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QUALITY STANDARDS OF FERROALLOYS VIEWED FROM THE STEEL INDUSTRY

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For the development of steel material in the iron & steel making industry, the improvement in quality design, specifically a component design has been taking the leading role so far in parallel with the progress of steelmaking process and in the course, the part supported by ferroalloys has been large and contrariwise, it has exerted a serious influence upon the ferroalloy specifications. This report outlines a relation between needs to higher-grade steel and ferroalloy specifications to make the interrelation clear and at the same time, describes the requirements mainly orientated from the customers' needs in connection with higher steel quality in future and the possible influences of this orientation on the ferroalloy quality. In addition, the ideas of application of various ferroalloy brands to the actual refining operation and the examples are herein described chiefly based on the data acquired in Kimitsu Works of Nippon Steel Corporation to which the author belongs.

Introduction

It is natural that in step with the development of iron & steel making technology, the manufacturing method, specifically the manufacturing process undergoes changes accordingly and the trend is noticeable especially in these 20 years. In such changes, the change in the steelmaking process has exerted a great influence upon the manufacture of ferroalloys indirectly as well as directly. For instance, the production, produced brands, specification of components, style of packing, etc. are influenced by the change and the tendency, though being different somewhat according to the nations, is common to the basic parts.

Such interrelation between iron & steel industry and ferroalloy manufacturing industry would become even closer from now on and it is not too much to say that the factors working as a trigger making the interrelation closer are controlled by the quality standard of steel products as well as the more sophisticated and complicated quality function requested from the customers of steel.

This report has been drawn up aiming at getting light on the trend of needs to various ferroalloys from the necessity of technical innovation in the iron & steel making industry demanded from the customers, taking account of the changes undergone so far in the steelmaking process and the influence on ferroalloys.

Trend of ferroalloy consumption in Japan

1. Transition of crude steel production

The worldwide production of crude steel increased remarkably from the year of 1960 on and experienced such transition as shown in Fig. 1. This tendency is exactly the same even in Japan and as seen from Fig. 2[1], the production surmounted a hundred million (100,000,000) tons to reach a peak in 1973. In the subsequent about 20 years, the production remained at almost the same level depending on the business trend and as the manufacturing process, a ratio of blast furnace–converter process decreased to become under 70% as the share in the crude steel

Fig. 1. World crude steel production from all processes and electric arc furnaces

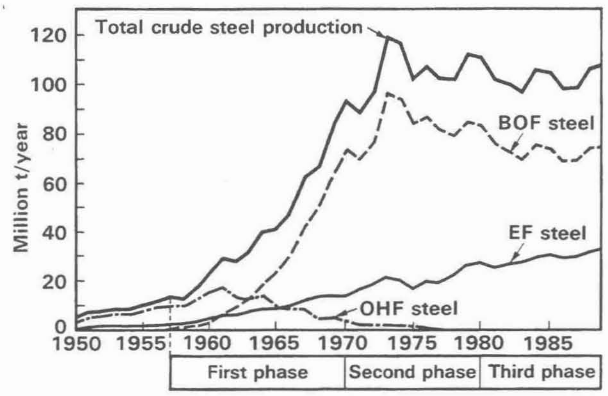


Fig. 2. Changes in crude steel production and refining processes in Japanese steel industry

production and instead, an electric furnace process has increased though being by slow degrees.

Taking a look at this movement in a little more detail, Phase 1 was up to 1973 encountered an oil crisis, in which the seaside ironworks with a large-scale blast furnace or a large-sized converter taking the chief equipment were completed one after another and as the outcome, a mass-production technology was established. Phase 2 was on/after 1973 where the oil crisis took place, during which the whole nation, one and all, directed the mind toward the resources saving and energy conservation in a condition that the production did not increase basically. The following Phase 3 was a term in which a great change was brought about mainly in the refining process and further, "Optimum refining process" was attained and varied technical improvements undertaken based on the refining process made progress.

2. Transition of ferroalloy consumption

The ferroalloy consumption, too has fluctuated naturally so far in correspondence with the change in crude steel production stated hereinabove and herein, the transition in the latest 7 years is shown every ferroalloy brand. Fig. 3 shows Mn-based ferroalloy, Fig. 4 does Cr-based ferroalloy and Fig. 5 does

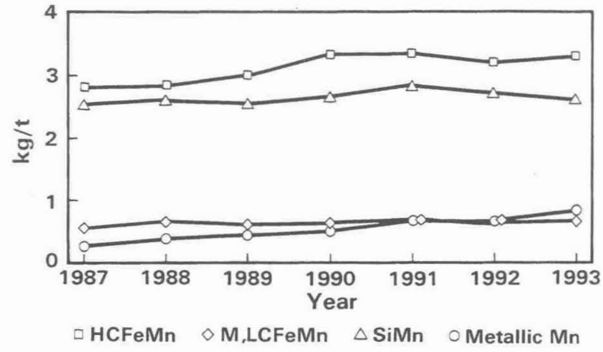


Fig. 3. Trend of consumption of Mn alloy

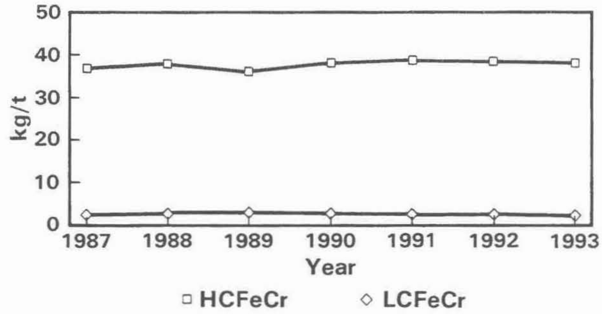


Fig. 4. Trend of consumption of Cr alloy in alloy steel

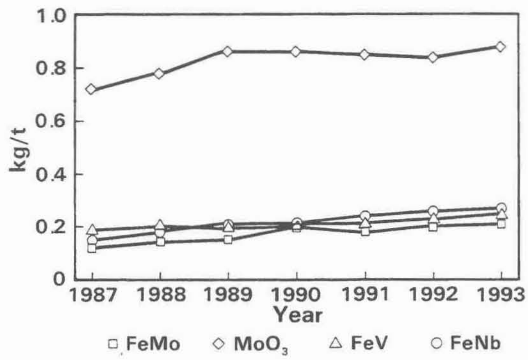


Fig. 5. Trend of consumption of micro alloys

other major elements (Mo, V and Nb)-based ferroalloys.

As to the Mn-based ferroalloy, the consumption tends to increase though being a very little as the unit consumption and especially, the tendency is clearly marked in metallic Mn. The reason will be described later in the column of the future quality trend of steel products and to put it in a nutshell, it is because that the necessity of Mn source containing no carbon has heightened with increase of low C-high Mn steel.

A great change is not seen especially in the consumption of Si- and Cr-based ferroalloys. On the other hand, when viewed from such elements as Mo, V and Nb and iron side, the consumption of source containing an element added in a small quantity is increasing little by little along with the needs to a high tensile strength steel or the strengthening of various mechanical properties. However in regard to Mo, the consumption is found to have increased/decreased very hard repeatedly even in the past. This is put down to the fact that since the fluctuation in price of Mo is heavier than that of other elements, the quality control division of iron & steel manufacturer is changing the design components of product.

Passage of steelmaking process and change of usage of ferroalloys

1. Passage of steelmaking process

The steelmaking process taking charge of a leading function in making steels was reformed of course with the object of reducing the costs and rather the main object was to meet the request of "Supply of high-grade materials" made from the customers. As mentioned above, the reform in the process of refining forming a nucleus of the steelmaking process got into the most active phase at Phase 3 in Fig. 2. Fig. 6 shows the history of reform of the refining function. To put it in a work, it can be said to be nothing else but "Division of refining function". Generally, the steelmaking & refining process is available for removing elements contained in molten iron just turned out of a blast furnace, that is, a hot metal to meet the product componental specification indicated from the customer. And, the function is represented by decarburization, desiliconization, dephosphorization, desulphurization and degassing. Each elementary reaction depends greatly on the reaction conditions including temperature, pressure, slag basicity and so on and besides, the most advantageous condition differs according to the elements taken as an object. Therefore, the history of attainment of optimum refining is the division itself of the refining process.

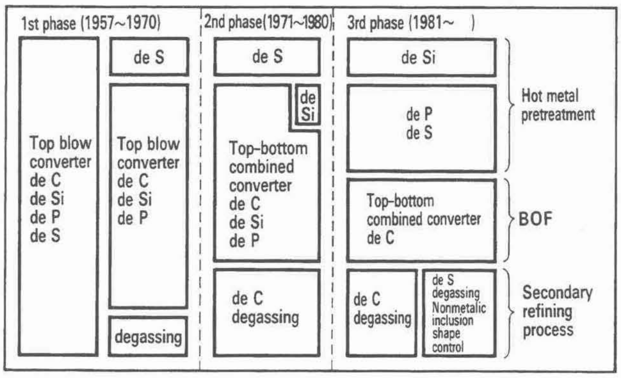


Fig. 6. Divided refining function

The elements having the worst influence on steels are phosphorus and sulphur and it may safely be said that the progress of a method removing these 2 elements is just the development itself of refining. Quoting an example of dephosphorization, this work has been done primarily by producing a large quantity of slag in a converter. And, the converter itself was changed to top & bottom blowing converters assuring higher reaction efficiency for decarburization and then successively the dephosphorization has come to be performed as a pretreatment at the phase of hot metal where the reaction conditions are better. Also, desulphurization has been transferred to the pretreatment of hot metal from the converter and in accordance with the growing needs toward further lowering of sulphur content, a ladle refining which is the next process of converter is in full use lately.

