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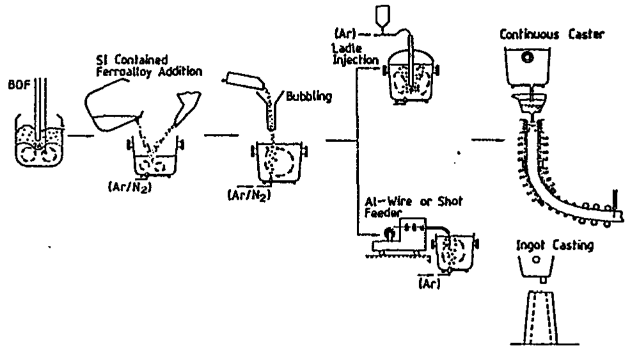
(54) **Si contained ferroalloy addition as a weak pre-deoxidation process in steel-making.**

(57) A weak pre-deoxidation process (W.P.D. process) for the production of aluminium- and titanium-killed steel.

In this process an adequate amount of a silicium-containing ferro-alloy is added to the molten steel during its tapping.

The ladle is subsequently transferred to an aluminium wire feeder or to a ladle-injection treating equipment for performing the final stage deoxidation process.



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Si CONTAINED FERROALLOY ADDITION AS A WEAK PRE-DEOXIDATION PROCESS IN STEELMAKING

This invention concerns with Weak Pre-deoxidation practice in steelmaking. Adding Si contained ferroalloy during tapping stage as weak pre-deoxidation practice, this new practice could achieve lower production cost and high quality steel products. For rimmed steel production very mino addition of deoxidizer results in higher free oxygen contain in molten rimmed steel, which would react with solute element in molten steel, a solid skin layer around the ingot surface is formed.

Such solid skin layer possessing good surface quality and soft characteristics will improve cold heading formability of the steel products whereas the inner part of rimmed steel could not provided for higher grade application because of its poor cleaniness.

High free oxygen in rimmed steel liquid, couldn't be casted by continuous casting process, casted ingot causes lower production yield. Rimmed steel couldn't be provided for special application for the reasons stated as above.

For fully killed steel, the deoxidizer (Al, Si, Ti, Mn) added during tapping process is oxidized by the free oxygen in molten steel. The reaction is shown below:

$$xM + y(O) = MxOy$$ M: Deoxidizer, such as Al, Si, Ti, Mn etc.

(C): free oxygen in molten steel

x,y: coefficient

Because of lower free oxygen after deoxidizing, the fully killed molten steel could be casted continuous casting process. Generally speaking, the production yield and internal quality of the continuous casted products is superior than that of ingot. Lower recovery rate and higher addition amount of deoxidizer for fully killed steel causes higher production costs and results in the residual of deoxidizing formations remained in steel. Such residual deoxidation formations is harmful to processing formability while the Weak Pre-deoxidation process could vanish the defects stated above and provides lower cost higher cleaniness and higher quality steel products.

Producting steel for cold working or forming applications by continuous casting, fully killed steel is usually adopted to avoid casting incident and blow hole formation in steel, Al and/or Ti is the major deoxidizer in continuous casting process. Killed steel for cold working or forming applications could be classified into Al-killed and Ti-killed steel according to the deoxidizer adopted. Al-killed steel as an example, in order to reduce work hardening effect, any Si contained ferroalloy could not be permitted to add into molten steel during steelmaking process, only Al is used as deoxidizer. Owing to the deoxidation reaction of Al ($2Al + 3[O] = Al_2O_3$), alumina cluster (Al_2O_3) forms in molten steel and remains in solid steel as inclusion, which could not be elongated during deformation, thus interfere the cold heading or working formability. The objective of this new process stated above is to overcome the shortness of deoxidation practice, that is to reduce work hardening effect. For conventional Al-killed steel, any Si contained ferroalloy could not be added during steelmaking. Such deoxidation concept is modified by this new deoxidation process, during tapping (of top blowing furnace, bottom blowing furnace, top and bottom combined blowing furnace or electric arc furnace) appropriate amount of Si contained ferroalloy could be added in the condition of no Si remained in molten steel. Free oxygen content of the molten steel in ladle could be reduced as Si contained ferroalloy added then the ladle is transferred to Al-wire feeder system or ladle injection treating station to proceed the final stage deoxidatio with Al and/or Ti killing, or other composition adjustment.

