RECENT DEVELOPMENTS IN CALCIUM ALLOY CORED WIRE IN STEEL PRODUCTION

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The control of sulphides and oxides and desulphurisation by injection of calcium alloys in liquid steel is used with success in ladle now for many years. In the last years, technique of Ca alloys cored wire was developed as an alternative for inclusions control.

A technology using a wire, not welded with a large diameter is described so that a feeder of the capstan type, making it possible to introduce big quantity of Ca alloys (SiCa - SiCaBa...) or other powdered products. This technique is intended to small foundry ladles or big steelworks ladles as a tool to treat medium tonnages. Treatment in tundish of casters is also possible.

Some results achieved in special steels for mechanical industry are given regarding mainly sulphides control by ladle addition.

1. INTRODUCTION

In the last 10 years, ladle injection treatment has been developed as a major tool for desulphurization and inclusions control, oxides and sulphides. All types of treated steels are cast in moulds or in casters leading to a high level of quality in the final product. It is the aim of the present conference to deal with the latest developments in this field.

The mechanisms of ladle injection are now well precised, and, specially the knowledge of suitable gas/product ratios is accurate enough to predicate better conditions for treatment and final results. Calcium alloys, mainly calcium-silicide are largely used in the injection process with a good success.

Nevertheless some limitations are specific to injection technique:

The tonnage to be treated must be large enough because of cost of investment and use, losses of temperature.

The capacity of ladles must be in the range of 15-20 T at least and use of basic lining is most often recommended.

The treatment is made mainly in ladle, the necessity of relatively big gas volume making it difficult to be used in small ladles and in the tundish of casters.

Also it is not possible to introduce separately product and gas to control tightly the quantity of inclusions eventually favourable to final properties (machinability for sample): "injected" steel is a clean steel.

In these conditions, a calcium cored wire appeared as a simple mean to control more strictly final inclusions. Calcium bullets (SCAT process) are intermediary between injection and core wire (1). Calcium and calcium alloys cored wires are derivated from the welding technology. Such wires are developed with feeders, generally, for treatment in full ladle (2), in bottom pouring (3), (4), in tundish of casters (5), (6).

The study of the formation and floating up of oxides and sulphides very often associated together, is well advanced (7), (8), (9). The treatment was applied to steels for sheets, plates, forgings (10), (11), tubes (12), produced in oxygen converters and electric furnaces. A survey of the technique and results was made recently (13).

Addition products are Ca metal and alloys (Al - Ca alloy) in a 5-7 mm steel tube. With the high vapor pressure of calcium at 1600°C, the emission of fumes and splashes is not thoroughly avoided: the use of free board is advisable e.g.

So, our development in cored wire was made with the purposes hereafter:

To use industrial powder of Ca alloys (SiCa - SiCaBa) with the screen analysis of the injection powders.

To limit by this way strongly, if possible to suppress, fumes and splashes (no free-board requested).

To use a wire with a big diameter, to have a maximum content of SiCa per meter. Aimed characteristics e.g. dia = 11 mm, SiCa = 130 g/m, SiCa = 45%.

To be able to add wires in all ladles from 5 to 150 T, possibly up to 300 T with a simple feeder, without any extra manpower (for ladles in the range 200 to 5000 kg, a small diameter wire 5-7 mm is produced). The treatment in tundish is also concerned.

To ensure by addition in ladle or in tundish a precise control of inclusions in the production of:

special steels (C, alloy steels) with Al content for improving machinability and cold forging properties (Calcium steels), including resulphurized steels up to 0.070%, produced by the route of ingots or continuous casting.

carbon steels cast in small billets casters with the aim to replace Al wire addition in mould by higher Al content in ladle (Al about 0.020%). In slab casters, in low-sulphur steels to have also possibility of maximizing properties by controlling inclusions.

