REVIEW ON LADLE METALLURGY IN STEELMAKING

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Treatment of steel in the ladle as a measure of supplementing melting shop metallurgy has had a long tradition. With the need for economical production of higher-strength steel, and with the requirement to rationalize and ensure a safe operation, an accelerated structural change began in the steel industry approximately 20 years ago, as a result of which ladle metallurgy emerged as an independent process step with the following new tasks:

Removal of unwanted accompanying elements from hot metal and steel heats to the largest possible extent, homogenization of temperature and concentration, precise chemistry control, inclusion control, improvement of the fluidity of steel heats, process optimization, and the improvement of productivity in ironmaking and steelmaking operations.

Injection, stirring and dipping of reagents into the metal bath are process technology elements of ladle metallurgy that are used for treatment of hot metal heats, whereas stirring, injection of gaseous and solid reagents, and application of vacuum are used for treatment of steel heats.

TREATMENT OF HOT METAL

For the production of high-grade steels and for an alleviated operation of the blast furnace and steelmaking shops, hot metal is desulphurized in the transport vessels by additions of soda ash, calcium carbide, magnesium, or lime. Lowering the percentage of silicon, nitrogen, and phosphorus in hot metal is possible by means of alkali and oxygen carriers.

TREATMENT OF STEEL

Stirring

Stirring systems are used, with inert gases being injected into the steel bath through one or several porous bottom bricks or through an injection lance.

Objective: improved homogeneity of chemistry and temperature, improved cleanliness, precise percentages of alloying elements and sulphur removal by means of active slags.

Injection treatment

A large extent of oxygen and sulphur removal, and the elimination of harmful inclusions, can be achieved in deoxidized heats through injection of calcium based reagents. The injection is done by blowing, spooling-in of coated Ca composite wire, or shooting. For the blowing process, *magnesium and slag mixtures are used in addition to Ca-carriers.*

Improvements achieved: oxygen and sulphur percentages can be reduced down to the detection limit.

Dispersed particles, detrimental to quality of steel can be converted into globular inclusion types making it possible to obtain improved toughness properties and a high degree of isotropy. Improved fluidity of the steel which enables the casting of billets from aluminium-killed heats on continuous casting machines. Increased productivity of the steelmaking shop is, due to the shifting of metallurgical reactions into the ladle.

Vacuum treatment

Treatment of steel by application of vacuum was originally developed for reducing the hydrogen content. This method enables the attainment of exact percentages of alloying elements, and the homogenization and cleaning of the heat. Systems for degassing partial quantities of steel, stream degassing and ladle degassing have assumed great practical importance. For the addition of larger quantities of alloying elements, and for instance for desulphurization, facilities with additional electrical heating systems have proved of value.

During the vacuum treatment, dissolved oxygen is removed without residues because CO is formed. Oxide inclusions are largely reduced, and favourable conditions are created for the separation of non-metallic phases.

The pressure dependence of the decarburization reaction makes it possible to decarburize steel heats with addition of oxygen, if necessary. This possibility is used for the production of low-carbon and/or high chromium stainless, acid-resisting, and heat-resisting steels.

INTRODUCTION

Treating steel in a ladle is as old as the use of ladles in steelmaking. Ladle treatments of hot metal and liquid steel, for instance for the purpose of desulphurization, deoxidation, and alloying, have been common practice at all times; also as early as that, steel heats were treated in the ladle to improve the cleanness by way of using premelted slags along the lines of the "Perrin process". Thus, as a supplementary measure in metallurgy, ladle treatments have had a long tradition.

As the structure of the steel industry changed about 20 years ago, with requirements for more economic production of higher-strength steels for new applications and with its necessity for rationalization and more reliable handling of all production operations, additional tasks arose for treating the heats outside the melting shop, which could no longer be solved in the previous, relatively simple mode of operation based on rough estimates. Production of new steel grades with improved properties presupposed thorough removal of disturbing elements from the steel. With a view to handling the orders reliably and warranting the fulfilment of specifications, among other things for continuous casting, it became necessary to meet enhanced expectations with respect to the homogeneity of concentrations and temperature; and the necessity of improving environmental conditions entailed the need for new, fully mechanized and precisely operating process stages.

Today, in modern steelmaking facilities, various kinds of ladle-metallurgical process stages are in operation. For the treatment of *hot metal* there are such technological elements as injection, stirring, or the dipping of reagents into the metal bath; for treatment of *steel heats*, use is made of stirring, injection of solids, and vacuum.

Today, the possibilities of ladle metallurgy are by far not exhausted yet. Many questions are still unanswered and at many places, investigations are being made at present with a view to its further refinement and improved utilization.

In the following sections a description is given of the possibilities of ladle metallurgy in making hot metal and steel with examples of their implementation in modern steelmaking.

HOT METAL TREATMENT

Treating hot metal in the ladle today is done for the purpose of desulphurization and, consequently, for a reduction in sulphur input when making the steel. Improvements obtainable in the steel by way of reducing its sulphur percentage are reflected in the properties and the surface quality of the metal(1). Therefore, in many steel mills, even for plain carbon steel production, use is being made today of hot metal with no more than 0.020% sulphur. In particular, it has been the increase in continuous casting for making plain carbon steel that has made a further reduction in sulphur necessary. To warrant a good surface quality and to prevent internal cracks from occurring in continuous-casting slabs, obtaining less than 0.020% sulphur in the steel was found to be necessary and less than 0.015% sulphur desirable. For making steels with particular property requirements, reliably achieving less than 0.03% sulphur in the hot metal is causing no difficulties if modern desulphurization processes are used.

Apart from a qualitative improvement of the steel product, external hot metal desulphurization may constitute a relief for the melting shop permitting a more favourable mode of operation with less basic slag (figs. 1 and 2). In the blast furnace[1-4], this allows the use of fuels (coke and oil) with higher sulphur content and achieving lower silicon percentages in the hot metal which permits the coke rate to be reduced and the performance to be increased.

For steelmaking[1,2] the use of hot metal with reduced silicon and sulphur percentages leads to a mode of operation with less slag and lower basicity resulting in improved iron yield and lining life.

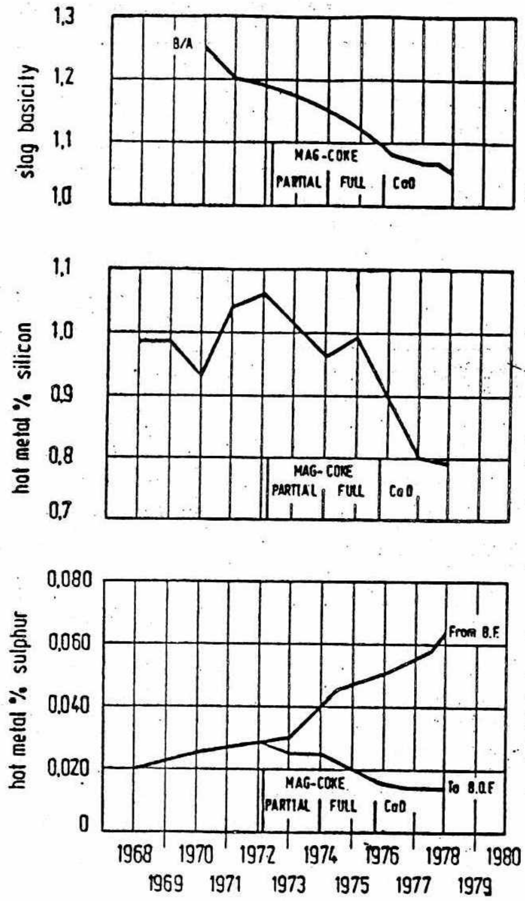


Fig.1 Blast Furnace Operation in Combination with External Desulphurisation[4]

For hot metal desulphurization, use is still being made today of the conventional method of addition of soda ash during refilling the hot metal as well as injection, stirring, and dipping of desulphurizing agents (fig.3).