This new process will increase the recovery rate of deoxidizer, decrease the amount of deoxidizer and ferroalloy consumption and save production cost. Because of less deoxidizer and alloy addition, deoxidized formations could be reduced that would remarkably improve the internal cleaniness of the steel products. The major premise of this invention is to add Si contained ferroalloy as weak pre-deoxidation process with the furance (such as top blowing type, botton blowing type, top and bottom combined type or electric arc furnace) or during tapping, then following by final stage deoxidation process by Al and/or Ti addition Al-wire feeder system and/or ladle injection treating station are the undeficient equipments for this new deoxidation process. After treating by Al and/or Ti with this new process, good shrouding system should be adopted during continuous casting or ingot teemming process to protect the molten steel from reoxidizing by the atmosphere. Consequently, cleaner steel could be acquired by this new process. The explanation of this new process proceeding with various installation is described as following flow chart (Fig.1):

This invention will be explained in detail with some figures and tables as following:

Fig. 2 shows the relationship between the amount of Si contained ferroalloy added and the free oxygen content before adding aluminium as a deoxidizer into the liquid steel (which has no residual Si).

In general, in order to prevent the liquid steel from containing residual Si, no Si contained ferroalloy could be permitted to add into molten steel to adjust the chemical composition in producing Al-killed steel, ferromanganese is usually added. But manganese itself is not a good deoxidizer. Therefore, if weak pre-deoxidation with Si contained ferroalloy is not performed before Al addition in producing Al-killed steel, the residual free oxygen content in the liquid steel will be very high and unstable.

Fig. 2 indicates that with appropriate amount of Si contained ferroalloy addition the free oxygen content in the liquid steel before Al deoxidation can evidently be lowered. By using this process, the recovery of deoxidizer can be improved and the oxides retained in the liquid steel after deoxidation can be reduced as well, thus the quality of bloom, slab and ingot can be improved.

Fig. 3(a) & 3(b) compare the Si content in the liquid steel between WPD Process and non-WPD Process. Fig. 3(a) shows the distribution of Si contents in the final molten steel treated by weak pre-deoxidizing with Si contained ferroalloy. Fig. 3(b) shows the distribution of Si contents in the final molten steel without WPD treatment.

Fig. 3(a) & 3(b) indicates the percent of the number of heats which contain Si less than 0.02% in the liquid steel by using WPD Process is 96.8%, while that of non-WPD Process is 95.8%. The data obviously shows that the proportion of Si content below 0.02% in the liquid steel of WPD Process is even a little bit higher than that of non-WPD Process. The Si content analyzed by spectroscope is total Si content (including silica), thus confirms that Si contained ferroalloy will not cause Si to be retained in the liquid steel. (It can also be confirmed by microscope.) While Si contained ferroalloy is added into liquid steel, Si will react with free oxygen first and forms silicon dioxide (SiO_2) particles, which distribute in the whole liquid steel. Manganese will then reacts with the oxygen around SiO_2 and forms Silicon-manganese oxides, which can float up almost completely after gas stirring. Therefore, it is the characteristics of the present invention that by adding appropriate amount of Si contained ferroalloy during tapping (or into furnace) the free osygen content can be reduced effectively before Al and/or Ti addition, without fearing of Si being retained.

Fig. 4 shows the comparison of the rate of Al recovery between Al-killed steel produced by Weak Pre-Deoxidation Process and conventional deoxidation process. For Al-wire feeder system, the rate of Al recovery was evidently increased by this invention as indicated in Fig. 4, that is due to the content of free oxygen in molten steel is remarkably decreased. Because of higher recovery rate of Al, caused less Al addition, deoxidation formations could be effectively reduced. Consequently, the internal cleaniness and surface quality of the steel product was remarkably improved by this new process.

Table 1 shows the comparison of free oxygen content between WPD Process and conventional deoxidation process before aluminum and/or titanium addition.

Purpose of this invention is to lower down the free oxygen content of molten steel as possible before the addition of deoxidizers (aluminum and/or titanium). (The key point of this process is to make sure that there is no silicon remained in the molten steel) The data listed in the table obviously show that after WPD Process treatment the free oxygen content can be greatly decreased before the addition of deoxidizers.

