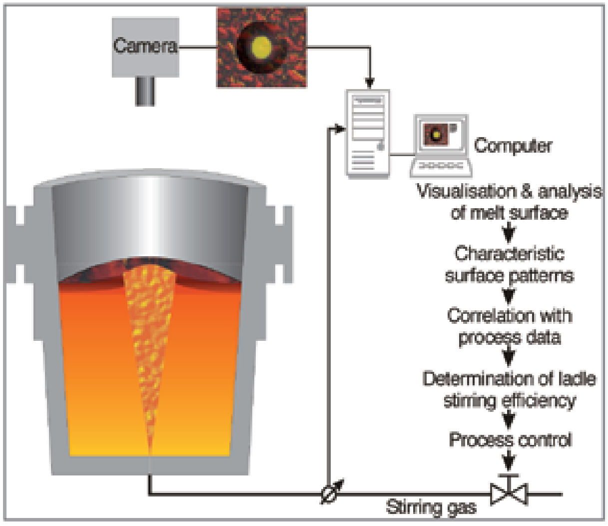

Fig. 9 - Monitoring the gas stirring process for improving the cleanness of steel by digital image processing.

Optical techniques for process monitoring offer an enormous potential for control of metallurgical processes. Saarstahl has developed in cooperation with BFI a new system for monitoring the gas stirring process by digital image processing. A conventional digital camera system equipped with infrared filter observes the melt/liquid steel surface during gas stirring *(fig. 9)* to control the stirring gas flow in order to ensure optimum steel cleanness.

A correlation between geometry of open-eye, turbulence structure of the surface and the gas flow rate has been identified *(fig. 10) (15)*.

The results from observation of melt surface can be used to determine the gas flow without any distortion caused by leakages in the gas pipes or damages of purging plugs. However, trials showed only a slight correlation between gas flow and steel cleanness.