2. FLUX-CORED WIRES FOR STEEL INDUSTRY

2.1 Main characteristics and manufacture.

Flux-cored wires for steel industry are manufactured by Bozel/Arbed/Mines et Métaux. They are made of a metal sheath which surrounds a powdered flux: as they are produced by a continuous process those wires can be delivered in any length.

These cored wires whose production is protected by several patents are either welded or folded pipes. It is obvious that welded pipes are perfectly moisture tight but the same moisture tightness is got with special folded tubes.

Indeed, wires do not consist of a plain overlap but very thin protection foil is put inside and closes the seam perfectly.

This thin foil is just located above the flux and maintained firmly against the seam of the pipe; in other cases, the powder is completely surrounded by the foil (Figs. 1,2&3).

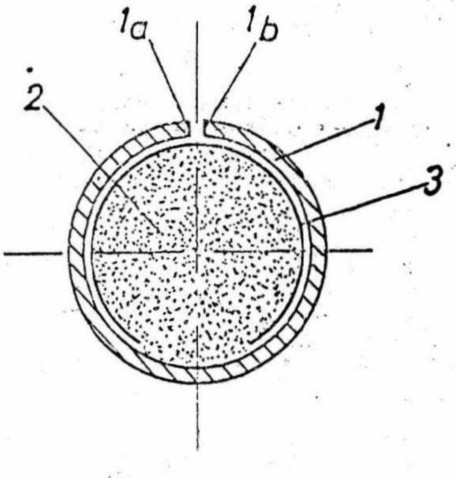


Fig.1 not welded

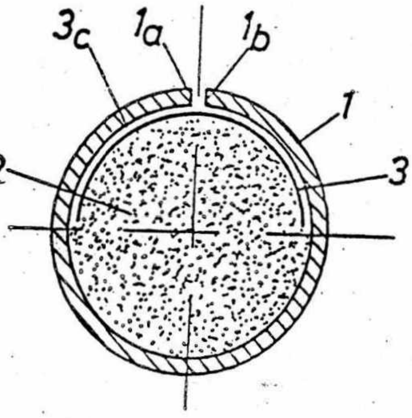
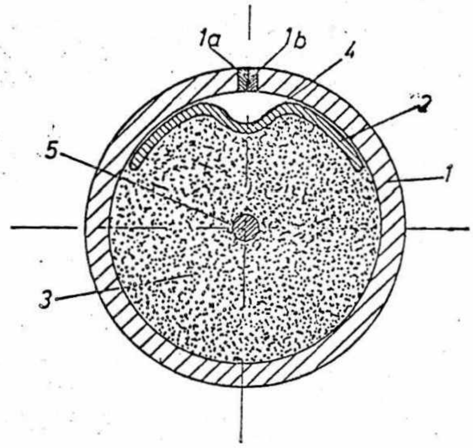


Fig.2 not welded



Some aspects of cored wires range

dia. 5 - 11 mm

Fig.3 possibly welded

Till now, the best results are achieved with two types of wire: first of all with the kind of wire with thin metal foil and also with plastic envelope but only on condition that the hydrogen content brought into the liquid steel doesn't bother. On the other hand, the plastic foil makes it possible to get a more important filling grade, that is to say a better ratio flux/metal. These flux-cored wires can be realised in several sizes for different uses; the usual sizes are 11-12 mm for injection into the ladle and 5-6 mm for injection into small ladles and tundishes. The table hereunder shows the main characteristics of the wires, depending on the kind and density of the powder, for instance here CaSi or CaSiBa.

The strip thickness has been chosen in order to get a high filling ratio and an ideal melting speed in liquid steel.

	ϕ 11 - 12 mm	ϕ 5 - 6 mm
Sheath thickness	0.5 mm	0.2-0.3 mm
Foil thickness		
Steel	0.2 mm	-
Plastic	0.025-0.075 mm	-
Flux weight	125-140 g/m	20-30 g/m
Total weight	285-300 g/m	70/75 g/m
Filling grade	43-48 %	26-30 %

These tubes are made from bright annealed and skin passed coils; the flux is introduced in the pipe during its formation by a continuous filling system; after the closing and compacting operation, these wires are coiled either on cardboard core or on a metal spool.