The conventional method of desulphurization by way of adding soda ash is simple to perform if used to a limited extent. Apart from reducing the percentage of sulphur, silicon, nitrogen, and phosphorus[5,6] are also lowered. However, it presents major deficiencies with respect to reliably obtaining low sulphur percentages. Besides, the soda ash reaction entails substantial losses of physical and chemical heat in the hot metal. Also when treating large amounts of hot metal, particular care must be taken to ensure removal of alkaline dusts and sludges for environmental protection. It is for this reason that the conventional soda ash process does not fit into the realm of modern ladle metallurgy.

table I: METHODS FOR THE DESULPHURISATION OF PIG IRON[7)]

Group process	locality of treatment	desulphurising agent	consumption kg/t from 0,100 to 0,020% S	from 0,040 to 0,010% S	from 0,030 to 0,005% S	treatment time side times min	temperature loss °C
teeming stream mixing processes							
sodaash desulphurisation	ladle (Blast furnace)	soda (liquid slags)	8to10	ca. 8	ca. 8	inapplicable	10 to 15
	mixer/ladle			ca. 8			10 to 15
	mixer/ladle/ ladle			ca. 6		ca. 10	25 to 35
mechanical mixing processes							
solid stirrer	B.F. runner	CaO (powdered lime)		3 to 5 CaC_2		10 to 20	ca. 20
	hot metal ladle	CaC_2					
hollow stirrer	hot metal ladle	Soda/lime (ca. 1:10)		1,5 soda			
KR (Japan)	hot metal ladle	CaO (CaC_2)		ca. 3	ca. 5		
pneumatic mixing processes							
immerged lance							
Europe, Japan	torpedo car or charging ladle	CaC_2+(Carbonate)	3to6	2,5 to 3	2,5 to 4	6 to 30	5 to 10
SU	torpedo car or open ladle	Mg and Mg + (CaO)		0,7 to 1,0	0,8 to 1,1		
plunging process (Magcoke)	hot metal ladle	magnesium-coke (ca. 45% Mg)		0,7 to 1,0	0,8 to 1,2	8 to 20 (10)	5 to 15

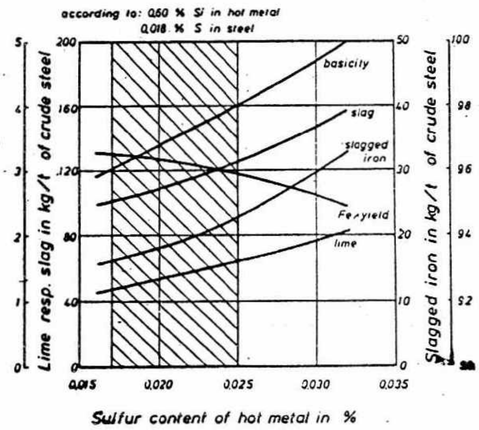


Fig. 2 Influence of the Sulphur Content of Hot Metal on the BOS-Process Parameters[1,2)]

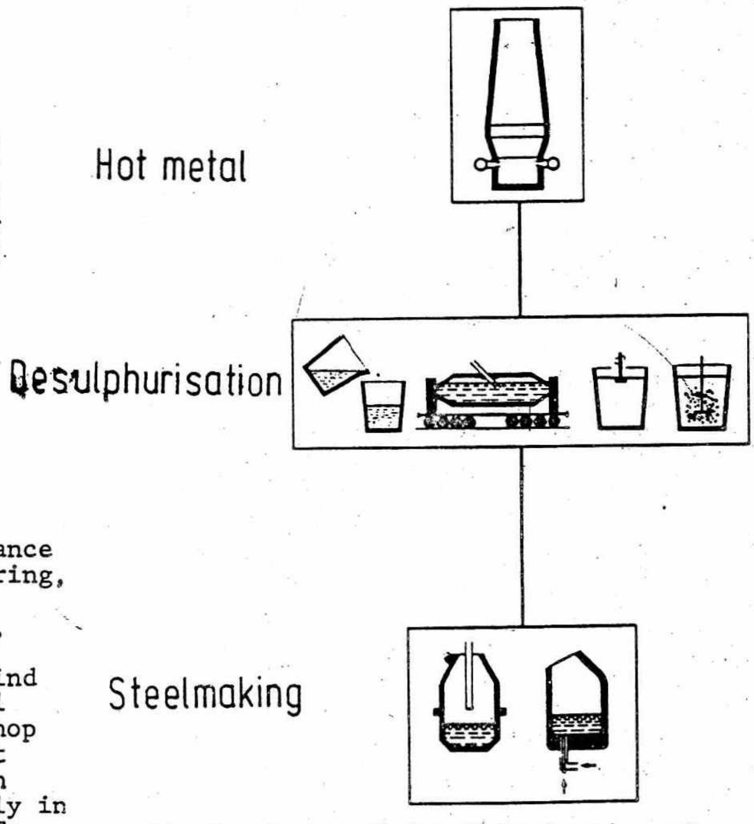


Fig. 3 External Desulphurisation of Hot Metal

Substantial practical significance can be found in the injection, stirring, and dipping methods[1)] of hot metal desulphurization when using calcium, magnesium and lime (table 1)[7)]. At present, using facilities of this kind is common practice in a modern steel mill. To provide the steelmaking shop uninterruptedly with low-sulphur hot metal, use is made of such injection facilities as are shown schematically in fig.4, or of stirring facilities. To make steel for particular requirements,

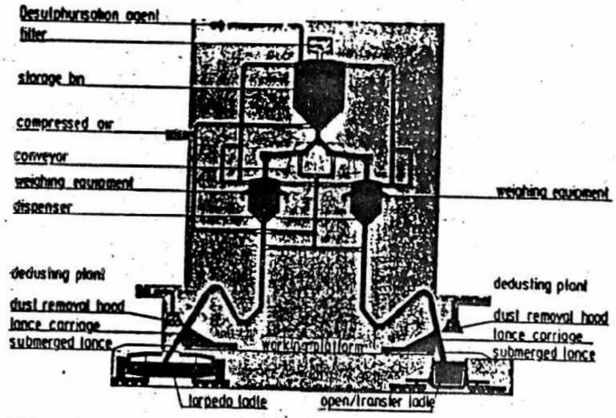


Fig.4 Hot Metal Desulphurisation (Diagrammatic Outline)

sulphur percentages in the hot metal as low as ≤ 0.003% are often obtained by additional injection or stirring treatments. Preferentially for batch-type supply of low-sulphur hot metal to the steelmaking shop, use is mostly made of methods employing hollow or solid-body stirrers or a plunging bell, using Mg-impregnated coke or similar materials.

A decision as to what method is to be preferred depends not only on the technical requirements but also on the availability and prices of the required desulphurizing agents at different places throughout the world. Present activities to further develop these methods are essentially aiming at obtaining more efficient desulphurizing agents.

Recently studies have been made in Japan[8-11] to demonstrate the possibility of "slag-free" refining of dephosphorized hot metal. It is well known[12,13] that a substantial reduction in phosphorus can be obtained under oxidizing conditions, for instance by way of treating the hot metal with soda ash or with similarly active slag mixtures on an alkaline basis from approx. 20kg/ton, or on the basis of alkaline earths (fig.5). However, the latter case requires much higher specific rates. Since such a hot metal is also largely exempt from silicon and sulphur, slag reactions in the converter are then no longer required or only to a limited extent, provided the remaining charging materials are exempt from contaminations as well. Such a refining operation which is meant for decarburization alone could become increasingly important for steelmaking in various

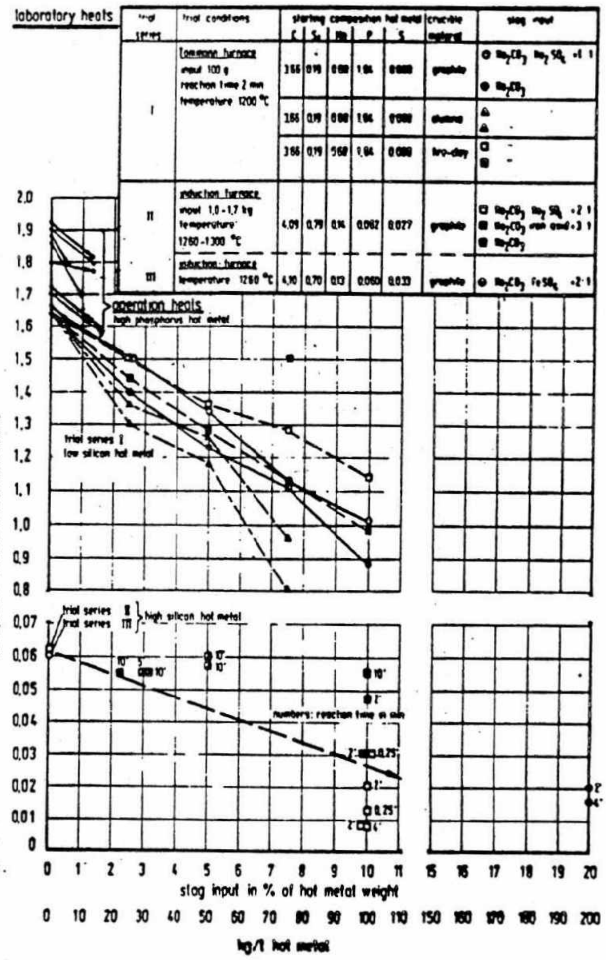


Fig.5 Influence of Different Reagents on the Reduction of Phosphorus in Hot Metal Heats[13]

respects, for instance to improve the yield, to reduce the slag volume and to improve the steel quality through lower phosphorus, sulphur and nitrogen percentages. However, a lot of questions remain to be answered before industrial maturity of such mode of operation is reached, such as the wear of refractories in the dephosphorizing vessel and the converter. And last but not the least, a practicable and economic solution must be found to the problem of preparation of a synthetic slag for recycling.

