



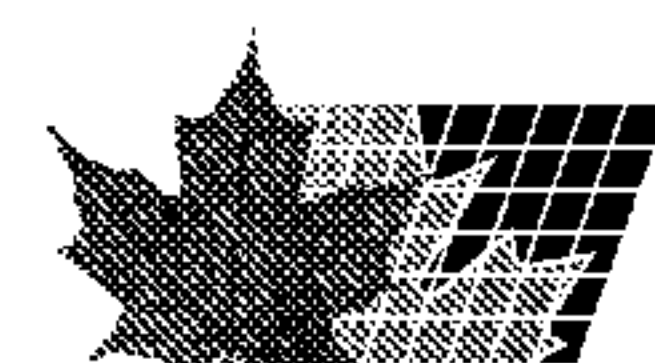
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(54) Titre : PROCEDE D'ALLIAGE DIRECT DE L'ACIER
(54) Title: METHOD FOR A DIRECT STEEL ALLOYING

(57) **Abrégé/Abstract:**

The inventive direct steel alloying method relates to the iron and steel industry and can be used for steel production by means of a direct alloying process. Said direct steel alloying method consists in making steel in a steelmaking vessel, alloying the thus produced steel with manganese reduced from oxides during the supply of a manganese oxides-containing material and a reducing agent and the interaction thereof. The manganese reduction is carried out in association with the reduction of other alloying elements from a material containing non-metallic compounds thereof and supplied on the molten metal surface. The reducing agent is added when the height of the layer of the supplied material which contains the non-metallic compounds of alloying elements attains 0.1-0.15 of the total layer height. A reduction temperature is maintained at a level of the flowing temperature of the supplied material, a permanent contact of the molten part of the reducing element with the molten part of the supplied material containing non-metallic compounds of alloying elements being also maintained. The reducing element is supplied in a quantity ensuring the required thermal characteristics of the mixture of the supplied material and the reducing agent. Said method ensures a high recovery of alloying elements by metal, reduces steel contamination with non-metallic impurities and improves the quality thereof.



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(54) Title: METHOD FOR A DIRECT STEEL ALLOYING

(54) Название изобретения: СПОСОБ ПРЯМОГО ЛЕГИРОВАНИЯ СТАЛИ

(57) Abstract: The inventive direct steel alloying method relates to the iron and steel industry and can be used for steel production by means of a direct alloying process. Said direct steel alloying method consists in making steel in a steelmaking vessel, alloying the thus produced steel with manganese reduced from oxides during the supply of a manganese oxides-containing material and a reducing agent and the interaction thereof. The manganese reduction is carried out in association with the reduction of other alloying elements from a material containing non-metallic compounds thereof and supplied on the molten metal surface. The reducing agent is added when the height of the layer of the supplied material which contains the non-metallic compounds of alloying elements attains 0.1-0.15 of the total layer height. A reduction temperature is maintained at a level of the flowing temperature of the supplied material, a permanent contact of the molten part of the reducing element with the molten part of the supplied material containing non-metallic compounds of alloying elements being also maintained. The reducing element is supplied in a quantity ensuring the required thermal characteristics of the mixture of the supplied material and the reducing agent. Said method ensures a high recovery of alloying elements by metal, reduces steel contamination with non-metallic impurities and improves the quality thereof.

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Опубликована

С отчётом о международном поиске.

В отношении двухбуквенных кодов, кодов языков и других сокращений см. «Пояснения к кодам и сокращениям», публикуемые в начале каждого очередного выпуска Бюллетеня PCT.