Spools of any weight can be produced but generally they contain exactly a flux weight enough for several heats.

For instance, the biggest spools till now contain 400-500 kg powder, that is to say about 850-950 kg cored wire (Fig.4).

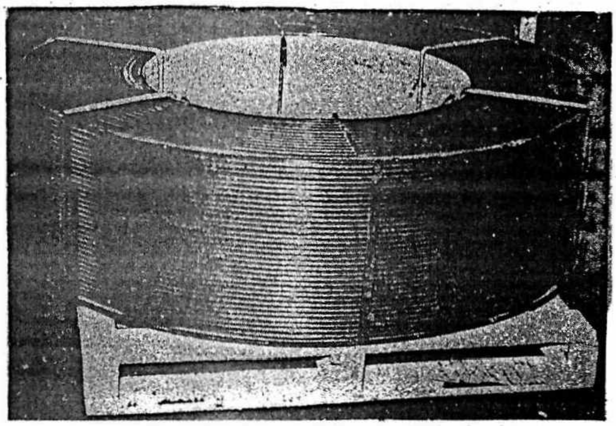


Fig.4 Spool SiCaBa cored wire wire dia. 11 mm / 900 kg

To avoid moisture on the wire, the spools are protected by a plastic foil and delivered on 2 tons wooden pallets (Fig.5).

The 5-6 mm wire is coiled on wooden or metal spools of about 250 kg **(Fig.6).**

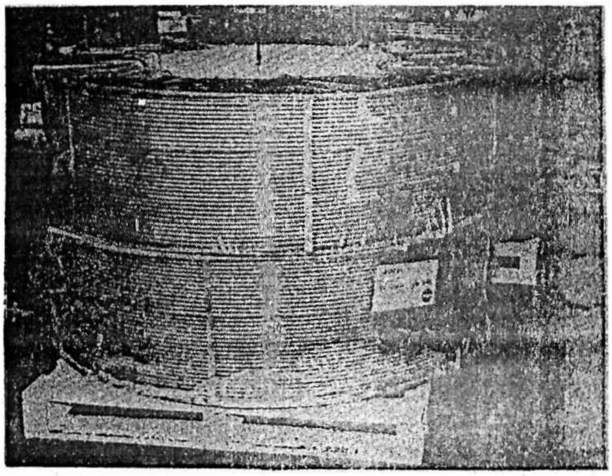


Fig.5 Typical deliveries

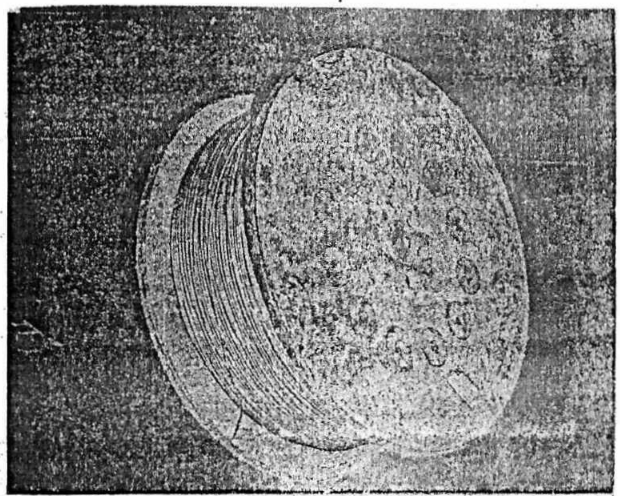


Fig.6 Spool SiCa cored wire
Wire dia. 5 mm / 250 kg

2.2 Feeders

The feeders for flux-cored wires are of two different types and sizes for 12 or 6 mm wires.