The amount of free oxygen content lowered can be controlled directly by adjusting the amount of Si contained ferroalloy addition. Owing to the decrease of free oxygen content, recovery of aluminum can be improved, cost can be lowered, and the quality of steel products can be improved remarkably.

Table 2 shows the comparison of typical chemical compositions between the general cold working Al-killed steel grade and the steel designed according to this invention for the same end use. The main difference is that typical chemical composition designed according to this invention has lower aluminum content than that of conventional Al-killed steel grade. The reason for this composition design is to decrease the inclusion formation of deoxidation to get cleaner molten steel. Because of more deoxidizers are added, more chances to form inclusions would result and the cost is also higher. Therefore, the principle of chemical composition design by this invention is to lower the addition of deoxidizers such as aluminum and/or titanium under the condition of no poor deoxidation and good formability. And with the aid of WPD Process, the amount of deoxidizers added can be decreased, cleaner steel and lower production cost will be resulted.

This deoxidation method is also suitable for any other kind of Al-killed steel grade.

Table 3 shows the comparison of estimated index of inclusions between different deoxidation processes. In respect of quality, the main prupose of WPD Process is to improve the internal cleaniness, and improve the quality of casted steel. The table obviously shows that under this new process, the estimated index of inclusions is much better than that of conventional process. It can also be sured that the WPD Process has much improvement on internal quality of casted steel.

Table 4 shows the comparison of grinding speed of billets between different deoxidation processes. In respect of quality, the WPD Process improves not only the internal cleaniness of the casted steel, but also its surface quality. Data listed in the table represent pieces of billets to be ground within unit time (per hour).

(The worse in surfacial quality, the bigger in area and depth should be grinding, so less pieces of billets could be treated within unit time in order to get same level of surfacial quality.)

This table shows that the grinding speed of billets treated by the WPD Process is faster than that of conventional deoxidation process. Therefore, the WPD Process can make much improvement on surfacial quality of casted steel, and save much surface conditioning cost.

III) Claims of this patent application:

1) This is an invention of deoxidation process for Al-killed and/or Ti-killed steel for Basic Oxygen or Electric Arc Furnace Steel making processes. It includes:

(1) After blowing end or during tapping of Basic Oxygen or Electric Arc Furnace Steel making, Si contained ferroalloy is added to the molten steel as weak pre-deoxidation agent.
— After adding optimal Si contained ferroalloy, the free oxygen content of molten steel can be lowered efficiently whereas silicon will not remain in molten steel. It is this method which not only increases the recovery of aluminum and/or titanium, saves much production cost, improves surfacial and internal quality of steel which is good for formability, but also keeps steelmaking operation in good stability.

(2) According to the statements of this patent application as mentioned in item 1, the feature of the weak pre-deoxidation process is its type of deoxidation which is executed after blowing end and before aluminum and/or titanium deoxidizers' addition.

(3) According to the statements of this patent application as mentioned in item 1, the weak pre-deoxidation process is quite different from that of conventional process. (conventional process is that Si contained ferroalloy can't be added as deoxidizing agent in Al-killed and/or Ti-killed steel to prevent from silicon retaining in molten steel). So addition of Si contained ferroalloy is a feature of this process.

CLAIMS:

1. A method for the deoxidation of molten steel produced in a furnace by a steelmaking process, which method comprises:

(a) subjecting the produced molten steel to a pre-deoxidizing treatment by adding to said molten steel a silicon-containing ferroalloy in an amount effective to partially deoxidize said molten steel; then

(b) treating the partially deoxidized molten steel with one or more deoxidizers and obtaining deoxidized steel without substantial retention of silicon.

2. A method according to claim 1, wherein the produced molten steel is subjected to the pre-deoxidizing treatment in the furnace after a blowing step or during a tapping step of the steelmaking process.

3. A method according to either of claims 1 and 2, wherein molten steel produced by a basic oxygen or electric arc furnace steelmaking process is subjected to the pre-deoxidizing treatment.

4. A method according to any one of claims 1 to 3, wherein the partially deoxidized molten steel is treated with a deoxidizer consisting of one or both of Al or Ti.