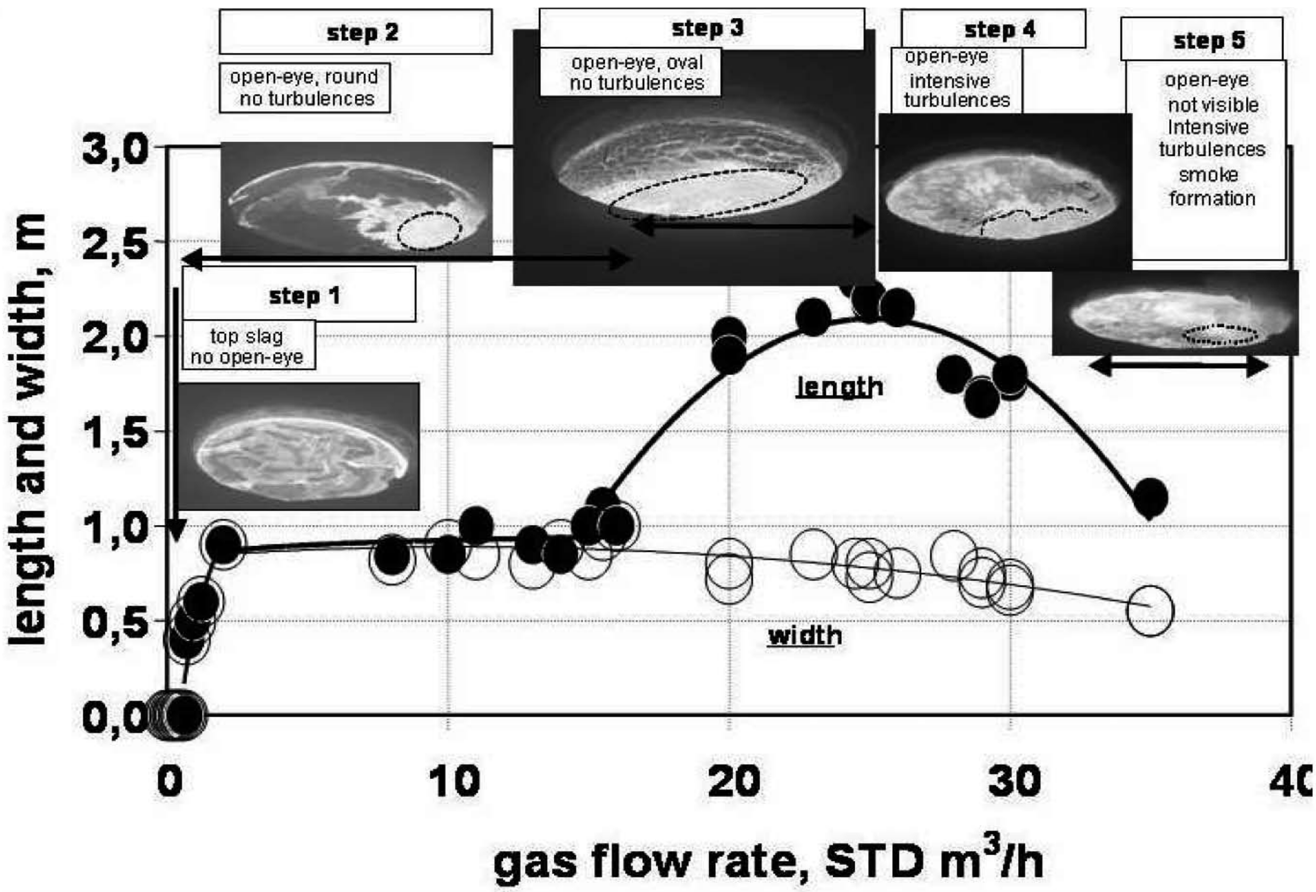

Fig. 10 - Correlation between open-eye, turbulence structure of surface and gas flow rate, 170 t ladle Saarstahl *(15)*.

Model based control concepts based on continuous measurement technology for secondary metallurgical processes are of special interest because analytical online observation is still not possible today. Dynamic models for online observation of the process are the precondition for model based control concepts. BFI, Düsseldorf, together with Voestalpine Linz, has developed a control concept for the RH process with oxygen lance. The dynamic process model covers decarburisation behaviour in connection with the oxygen removal, dehydrogenation, denitrogenation and the evolution of the steel temperature. The model was recently extended to the RH operation with oxygen input via a top lance.

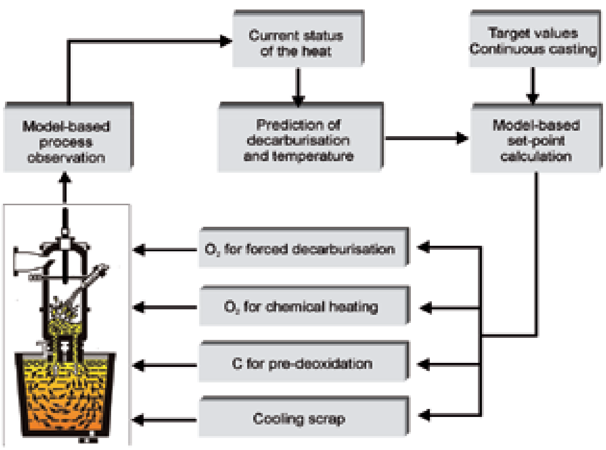

Fig. 11 - Structure of model based control concept for the RH process with oxygen lance.

Within the dynamic control concept, the thermodynamic model calculates the current process status online and predicts the decarburisation and temperature evolution *(fig. 11) (16)*. Through comparison with set-points of the continuous caster, a decision is made whether it is necessary to add oxygen for forced decarburisation or for chemical heating, coal for predeoxidation, or scrap for cooling. The control system improves the achievement of the target temperature while on the average reducing the consumption of oxygen for blowing and aluminium for deoxidation.

Slag carry-over while ladle taping is a tremendous problem for cleanness of steel. Lately, ThyssenKrupp Steel and Amepa have developed a new slag detection system to prevent slag carry-over especially before ladle change, when the ladle level is low *(fig. 12)*. A transmitter and a receiver coil are wrapped around the ladle outlet, above the slide gate.

Charging the transmitter coil with alternating current induces eddy current in the melt. Amplitude and local distribution of the induced eddy current depend on the electric conductivity of the melt, which means it is sensitive to presence of slag. The current eddy in the melt induces itself a voltage in the receiver coil, correlating to amplitude and geometric distribution of the current eddy in the melt. The signal is used to close the slide gate if slag is detected. Today, after some optimisation, the new system is able to prevent slag carry-over to more than 86% with a steel flow of 130 kg/s *(17, 18)*.