(57) **Реферат:** Способ прямого легирования стали относится к области черной металлургии, и может быть использовано при производстве стали с использованием приема прямого легирования. Способ прямого легирования стали включает выплавку металла в сталеплавильном агрегате, легирование стали марганцем путем восстановления его из оксидов при подаче материала, содержащего оксиды марганца и восстановителя и их взаимодействии, при этом восстановление марганца из оксидов осуществляют с восстановлением других легирующих элементов из подаваемого на поверхность жидкого металла материала, содержащего неметаллические соединения этих элементов и/или с восстановлением марганца из материала, содержащего другие неметаллические соединения марганца, восстановитель начинают вводить при достижении высоты слоя подаваемого материалов, содержащего неметаллические соединения легирующих элементов, равной 0,1-0,15 общей высоты слоя, при этом поддерживают температуру процесса восстановления, равную температуре плавления подаваемого материала, обеспечивают постоянный контакт расплавленной части восстановителя и расплавленной части подаваемого материала, содержащего неметаллические соединения легирующих элементов, причем восстановитель подают в количестве, обеспечивающем требуемую термичность смеси подаваемого материала и восстановителя. Предлагаемый способ обеспечивает высокое усвоение металлом легирующих элементов, снижает загрязненность стали неметаллическими включениями и повышает ее качество.

METHOD FOR DIRECT STEEL ALLOYINGField of the Invention

The present invention relates generally to ferrous metallurgy and is suitable for production of steel using direct alloying techniques.

Background of the Invention

The tendencies for improvement of steel quality, in particular, for production of steel having a low and ultra-low content of carbon, gases and impurities are presently gaining in importance in the world practice, this evoking changes in the existing methods of melting, predominantly in out-of-furnace treatment, for bringing the steel to desired parameters before casting. In this connection, requirements are being toughened to reaching a predetermined composition of steel with simultaneously narrowed ranges of each of the elements. For this reason, methods and process steps ensuring a controlled degree of recovery of alloying and modifying additives by steel are taking on great significance.

In view of the fact that the conventional practice of making steel comprises melting a low-carbon product in steel-making vessels irrespective of the steel grade to be produced, followed by bringing the product to desired parameters at steel-refining systems, the necessity emerges to deoxidize the low-carbon product prior to alloying. In this case the metal is inevitably saturated with non-metallic impurities, oxide products of the deoxidation reactions, and to modify or remove

the oxide products additional measures are to be taken that require energy and material costs. The next step of out-of-furnace treatment, alloying the steel, is also accompanied by formation of some amount of non-metallic impurities. Use of the materials that do not form non-metallic impurities, such as coke or coal, for pre-deoxidation of steel entails great heat losses which must be compensated for by reheating the carbonaceous semi-product before discharging, this resulting in surplus costs and impairing the quality of the steel.

A conventional method for alloying steel with manganese comprises melting a steel in a steel-making vessel, tapping the steel into a ladle, charging alloying materials and blowing an inert gas, wherein a low-phosphorous, manganese-containing slag of ferroalloy industry, a reducing agent and lime are charged into the ladle on the melt surface after tapping the metal in the amount providing a slag basicity in the range of 2.0-3.5, and oxygen is then injected for 3 to 30 seconds on the molten bath surface (SU 1 044 641, Int.Cl.C21C 7/00, 1983).

The conventional method is however unsuitable for production of a high-quality steel because the simultaneous delivery of the oxide material containing the alloying agent, manganese, the reducing agent and lime into the casting ladle on the carbonaceous semi-product surface after tapping thereof from the steel-making vessel, and subsequent blowing of oxygen make the control of the steel alloying process with manganese difficult, thereby preventing the attainment of a high degree of manganese recovery by steel and a high desulfurization degree.

Reduction in sulfur content in the steel is provided by treating with desulfurizing materials after deep pre-deoxidation of the metal, this requiring maximum contact between the desulfurizing materials and the metal, e.g. by vigorously stirring them.

In the conventional method, the high-basicity slag formed after direct alloying of the steel with manganese, while exhibiting a certain sulfide capacity, fails to provide deep steel desulfurization due to the absence of vigorous stirring.

The method is therefore unsuitable for obtaining a low sulfur content in steel.