5. A method according to any one of claims 1 to 4 wherein after the pre-deoxidizing treatment, silicon oxides are separated from the partially deoxidized molten steel.

6. A method according to claim 5, wherein the silicon oxides are separated by gas stirring or bubbling.

7. A method according to either of claims 5 or 6 wherein after separation of the silicon oxides, the partially deoxidized molten steel is contained in a ladle and is treated with one or both of Al or Ti added by use of ladle injection treatment equipment or an Al wire or shot feeder.

8. A method according to any one of claims 1 to 7, wherein the free oxygen content in the partially deoxidized steel is controlled by adjusting the amount of silicon-containing ferroalloy added during the pre-deoxidizing treatment.

9. A method according to any one of claims 1 to 8, wherein the obtained de-oxidized steel is continuously cast into steel products.

10. A method for the deoxidation of molten steel produced by a basic oxygen or electric arc furnace steelmaking process, which method comprises:

(a) after tapping the produced molten steel into a ladle, subjecting the produced molten steel in said ladle to a pre-deoxidizing treatment by adding to said molten steel a silicon-containing ferroalloy in an amount effective to partially deoxidize said molten steel;

(b) separating silicon oxides from the partially deoxidized molten steel by gas stirring or bubbling in the ladle;

(c) treating the partially deoxidized, substantially silicon-free molten steel in a ladle with a deoxidizer consisting of one or both of Al or Ti to obtain deoxidized molten steel.

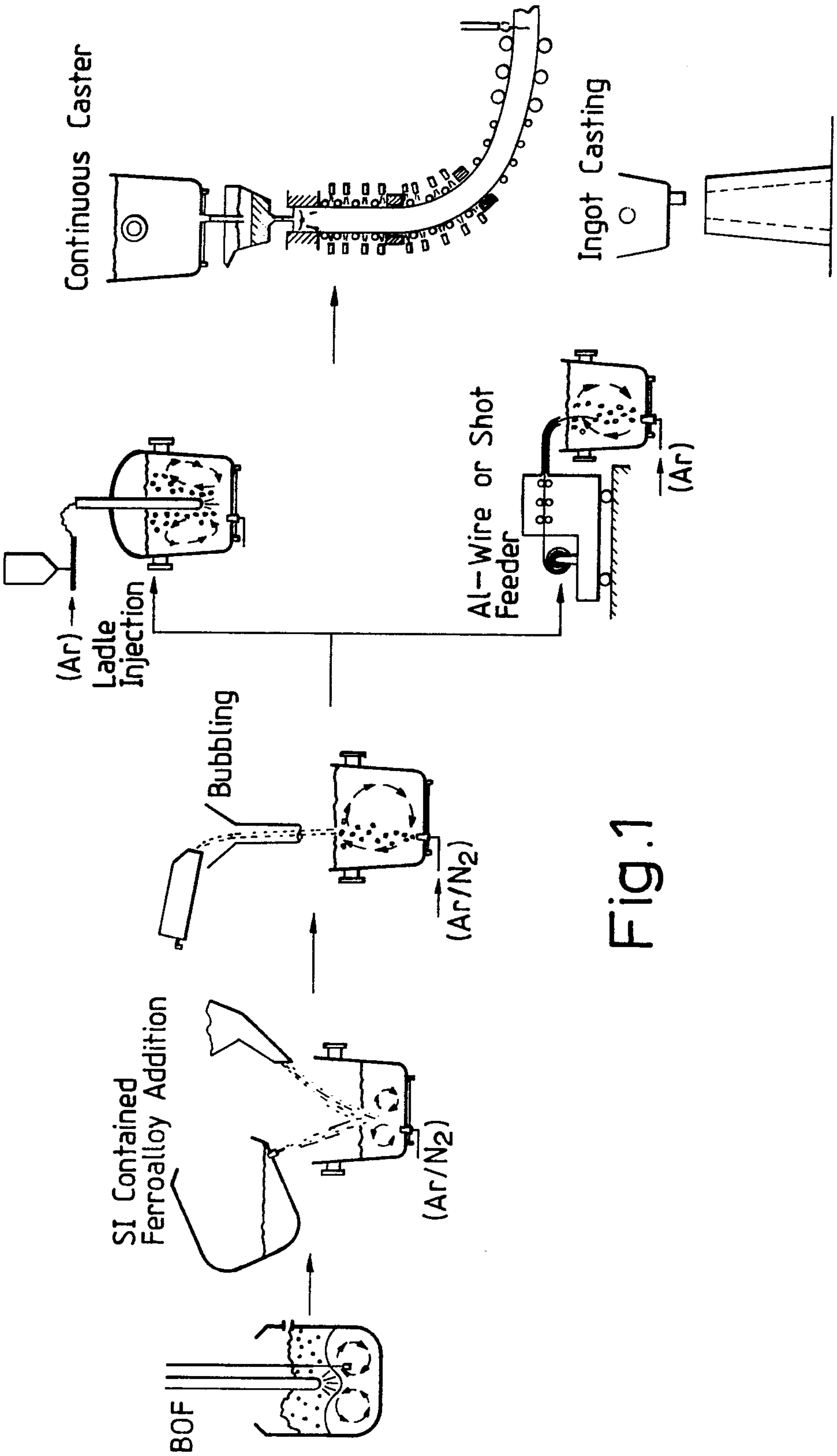
BOF
SI Contained Ferroalloy Addition
(Ar/N2)
Bubbling
(Ar/N2)
(Ar)
Ladle Injection
Al-Wire or Shot Feeder
(Ar)
Continuous Caster
Ingot Casting