On the one hand, the tendency is similar even in the electric furnace industry. Fig. 7[2] shows a transition of a ratio of the ladle refining treatment in the steelmaking process by an electric furnace. To make the grade of properties requested on steel higher or reduce the manufacturing costs, the actual condition is such that even if the process becomes more intricate, it is obliged to still put another process.

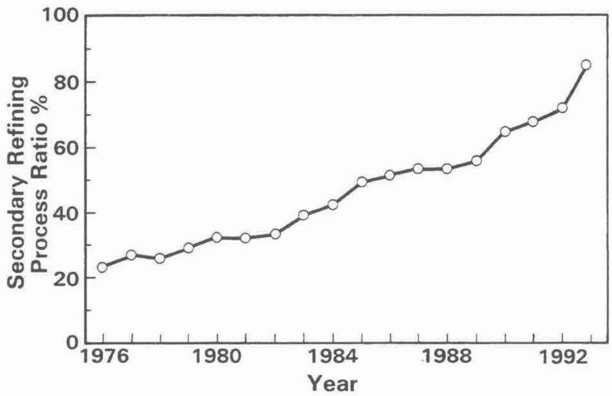


Fig. 7. Trend of secondary refining process ratio in electric furnace

2. Features of new process of converter steelmaking method

Taking up 2 major techniques composing the new process of converter steelmaking method, there will be given a brief description of the influence on ferroalloys.

At the beginning, the refining flow at Kimitsu Works of NSC is shown in Fig. 8 as a typical example of the recent refining process. This form was applied to the actual operation for the first time in the beginning of the 1980's and thereafter, it was constricted into the present form through some continued improvements. The features are typified by "Pretreatment of hot metal" and "Top & bottom blowing converters" and these are described below.

"Pretreatment of hot metal" is essentially a process provided newly and performed before the treatment with converter because it is unable to respond to the supply request of exctremely low P steel when the refining is done only with the conventional con-

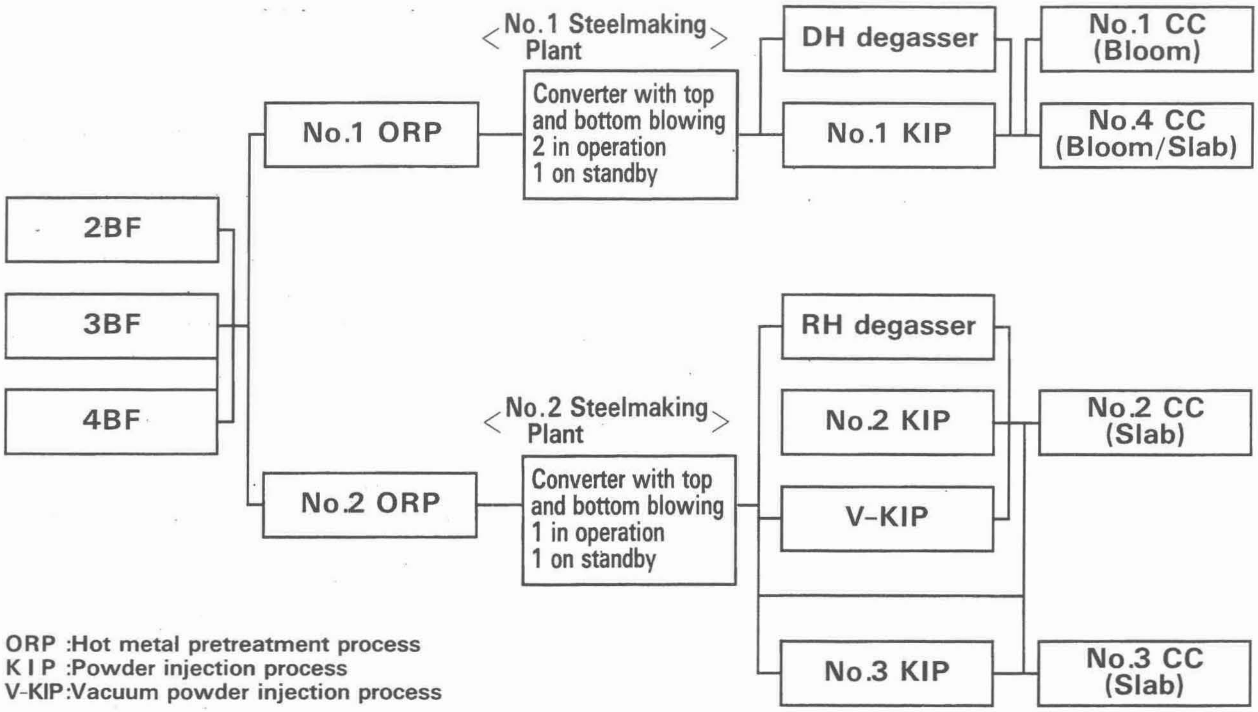


Fig. 8. Block flow diagram of refining in Kimitsu Works

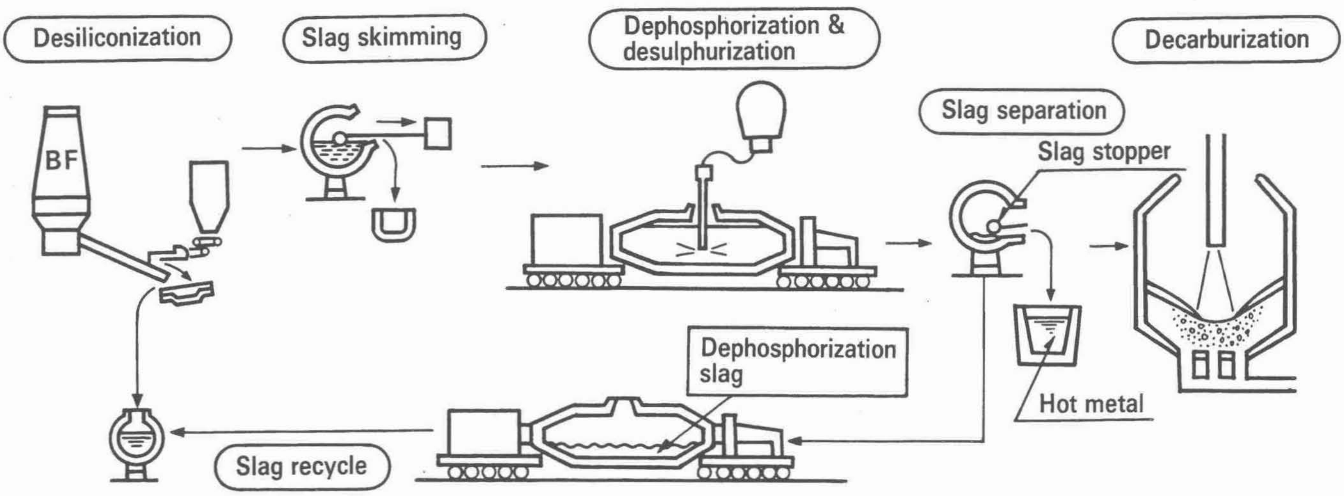


Fig. 9. Optimized refining process (ORP)

verter. By releasing the converter from such reaction as desulphurization or dephosphorization, a great effect was brought about in raising the productivity of converter as well as reducing the refining cost as a total. The hot metal pretreatment system in Fig. 9[3] is also a paradigm of Kimitsu Works and an oxidized metal is in use as a dephosphorizing agent. This material is an iron oxide in general and it leads even to the effective use of wastes produced in the Works, e.g., mill scale, dust, etc. Viewed from a relationship with ferroalloys, there is a case where a manganese oxide, i.e., manganese ore is used in place of iron oxide. This results in Mn concentration in hot metal becoming high and a substitute effect of Mn ferroalloy used after the converter process being gained consequently. Whether to apply this operation depends on the unit prices of Mn ore and Mn-based ferroalloy and it is limited to a case where the former becomes under about 1/2 of the latter in regard to the unit price per Mn pure part. When given by a numerical expression, it can be represented as shown by an equation 1.

$$a_{ore}/a_{alloy} \leqq Y_{ore}/Y_{alloy} \quad \cdots\cdots(1)$$

Where, "a" and "Y" denote an unit price and Mn addition yield per Mn pure part. Y_{ore} and Y_{alloy} are about 0.45 and 0.90 respectively in the converter process.

"Top & bottom blowing converters" is a process having together the respective merits of the conventional top blowing converter and a bottom blowing converter applied at some steelmaking plant in the world in the 1970's. This process was started to adopt widely in the world mainly from the latter half of the 1970's and at present, it has settled as a modern steelmaking process. Fig. 10 shows the conceptual drawing of the three parties. The most notable feature of this process lies in both early producing effect of slag by top blowing and increasing effect of reaction efficiency secured from powerful slag/metal stirring by bottom blowing. This provides more reduction of the amount of slag in the converter than it had ever been before and the effect becomes even more marked if only the concentration of phosphorus or sulphur of hot metal is lowered prior to charging into the converter with the aforesaid "Pretreatment of hot metal". Fig. 11 shows a relation between a ratio that Mn ore added in the converter melts down to turn to a component in molten steel, what is called, Mn yield and amount of slag, from which it becomes clear that Mn ore has been reduced by a strong bottom blowing and stirring power of the converter. When given by a numerical expression, it can be represented as shown by an equation 2.

$$\log\frac{(\%MnO)}{[\%Mn]} = -1.79 + 1.07\times\log(\%T\text{-}Fe) + 3.980\times\frac{1}{T} - 0.048\times\log(\%CaO/\%SiO_2)$$

Mn recovery

$$= \frac{1}{1+\frac{55}{71}\times\frac{1}{1000}\times\frac{(\%MnO)}{[\%Mn]}\times \text{Slag volume}} \qquad (2)$$

With regard to the improvement of high-purity steel manufacturing process ability which is primary object of introducing the new refining process, it has hitherto followed the requirement put forth from the customers at a pace more than anticipated as shown in Fig. 12[4]. Even for not only such elements as phosphorus and sulphur in molten steel but also oxygen and nitrogen which are a so-called gas component, the effect is noteworthy.