The oxygen injection on the metal surface increases oxygen content in the metal when directly alloying the steel with manganese, and this raises the reducing agent consumption, reduces manganese recovery by molten metal, aggravates desulfurization conditions, and increases contamination of the steel with oxide and sulfide non-metallic impurities, i.e. impairs the quality of the steel.

The joint delivery of materials into the casting ladle upon tapping the carbonaceous semi-product therein reduces recovery of the alloying element, manganese, and this fact, in combination with the impossibility of controlling the alloying process speed, impairs the steel quality.

When making steel according to the conventional method, the efficiency of a steel-making vessel is reduced as compared to that of the method of alloying steel with ferroalloys because all the materials are charged into a casting ladle upon tapping

the carbonaceous semi-product therein, this making the alloying process longer as the additional time is spent for melting the charged materials.

Manganese in the low-phosphorous manganese-containing slag of ferroalloy production is in the form of a chemically strong compound, MnSiO_3 . When lime is consumed in the amount providing a slag basicity of 2,0-3,5, and delivered into the casting ladle together with the low-phosphorous manganese-containing slag before the beginning of manganese reduction, strong compounds with a high melting point (over 1400°C) are formed in the slag along with calcium silicates and free lime. While the presence of lime contributes to destruction of chemical bonds in manganese silicate when it is reduced with silicon, nevertheless refractory calcium silicates Ca_2SiO_4 and Ca_3SiO_5 are formed in the slag and cause a high melting temperature of the slag, this factor increasing the slag viscosity, decreasing the manganese recovery degree, increasing the content of non-metallic impurities and impairing the quality of the steel.

Furthermore, the oxide material containing manganese as the alloying material, used in the conventional method, is expensive and power-intensive as the great amount of electric power is consumed for its production.

Another conventional method of making steel comprises melting a steel in a steel-making vessel, deoxidizing, alloying, producing a molten metal containing silicon and aluminum as reducing agents, adding an oxide mixture containing manganese and calcium oxides in a ratio of $\text{CaO}/\text{Mn}_x\text{O}_y=0,6-1,2$ to the molten

metal, treating the molten metal in a casting ladle with the slag formed when manganese is reduced with silicon and aluminum dissolved in the metal, said treatment being carried out by holding the molten metal under a slag having a basicity of $\text{CaO/SiO}_2=0,7-1,8$, and further adding a silicon-containing reducing agent to the molten metal, along with the oxide mixture (RU No.2096491 C1, Int.Cl.C21C 7/00, 1997).

The pre-deoxidation and alloying of the metal in the method is carried out in a steel-making vessel in the presence of an oxidizing slag and with a highly oxidized metal. This not only results in excessive consumption of oxidizing and alloying agents that react with iron oxides in the slag, but also increases contamination of the metal by hardly removable non-metallic inclusions: silicates, aluminates and sulfides of manganese and iron. In the method, the metal is then treated in the casting ladle by reducing manganese from its oxides while a silicon-containing reducing agent, ferrosilicon, is added into the ladle. The manganese reduction method is carried out in a diffusion regime, this inevitably requiring additional time for its performance. In addition, the amount of silicates, aluminates and sulfides formed previously in the steel-making vessel increases due to the addition of silicates newly formed in the manganese reduction. In the absence of means for globularizing the inclusions and in the presence of the high-silica slag formed on the metal surface, the method fails to provide removal of the non-metallic inclusions from the metal body into the slag, this resulting in increased contamination of

the metal with oxide and sulfide inclusions and impaired quality of the metal.