2.2.1 *The 12 mm wire machine* is essentially made of the following parts (Fig.7).

- a wire reel on which the spool is placed horizontally
- an input guide to lead the wire from the reel to the capstan
- a V groove capstan which drives the wire

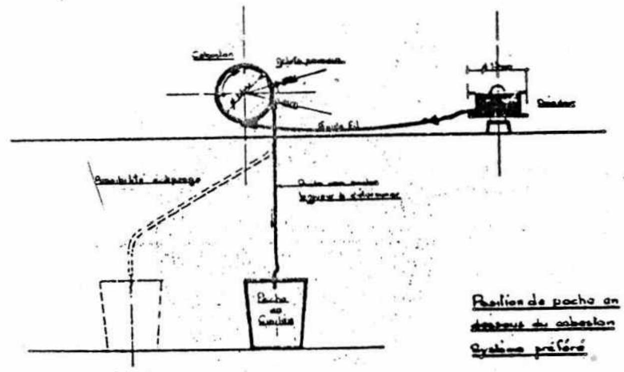


Fig.7 Capstan feeder for direct ladle addition

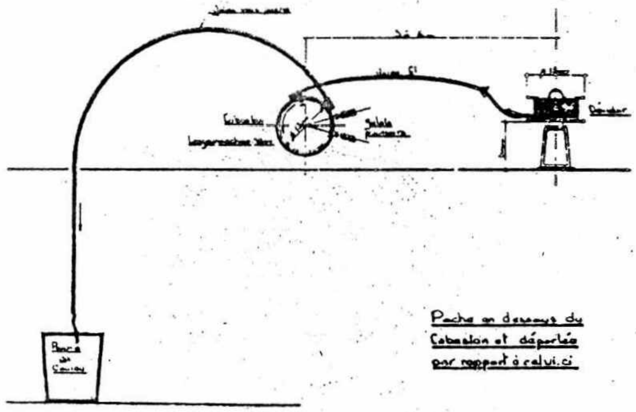


Fig.8 Capstan feeder for indirect ladle addition

- a kit of two or four pressure rolls pushed by pneumatic pistons to clamp the wire in the V groove
- an output guide to conduct the wire to the ladle

The machine is also equipped with all kinds of accessories, for instance:

- electronically controlled DC motor
- permanent and pneumatic emergency brakes
- potentiometric speed control
- round per minute or wire length electronic counter, etc.

It is interesting to note that this machine allows the feeding to be done in 2 different ways either by pushing down the wire when the machine is located just above the ladle (Fig.7), or by pushing up with the machine on a platform beside the ladle (Fig.8).

This machine is able to run continuously from very low speed up to speed in the range 120 and 200 m/min which means an alloy quantity of about 15 and 25 kg/min.

With the wire dia 11 mm, conditions of treatment are (for SiCa, SiCaBa 1.3 kg/T addition).

2.2.2 *For 5-6 mm wire* the machine is naturally more simple and compact and is essentially made of the following parts:

- a wire reel
- wire feed rolls pulling the wire
- an output guide to the steel bath

This machine is also provided by some accessory kits such as electronic rpm counter, potentiometric speed control from 0 to 80 m/min and so on.....

With this kind of machine, it is possible to add alloy quantities of about 0.2 to 2 kg/min depending on work conditions (steel tonnage to be treated, allowed time for treatment, bath depth and so on.....).

With a wire dia 5 mm conditions of treatment are (for SiCa 1.3 kg/T addition):

3. METALLURGICAL RESULTS

Some results achieved when using calcium silicide wire are discussed:

Control of inclusions in Medium Carbon steel with fine grain, cast in ingots.

Control of inclusions in Carbon steels cast in continuous casting.

3.1. Inclusions control in XC 38 grade with Al controlled grain (ingots)

The aim is with a 30 T electric furnace, using a cored wire dia 11 mm (130 g/m), in the full ladle with addition of SiCa= 1.5 kg/T:

To replace the 2 slags process including a long furnace refining time by one slag process.