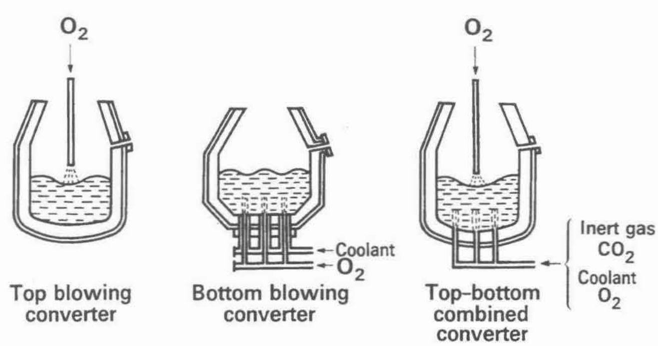


Fig. 10. Conceptual drawing of various converter processes

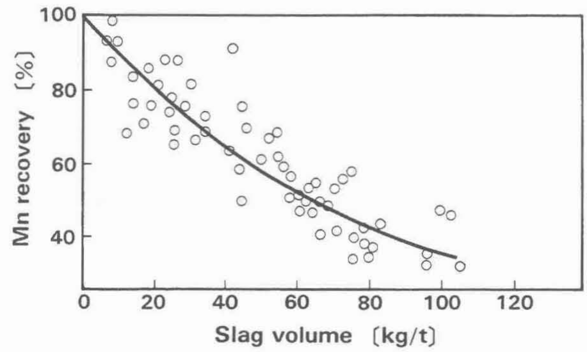


Fig. 11. Relationship between Mn recovery and slag volume

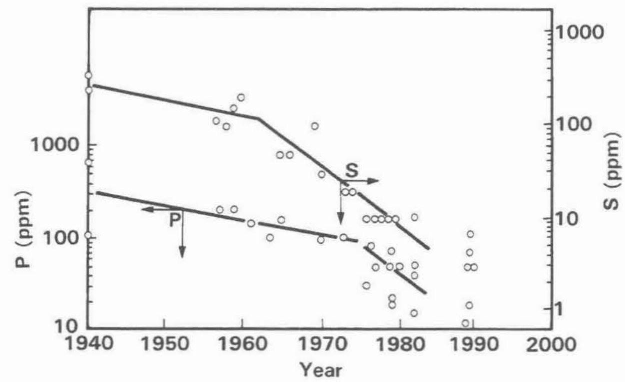


Fig. 12. Transition in P and S contents

3. Feature of new electric furnace steelmaking process

An electric furnace steelmaking technology has been making steady progress since the 1970's. Table 1[5] shows the major technologies available currently, in which three technologies introduced below are those to be noted in particular.

A refining process performed outside the furnace has allowed the functions to divide by installing an arc equipment used to heat a ladle. To put it in detail, this process gets an electric furnace to discharge its melting and heating functions and a ladle furnace to fulfill its refining and temperature adjusting functions, although it has so far been customary to let only the electric furnace undertake all refining functions. By dividing the functions in this way, the increase of refining speed and stability in quality have been assured as the effect.

A scrap preheating process is such that scrap is preheated by making efficient use of waste gas coming out of the electric furnace itself, which has brought about the effect improving the unit consumption of electric power more than 10%.

A technology which is most noteworthy these few years is a direct-current electric furnace, which has contributed to the prevention of flickers and the reduction of various costs as well. The introduction of such new technologies, specifically the

Table 1. Introduction of new steelmaking technologies and effects

Item \ Effect	Year of introduction	Improvement of yield	Improvement of unit consumption			Productivity	Improvement of quality
			Electric power	Refractories	Electrodes		
Formed slag operation	1975	◎	◎				
Refining process performed outside furnace	1977					◎	◎
Scrap preheating	1978		◎			○	
Long arc operation	1982		◎		◎	◎	
Operation without slag off	1984	◎					
Hearth bottom tapping	1985		○	◎			◎
Electrode spray cooling	1985				◎		
DC electric furnace	1988		◎	◎	◎	◎	
Water-cooled oxygen lance	1992		○			◎	

◎ : Greatly effective
○ : Just about effective

employment of said refining process performed outside the furnace has enabled heating, stirring, reduction refining and non-oxidizing atmosphere control. As regards a relation with ferroalloys, it has been designed to add more controllably ferroalloy than it had ever been before and accelerate the ferroalloy melting and further, the narrow range control of components has become possible.

Technical ideas of best selective use of ferroalloys and examples

1. Principle of best selective use of ferroalloys

The elements added to steel as a ferroalloy have a number of different sorts of chemical properties and consequently, the technical ideas regarding the addition differ depending on the elements. The principles common to each element have been shown together in Table 2 below.

Table 2. Common principles of ferroalloy addition

1) Yield of addition as molten steel components must be maximum.
2) Inclusions produced with addition, such as oxide, nitride and sulfide must be minimum.
3) Change in molten steel temperature coming about in line with addition must not act as an obstacle to the process.
4) Other refining reactions must not be obstructed.

Then, the principles provided every element are described. What is the most important is to set the optimum conditions of addition, that is, an adding place, adding method and size of lot added at one time according to the magnitude of chemical affinity with oxygen. In Table 3 below, the features of each element and the principles of addition provided every element have been shown by putting them together.

Table 3. Features for addition of ferroalloys every element

	Affinity with oxygen	Yield stability	Possibility of generation of inclusions
Mn	Medium	Medium	Medium~High
Si	Large	High	High
Cr	Medium	Medium	Medium
Nb	Medium	High	Low
V	Medium	High	Low
Ti	Large	Low	High
Ni	Small	High	Low
Mo	Small~Medium	High	Low

Then, let's take a look at a detailed operation in regard to typical elements.

(Mn)

Mn is in use widely for most products as an element available for raising the strength of steel and this can be said to be the most representative ferroalloy by reason of the fact that its chemical property is almost similar to that of iron. Because the affinity with oxygen is virtually medium and additionally, the amount to be added is large, the stability of yield is also good relatively. The fact that the amount to be added is large bespeaks that the influence of other components coming from Mn-based ferroalloy is serious and this constitutes a

factor which complicates the kinds of Mn-based ferroalloy.
At present, the elements becoming material for discussion in particular are carbon and phosphorus. The performances requested from the customers to strengthen especially for steels are "Deep drawability" and "High strength and Cold toughness". Required for the former is that carbon and nitrogen are low and for the latter, a low carbon equivalent at high Mn concentration and an extremely low phosphorus are required. These requirements have all the influence on the specification of ferroalloy.

Table 4 shows the brands of Mn-based ferroalloy used in Kimitsu Works of NSC and the major steel materials to be applied.

Table 4. Brands of Mn-based ferroalloy & major steel materials to be applied

Steel materials	Typical components	Brands of Mn-based ferroalloy to be used
Deep-drawing steel sheets for automobiles	Extremely low C -Low Mn-Low N	Low C-Fe-Mn
Steels for offshore structures	Low C-High Mn -Extremely low P -Extremely low S	Low C.Low P-Fe-Mn or Metallic Mn
Hard steel wire rods	High C	High C-Fe-Mn Si-Mn

Especially for the steels used for the offshore structures, it is absolutely necessary to use Mn-based ferroalloy of low C,low P-Fe-Mn. The reason is that a very low phosphorus concentration is necessary compared with ordinary steels for fulfilling low-temperature toughness required for the steel of this type. Fig. 13 shows the influence of concentration of phosphorus contained in the steel on the cold toughness of high-tensile steel. In the most stringent application at present, the concentration of phosphorus contained in product is demanded to be less than/equivalent to 0.005%. And, even for keeping a level obtained by the hot metal pretreatment and the dephosphorization refining at the converter, it needs to restrain the input of the phosphorus from the ferroalloy as minimally as possible.

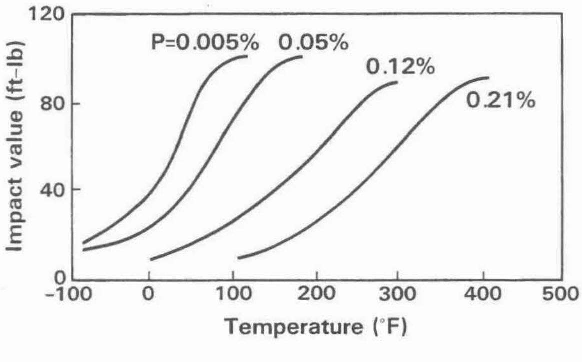


Fig. 13. Influence of phosphorus on impact property of carbon steel (J.A. Rinebolt)

(Ti)
Ti is such element that since it has a very strong affinity with oxygen and also the amount to be added is small, the yield is unstable and the highest degree of addition technique is required. In the conventional refining process in which refining function has not been divided yet, Ti has been added during tapping after completion of the refining at the converter and as the brand then, a relatively large-sized and good-shaped Ti had ever been used. For instance, a compact Ti or Fe-Ti is a typical element. However, with the recent expansion of employment of a micro-alloying technique, Ti componental control at a very small quantity and narrow range has become necessary and the customary adding method has no longer been able to adopt.