The method creates unfavorable conditions for manganese reduction as the addition to the molten metal of the oxide mixture in which the ballast additive (CaO) is from $1/2$ to $2/3$ of the total mixture quantity aggravates melting conditions, increases time and heat spent for melting thereof, which is of considerable importance when a reducing agent charged together with the oxide mixture is a material (silicon) having a lower activity as compared to aluminum. The use of a silicon-containing reducing agent is associated with possible local overheating of the mixture with the reducing agent, hence, with floating thereof on the molten slag surface and intensive reaction with atmospheric oxygen. Despite the fact that losses of the silicon-containing reducing agent into the gaseous phase are negligible, the silicon oxides formed in the manganese reduction reaction aggravate the thermodynamic conditions of manganese reduction, this leading to increased consumption of calcium-containing oxides (lime) and increased energy consumption for heating the oxide mixture. The thermal characteristics of the oxide mixture, even in combination with aluminum and silicon preliminary added to the molten metal, fail to provide spontaneous reduction process, and the additional consumption of the silicon-containing reducing agent to provide the compensating chemical heat impairs the manganese reduction performance due to the increased SiO_2 portion in the slag.

SUMMARY OF THE INVENTION

The object of the present invention is to provide an improved method of direct alloying of steel by optimizing the manufacturing process. The invention ensures favorable physical, chemical and temperature conditions for synchronously melting the charged materials and carrying out the reduction, this improving the recovery of alloying elements by the metal, reducing contamination of the steel by non-metallic inclusions and improving the quality of the steel.

The object of the invention is attained in a method for direct alloying of steel, comprising the steps of: melting a steel in a steel-making vessel; alloying the steel with manganese reduced from oxides during addition of a material containing manganese oxides and a reducing agent and reaction therebetween, wherein according to the invention the manganese reduction from the oxides is carried out in association with reduction of other alloying elements from a material containing non-metallic compounds of the elements and charged on the metal surface, and/or with reduction of manganese from a charged material containing other non-metallic manganese compounds; the addition of a reducing agent starts when the layer height of the charged material is from 0,1 to 0,15 of the total layer height; the reduction temperature is maintained at the level of the melting temperature of the charged material and the reducing agent; constant contact is provided between the molten part of the reducing agent and the molten part of the charged material containing non-metallic compounds of alloying elements, the

reducing agent being delivered in the amount ensuring required thermal characteristics of the mixture of the charged material and the reducing agent.

The material containing non-metallic compounds of alloying elements preferably comprises oxides or carbonates of the alloying elements, or combinations thereof.

The reducing agent is preferably aluminum-containing, or silicon-containing, or carbon-containing material, or a material containing a group of alkaline-earth metals, or combinations thereof.

The charging of the material containing non-metallic compounds of alloying elements is preferably carried out continuously or in batches, each batch being no less than 0,1 of the total consumption.

In a direct steel alloying method carried out in a steel-making vessel, it is preferable to further add a slag-forming material, and the carbon-containing material used as reducing agent is preferably added in the amount selected from the ratio of $1:(0,18-0,20):(0,10-0,12)$ of the material containing non-metallic compounds of alloying elements, the slag-forming material and the carbon-containing material, respectively, when the molten metal reaches a temperature exceeding the tapping temperature by a value determined from the expression: $\Delta t = 33[Mn]$, where: Δt is the value in excess of the tapping temperature, °C; $[Mn]$ is the quantity of reduced manganese, in percent by weight; 33 is the empirical coefficient, and the oxidizing slag is preferably removed from the steel-making

vessel.

When alloying steel in a steel-making vessel, the material containing non-metallic compounds of alloying elements, the slag-forming material and the carbon-containing material are preferably charged in batches, the weight of each batch comprising all the supplied materials being 0,01-0,02 of the molten metal weight.

When a direct steel alloying method is carried out in a casting ladle, it is preferable to preliminary charge a carbon-containing material into the ladle; the reducing agent is preferably aluminum; in the alloying process it is preferable to additionally add lime as a slag-forming material, the components being preferably taken in the following ratio, in percent by weight: the materials containing non-metallic compounds of alloying elements 56-65; aluminum 12-16; carbon-containing material 5-7, lime - the balance.

When alloying steel with chrome in a casting ladle, the non-metallic compounds of other elements are preferably chrome compounds which are to be charged into the ladle during tapping the molten metal; and to increase manganese and chrome content for every 0,1 percent in the resulting steel, chrome oxides are preferably added in an amount selected from a manganese-chrome ratio of from 1,1 to 1,2 in the material containing non-metallic compounds of these elements, and aluminum used as a reducing agent is preferably added together with calcium carbide in a ratio of 1:(2,9-3,2).