Fig.1

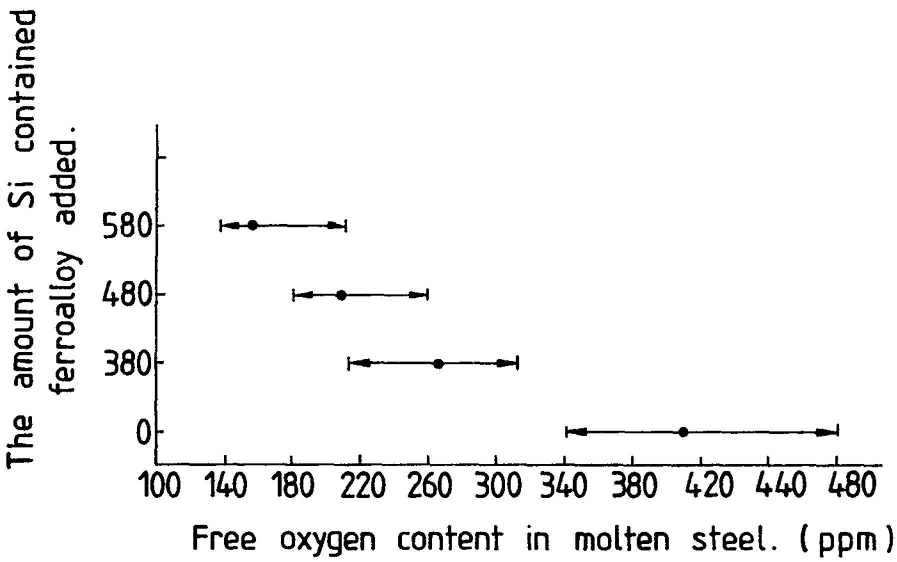
The amount of Si contained ferroalloy added.
580
480
380
0
100 140 180 220 260 300 340 380 420 440 480
Free oxygen content in molten steel. (ppm)