(Cr)
Cr is an element used widely round a stainless steel and herein, as an example of the optimum usage of this element, a process will be introduced which supplies molten ferrochrome from the ferrochrome manufacturing plant installed nearby the steelmaking plant to the steelmaking furnace. This process embarked on its commercial operation in 1970 at Shunan Works of Nisshin Steel Co. and it is now in operation. The manufacture of ferrochrome is being undertaken by Shunan Denko Co. and the principle of manufacture is as follows; pellets are made from low-priced, low-grade powdery chrome ore and coal material and after drying and heating in a kiln, these pellets are turned to SRC (Solid-state Reduction of Chrome ore) pellet obtained by reducing about 60% of oxide of Cr and Fe and the pellet is charged into an electric furnace in as-hot condition to manufacture a ferrochrome. After this, receiving the metal into a ladle, this is hot-charged as it is directly into the steelmaking furnace of the steelmaking plant. Fig. 14[6] shows a general view of the process. The annual manufacturing capacity of ferrochrome is 60, 000 tons, and the components are; Cr: 56.5%, Si: 2.0%, P: 0.025%, C: 8.2% and S: 0.020%.

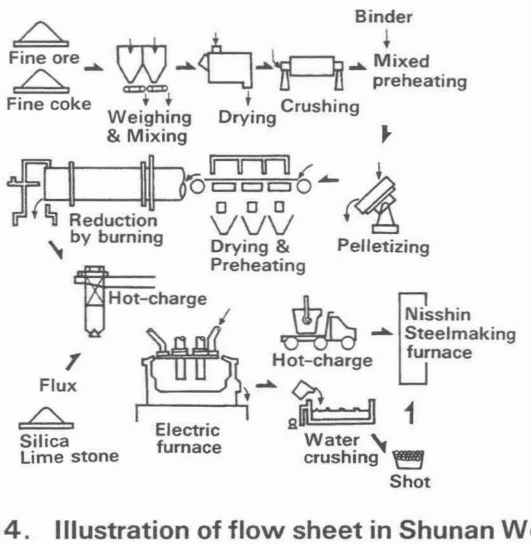


Fig. 14. Illustration of flow sheet in Shunan Works

In an operation requiring to add a large quantity of ferroalloy viewed from the steelmaking plant, such problem arises that the refining temperature becomes high because of considerable temperature drop and the employment of this ferroalloy hot-charging method can be said to bespeak one solution.

2. Rules of best selective use of plural componental elements and examples

Some componental elements do not always correspond to an ferroalloy brand of one kind and they are corresponding with selective use of a few brands. There will be given herein a description taking up the cases of Mn and Si as an example.

Generally, to get a plurality of ferroalloy brands and a plurality of componental elements to correspond with each other in the most reasonable way, the operation is going on following the rules given below.

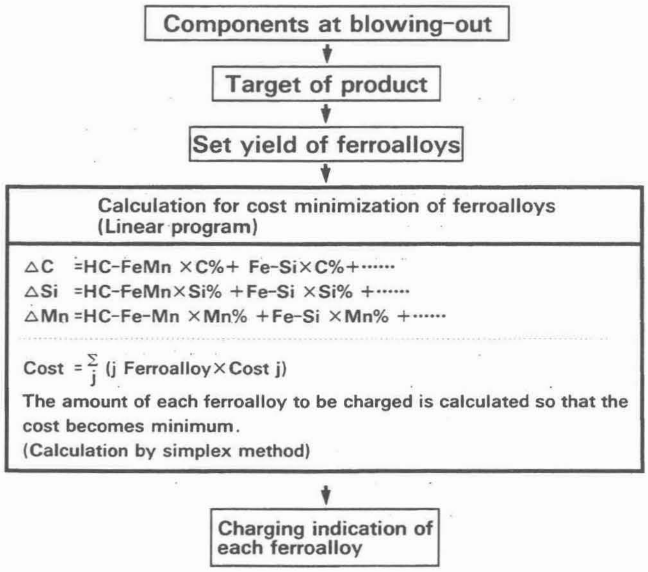
Step 1 Determination of conditions of use of ferroalloys restricted in terms of quality and operation
<Example> Brand not permitted to use (Mainly restriction on quality)
Restriction on proportional division of quantity of use set by brands (Cause of temperature drop, etc.)

Step 2 Calculation of optimum use made by using linear program

Then, an example of the linear program is shown in Table 5. The key logic of optimization is cost minimization in principle and coming down to facts, it has been set up every steelmaking plant. Provided that the components are made clear before adding the ferroalloys in the case of manufacturing, speedy and stable calculation of optimization becomes possible by processing a difference between final component aimed value and component value obtained before addition of ferroalloy with this program.

Fig. 15 shows a concrete example of a case where calculation was made by using this logic. In some plants, the work of the preparation for supply of the necessary ferroalloys and the addition of them is being done in a full automatic way according to this

Table 5. Flow chart of L/P calculation of ferroalloys



	[C]	[Si]	[Mn]
End point	0.05	0	0.15
Ladle aim	0.12	0.25	1.50
Upper limit	0.15	0.30	1.60
Lower limit	0.10	0.20	1.40

Alloy	HCFeMn	LCFeMn	Si-Mn
Calc.	1272	0	5237kg/heat
Set	1272	0	5237
Yield	95	95	95%

[C]	[Si]	[Mn]
0.05	0	0.15
0.09	0.25	1.50
0.12	0.30	1.60
0.07	0.20	1.40

HCFeMn	LCFeMn	Si-Mn
0	2385	3615 kg/heat
0	2385	3615
95	95	95 %

[C]	[Si]	[Mn]
0.05	0	0.15 %
0.08	0.25	1.50
0.11	0.30	1.60
0.06	0.20	1.40

HCFeMn	LCFeMn	Si-Mn
0	2385	3615 kg/heat
0	2385	3615
95	95	95 %

Chemical content (%)

	C	Si	Mn
HCFeMn	6.85	0	74.50
LCFeMn	0.86	0	81.00
Si-Mn	2.20	14.50	60.70

Fig. 15. Example of calculation results of ferroalloys

calculation, which can decrease the number of the required operaters substantially to the minimum. The answer given by this program depends largely on C, Si or Mn contained every steel and it often exerts the influence on whether to use Fe-Si or make efficient use of a part of Si-Mn especially as Si source.

Moreover, it can make an additional remark that the weight of all-added ferroalloys can be reduced more by making use of Si-Mn as much as possible, thus resulting in the temperature drop becoming lesser and the addition time becoming shorter, which is advantageous viewed from the operation.

3. Rules of best selective use of ferroalloys and ores, and examples

For adjusting the componental elements necessary for steels to a predetermined level, a method making full use of ores is widely available which exists as a method opposed to the method using ferroalloys. Fig. 16 shows a transition in the actual results of use of Mn-based ore. Though the use of these ores was almost zero in the 1970's, it reached 20% of the total Mn part in the actual results obtained in the whole Japan in 1993. This tendency can be verified technically by the fact that the yield of Mn has increased as the result of a refining process having been materialized which is performed by lessening the amount of slag with introduction of the hot metal pretreatment and top & bottom blowing converters as described hereinabefore, in other words, the absolute amount of MnO getting into the slag has decreased drastically corresponding Mn distribution shown by (MnO)/[Mn]. Moreover, the use of Mn ore working as an oxygen source for an dephosphorizing agent in the hot metal pretreatment won't pay off unless otherwise the price of Mn ores is considerably low because the conditions for making full use of ore are severer than those at the inside of converter in terms of cost. In fact, the amount of use is decreasing sharply with the year of 1992 as a boundary and accordingly, a ratio with Mn-based ferroalloy is also lowering.

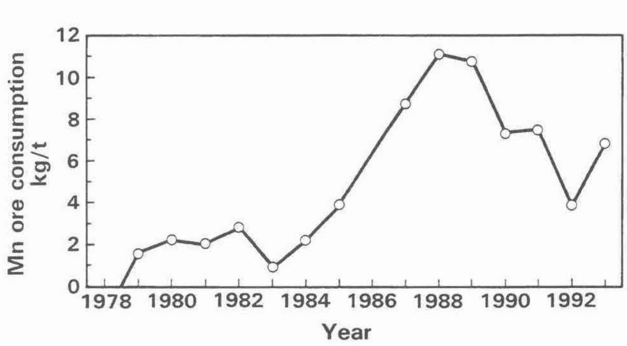


Fig. 16. Trend of Mn ore consumption in Japanese steel industry

As to Cr, the use of Cr ore is becoming general with a special steel, specifically a stainless steel as an object and a large quantity of it is now added into the converter. Fig. 17 shows the operation flow at the top & bottom blowing converter in Chiba Works of Kawasaki Steel Corp. A small-lump coke and chrome ore (pre-reduction pellet) are added to hot metal given pre-treatment of dephosphorization and desulphurization for refining with the top & bottom blowing converter and thereafter, slag is separated by tapping once. The metal is decarburized further by another top & bottom blowing converter, whereby a stainless steel can be produced. This is in practical use as a high-speed manufacturing technology at a large-sized converter.

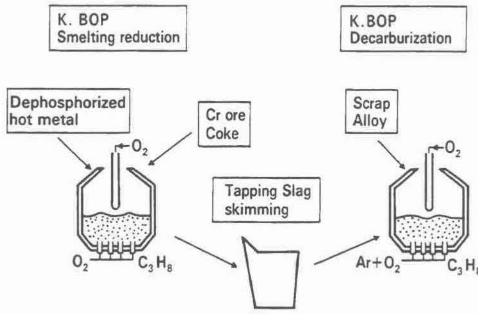


Fig. 17. Schematic illustration of stainless steel production system in Chiba Works with the use of smelting reduction process

Fig. 18 shows the changes in unit consumption of chrome ore consumed so far by the iron & steel making companies in Japan, from which it is to be understood that, not limited to the stainless steel, the consumption is 2 to 3 kg/t even if calculated taking the whole amount of crude steel as a denominator and a pretty amount of Cr component is supplied from the ore.