To eliminate alumina stringers and to globularize sulphides in the range S - 0.015%/0.030%.

Table I

To be treated	Vm/sec wire speed	T min time of treatment
Ladle 25 - 30 T	1,2-1,5	4 - 6
40 T	1,6-1,8	5 - 6
80 T	2,0-2,3	6 - 7
150 T	2,8-3,0	10
Tundish (bloom caster) 5T, depth = 800 mm, ladle = 60 T	0,25	50 - 60
(x) for ladles 300 T	2 wires	v = 2,8 - 3,0 m/min t = 10 min

Table II

To be treated	V m/sec wire speed	T min time of treatment
Ladle 20 T (2 wires)	1	7 - 9
Furnace 2 000 kg	0,25/0,35	6 - 8
Tundish (billet caster) 2 T, depth = 300 mm, Ladle = 30 T	0,3	75 (SiCa = 1 kg/T)

To achieve a partial desulphurisation in ladle.

The conditions are:

a) analysis C = 0.38% Mn = 0.65%
Si = 0.30%
P $<$ 0.020% S = 0.030%
Al = 0.040%

b) steelmaking: furnace 30 T
ladle high alumina
preheating = 700°

- Usual practice includes: melting - decarburization with slag off.

  FeSi - SiMn blocking. New slag addition and reduction.

  Refining up to "white slag" tapping.

  In ladle: additions
  FeSi - FeMn - SiCa-Al
  argon purging 3 to 5 min

  Teeming: bottom pouring of 1300 kg square ingots.

- Tests heats A-B-C (Table III): in these heats steelmaking is modified in suppressing the long refining period in furnace by a short time in furnace with cored wire treatment in ladle.

In furnace, after total (heats A,B), or very partial deslagging (heat C), a lime addition is made, melted rapidly. In ladle metal and slags are tapped, slag being reduced by Al addition.

Process in ladle is following:

1. argon bubbling 1-2 min medium intensity.

2. wire feeding with low intensity bubbling total time = 5-6 min, speed = 1.2 m/sec.

3. post bubbling: about 3-4 min.

3.1.1 Results (Table III)

In furnace, time saving is about 30 min in refining period and the total ladle desulphurisation rate may reach 30-40%, with a temperature drop of 30° for a treatment of 10 min.

Examinations on the flats from Ca treated ingots confirmed the following points:

a) Inclusions: countings for B inclusions (alumina are better than with 2 slags process, only the finest inclusions being observed.

Silicates (C type) are eliminated.

Globular inclusions D type are low.

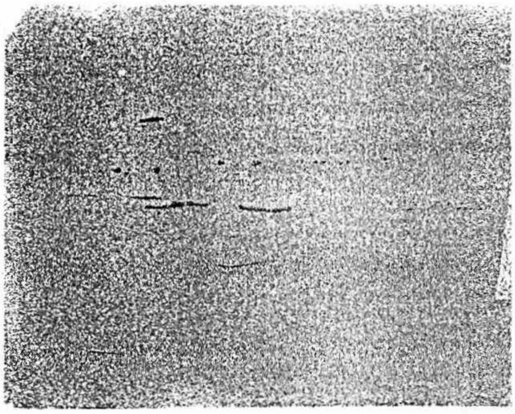
In the reference heat (figs.9 & 10) manganese sulphides and oxides (mainly alumina) are the most often apart, and many stringers are