Fig.2

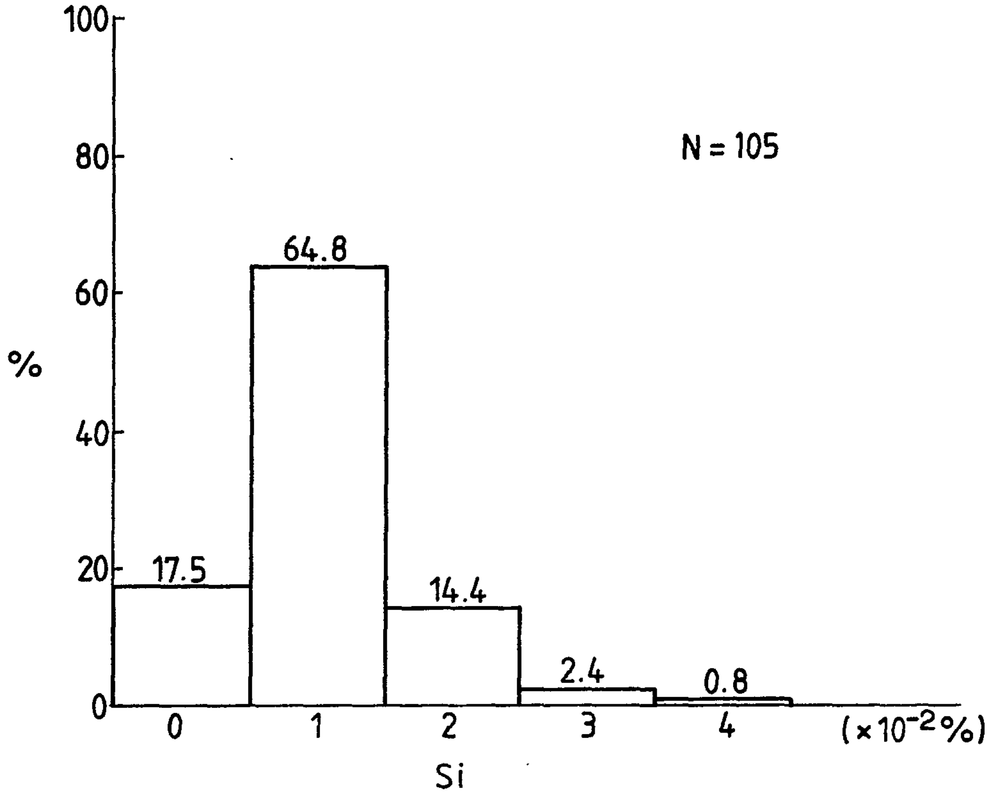
100
80
60
40
20
0
%
N = 105
64.8
17.5
14.4
2.4
0.8
0 1 2 3 4 (×10⁻²%)
Si

Fig.3a

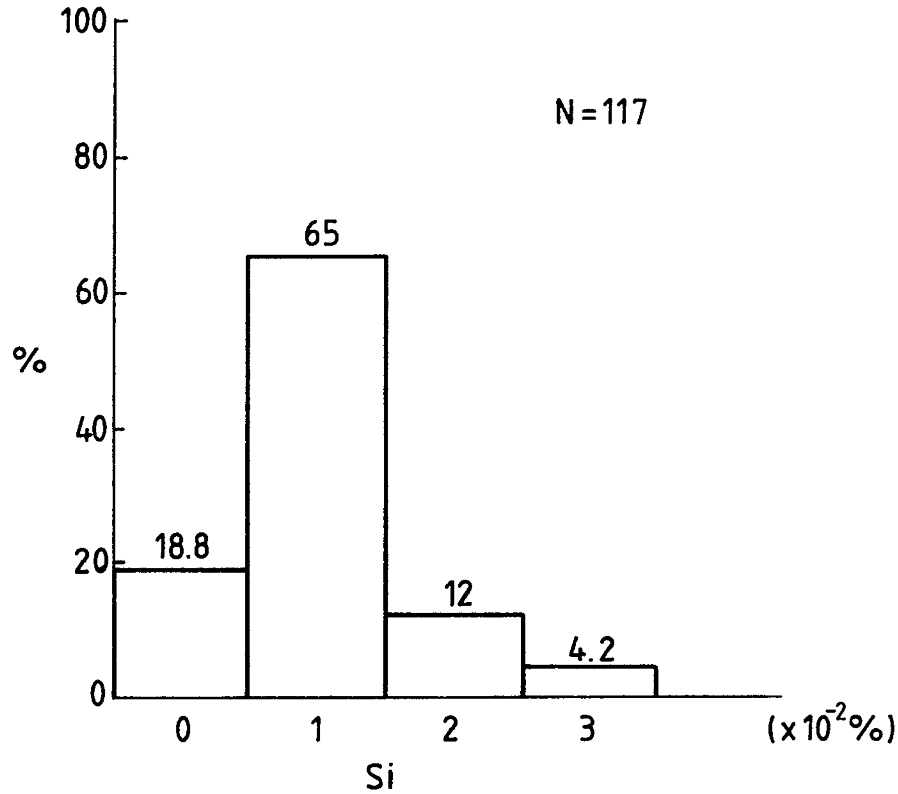
100
80
60
40
20
0
%
N=117
65
18.8
12
4.2
0
1
2
3
(x10^{-2}%)
Si