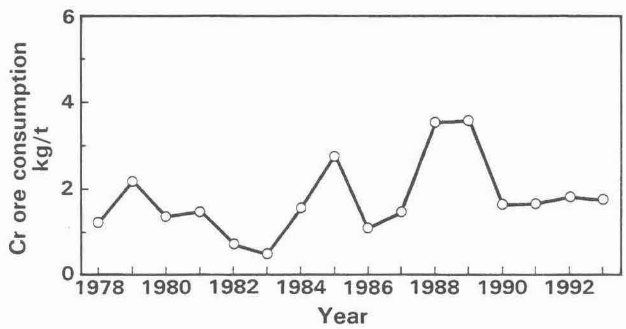


Fig. 18. Trend of Cr ore consumption in Japanese steel industry

4. Micro-alloying technique

A description has been given so far about Mn, Cr and Si, what is named, elements added in large quantities among the ferroalloys used in the iron & steel making industry. To meet the requirement from the customers to improve the properties of steel, a

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	O
1	1H																	2He
2	3Li	4Be											5B ◎	6C ○	7N ○	8O ○	9F	10Ne
3	11Na	12Mg											13Al ◎	14Si ○	15P ◎	16S ○	17Cl	18Ar
4	19K	20Ca ○	21Sc	22Ti ◎	23V ◎	24Cr ○	25Mn ○	26Fe	27Co	28Ni	29Cu ○	30Zn	31Ga ○	32Ge ○	33As	34Se ○	35Br	36Kr
5	37Rb	38Sr	39Y ○	40Zr ○	41Nb ◎	42Mo ◎	43Tc	44Ru	45Rh	46Pd	47Ag	48Cd	49In	50Sn ○	51Sb ○	52Te ○	53I	54Xe
6	55Cs	56Ba	57La ○	72Hf ○	73Ta ○	74W ○	75Re	76Os	77Ir	78Pt	79Au	80Hg	81Tl	82Pb ○	83Bi ○	84Po	85At	86Rn
7	87Fr	88Ra	89Ac ∫															

◎: Elements assuring quite great micro-alloying effect

○: Elements affording recognizable micro-alloying effect

Micro-alloying technique: One technique available for improving properties of metallic material or making quality higher with elements added in very small quantity

Fig. 19. Description of micro-alloying elements

micro-alloying technique has been adopted. It is a precondition for the most steels to provide them with a basic property, that is, general properties necessary for the steels from a condition almost similar to a pure iron. To have these steels display the further stepped-up mechanical properties or other special performance, another technique is needed. This micro-alloying technique can define as "Improvement of properties and assurance of higher quality of metallic materials with elements added in very small quantity". A ladle refining materialized as a part of the division of refining process has allowed the technique to apply to the actual operation.

Fig. 19[8] shows the elements taken as the object of micro-alloying on a periodic law table. It indicates that basically, the elements of IV, V and VI groups in the periodic law table have a great effect mainly on the improvement in strength of the steels. A double circle denotes the elements strengthening the steel material by the micro-alloying effect, that is to say, by adding in a very small quantity and also, a single circle does the elements producing their own effect. Ti, C, Cr, Nb and Mo are the elements bringing about a marked effect.

As a steel is cooled down from about 1,000°C, a crystal structure, e.g., Austenite or Ferrite comes on and in this process, such elements deposit and disperse into the crystal of steel finely as a carbide or nitride, thus promising the effect mentioned above.

5. Change in conditions of use of ferroalloys based on change of steelmaking process

The above-mentioned method adding various ferroalloys to the steels has undergone changes while being influenced with the development of the steelmaking process. Table 6 shows together the technical improvements undertaken in this period in connection with the addition of ferroalloys.

As a representative refining process, a typical example of the latest addition method is shown below as

Table 6. Necessity of technical improvements for addition of ferroalloys and corresponding steps

(Improvement needs on addition of ferroalloys)

- Increasing the addition yield to the maximum
- Decreasing the produced inclusions to the minimum
- Lessening the change in molten steel temperature to the minimum
- Preventing a harmful influence on other refining reactions
- Making the component range narrower

⇨ (Corresponding technical improvements)

- Dividing the addition process
- Decreasing oxygen content in steel before addition
- Cutting off interaction with slag in case of addition

to Mn-based ferroalloy on the basis of hot metal pretreatment-top & bottom blowing converters -ladle refining (degassing)-casting. (See Fig. 20)

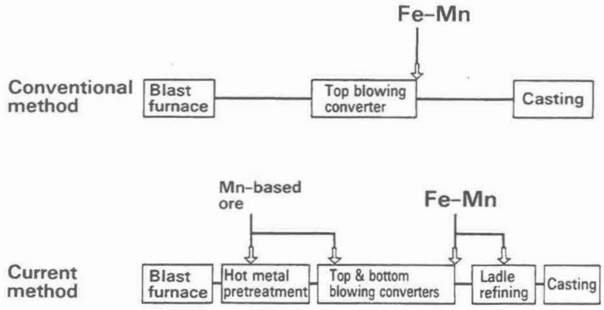


Fig. 20. Typical example of recent adding method of Mn-based ferroalloy

With full use of the equipment introduced for attaining optimum refining, the addition has become made at a few places though it was done at only one place in the past. This has permitted the control of components to be made at even higher accuracy. Fig. 21 shows a transition of the severest target of components in Kimitsu Works of NSC in regard to Mn and Nb and because of transfer to the process shown in Fig. 20, a sufficient process capacity has been maintained successfully.

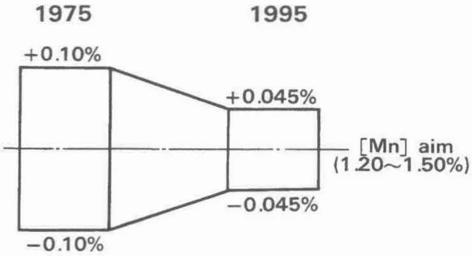


Fig. 21. Trend of [Mn] spac allowance in steel

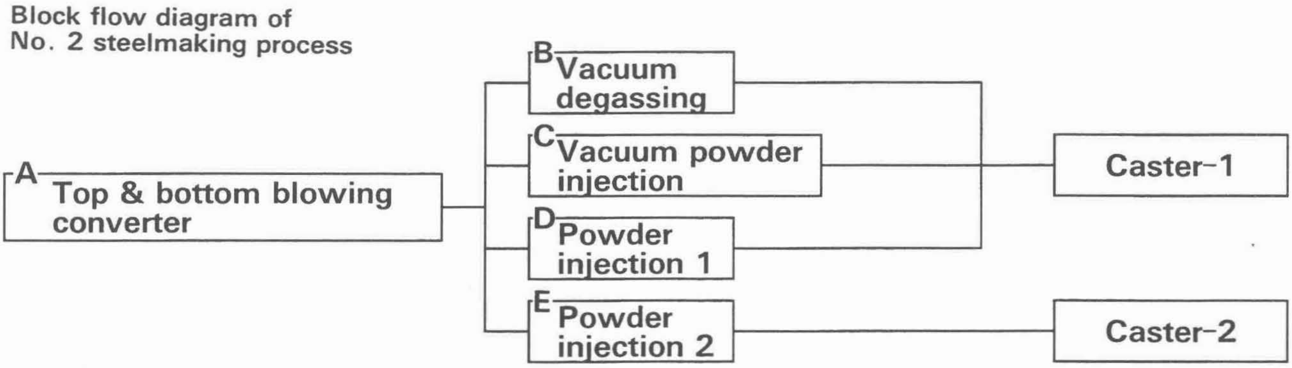
6. Actual results of ferroalloy consumption by processes

Taking the above-mentioned facts into account, the actual results of ferroalloy consumption by processes of various ferroalloys obtained on the premise of the existing process have been put together below. (Fig. 22)

Future development forecasting of steel manufacturing process

1. Future technological forecasting of refining process

As a process matching with the blast furnace-converter process and the electric furnace process, both of which are the main process for the current steel



Unit : kg/t-process

		A	B	C	D	E
Production (Thousands(ton)/M)		363.0	162.4	3.8	56.2	171.6
Description of ferroalloy	Ferroalloy brand					
Mn	Mn ore	1.16	0	0	0	0
	HCFeMn	1.94	0.71	0.77	0.16	0.37
	M,LCFeMn	1.12	0	0	0.02	0.09
	Metallic Mn	0	0.40	1.33	0	0
	SiMn	2.95	0	0	0	0
Si	FeSi	0.72	0.33	0.31	0.07	0.03
Nb	FeNb	0.01	0.12	0.68	0	0
V	FeV	0.01	0	0	0	0
Ti	Al-V-Fe-Ti	0.01	0.33	0.22	0.003	0
Cr	HCFeCr	0.13	0	0	0	0
	LCFeCr	0.002	0	0.06	0	0
Ni	Ni	0.02	0	0	0	0
Mo	FeMo	0.002	0	0	0	0
	MoO_3	0.10	0	0	0	0

Fig. 22. Actual records of ferroalloy consumption in each process

making, the research of a smelting reduction process is making a forward move and even in Japan, the development is going under participation of each company of iron & steel making industry as a national project. This is a process which makes a steel from an iron ore by direct reduction and can offer various anticipated advantages. Fig. 23 shows the outline of the process and in brief, its mechanism is as follows; a raw iron ore is reduced several tens percent by a reducing gas coming out of a smelting reduction furnace at a pre-reduction furnace installed at the upper portion and then gets into the smelting reduction furnace having a shape like a converter, where the ore is reduced continuously to turn to a hot metal whose carbon content is about 4% and temperature is about 1,500°C. From the year of 1993 on, a pilot plant is in operation at Keihin Works of NKK.