TREATMENT OF STEEL HEATS

Steel heats are subjected to post-treatment in order to reach desired chemical composition, inclusion morphology, and temperature of the steel bath which will ensure ultimately properties of the desired grade of steel. This permits

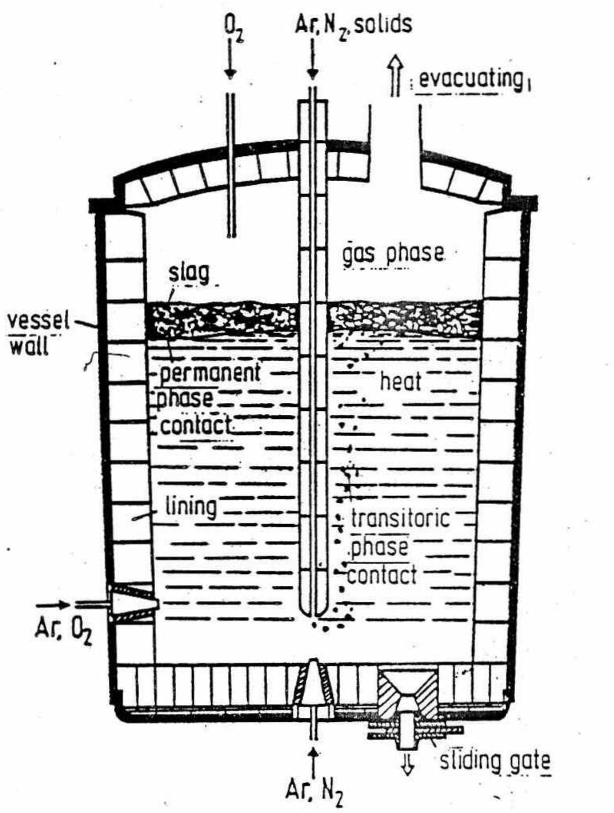


Fig.6 Possibilities for Post-Treatment of Steel (Model Reactor)[14]

steels to be produced today on a large scale production of which so far has been considered possible only at great expenses in the melting vessel, or not at all. Substituting the ladle for the melting vessel for metallurgical treatment means an increase in capacity of the melting vessel. The technological elements, such as the stirring treatment, the injection of gases and solids, and the evacuation are illustrated by the model reactor[14] shown in fig.6. The metallurgical results obtainable in this way are decisively governed by such thermodynamical limiting conditions as the impact produced by addition of solids through a permanent or transitoric phase contact, the structure and the composition of the slag and gaseous phases, and the refractory lining of the ladle. Examples of a practical solution for the use of these technological elements are shown in fig.7.

Stirring Treatment

Stirring a steel heat is the simplest kind of steel post-treatment in the ladle. It is aiming primarily at

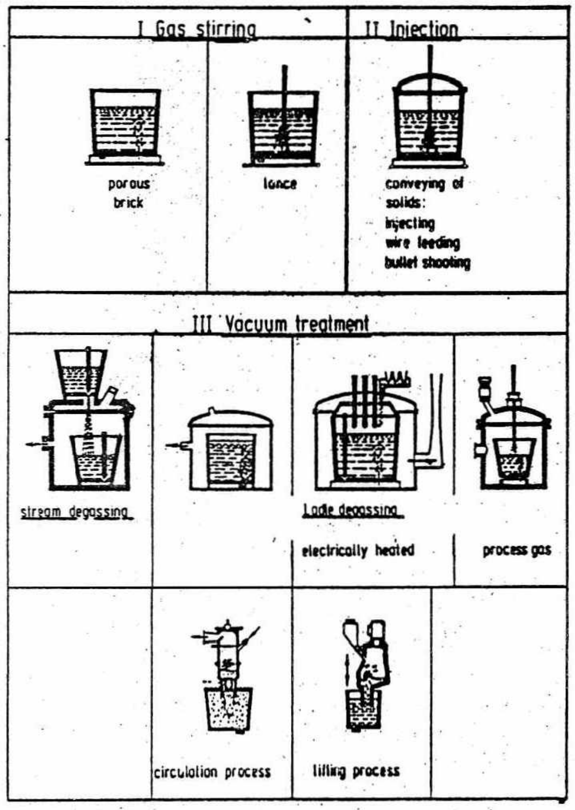


Fig.7. Processes for Post-Treatment of Steel

homogenising the temperature and composition of the heat, which is a prerequisite for smooth operation, especially for continuous casting. Various stirring systems are in use today. Widespread use has been reported of one or several porous bottom bricks in the ladle bottom or wall, through which inert gases - argon or nitrogen - are introduced into the heat. Stirring by means of an injection lance is also widespread and frequently preferred for reasons of safety.

Attainment of the required temperature is achieved by way of cooling the heat during stirring and reinforced by way of adding cooling scrap. Precise control of the required analysis - micro-alloying, among other things - is achieved by way of adding alloying elements into the flushing spot. The concentration margins that can be complied with by way of stirring are shown in table 2.

Reports from Japan[15] mention modified processes and the potential reduction in concentration margins, for instance those of aluminium (fig.8).

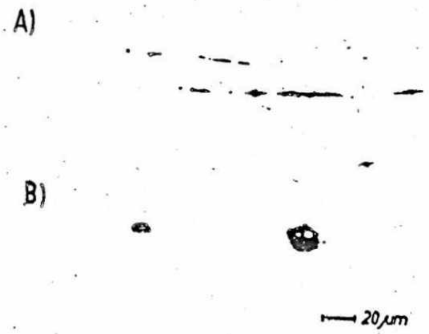


Fig.9 A) Non-Metallic Inclusions in a 50-MM plate made of a Conventionally Molten Steel (Long Lines), and B) A Plate Made of a Steel Treated According to the TN Process (Globular Inclusions)[17]

cause anisotropy of the steel, particularly in flat-rolled products. In the case of calcium treatment, these types of inclusions turn into calcium aluminates which coagulate and precipitate well, with a low melting point and a complex structure. In this way, the steel becomes not only cleaner but the remaining inclusions become less dangerous because they are globular and non-deformable at rolling temperatures.

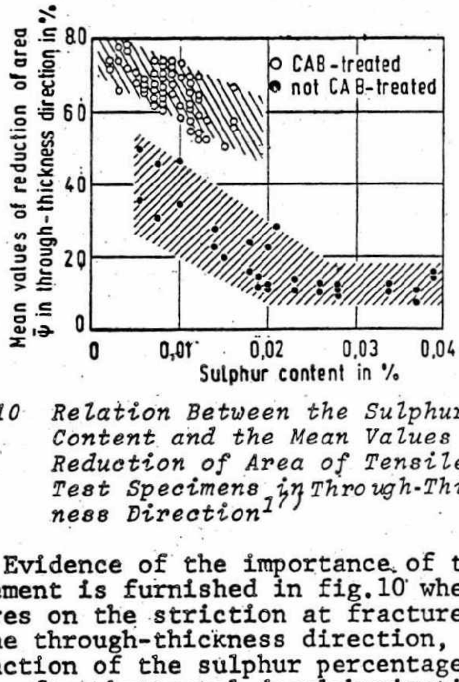


Fig.10 Relation Between the Sulphur Content and the Mean Values of Reduction of Area of Tensile Test Specimens in Through-Thickness Direction[17]

Evidence of the importance of this statement is furnished in fig.10 where figures on the striction at fracture in the through-thickness direction, as a function of the sulphur percentage in heats after hot metal desulphurization and in steel heats after calcium treatment, are compared with each other. This comparison[17] shows that a reduction to lower sulphur percentages alone is not sufficient to obtain maximum striction figures. It is more important and necessary to reduce the dependence of the mechanical properties upon the orientation by way of changing the shape of the inclusion.

Apart from calcium which tends to change the morphology of oxide and sulphide phases, there are elements which cause the shape of sulphides to change in the steel heat in the presence of small concentrations. These include titanium, zirconium, rare-earths and tellurium. Using these elements is often difficult, but it can bring improvements wherever the quality of steel is impaired as a result of an anisotropy of the properties caused by sulphides. Since the various elements differ from each other with respect to their impact on the sulphide shape and the effect on the mechanical properties, their use must be adapted to the steel properties desired.

As a result of an increase in steels with particular toughness requirements various processes and injection systems have been developed in recent years for adding alloying elements, in particular those based on calcium as well as on magnesium and active slags.

Powder Injection

Widespread and manifold use has been noted for the injection processes, for which the scheme of a TN-type facility is shown in fig.11. In the TN-process[18-20] which has been in operation for more than 10 years worldwide, and in similar follow-up developments[21] in various countries throughout the world, powdered substances of the kind shown in table 3[22] are injected into the deoxidized heat by means of a ceramic lance using a stream of inert gas.

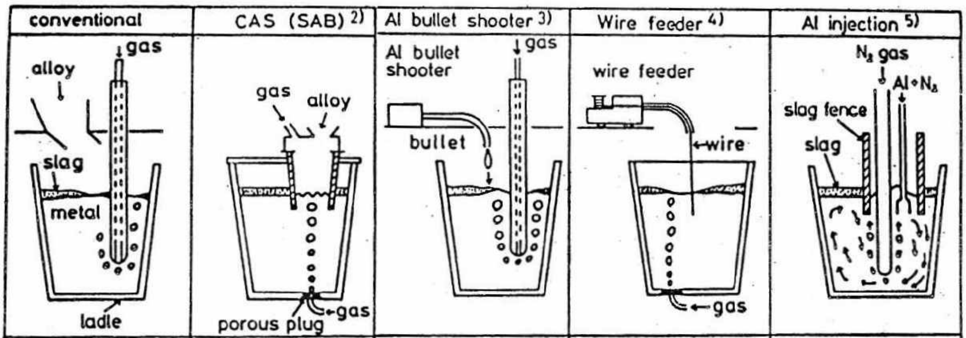
The reaction of the injected elements is extremely efficient as a result of the transitoric phase contact and the permanent phase contact with the basic top slag of the liquid bath (fig.12)[23].