When alloying steel with chrome in a casting ladle, the

material containing chrome oxides is preferably a converter slag of the medium-carbon ferrochrome production.

The method in accordance with present invention relies on the idea of implementing the principle according to which the reduction of temperature in the reaction zone contributes to increasing the reaction equilibrium constant, hence, increases the reaction completeness; to this end a method in accordance with the present invention ensures the following conditions:

1. Minimum temperature of the direct alloying process in the alloying element reduction reaction zone at a minimum viscosity of the forming slag and a high slag sorption capacity in respect of the reduction reaction oxide products - oxides of active elements included in the reducing agent.

2. Permanent presence in the reaction zone throughout the reduction process of the starting reaction components: a material containing manganese oxide and non-metallic compounds of other alloying elements, and/or containing other non-metallic manganese compounds and a reducing agent.

3. Effective withdrawal from the reaction zone of the reaction product, the reduced alloying element, into the metal body, and the formed oxides of the reducing agent active elements into the slag phase.

As the alloying elements are soluble in molten iron, and e.g. manganese is infinitely soluble in molten iron, the reduced manganese microparticles are instantly absorbed by the molten metal, and convective flows, always existing in the molten metal body, carry away the layers enriched with the reduced element

into the molten metal body, thereby averaging the composition in respect of the alloying element, manganese. Other reducible alloying elements in the presence of the reduced manganese microparticles also intensively dissolve in the metal body since the reduction occurs in the liquid-phase conditions, hence there is no obstacles to their dissolution in the molten metal.

The reducing agent is added in the amount providing the desired thermicity of the charged mixture containing manganese oxides, non-metallic compounds of other alloying elements, and/or containing other non-metallic manganese compounds, and a reducing agent.

For spontaneous reaction of reduction of elements from oxides and carbonates, a certain resource of potential heat of a particular material mixture comprising non-metallic compounds of alloying elements and a reducing agent is required, which resource would provide not only melting the starting materials and reducing the alloying elements, but also effective separation of the metal and slag phases being formed. In direct steel alloying using materials containing non-metallic compounds of alloying elements in the form of oxides and carbonates of the alloying elements, and the reducing agent, favorable thermal conditions of the reduction process are created, since along with the exothermic reduction reaction heat the additional heat sources are provided by the molten metal, inner surfaces of the steel-making vessel, etc. In this case, along with a definite quantity of heat supplied into the reaction zone, the conditions are provided that prevent inflammation of highly active

elements, reducing agents, and removal thereof to the gas phase. Therefore the thermicity of each particular mixture are experimentally selected so that to provide the spontaneous reduction reaction at minimal loss of the reducing agent.

Being added, the reducing agent is first covered on the surface by slag and metal. But as the reducing agent melting point is lower than that of the metal and slag, the reducing agent melts and the process is accompanied with breaking the adhered crust, so a permanent contact is provided between the formed molten part of the reducing agent and the homogeneous component of the alloying materials being melted, the contact being constantly maintained by the heat of exothermic reactions of alloying element reduction. This provides synchronous processes of melting of the charged materials and reduction of the alloying elements.

Detailed Description of the Invention

A method of direct alloying of steel is accomplished in the following manner.