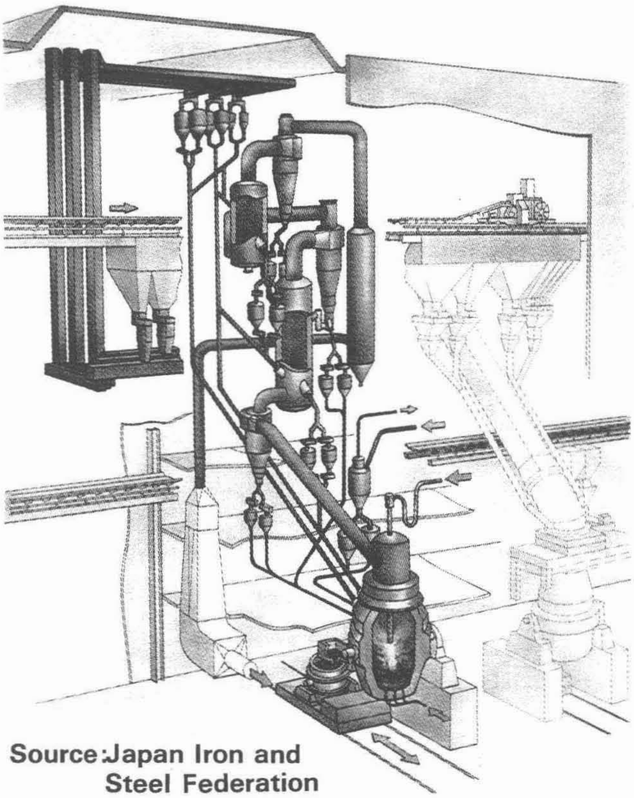


Fig. 23. Example of direct Iron ore smelting reduction

Next, a description will be given referring to a technology which turns a scrap to an iron source including little impurities. As shown in Fig. 24[9], generation of scrap is increasing more and more in Japan and quite a large quantity of it is being processed well mainly at the manufacturers possessing electric furnaces, needless to say the manufacturers equipped with converters. However, a point in question is that the amount of waste scrap hard to reuse increases and the cause lies in that such scrap includes other impure elements than iron in quantities. Therefore, a procedure is under examination which eliminates Sn, Cu, Ni and Zn and further the

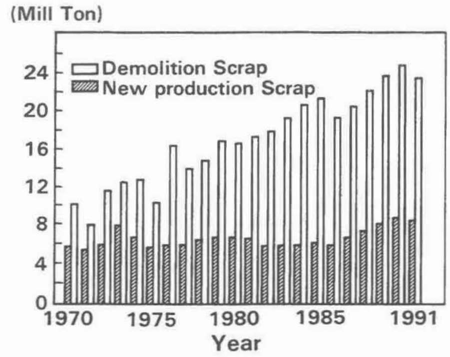


Fig. 24. Purchased scrap (domestic)

elements effective for the aforesaid micro-alloying by a physical or chemical technique and regenerates a high-purity resource composed only of 5 elements, i.e., C, Si, Mn, P and S, as shown in Fig. 25.

In Japan, it is aimed at establishing the technology during the twentieth century; however this is never an easy development in terms of technique and it needs to watch the progress from now on.

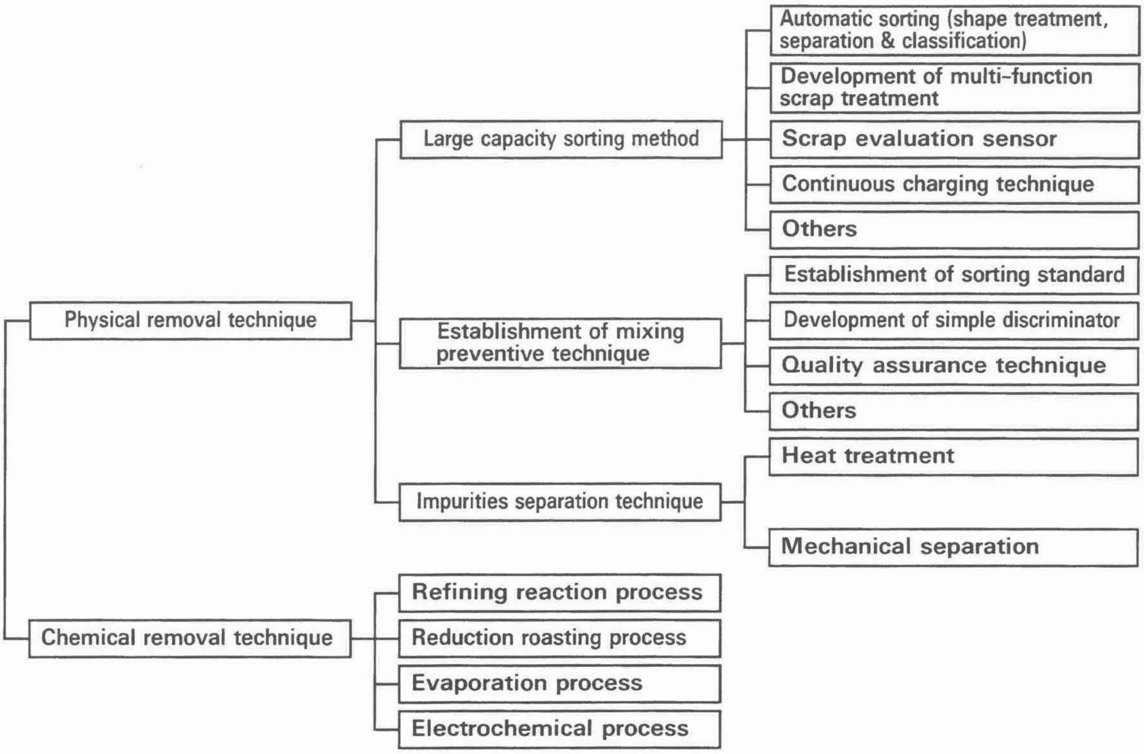
2. Future technological forecasting of rolling technology

The development of rolling technology is extending over quite in a number of different directions and herein, it will be discussed limiting to a technology having the influence directly on the consumption and quality of ferroalloys.

The role of rolling process in the past was mostly to simply change the shape of materials and make adjustments and lately, it has become necessary absolutely even as a technique available for adjusting and raising the quality, that is, the mechanical properties. Especially for the rise in strength, it has made the greatest headway.

From the latter half in the 1970's on, a controlled rolling has become employed widely. This technique was fully utilized for manufacturing the material for line pipes used under low temperature. By controlling the temperature of steel plate to a proper temperature lower than ordinary level before rolling to perform a powerful screw-down, it has become possible to supply a material having superior quality even with fewer alloy components.

In recent years, a Thermo Mechanical Control Process has been adopted as a further forward move. Fig. 26 shows the process image and also Fig. 27 shows a transition of the amount of steel to be manufactured, This process has been made up by combining additionally an accelerated cooling process of steel plate after rolling and it is a technique indispensable for manufacturing high-grade steel plates at present. (Fig. 28) Moreover, this technique is not only applied to the manufacture of steel plates but put into use even for coils in future. The prog-



Source : New Steelmaking Technology Research Institute

Fig. 25. Technology for removing impurities from scrap

ress of this technique brings about the effect which decreases the consumption of Mn used as an element raising the strength and instead increases the consumption of the micro-alloying element stated hereinbefore.

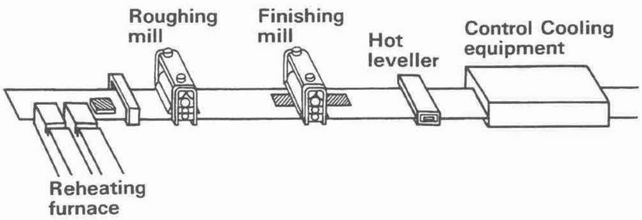


Fig. 26. Arrangement of thermo mechanical control process equipment

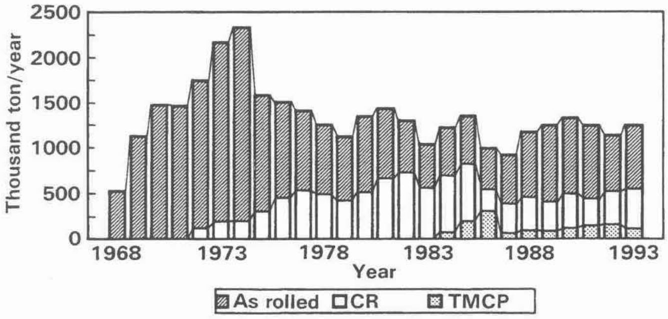


Fig. 27. Changes of past records of plate hot rolling in Kimitsu

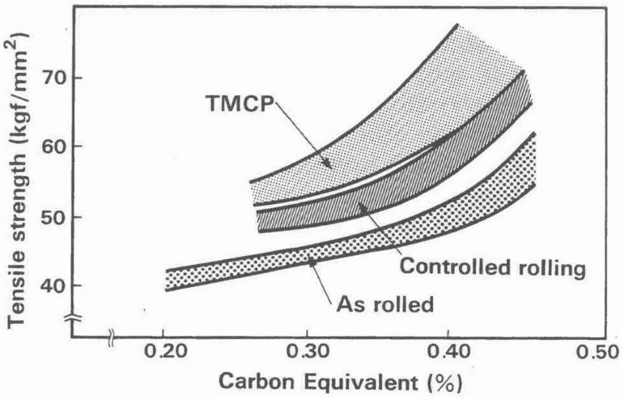


Fig. 28. Tensile strength of TMCP steel plate

3. Forecasting of trend of requirements set out of customers

First, an attempt will be made to forecast starting from the automobile manufacturer which is the top user of steel products. Table. 7 shows the description of major steels used for automobiles and it is a movement toward "Lighter automobile" that the iron & steel making industry is affected in the greatest degree. It is now crying out worldwide for reducing the fuel consumption of automobiles and the reduction in fuel consumption has been set partially as a bill. This requires the measures in both aspects of a fuel cost curtailing technique and a body weight reducing technique at the side of the automobile manufacturers themselves, and the latter technique, as a matter of course, is related to making the