The sulphur and oxygen percentages attainable within a few minutes are within a range of only a few ppm; however, for the performance in acid and basic ladles they differ from each other. Therefore, for steels with

Table II: ADJUSTABLE LIMITS IN CHEMICAL COMPOSITION OF GAS STIRRED HEATS IN % (LADLE SAMPLING, 95 % SIGNIFICANCE)

C-content in %	≤ 0,20	0,21-0,40	0,41-0,70	0,71-1,20
C	± 0,03	± 0,03	± 0,03	± 0,04

Alloy content in %	≤ 0,20	0,21-0,60	0,61-1,20	1,21-2,50	2,51-12,0
Si	-	± 0,08	± 0,10	± 0,13	-
Mn	-	± 0,07	± 0,08	± 0,13	± 0,5
Cr	± 0,04	± 0,07	± 0,08	± 0,13	± 0,25
Mo	± 0,03	± 0,04	± 0,08	± 0,10	-
Ni	-	± 0,05	± 0,08	± 0,13	± 0,15
V	± 0,03	± 0,05	-	-	-



	CAS (SAB)	Al bullet shooter	Wire feeder	Al injection
	[Al] total in tundish	[Al] sol in product	[Al] sol in mold	[Al] total in tundish
	$\bar{x}$ / σ	σ	$\bar{x}$ / σ	$\bar{x}$ / σ
C*	0.063% / 0.011%	0.0175%	0.047% / 0.011%	0.047% / 0.0137%
N*	0.063% / 0.009%	0.0057%	0.043% / 0.008%	0.040% / 0.0086%

C*; Conventional, N*; New practice, $\bar{x}$: average, σ: standard deviation.

Fig. 8 Modified Argon Stirring Processes for Low Carbon Aluminum Killed Steels[15)]

Stirring treatment removes non-metallic phases, thus improving the cleanliness of the steel. Besides, minor reductions in hydrogen concentrations are observed. If reactive slags are added during stirring, for instance mixtures of lime and fluorspar, especially while using basic linings in the ladles, a reduction in sulphur can be achieved[16)].

Injection Treatment

Sulphur which highly adversely affects the properties and the surface quality of steel products as a result of the kind of inclusions it forms, can be removed only to a limited extent by simple stirring in the ladle. For substantial desulphurisation of steel heats, which presupposes a low oxygen potential of the metal/slag system, pertinent steps must be taken to reduce or to remove the oxygen. Such a step is also mandatory to improve the oxidic cleanness. Therefore, processes are being used today that are capable of reducing both sulphur and oxygen to the very limit of their detectability in basic lined ladles. Substances that have given excellent results in such treatments were found to be, above all, calcium-bearing alloys. The clear-cut improvements in toughness, obtainable in this way, such as elongation, striction, and impact strength, are attributable to an improvement in sulphide and oxide cleanness and to the transformation of quality-impairing oxide and sulphide phases into less dangerous types of inclusions.

Fig. 9[17)] shows such quality-impairing lines of inclusions in conventional steel, made up of manganese sulphides and alumino silicates, which

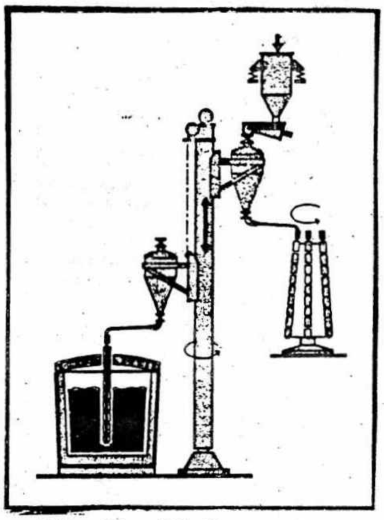


Fig. 11 TN-Process

Table III: DESULPHURISATION AGENTS FOR POWDER INJECTION[22)]

desulphurisation agent	composition	injected kg/t	amount of agent for $\frac{\Delta S}{S_0}=0.90$ kg/t
SiCa	62 % Si, 0.8% Al (30 % Ca)	2 - 4.5	3.87
Calcium carbide	90 % CaC_2, 15 % CaO (50 % Ca)	1 - 3	2.32
Calcium cyanamide	55 % $CaCN_2$, 33 % CaO, 12 % C (28 % Ca)	0.4 - 1	(4.22)
Mg (CaO/CaF_2)	5 - 20 % Mg	1 - 3	2.2
CaO/CaF_2	90 % CaO, 10 % CaF_2	3 - 6	3
CaO-Al_2O_3	50 % CaO, 50 % Al_2O_3	1 - 5	4
CaO-Al_2O_3-CaF_2	70 % CaO, 20 % Al_2O_3, 10 % CaF_2	1 - 5	3

high property requirements, basic ladles should be used, if possible.

The treatment lasts for about 10 minutes. Depending on the amount of additions and the ladle condition, a temperature loss of approx. 35°C must be anticipated during the treatment. The hydrogen percentages tend to rise; therefore, care should be taken to see that dry materials are used. For steel grades susceptible to hydrogen effects this should be followed by vacuum treatment.

Injection processes have given excellent results in making high-strength structural-steel plate grades, forging grades, and wire grades. For tube steels, it is the improved directional toughness behaviour at low temperatures (fig.13)[24)] and the increasing resistance against hydrogen induced cracking (HIC) that are of great practical significance for the off-shore drilling application and pipeline construction.

The injection of solids has found widespread use in recent years, more than any other used in ladle metallurgy.

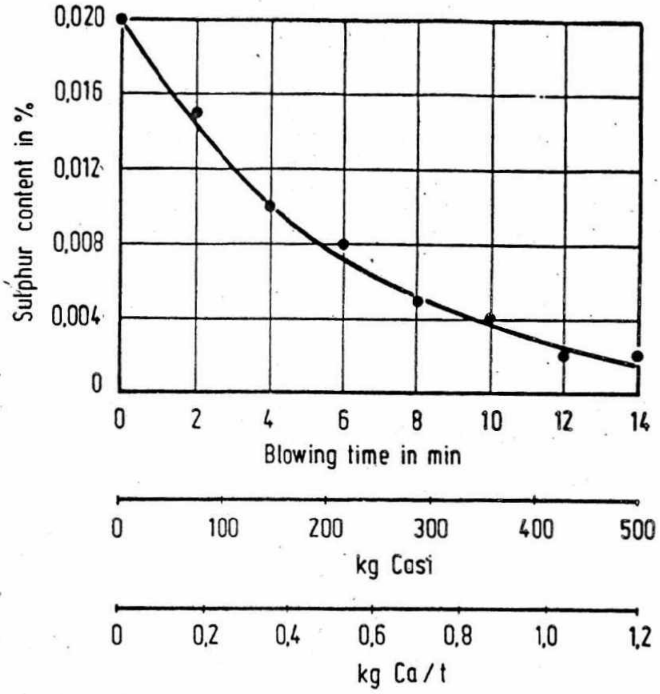


Fig.12 Decrease of Sulphur Content During CaSi Blowing into a 120 T-Dolomite Ladle[23)]

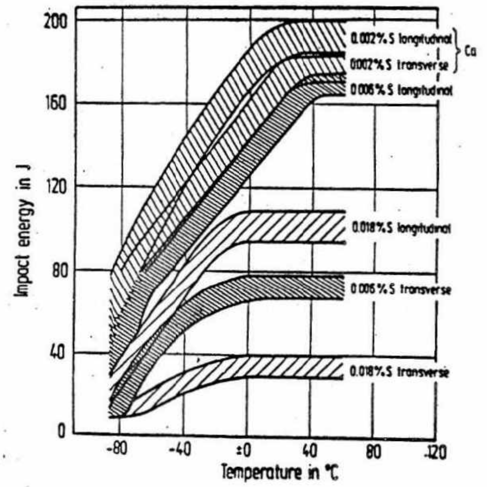


Fig.13 Influence of Sulphur Content and Sulphide Shape Control on the Charpy V-Notch Energy of 8 and 10 MM Thick x 52 Hot Strip[24)]

Apart from improving the quality of flat rolled products, it is being used today for nearly the entire product range. In particular the surface quality (fig.14)[25)] can be improved. The relatively simple way of operating the facility as well as the high attainable degree of cleanness and the good fluidity of the steel produced (fig.15)[26)] make it possible today for any producer of plain carbon

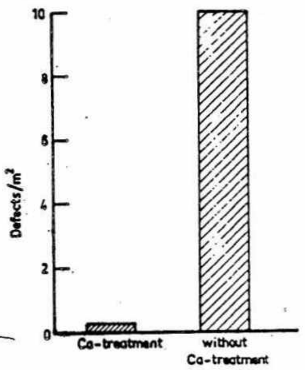


Fig.14 Defects on the Surface of Fine-Ground Plates[25)]

steels to include in their product mix even such highgrade steels as used to be made previously in electric arc furnaces only. Electric steelmaking shops prefer these methods, in particular for expanding the capacity of the melting shop and for stepping up continuous casting.