TABLE III

XC 38 TREATED WITH SICA CORED WIRE

RESULTS	HEAT A		HEAT B		HEAT C	
SULPHUR %	0,029 %		0,015 %		0,020 %	
Micrographic cleanliness						
worst area						
A Type H	2		2		2	
" B	2		2		2	
B Type H	2		1		2	
" B	1		3 (center)		1	
C Type H	0		0		0	
" B	0		0		0	
D Type H	1,5		1,5		2 Heavy	
" B	1,5		1,5		1,5 Thin	
Inclusions counting Type B						
type 1	7		7		26	
type 2	1		0		1	
type 3	0		1		0	
[Reference Heat type B/Type 2 (2 slags)]	(10)		(10)		(10)	
- Sulphides globularisation rate	flats 80 x 100 mm		flats 70 x 80 mm		flats 80 x 150 mm	
Head	> 50 %		≥ 90 %		90 %	
Bottom	85 %		≥ 90 %		100 %	
- Impact tests						
KCUL daJ/cm^2	(H)7,4	(B)7,4	(H)8,8	(B)8,4	(H)4,4	(B)5,2
KCUT daJ/cm^2	(H)4,1	(B)4,6	(H)6,1	(B)6,1	(H)4,1	(B)4,0
ratio KCUT/KCUL%	55	62	69	75	93	77
[reference heat %]	(≃31)		(≃49)		(≃43)	

H = Head of ingot
B = Bottom



x 100

Fig.9 reference heat

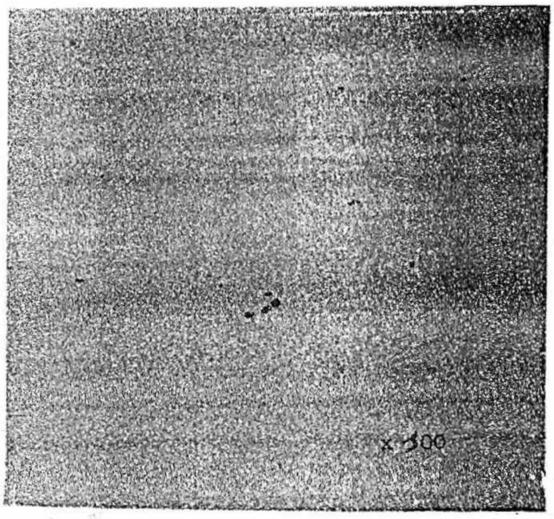


Fig.11. treated with SiCa

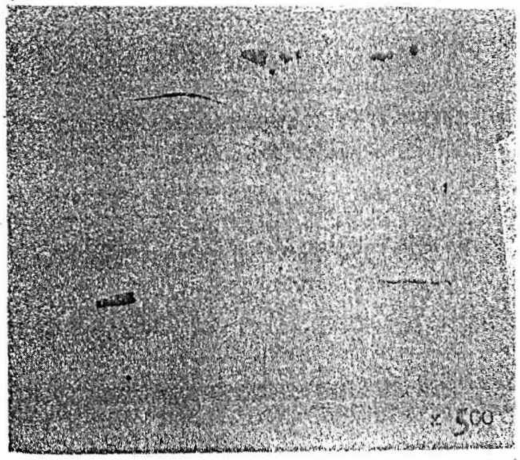


Fig.10 reference heat

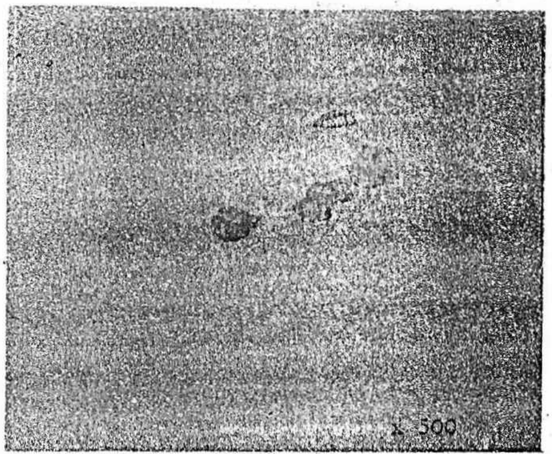


Fig.12 treated with SiCa

XC 38 oxides and sulphides in flats 70 x 80 mm (heat B)

present. In the tests heat B (figs.11 & 12), alumina inclusions are replaced by aluminates rich in calcium, round, in the form of a nucleus surrounded by manganese - calcium sulphides also globularized: the rate of globularisation for sulphides is high (a sulphide is counted as "globular" if ratio length/thickness is less than 1.5) and results in good isotropy of the flat.