Table 7. Steel sheets for automobiles

- **Hot-rolled high-strength sheets**
  (50 & 60kg high-tension steel sheets):
  For running mechanism(Wheels, Members, Trailing arms, etc.)
- **High-strength cold-rolled sheets**
  Ultra-deep drawing type high-strength sheet (Ti-Sulc):
  Fenders & Quarter panels
  High r-value type high strength sheet (P-added Al-k):
  Outer sheets & doors
  General working-use high-strength sheet (C-Si-Mn steel):
  Bumpers & Impact bars
- **Cold-rolled sheet for automobiles** (Ti, Nb-Ti Sulc):
  Bodies

steel products thinner, that is, lighter. However, on the assumption that the steel products are made thinner, it cannot be guaranteed whether the strength can be maintained with the conventional steel and as the result, it is necessary to put forward the development of a steel having a new performance. Further in addition, giving thought to that it also needs to provide the steel with good workability, a target is to "supply a steel sheet having such contrary character as high strength-high workability". To this target, an action would be taken to respond with a steel made on the basis of "Interstitials Free Steel". To assure high strength with the interstitials, in other words, with an extremely small quantity (for instance, 10 to 15ppm or less, respectively) of carbon and nitrogen, a large quantity of manganese content from 1.0% to 1.5% or thereabout (usually, 0.1 to 0.4%) is required. Thus, it is unable to meet the requirement with the use of an ordinary ferroalloy brand, that is, Fe-Mn-based ferroalloy and the efficient use of metallic manganese would become a precondition. There is also a limit on the measures of refining with lower content of nitrogen and it is hoped to decrease the nitrogen content in ferroalloy.

Then, as for a plate, there are the requirements of a steel meeting more the environments where it is used actually and damaged little in case of emergency in addition to the current of mechanical properties such as high strength, high weldability and cold toughness which have been requested so far from the customers, and such tendency would become growing. As an example, a description will be given taking a fire resisting steel. Table 8 shows the concept. If a steel structure is attacked by a fire, the yield proof of the steel greatly lowers, therefore, the steel has to be covered thickly with a refractory material by all means. As this step, a steel has been developed which is given the properties available as a boiler-use steel plate and at the same time, able to maintain a yield of 2/3 at ordinary temperature even at 600°C by using such added elements as Cr, Mo or Nb. It is clear that hereafter, even severer working environments and conditions are indicated and it would be obliged to supply a steel having a new performance every time as required.

As a problem which is important and besides has a great influence in a global scale in connection with the working environments, there is a question related to the oil resources. What is significant in particular is a large-diameter steel pipe and from the viewpoint that it is used for transporting crude oil or LNG, it becomes necessary to make designs for the steel taking account of the influence of components contained in oil or LNG as well as the working environments.

To put it in more detail, a transported substance turns into a sour gas as time goes on and when CO_2 or H_2S is contained, it constitutes a factor bringing various disadvantages. Fig. 29 shows the change in the properties required for the quality of line pipe

Table 8. Fire resistant steel

Steel construction building:

Steel strength lowers due to heat in case of fire.

⇩

As step preventing strength from lowering, steel must be protected with fire-resisting covering(about 5cm in thickness). (Building Standard Law)

⇩

"Bellow 350°C" in "Specification of fireproof construction" must be secured.

⇩

Fire resistant steel:

At high temperature, properties of boiler-use steel material must be maintained and at ordinary temperature, the same properties as those of conventional construction-use steel material must be displayed. (Addition of Nb, Mo and Cr)

⇩

About 2/3 of specified value at ordinary temperature must be guaranteed.

⇩

Outside steel frame of building whose fire-resisting covering thickness is about 1/3 of conventional one is possible even if there is no covering.

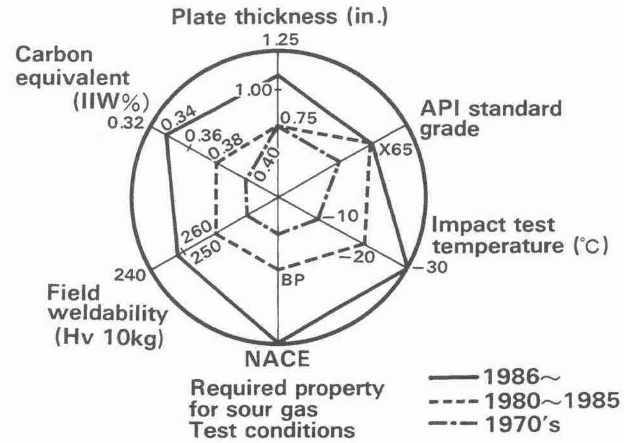


Fig. 29. Changes of properties required for material in line pipe material

material. The change in 10 to 20 years is rapidier than anticipated and speaking of the above-mentioned antisour gas property, in view of that the places where the line pipe is used are in a considerably gruelling circumstances, e.g., Arctic area, a very stringent inspection has been obliged to perform on the steels and steel pipes for preventing a social irreparable trouble, a so-called burst accident or the like. This inspection is performed for checking if there are cracks in the weldment of steel pipe by using an acidic solution whose pH is 3.0 to 3.5 or so (called NACE reagent). To allow the steel pipe to pass the inspection, as a step which prevents generation of cracks in the weldment of steel pipe, it needs in every way to make the existence of hydrogen quite little in addition to a thorough elimination of phosphorus and sulphur out of the steel. Also, as will be apparent from Fig. 29, even for improving a weldability in low-temperature atmosphere or making a cold toughness (guaranteed at temperature of -30 °C) severer, decrease of carbon equivalent is an absolute must and there is a tendency that the manufacture at X65 of API standard, according to the circumstances, more than X70 with low carbon content of 0.03 to 0.04% is required along with making the necessary strength higher. In this case, it is indispensable to combine intricate added elements conforming to higher Mn and a quality design worked out according to the performance demanded every project is needed. At any rate, it would be inevitable to make hydrogen content lower as already stated hereinbefore.

Quality standard of ferroalloys and future expectation

1. Actual condition of quality standards of ferroalloys

The steel manufacturing process and higher quality of steel products described in detail so far have been supported by raising the quality standards of ferroalloys which serve as the base of quality design. It cannot be denied to be certain that this brought severer and more complicated quality standards of ferroalloys and now, it has been characterized as a significant basic condition for the steel manufacture.

At the beginning, the current quality standards of ferroalloys will be discussed. The standards are not always unified yet by nations, companies and steelworks and in fact, they have been determined according to the scale and shape of refining vessel and the steels to be manufactured. Also, when the discrete conditions including molten steel temperature, adding atmospheric condition, adding place, etc. are taken into account it is in fact quite hard to prescribe the unified specification. Thus in this report, it has been decided to make a statement round the example of Kimitsu Works of NSC. Moreover, the example is such that the data are ample and what is more, the actual adding conditions have already been made clear and there is no room allowing imagination to inflame in the arena of discussion.

Table 9 shows quoting the example of Mn-based ferroalloy used most generally. Taking a look at the ferroalloy in the aspect of composition of compo-

Table 9. Specification of Mn alloy

	Example of converter steel maker		Example of EF steel maker
	HCFeMn	LCFeMn	HCFeMn
Content Mn Important other elements	73~78% P,S,Si	90~95% C,P,S,Si	75~78% P
Shape	10~50mm	10~50mm	10~100mm
Surface	water less	water less	water less

nents, a low-carbon and high-manganese content steel stated before has increased in both sheet and plate. Therefore, in addition to such combination as general high-carbon Fe-Mn and low-carbon Fe-Mn, a low-P and low-C brand and metallic manganese have been applied, and the amount is as shown in Fig. 3. In this case, since the range of component design of steel material becomes narrower inevitably to satisfy together the material properties including the strength, toughness and workability, dispersion in components of ferroalloy has also been controlled as indicated in Table 9.

On the other hand, specifications of the shapes have been shown together in Table 9 and taking account of acceleration of melting of ferroalloy in the converter and ladle refining processes or prevention of scattering in the case of addition, a proper range has been set. In particular, there are some plants in which the upper limit of size has been more restricted on account of a relation with automatic feeding or the performance of weighing machine.

As other specifications, an agreement has been made in regard to a sticking moisture content and surface oxidized condition, and the details are as shown in Table 9. It goes without saying that the these are effective as the measures for meeting the manufacturing needs of the aforesaid low-hydrogen steel or cutting off an oxygen source and oxidic inclusion source.

On the one hand, to clarify the influence on the specifications of Mn-based ferroalloy according to difference in process, the specifications at the manufacturer equipped with an electric furnace have been shown in a right half of Table 9 above.

According to difference between steels to be manufactured by the converter process and electric furnace process, there is found a difference in brand and size of Mn-based ferroalloy to be used. LC-Fe-Mn ferroalloy is mainly used in the converter process and as for the size, too, the range for the converter process tends to be narrower than that for the electric furnace process. However, even in the electric furnace process, difference with the converter process is deemed to rather lessen due to the change of charging method of ferroalloys or the increase of addition ratio in ladle refining.