Recent developments in injection metallurgy have shown that the improved fluidity of ladle-treated steels open up new possibilities, in particular for making high-grade steels through continuous billet casting. So far, continuous billet casting was predominantly used for making Mn/Si-deoxidized

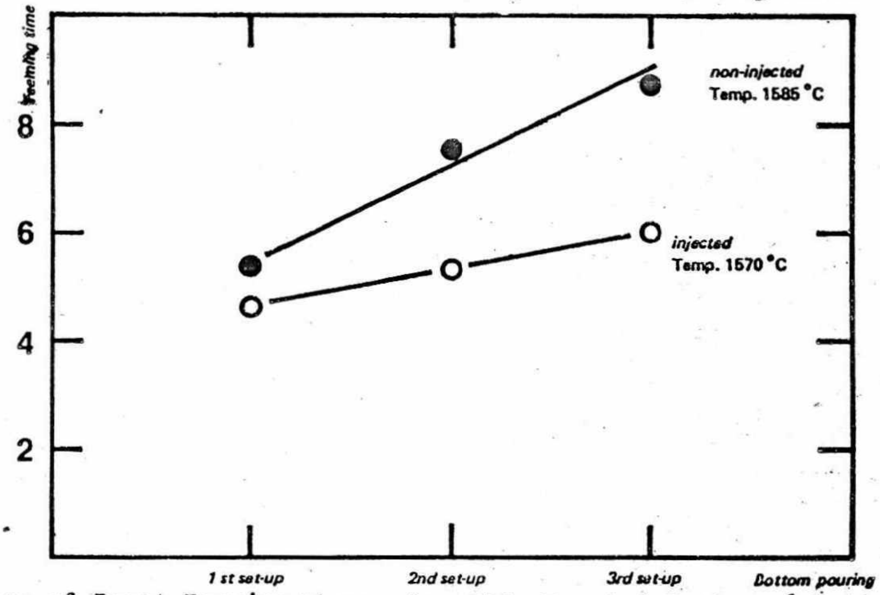


Fig.15 Comparison of Ingot Teeming Times, for SiCa Treated Heats and Untreated Heats[26)]

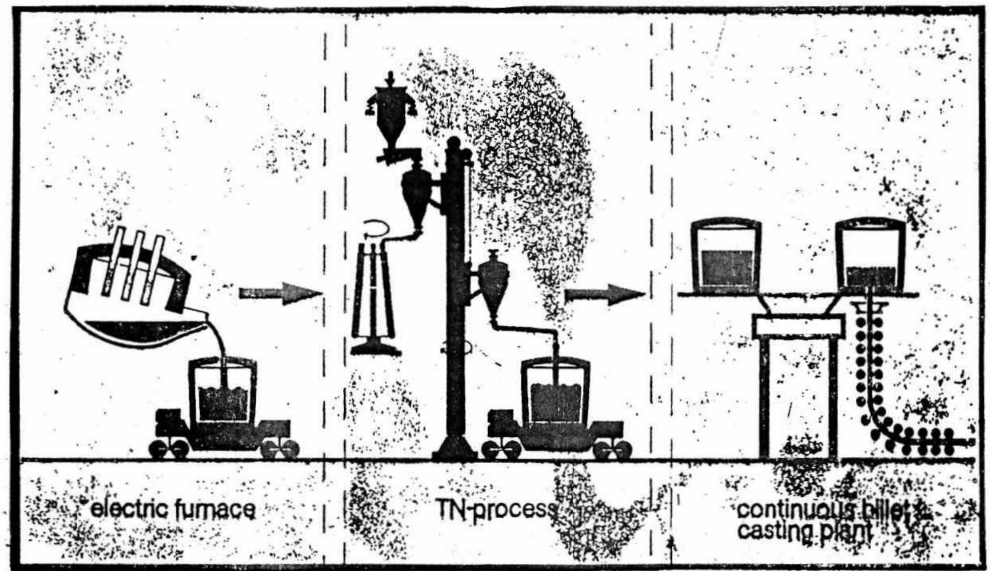


Fig.16 TN-Process and Continuous Billet Casting

basic grades. Aluminium-killed steels caused the tundish nozzles to be plugged as a result of alumina precipitations having a high melting point. Necessary aluminium additions to prevent the formation of pinholes could, at best, be made by feeding aluminium wire into the continuous casting mould. However, the quality improvement obtainable in this way is only a limited one because of the irregular aluminium distribution in the billet. Evidence has now been furnished, showing that the disturbing alumina precipitations of aluminium-deoxidized heats can be prevented by way of injecting calcium-bearing alloys, and that aluminium-killed steel grades can be smoothly poured[27,30], regardless of the carbon percentage. Fig.16 shows the process route from the electric furnace to the TN facility and the continuous billet caster in the new electric steelmaking shop at Thyssen Niederrhein AG with its two 120-ton UHP electric arc furnaces (80 MVA each) and a 6-strand continuous caster where both Mn/Si-killed and aluminium-killed high-grade steels are made without any trouble during pouring.

In conjunction with steelmaking in electric furnaces, injection methods offer further economic advantages as against the conventional single-step electric furnace operation. Adopting the double-stage mode of operation - namely performing the deoxidation, desulphurization, and alloying in the ladle - permits the capacity to be increased by more than 30%[31]. In the case of the double-stage mode of operation, the electric capacity of the furnace is fully available for melting scrap and the necessary refining. The difficult tasks of deoxidation and desulphurization in the electric furnace vessel which is unfavourable for such metallurgy work is moved into the ladle where ideal conditions are encountered for an exchange of the substance through the process of injection. Work done at present to further develop the injection method is now concentrating on studies to control the formation of inclusions through the injection of specific kinds of elements and the sequence thereof, with a view to applying them to other steel grades.

Fig. 17 shows how to minimize negative aspects of the process, for instance nitrogenizing the heat in case of injection of CaSi. Adding powdered slag causes the nitrogenizing effect to be negligible[23].

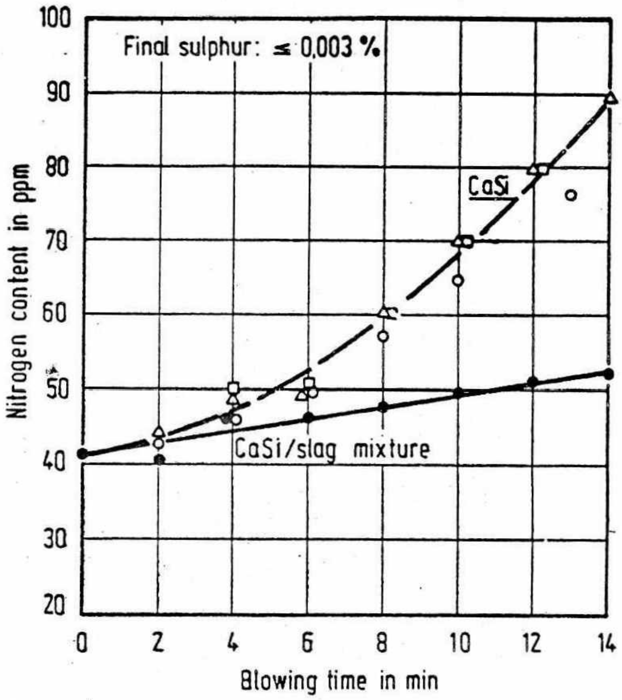


Fig.17 Nitrogen Pick up During Injection of Desulphurising Agents into a 120 T Dolomite Ladle[23]

Wire Injection

Based on success achievable by means of calcium additions to improve the properties of the steel, injection methods have been developed in Japan in recent years to introduce calcium-bearing elements by way of bullet-shooting and calcium compound wires by way of feeding. Both the bullet-shooting and the wire feeding methods are modifications of the industrially proven method of adding aluminium (fig.8).

With the bullet-shooting method - SCAT-Process[32] - CaSi contained in an aluminium capsule is shot deep into the ladle by means of high-pressure gas; to provide good distribution, the heat is simultaneously stirred with argon.

With the wire feeding method[33-35] specially designed, sheathed calcium compound wires can be introduced continuously into the ladle, the centre riser or the tundish during continuous casting by means of a feeding machine. The feeding rate can be varied from 0.05 to 5.1 m/s by means of a regulating mechanism. For big tonnages, it is recommended to reel in 2 or more wires. Calcium compound wires are available today in thicknesses up to 11 mm. They consist of an independent internal body made up of calcium and aluminium, surrounded by sheet metal sheathings 0.2 mm in thickness. Apart from this, filling wires are also used with fine-grained CaSi. During the injection into the ladle, inert gases are again used for stirring with a view to obtain thorough mixing.