b) Mechanical properties: Isotropy is estimated by the relation.

$$\frac{\text{Transverse toughness}}{\text{Long toughness}}$$

As observed in Table III, the sulphides globularisation increases strongly the isotropy, even at a sulphur level of S = 0.030%. Also in heat C, with a medium cleanliness in B inclusions (due to very partial deslagging), isotropy is very high.

3.1.2 Developments: other parameters are now well experienced:

Necessity to have adequate and reproducible argon purging cycle in ladle to keep wanted final oxysulphides.

High fluidity of treated steels ensuring a regular velocity of casting specially well fitted to bottom pouring and continuous casting.

Possibility of using fireclay linings.

Improvement of inclusions fineness when using SiCaBa alloys (Ca content = 30-50 ppm).

Last achievement of Ca steels with good fatigue and cold formability properties should be also possible by this way (14), (15).

3.2 Inclusions control in continuous casting

Two addition places were tested: ladle / tundish

3.2.1 Ladle addition of SiCa cored wire

The aim is to make it possible to cast quality steel with Al 0.015% in conditions hereafter:

one slag fast process in electric furnace.

addition of SiCa = 1.5 kg/T about with wire dia 11 mm.

billets Ø 130 mm with open nozzles dia 14 mm and complete suppression of Al wire in mould.

First results indicated:

Excellent fluidity without nozzle clogging for Al level = 0.015%.

Decrease of soluble oxygen from 20 down to 5 ppm by wire introduction.

No appearance of subsurface blow-holes.

Possible developments will be to increase Al up to 0.025% for grain refining, with a small nozzle gas shrouding.

3.2.2 Tundish addition of SiCa cored wire

First trials were made to improve castability and cleanliness of steels cast with submerged or shrouded nozzles.

(wire Ø 5 mm SiCa = 20 g/m SiCa = 25%).

In alloy steels, an addition of SiCa = 1 kg/T was sufficient to be got rid entirely of nozzle clogging and to ensure a constant speed of casting, even in small and shallow tundish. In this case, treatment is achieved by introducing wire in oblique direction following the tundish axle. Final content of calcium is in the range 30-50 ppm with very low soluble oxygen content and good control of alumina and sulphides.

Developments will be made to work with open nozzles to increase Al content in ladle and in slab casters with the aim to achieve good surface and subsurface quality with an excellent cleanliness.

4. CONCLUSIONS

A development of cored wire, containing calcium industrial alloys like SiCa, SiCaBa powder is described.

Two types of wires are developed with suitable feeders:

a) diameter 11 mm for ladle treatment from 5 up to 150 T, possibly bigger.

b) diameter 5-7 mm for small ladles and specially for tundishes of casters.

Some achievements are discussed:

Treatment without fumes and splashes and no extra manpower.

Ladle treatment for controlling oxides and sulphides in fine grain steels (C and alloy steels) with elimination of alumina stringers, control of sulphides morphology, also in resulphurized steels, allowing to control transverse properties, machinability and cold forming.

Tundish treatment for limiting nozzle clogging in carbon steels, cast with open nozzle and small gas shrouding, and Al content superior to 0.015%. Cleanliness, soundness, cast conditions are improved.

Actual developments for cored wire are:

a) delimitation of quantity, of alloys to be added and gas -

purging conditions to control quantity and composition of inclusions.

b) tight reliability of properties in the final products.

c) possibility of increasing Al content in steel for billets casters without nozzle clogging, allowing production of Al grain refined steels.

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"inclusions control in XC 38 grade"

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