Molten iron is charged into a steel-making vessel, such as an oxygen converter, shaft arc furnace, etc, and then slag-forming materials (lime, dolomite, spar) are added, and oxygen is blown into the melt. After removing the oxidizing slag, a material containing manganese oxides, non-metallic compounds of other alloying elements, and/or containing other non-metallic manganese compounds is charged on the molten metal surface. The material containing non-metallic compounds may be manganese ore, concentrate, sinter, slag of ferroalloy production, etc. The

non-metallic compounds of other alloying elements may be compounds containing oxides of alloying elements, e.g. niobium, titanium, molybdenum, chrome, etc., or carbonates of alloying elements, e.g. titanium oxycarbonitride, niobium carbonates, groups of alkaline-earth metals, etc, or combinations thereof. The delivery of the material containing non-metallic compounds of alloying elements is accomplished continuously or in batches, each batch being no less than 0,1 of the total consumption, depending of a predetermined composition of the steel. The batch supply of the material containing non-metallic compounds of alloying elements is dictated by the necessity to provide synchronous melting of the supplied material and reduction of alloying elements therefrom. Reduction of the charged material batch below 0,1 of the total consumption will hamper the melting process because the materials are slagged and this increases the melting time, leads to inefficient use of the reducing agent and decreases recovery by the molten metal of elements reduced from the material containing compounds of alloying elements.

As the layer height of the supplied material containing non-metallic compounds of alloying elements reaches 0,1-0,15 of the total layer height, addition of the reducing agent is started and continued in the course of further charging of the materials.

The reducing agent is aluminum-containing, or silicon-containing, or carbon-containing material, or a group of alkaline-earth metals, or combination thereof. Depending on the selected reducing agent, its fractional composition may vary

from 1,0-3,0 mm to 20-50 mm and greater. The reducing agent is added in the amount providing the desired thermal characteristics of the mixture of the charged material and the reducing agent.

Addition of the material containing manganese oxides, non-metallic compounds of other alloying elements, and/or containing other non-metallic manganese compounds is dictated by the necessity of providing the melting temperature of the material below the molten material temperature.

These measures ensure, when homogeneous component of melting material is formed and the reducing agent is added in due time, intensive start of the reduction process, and synchronous processes of melting the supplied materials and reducing the alloying elements, which improves recovery of alloying elements by the metal, decreases steel contamination with non-metallic inclusions and improves quality of the steel. Effective use of the reducing agent is provided by simultaneous melting of the material containing non-metallic compounds of alloying elements and of the reducing agent. This promotes intensive performance of the liquid-phase reduction reaction of alloying elements.

The addition of the reducing agent in the process of charging a material containing non-metallic compounds of alloying elements provides early start of the reduction process and permanent contact between the molten part of the reducing agent and the formed homogeneous component of melted material containing non-metallic compounds of alloying elements,

synchronous process of melting the supplied materials and reduction, thereby preventing transition of the reduction process to diffusion regime accompanied by low speed and completeness of the reduction process, increased consumption of the reducing agent, contamination of the metal with non-metallic inclusions and degradation of steel quality.

Addition of the reducing agent is preferably started when the layer height of the charged alloying material reaches 0,1-0,15 of the total layer height, because the reducing agent melting point is lower than the melting point of the material containing non-metallic compounds of alloying elements. When the reducing agent is added earlier than the layer height of the material reaches 0,1 of the total layer height, the material will not have time to melt and form a homogeneous phase, hence the molten reducing agent could not participate in the reduction reaction, this resulting in inefficient use thereof. Addition of the reducing agent when the layer height of the material containing compounds of alloying element is more than 0,15 of the total layer height is also inadvisable as the intensive formation of a homogeneous phase of the charged alloying material would disturb the synchronous manner of melting the alloying materials and the reduction process, this resulting in decreased recovery of alloying elements by the molten metal, contamination of the metal with non-metallic inclusions and impaired steel quality.

Reduction of the alloying elements is carried out at the melting temperature of the material containing manganese oxide,

non-metallic compounds of other alloying elements, and/or containing other non-metallic manganese compounds.

This is dictated by the fact that in the presence of the homogeneous component of the alloying materials and the molten part of the reducing agent the reduction completeness increases and the temperature is minimized, which fact contributes to recovery of alloying elements by the metal, reduces contamination of the steel with non-metallic inclusions and improves the quality of the steel. No temperature increase above the melting temperature of the material according to the invented method occurs because the reduction process substantially ends when melting of the charged material is over.