The SCAT and the feeding methods essentially aim at improving the quality by way of changing the morphology of oxide inclusions in the steel. Since compound wires are usually relatively expensive, for low-sulphur steels, other desulphurising methods should be used to attain low-sulphur in steel. As in the case of the powder injection methods, a ladle should be used with basic lining, and a top slag should be provided to pick up the reaction products, if possible. The possibility of improving the quality of steel products even with small amounts of calcium by way of feeding compound wires into the tundish or the centre riser, has caused the feeding method to find widespread use. In this case, the desulphurization is usually performed by way of desulphurizing the hot metal or by providing a slag treatment in the teeming ladle. Therefore, when looking for the most economic method, both the objective and the entire process route must be considered here. Last but not the least, due consideration must be given to the fact that, in spite of the ease of performance, the prices of the wires are relatively high and the use of the same is economically justifiable only if the properties desired are obtainable with minimum additions of calcium.

Use of Vacuum

Hydrogen as the cause of quality-impairing flakes in the steel products gave rise to the development of degassing methods. Degassing of the teeming jet adopted as early as in the 1950s by Bochumer Verein permitted for the first time to reduce the hydrogen percentage in industrial heats to approx. $\leq$ 2 ppm, i.e. the limit beyond which there is a risk of flake formation, using a vacuum chamber with pressures up to 1.3 mbar. For making such steel grades susceptible to flaking, for instance forgings, plates, rails, and steel castings, this has made possible to eliminate completely or partially such process steps as are expensive and hard to control, i.e. cooling on hot beds or diffusion annealing in the forging and rolling shops.

Today, vacuum facilities of different designs are standard equipment in modern steel mills[36]. As modern ladle metallurgy advanced, additional tasks have been added to the original ones of hydrogen reduction. These encompass such steps as vacuum deoxidation, extreme decarburization, homogenization, slag treatment, and alloying.

Nowadays, vacuum methods are frequently used for deoxidation or extreme decarburization, which is possible by way of CO formation since the decarburization reaction is a function of pressure. The improvement obtainable in oxide cleanness is established in the removal of soluble oxygen without residues, in complete reduction of oxide inclusions, and in favourable conditions for the precipitation of non-metallic phases. Here, decarburization of steel heats can go to as little as 0.001% C, with the addition of oxygen-bearing elements or pure oxygen, if necessary.

For practical steelmaking, the jet or stream degassing methods continue to be of particular importance, in particular the ladle degassing method and the vacuum degassing methods for partial qualities, as shown in fig.18.

During stream degassing, the pouring jet is torn apart in vacuum, thus creating large reaction surface that permits degassification to extremely low percentages. This method is of great importance for casting big forgings.

Slag treatment is possible during stream degassing when using a second ladle. It was along the lines of the method shown schematically in fig.19 that the first powder injection treatments were performed in 1969 on industrial heats for making plates with particular toughness requirements[22]. Using two ladles permits complete retention of high-oxide furnace slags in the tapping ladle, thus creating optimum conditions for thorough deoxidation and desulphurization during the ensuring injection treatment in the teeming ladle.

Ladle degassing facilities have found widespread use in particular for treating small and medium tonnages (fig.20). The steel ladle which is placed into a vacuum chamber must be

Vacuum treatment

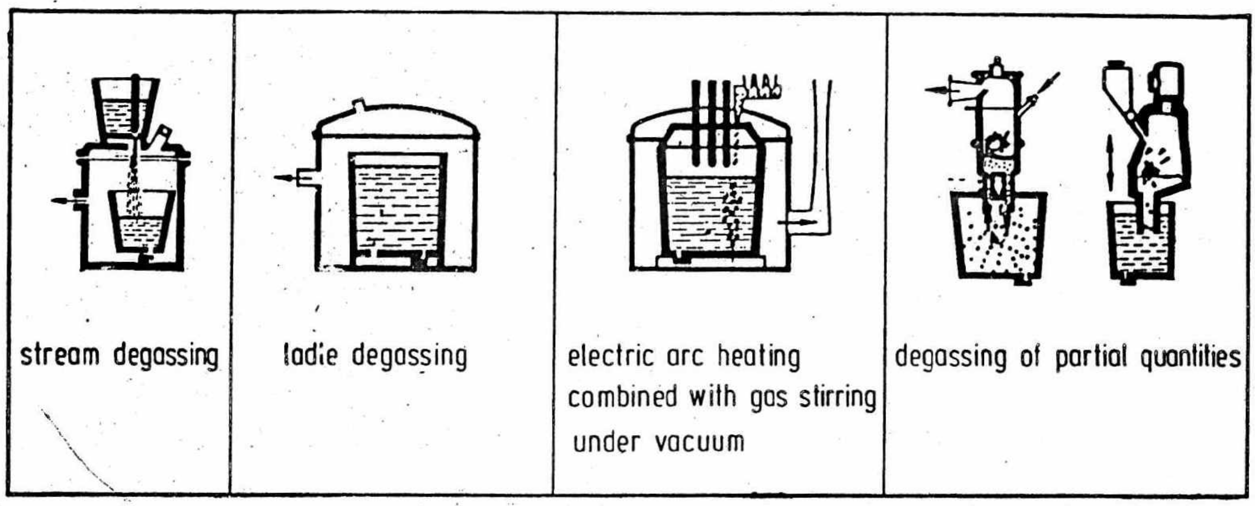
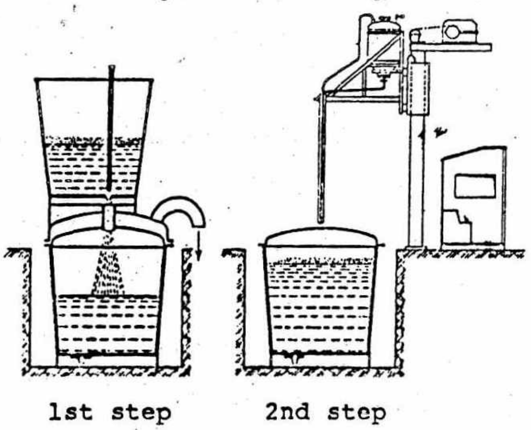


Fig. 18 Technological Solution for Post-Treatment of Steel



← *Fig. 19 Arrangement for Vacuum Degassing and Injection of Powdered Materials at Thyssen Niederrhein*[22]

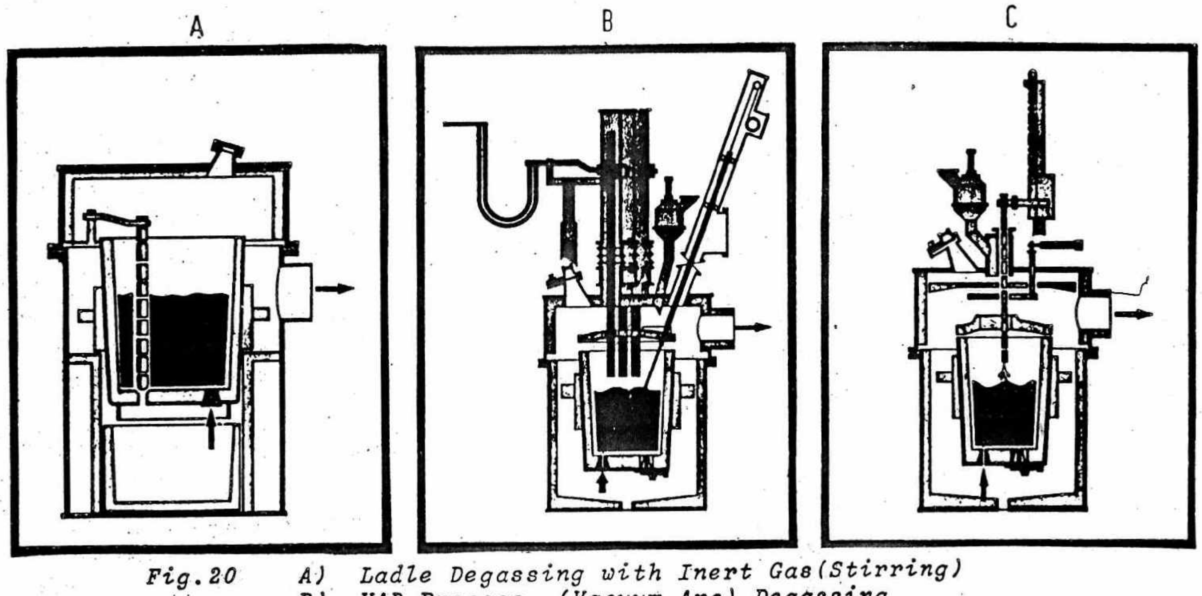


Fig. 20 A) Ladle Degassing with Inert Gas (Stirring)
B) VAD Process (Vacuum Arc) Degassing
C) VOD Process (Vaccum Oxygen Decarburisation)

flushed intensively with argon to support the degassing reaction. Combined with the injection metallurgy, this method has become particularly important for electric steelmaking. In this case, the crude steel made in the electric furnace is subjected to an injection treatment in the ladle and then to ladle stand degassing with a view to reducing the hydrogen content. The quality of the steels made in this way meets maximum requirements and compares favourably with the steel made along the lines of the electric-slag remelting process (fig. 21)[28].