Fig.3b

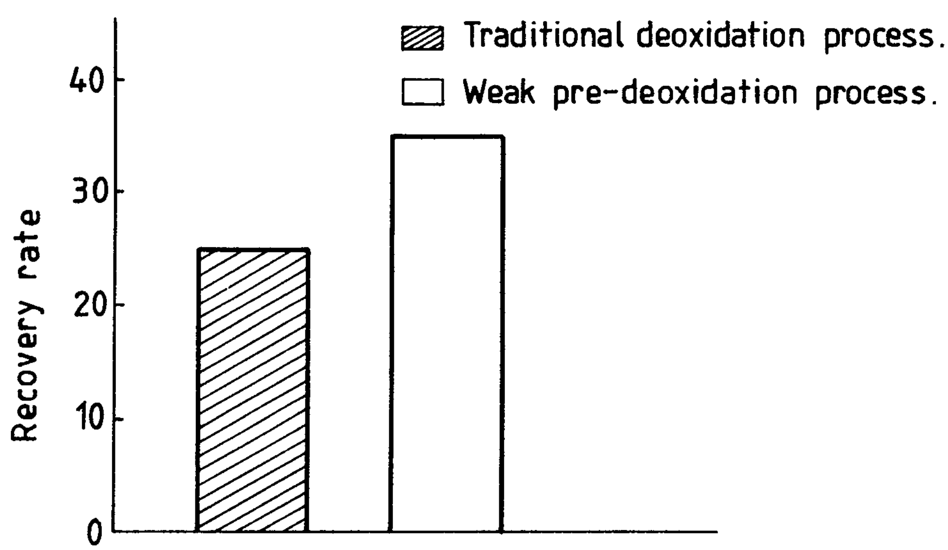
Traditional deoxidation process.
Weak pre-deoxidation process.
40
30
20
10
0
Recovery rate

Fig.4

Table 1. Comparison of free oxygen content before deoxidation between Si contained ferroalloy addition and no addition.

Type of deoxidation	Si contained ferroalloy addition	No addition of Si contained ferroalloy
Ratio	1	1.88

Table 2. Comparison of typical chemical composition between cold working use steels. (%)

	C	Si	Mn	P	S	Al
General steel grade	0.05	0.01	0.32	0.012	0.010	0.030
Designed steel grade	0.05	0.01	0.32	0.012	0.010	0.012

Table 3. Comparison of estimated index of deoxidizing inclusions between different deoxidation processes.

Types of pre-deoxidation / Types of inclusions	Si-contained ferroalloy addition	No addition of Si contained ferroalloy
Silica	0.21	0.29
Alumina	0.23	0.48

Remark: Estimated index value 0~4, 0 is the best.

Table 4. Comparison of surfacial grinding speed of billets between different deoxidation processes.

Types of deoxidation \ Grinding situation	Grinding speed pieces/hour	Ratio of grinding speed
Si contained ferro-alloy addition	165	4.23
No addition of Si contained ferro-alloy	39.0	1

Remark: Depth of defects to be ground are more than 1.2mm

Table 5. Comparison of quality characteristics between different types of deoxidation for same cold working use steel. (Typical)

Types of deoxidation \ Characteristics	Surfacial quality	Inclusions	Electro-plating	Errosion of dies
Si containes ferroalloy addition	O	O	O	O
No addition of Si contained ferroalloy	O	△	O	O

Remarks: 1. O means good, △ means bad.

2. Surfacial quality means the comparison of rods after surfacial grinding.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 84 30 3555

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-2 705 196 (F. WEVER et al.) * Claims 1,2 *	1-5,8	C 21 C 7/06
Y		6,7	

X	DE-C- 957 665 (MAX-PLANCK-INST.) * Whole document *	1-5,7-10	
Y		6	

Y	FR-A-2 387 292 (INSTITUT DES RECHERCHES) * Claims 1,7-10 *	1,6,7	
	---		TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	DE-C- 969 295 (HOESCH)		C 21 C

A	EP-A-0 002 929 (USS ENGINEERS)		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11-01-1985	OBERWALLENEY R.P.L.I

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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