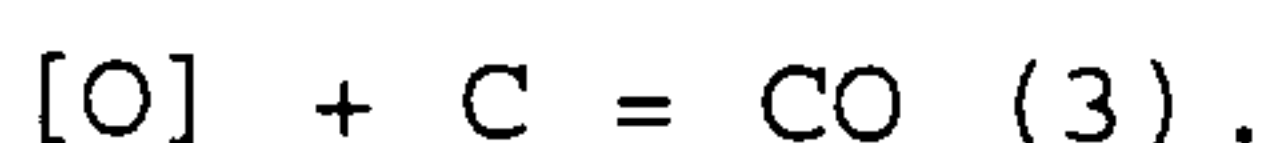
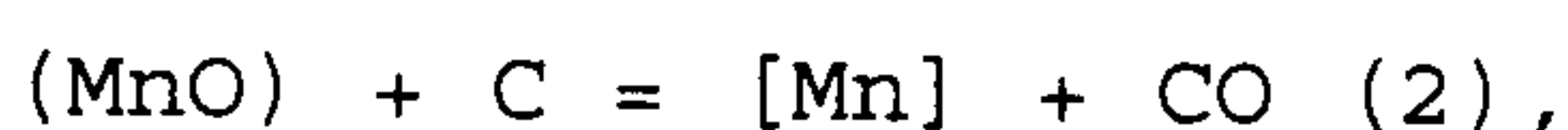
The provision of permanent contact between the molten part of the reducing agent and the homogeneous component of the melting material containing non-metallic compounds of alloying elements in accordance with the invented method is needed to maintain high speed and completeness of the reduction process.

When a direct steel alloying process is carried out in a steel-making vessel, such as a converter, upon termination of the refining blowing period and reaching the molten metal temperature in excess of the tapping temperature, the oxidizing slag is withdrawn. Additional heating of the molten metal is dictated by the necessity of reducing the oxidizing slag viscosity before tapping and compensating for the heat loss resulting from the endothermic reaction of carbothermic reduction of alloying elements from the material containing non-metallic compounds of alloying elements. The value by which the

molten metal temperature should exceed the tapping temperature rated for each particular steel grade is determined from the expression: $\Delta t = 33[Mn]$, where: Δt is the value in excess of the tapping temperature, °C; $[Mn]$ is the quantity of reduced manganese, percent by weight; 33 is the empirical coefficient. Upon heating the molten metal to the required temperature value the oxidizing slag is removed, and processes of resulfurization and rephosphorization of the metal in the steel-making vessel are brought to minimum in the following treatment. Then a material containing non-metallic compounds of alloying elements, and a slag-forming material such as lime, and a carbon-containing material used as a reducing agent are charged into the steel-making vessel in batches, the weight of each batch being from 0,01 to 0,02 of the molten metal weight. The material containing non-metallic compounds of alloying elements is lump ore, concentrate, agglomerate, preferably with 20-50 mm fractional composition, the slag-forming material is a freshly burned lime, and the carbon-containing material added as a reducing agent is coke, coal, silicon carbide, calcium carbide, or combinations thereof. The carbon-containing material is added in the amount selected from the ratio of $1:(0,18-0,20):(0,10-0,12)$ of the charged material containing non-metallic compounds of alloying materials, the slag-forming material and the carbon-containing material, respectively. This ratio is dictated by the necessity of providing a continuous process of direct steel alloying. Increase in the consumption of the slag-forming and carbon-containing materials decreases the amount of the material

containing non-metallic compounds of alloying elements charged into the steel-making vessel, reduces recovery of the alloying elements by the molten metal, increases slag heterogeneity, aggravates heat and mass exchange processes, all this impairing the steel quality characteristics due to the increased content of non-metallic inclusions. Reduction in the charged material ratio below 1:(0,18-0,20):(0,10-0,12) reduces the addition of CaO oxides into the steel-making vessel, aggravates physical and chemical conditions of the reduction process, decreases degree of recovery of reduced alloying elements by the molten metal, and impairs the quality of the steel.