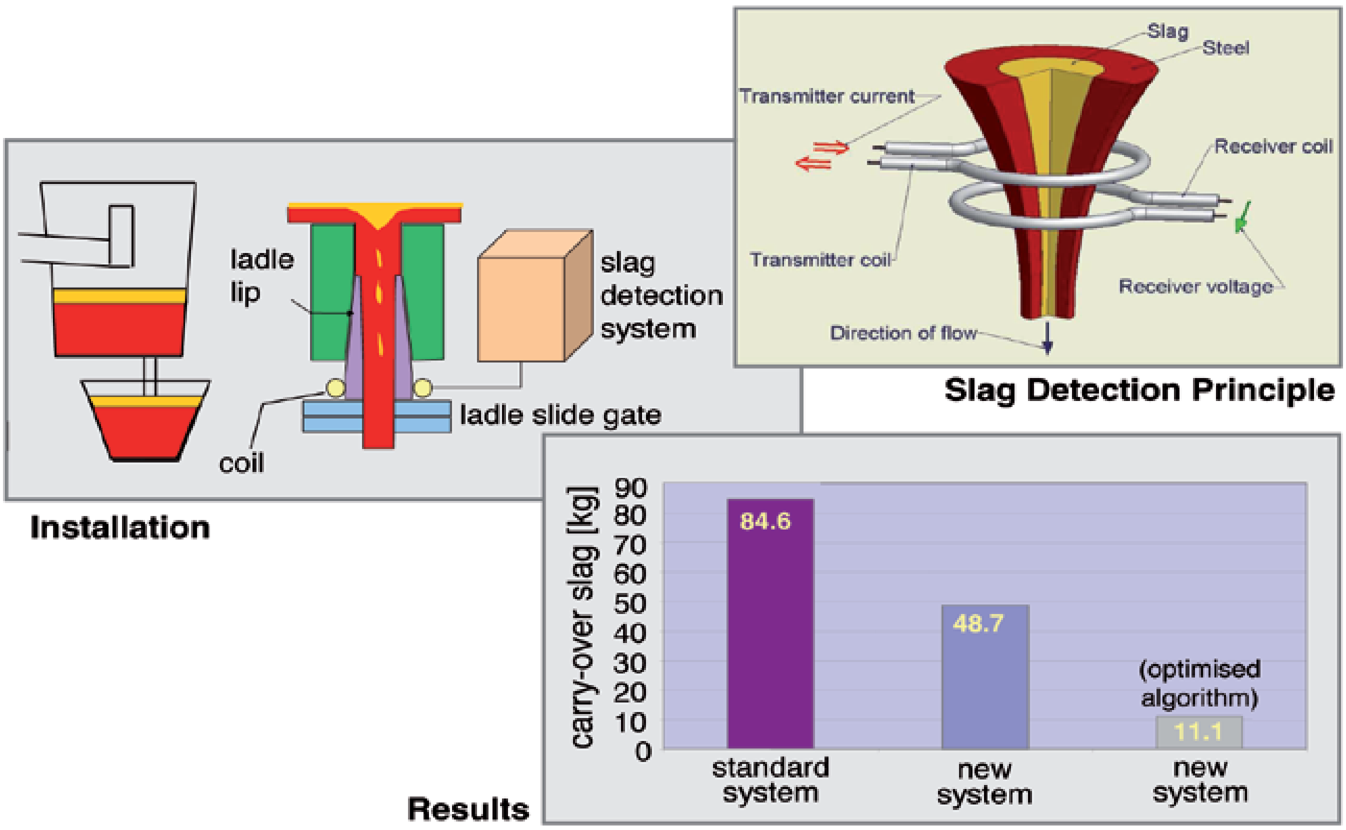

Fig. 12 - Reduction of slag carry-over by a new slag detection system at TKS; a) installation; b) results.