2. Expectations to future ferroalloy quality

Table 10 shows together the expectations to the future ferroalloy quality. The details will be explained individually below.

1) Trend on components

First of all, as to the components, it is intended to emphasize two points. One point is to decrease a gas component in no half-and-half way. As described so far detailedly, the conventional components have created a material round the metallic

Table 10. Expectations to future ferroalloy quality

Items	Expectations to ferroalloy quality
Components	1) Decrease of gas components(nitrogen and hydrogen) 2) Suppression of tramp elements 3) Reduction of dispersion in each
Shape	The necessity for supplying as a fine material might arise.
Surface properties	A special surface treatment (for example, a coating treatment) might be given.

elements chiefly and with further increase of the requirements to the material, more advanced quality design becomes necessary. Even in the sense, it is hoped to decrease various gas components or make control at a narrow range. What is most important in the gas components is nitrogen. Nitrogen is an interstitial element similar to carbon and harmful for manufacturing a deep-drawing sheet for automobile use. Fig. 30[10] shows the influence of carbon on workability and in future, it may be demanded to decrease the sum of carbon and nitrogen components below 15 ppm.

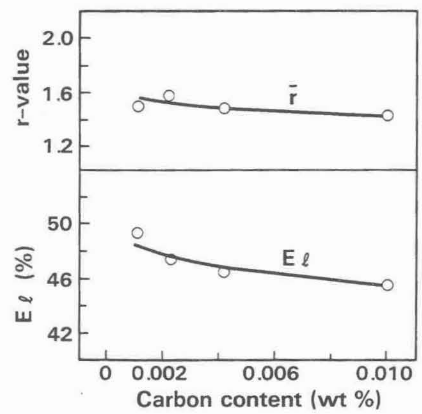


Fig. 30. Effect of C content on mechanical properties and their planar anisotropy of laboratory-made steels without alloying elements

Also, as to hydrogen, a moisture content becomes material for discussion as a matter of course. In a high grade steel, specifically in a thick plate or a large-diameter pipe, cavities attributable to hydrogen are produced in the progress of the product manufacturing process and results in these materials turning to scrap. Fig. 31 shows the example. It is necessary, for a very thick plate exceeding 100 mm in thickness, to control the hydrogen contained in molten steel under 1.5 ppm before casting.

A second point concerning the trend of components is to suppress a tramp element thoroughly. As already stated before, the increase of scrap available as the major raw material source in the future iron & steel making industry leads to the rise of a so

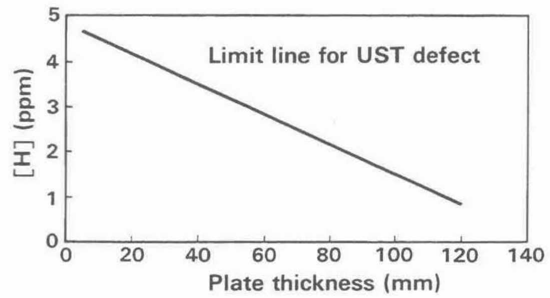


Fig. 31. Example of relation between plate thickness & hydrogen concentration in steel of plate and limit of generation of UST defects

-called tramp elements such as Cu, Sn, As and Sb, resulting in a restriction that scrap is unusable being imposed on the applications for which workability is required. It is aimed at establishing a technology for eliminating these elements as the development technology, however there is found no method enough to pay off at least industrially. It is thus hoped to decrease the above-mentioned tramp elements as much as possible, which are contained in ferroalloys serving as a very weighty additive to molten steel.

A third point regarding the trend of the components is to lessen dispersion of components of each ferroalloy. The requirements set out from the customers to narrow the range of components are growing steadily and for meeting the requirements, it is necessary to reduce dispersion of each component at the phase of molten steel. For this reason, it is of urgent necessity to establish and introduce a speedy analyzing technology of molten steel and in the important process, analysis by the operator and a dynamic control of the amounts of ferroalloys to be added based on the analysis results have already been performed. Fig. 32 shows the outline. An elementary technology which would be indispensable hereafter is to make a ferroalloy whose components have been controlled to a high degree at a narrow range and grasp the changes taking place every hourly at the refining progress phase.

2) Trend on shape

Then, the future needs about the shape can be estimated as follows. At present, addition of ferroalloys into molten steel is mostly performed by a simple addition method, that is, a method which drops the ferroalloys by gravity from an exclusive hopper installed above the furnace after weighing and conveying. In the progress of the addition method from now on, there is possibility of the change being demanded for the shape. In other words, for raising the addition yield of ferroalloys and feeding them into molten steel while evading reaction on slag, an injection method might be employed. There is an experience that this injection method had even been taken as a test for Mn ore or some elements added in a small quantity, for example, Ti, Al, etc. and this method may be adopted partially sooner or later. Assuming that this method is employed, the ferroalloys must then be changed into a fine material in shape and the size must kept as uniformly as possible. However, as to whether this addition method is used on a full scale in future, there is a need to watch the trend later on.

3) Trend on surface properties

A sphere meaning the surface properties is wide and a clear-cut trend can not always be estimated, how-

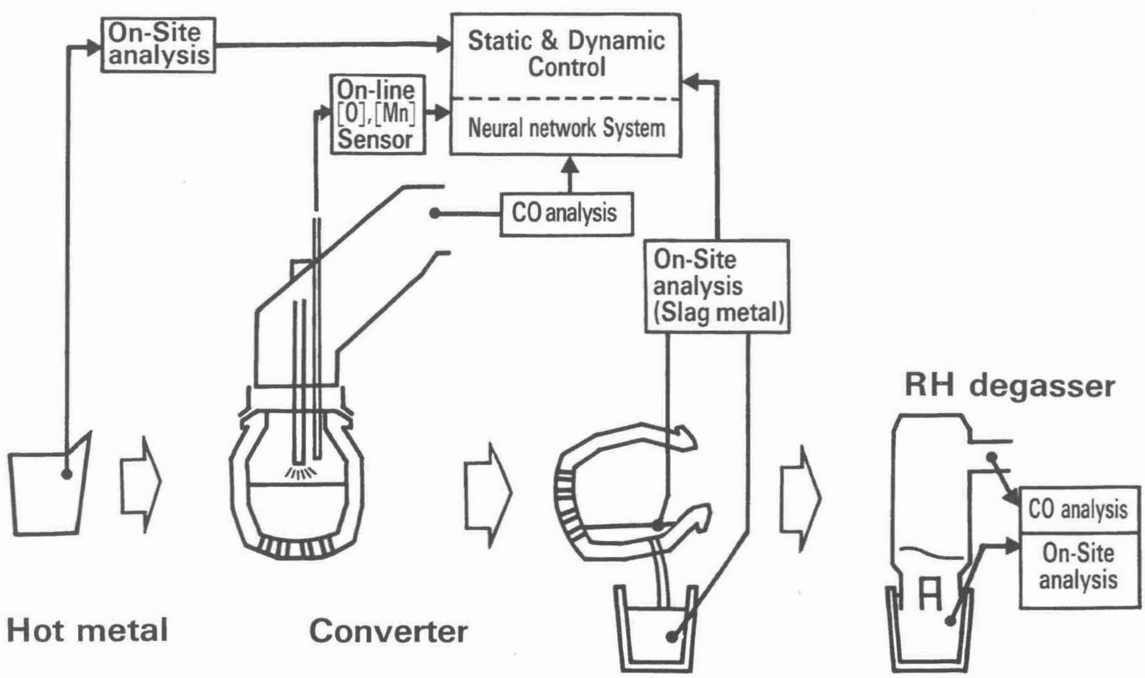


Fig. 32. Schematic illustration of content narrow range control

ever there may be some influence according to the change in the addition process of ferroalloys. Namely, with the expansion of kinds of the steel products to be turned out or the detailed setting of delivery date, reduction in manufacturing lot is going forward and in consequence of it, there is a tendency that the addition process of ferroalloys is put just before casting. It is of course a prerequisite that the majority of ferroalloy be pre-added in the refining process that is the main in the manufacturing process. And for a final adjustment on the components or making the components according to the properties, the ferroalloys may, for instance, be added into a tundish in the case of continuous casting and in fact, this method has been taken at some plants. In this case, there is a fear of impurities contained in ferroalloy, e.g., non-metallic oxide or something like that being taken into molten steel in its original form, which could exert a unfavorable influence on the molten steel as an inclusion. It is therefore desirable to decrease such impurities in ferroalloy and at the same time, give a special treatment, preferably a surface coating for preventing debasement of the quality in transport and storage after having been manufactured. At any rate, this argument is applied to some ferroalloys and it is an argument providing the possibility. It is judged that there is a need to propose the necessity timely and quantitatively even at the side of iron & steel making industry.

Summary

The performance required for steel product is becoming higher and higher every year with the changes in social environments and the technological progress in the associated industries. To respond to the performance becoming higher, various process innovations have been undertaken so far. In this course of progress, it has become necessary to improve the composition of components working as the most important factor deciding the inherent character of steel and make a new componental design and the today's state has been assured with a great contribution and cooperation of the ferroalloy industry. From now on, it is certain that such movement that the required properties become higher is promoted more and more and it would be necessary to continue the exchange of information with closer cooperation between both industries.

In this report, examination and study have been made round the change of ferroalloy addition technology which have taken place inevitably up to now according to the above-described process innovations, and the influences on the ferroalloy specifications and at the same time, with estimation of change(s) which might come about in future, further requirements to the ferroalloy quality have been discussed together including the expectations raised form the iron & steel making industry. Though it can not necessarily be concluded that such change comes with a probability of 100%, it should be characterized to be an important theme to be discussed at both industries hereafter as the possibility toward the future.

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