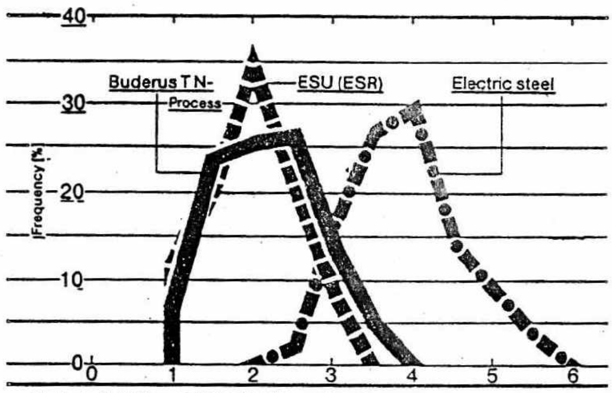


Fig. 21 Comparison of the Frequency Distribution for Purity (M Value=Mean Maximum Inclusion Size) of Various Steel Production Processes[28]

For vacuum treatment, due notice must be taken of a temperature loss resulting from addition of large amounts of alloying elements and the performance of the injection and slag treatments, which usually can be compensated for by increasing the tapping temperatures accordingly. Wherever this is not possible, for instance as a result of insufficiently rated electric furnace capacity, or inferior brick quality of the refractory lining or difficulties in obtaining low phosphorus percentages, additional electric arc ladle heating can help to solve the problems. Heating by ladle furnace as a separate step besides the vacuum treatment, for instance ASEA-SKF-process as well as combined heating and vacuum degassing-VAD-process, is today in widespread use.

Processes like VAD-Vacuum-Arc-Degassing (fig. 20) permits the conduct of the heat under vacuum up to several hours, depending on the requirements. This allows to get very low oxygen and sulphur percentages to be obtained and temperatures losses to be compensated for by way of deoxidizing and desulphurizing slag treatment.

With regard to the necessary equipments for getting low oxygen and sulphur steels the injection processes are less expensive. On the other hand, injections don't allow hydrogen reduction in the same step, but inclusion control leads to further improvements. A decision on process route to be preferred, in the ultimate analysis, depends on the technical requirements and cost of steel production.

Another field of application of ladle metallurgy is present day manufacture of low-carbon, high-chromium, corrosion-resistant, acid-resistant or high-temperature steels. When refining under vacuum, for instance along the lines of the VOD method - Vacuum-Oxygen-Decarburisation, (fig. 20) at the usual melting temperature of 1700°C, the required carbon percentages of less than 0.03% are obtained without causing any major chromium slagging to occur (fig. 22)[38]. Identical results can be obtained when using oxygen for partial-quantity degassing (RHO method) and the blowing processes (AOD and CLU process), by way of lowering the partial pressure of oxygen using oxygen/inert-gas mixtures.

Partial-quantity methods have found widespread use in BOF steelmaking shops of great capacity and big heat units of up to 400 tons. With more than 140 installations, these methods represent by far the biggest treatment capacity of all vacuum processes.

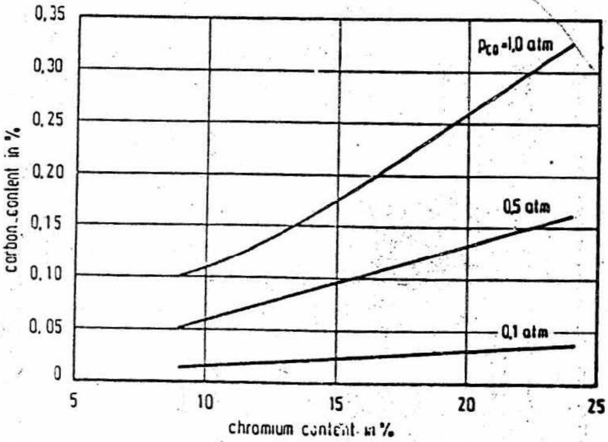


Fig. 22 Dependence of the Chromium-Carbon-Equilibrium from Carbon Monoxide Pressure (1700°C)[38]

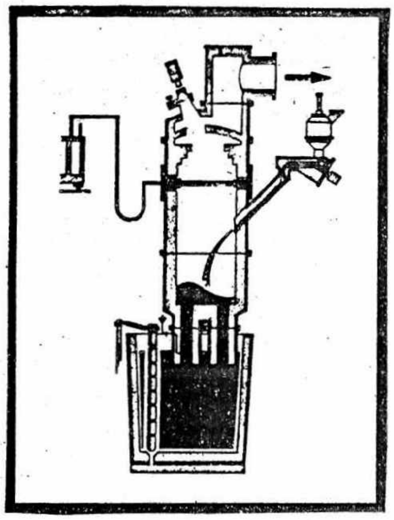


Fig.23 RH Circulation Process

It was in the 1950s that the DH method was developed by the Dortmund-Hörde division of Hoesch-Hüttenwerke AG, and the RH method as a joint venture of Ruhrstahl and Heraeus in the shops of Thyssen Henrichshutte AG. Today RH stands for: refining process Henrichshütte. When applying these processes, part of the steel heat is exposed to particularly low pressure. With the DH method, the partial quantity is discontinuously exposed to the vacuum by way of lifting and lowering of the vacuum vessel; with the RH method using argon as a carrier gas, the steel circulates uninterruptedly through the vacuum chamber; fig.23.

The methods are characterized by circulating rates of 25 to 125 tons/min., depending on the weight to be treated. The vacuum vessels which are lined with magnesite-chromium bricks specifically designed for this purpose are brought up to 1500-1600°C by means of graphite bar resistance heating to keep the temperature loss as low as possible during the treatment. Favourable conditions for kinetics of the reaction are ensured by the low pressure, the turbulence, and the big reaction surface of the steel, particularly when using carrier gas, so that short process times of 10 to 20 minutes are sufficient to obtain the desired results reliably. Alloying elements are fed into the steel under vacuum from automatically controlled bins and weighing equipments. This permits rapid dissolution and homogenization, with no disturbing effect being exerted by the slag.

Apart from using these vacuum methods to remove hydrogen, to determine the steel composition and to improve the cleanliness, the following tasks can be fulfilled:

1. *Extreme alloying*, for instance carbon up to 0.7%, Mn up to 1.2% and Si up to 3%.

2. *Aluminium-free de-oxidation* for making wire grades and forging steels in big ingots.

3. *"RH-light treatment"* for handling strand-cast, aluminium-killed steels in deep-drawing or tin plate sheet grades.

4. *RH-OB or RHO treatment* for refining stainless steels under vacuum. The oxygen is blown into the circulating steel under vacuum by means of lances.

The RH and the DH methods, with the injection methods as separate steps, are used in combination to perform the slag treatment and the inclusion control. Fig. 24[22] shows the toughness figures for the St 36 steel sheet grade, obtainable by way of combining the TN and RH processes as against conventional production, using as an example the dependence of the determined impact strength upon the test temperature and the sulphur percentage. For low sulphur percentages and up to a test temperature of -80°C, the T/L ratio is higher than 0.9. As the sulphur percentage increases and the test temperature decreases, the T/L ratio is getting smaller, i.e. the anisotropy of the sheets increases. In contrast, normal production with 0.015 to 0.020% S at ambient temperature presents an impact strength on longitudinal specimens of 125 J and a T/L ratio of only 0.6. Fig.25[39] shows the toughness figures obtained from a combined use of the TN and DH processes at Fabrique de Fer Belgium, showing the scatter band of striction figures in the through-thickness direction as a function of the sulphur percentage in plate of the St 52.3 and API X 60 grades.

There is considerable literature evidence for the successful use of vacuum installations combined with powder injection installations. Therefore, further details are not required here.