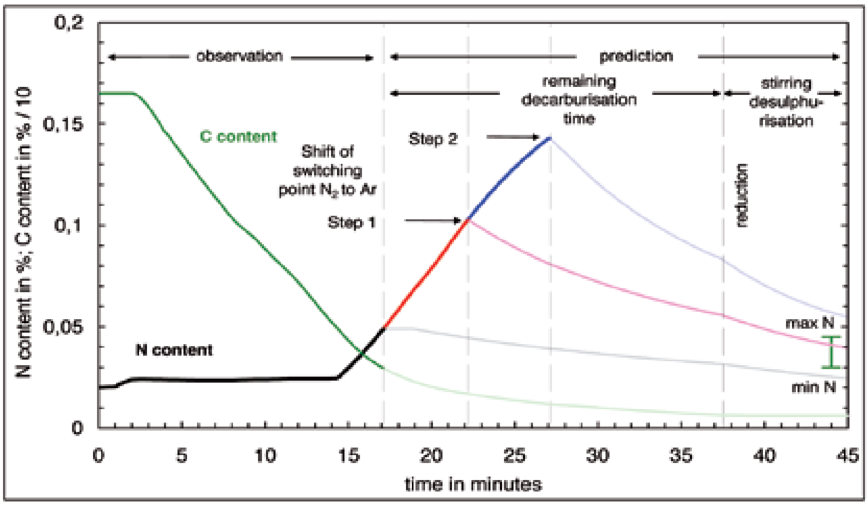

Fig. 13 - Model based dynamic control of AOD converter process, simulation of switching point between N_2 and Ar.

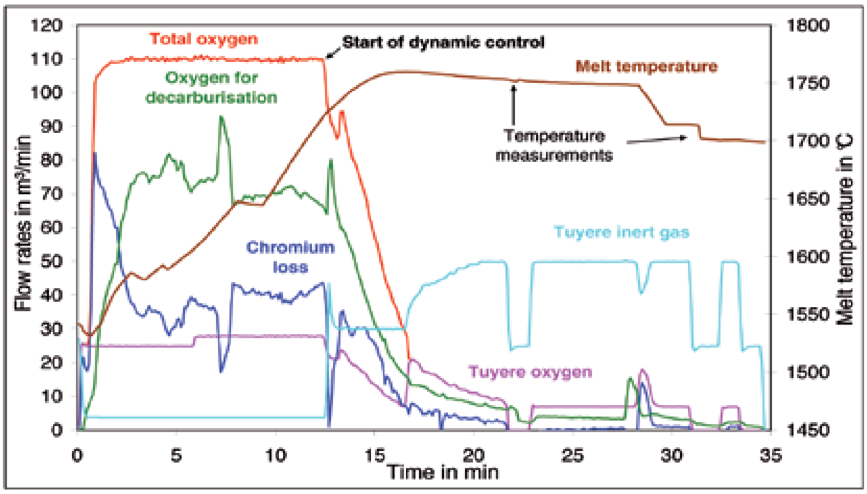

Fig. 14 - Model based dynamic control of AOD converter process, dynamic control of oxygen supply.

A second example for the benefit of model based dynamic control concepts has been developed and implemented at ThyssenKrupp Nirosta in Bochum in cooperation with BFI at the AOD converter for refining of high chromium stainless steel. Again, precondition for the control concept is a dynamic process model. In this case, it is describing the status and progress of decarburisation, nitrogen content and melt temperature evolution. In the final decarburization phase, the thermodynamic model allows to compute carbon and nitrogen content and the melt temperature very precisely. For the carbon content the standard deviation of the model error is about 0.01%, for the nitrogen content about 0.007% and for the melt temperature about 1% *(19)*.

A dynamic inert gas control by determining the optimal switching point between nitrogen and argon supply is decisive to adjust the target nitrogen content under minimum costs. For an example heat, *figure 13* shows the effect of shifting the switching point between nitrogen and argon in two steps, with a partial substitution of argon by the cheaper nitrogen. Criterion for the switching point is the model predicted final nitrogen content *(20)*.

A further important point for dynamic control of the AOD process is the oxygen input *(fig. 14)*. In the first phase of treatment, oxygen is supplied with the maximum flow rate to achieve decarburisation as fast as possible.

From online observation it can be detected when the oxygen demand for decarburisation goes down and thus the chromium loss increases. From this point on, the oxygen supply is dynamically decreased according to the reduced demand for decarburisation, which can be calculated from the thermodynamic model. Due to the steady decrease of the oxygen input according to the observed demand for decarburisation, taking into account in parallel the chromium oxidation required for temperature increase, the chromium loss is minimised. The diminished chromium loss is accompanied by lower consumption of reducing agents and slag formers.

CONCLUSIONS

In Germany the secondary metallurgy is applied in all steelworks and the operation of these facilities is a precondition for flexible production of various high grade steel products. There are for example today in total 32 vacuum degassing plants and 29 ladle furnaces in operation with heat sizes of up to 400 t per module. In the past years the efficiency of steel treatment and the steel cleanness has been significantly improved. The new developments show the potentials when using new advanced methods for controlling the processes, for example the computational fluid dynamics or model based control concepts only to mention some.

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