Test Temperature °C	Impact Energy in J of StE 36 plates, 18 to 41mm, ISO-V-Sampels				
	TN-treated				untreated
	l/t	l/t	l/t	l/t	l/t
R.T.	267/263	276/268	262/251	230/212	125 / 75
± 0	266/250	270/259	265/245	240/200	
-20	254/242	269/250	260/230	225/190	
-40	233/217	225/209	230/195	203/155	
-60	212/198	198/182	182/146	162/123	
-80	188/175	157/142	162/130	158/115	

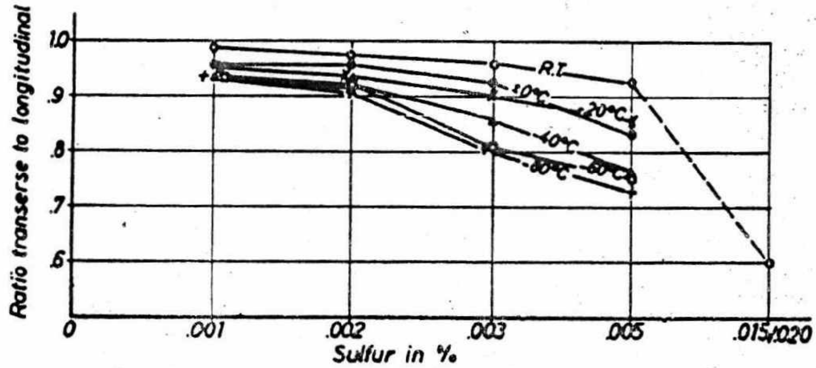


Fig.24 Effect of TN-Treatment on Impact Energy of STE 36 Plates[22)]

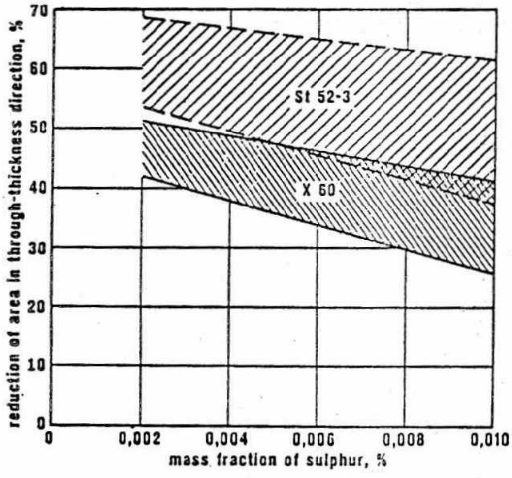


Fig.25 Reduction of Area in Through-Thickness Direction Related to Sulphur Content for Steels ST 52-3 and X 60[39)]

The fast spreading of post-treatment facilities demonstrates convincingly that use is made of the possibilities in ladle metallurgy to improve the competitive situation. Increasingly, post-treatment steps are included in the production flow of steel mills. The trend is to leave with the steelmaking shop only the task of melting and refining, possibly the dephosphorization and overheating.

The product of this primary metallurgy is a "crude steel" in the purest sense of the word, with sufficiently low carbon and phosphorus percentages. The final attainment of correct steel analysis conforming to the envisaged use - deoxidation, alloying, homogenization, and temperature control, as well as desulphurization, inclusion control, or degassing - is achieved in separated steps of ladle metallurgy which are controlled by probe measurements to determine the temperature, the chemical composition of the steel bath and the oxygen activity as illustrated in figs. 26[40)] and 27[41)] showing a combined installation for powder injection and vacuum treatment.

Finally, mention will be made of the present use of ladle metallurgy at Thyssen AG.

The divisions of Thyssen AG are located in the Rhein-Ruhr area of the Federal Republic of Germany. Its crude steel capacity is approx. 16 million tons per year. Fig. 28 is meant to provide an idea of the use of ladle metallurgy in these divisions:

1. The hot metal produced, i.e. approx. 1 million tons per month, is desulphurized to approx. 0.018% S by way of injecting calcium carbide

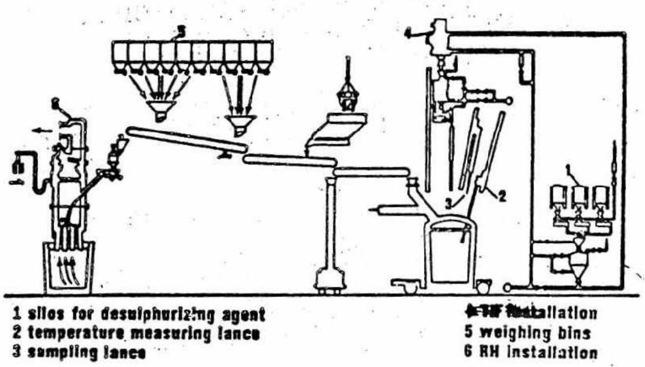


Fig. 26 Schematic Layout for Ladle Metallurgy[40)]

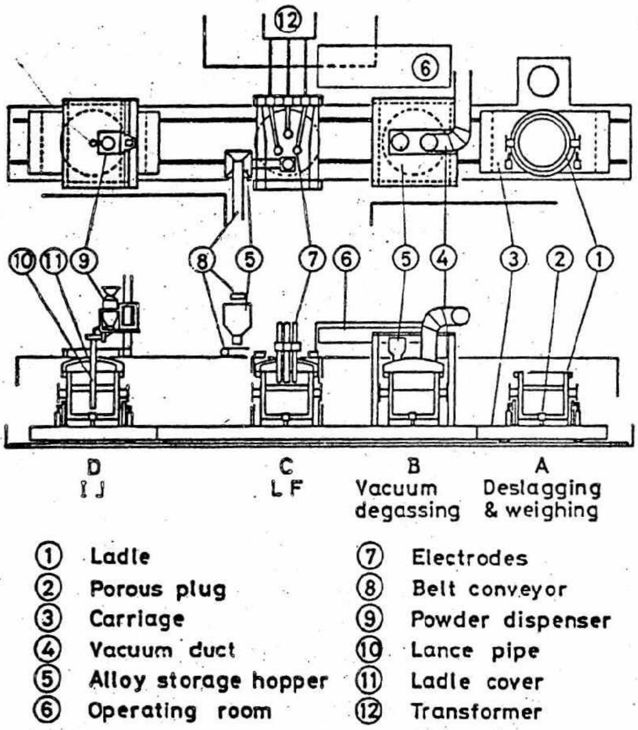


Fig. 27 Layout of Ladle Refining Equipment[41)]

mixtures into the torpedo ladles on their way from the blast furnace to the steelmaking shop.

2. In addition, injection or stirrer methods are used in all steelmaking shops to further reduce the sulphur percentage in the charging ladle, when required. Here, depending on the requirements for the steel grade to be produced, percentages of as far as $\leq 0.002\%$ are obtained.

3. In all steelmaking shops, inert gases are used for stirring the steel in the teeming ladle for the purpose of homogenization.

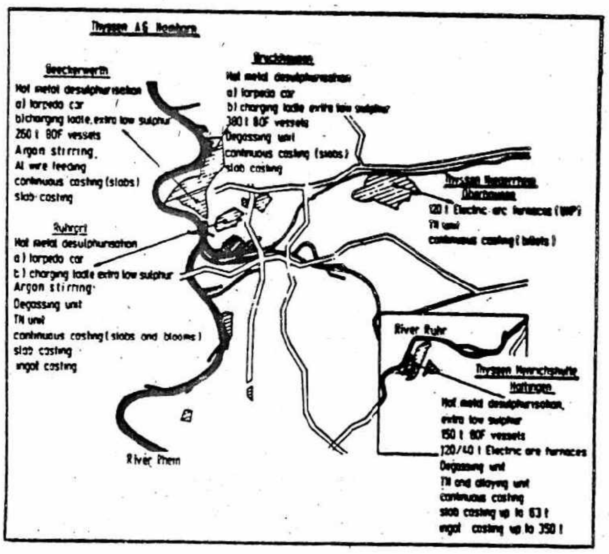


Fig. 28 Steel Making and Ladle Metallurgy Within the Thyssen Divisions

4. In the steelmaking shops of the Hattingen and Oberhausen divisions there are efficient TN installations for making high-grade steels with particular requirements. In the Oberhausen division, each heat is subjected to an injection treatment for producing continuously cast billets. In the Ruhrort division, injection facilities are being operated along the lines of the TN process, especially for the injection of alloying elements also.

5. Vacuum facilities are in operation in the Bruckhausen division - a DH installation for treating 400-ton LD steel heats - and in the Ruhrort and Hattingen divisions - RH installations for treating 100 to 160-ton electric-furnace and LD steel heats.

6. A combined TN/RH treatment is used in the Hattingen division for making plate and forging steel grades.

The examples of application shown here are meant to illustrate the importance of ladle metallurgy in a steel mill. Other methods may be more advantageous in other steel mills under different conditions and assignments. What is certain, however, is the fact that today's requirements for making high-grade steel cannot be met any more economically without using ladle metallurgy.

CONCLUSION

Increasing use is being made of ladle-metallurgical processes and process combinations for steelmaking. This trend was triggered by an increasing demand for improved steel products, the necessity of low production costs, and process steps which are compatible with environmental protection. It is through desulphurization of hot metal in the ladle that the steelmaking shop is being provided today with charging materials that presnet the required sulphur percentages. This permits the blast furnace and the steelmaking shop to operate more economically. In modern steelmaking shops, depending on the present assignments, different post-treatment methods or combinations of methods are being used. This allows steels of high quality to be produced in tonnage steel mills that used to be made previously along the lines of expensive methods using a reducing slag.

The demand for steels of ever increasing strength will continue in the future as well. The possibilities involved in ladle metallurgy are certainly not completely exhausted yet. For example, the use of injection metallurgy for making high-grade steels for billet casters is one of the recent progresses made. Although the technical design of the different ladle-metallurgical processes have reached a high degree of development, combinations of methods are likely to develop still further. The steelmaking shops will increasingly take care of melting and refining whereas the finishing steps of steelmaking will be handled by a centrally located treatment stand in accordance with the requirements stipulated by the final use of the steel.

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