The material containing non-metallic compounds of alloying elements, e.g. manganese, and lime, supplied on the molten metal surface, are melted, and chemical reactions take place between carbon as a reducing agent and oxygen of the slag-metal two-phase system, e.g.



Gas product of all three reactions is carbon monoxide which bubbles the slag and intensifies its refining ability and upper metal layers, thereby contributing to vigorous absorption of reduced elements by the base metal.

Endothermic nature of the reactions between carbon and oxygen contained in the metal and slag does not inhibit the reactions because the metal is preheated before the beginning of the direct alloying process to a temperature higher than the

tapping temperature, depending on the desired quantity of the reduced element, e.g. manganese.

The weight of each charged material batch equal to 0,01-0,02 of the molten metal weight is dictated by the necessity of provision of uniform reduction process. Reduction in the batch weight below 0,01 of the molten metal weight will aggravate the reduction process thermal conditions and, hence, the mass exchange process, due to the reduced amount of gaseous carbon monoxide formed in the process of deoxidation of the molten metal and reduction of the alloying elements by carbon which bubbles the slag and the molten metal surface layer, this impairing the completeness of the alloying element reduction and deteriorating the refining process, and the finished metal quality will be worsened due to the increased content of non-metallic inclusions.

Increase in the batch weight above 0,02 of molten metal weight is also unadvisable as this will disturb the heat exchange processes and lead to degradation of the slag-forming process due to great additions of slag-forming materials contained in the charged material, which results in thickening the slag, increases the slag heterogeneity, decreases the recovery of alloying elements, and deteriorates the refining process, thus, the metal will have an increased amount of non-metallic inclusions and the quality of the steel will be impaired.

Upon the conducted direct alloying process, a low-oxidized metal is discharged from the steel-making vessel. Therefore, the

process of bringing the metal to a predetermined composition can be regulated owing to the small and forecasted amount of oxygen dissolved in the metal. This drastically reduces the number of iterations in order to observe the narrow content range for any one of the alloying or modifying elements.

When performing the direct alloying process in a casting ladle, a carbon-containing material is first charged into the casting ladle at the beginning of tapping the molten metal from a steel-making vessel, then a material containing non-metallic compounds of alloying elements, a reducing agent such as aluminum, and a slag-forming material such as lime are charged in the following ratio, in percent by weight: materials containing non-metallic compounds of alloying elements 56-65; aluminum 12-16; carbon material 5-7; lime - the balance.

The delivery into the casting ladle of a carbon-containing material such as coke or coal in the amount of 5-7 percent by weight of the total consumption of the materials charged into the ladle provides deoxidation of the metal to desired values of oxygen content in the finished steel.

Furthermore, combination of deoxidation and alloying processes with tapping the metal into a casting ladle reduces time of alloying, thereby decreasing the melting cycle. The reduction in carbon-containing material content in the materials charged into the ladle does not lead to the desired deoxidation level, while the increase in its content above 7 percent results in cooling the metal in the ladle, as the heat generated by the exothermic reaction is insufficient to compensate for the heat

loss caused by the endothermic reaction between carbon and oxygen of the metal.

The addition of the material containing non-metallic compounds of alloying elements in the amount of 56-65 percent by weight ensures a predetermined concentration of alloying elements in the steel. The addition of less than 56 percent by weight of the material containing non-metallic compounds of alloying elements increases consumption of the reducing agent, aluminum, and consumption thereof for additional metal deoxidation accompanied by formation of hardly removable non-metallic aluminate inclusions, this aggravating the steel casting process and impairing the quality of the steel. The increase in the material consumption above 65 percent by weight lowers the degree of recovery of alloying elements therefrom.

Consumption of aluminum in the amount of 12-16 percent by weight provides a high degree of recovery of alloying materials, while the reduced temperature in the reaction zone as compared to that of the metal substantially excludes the formation of AlO and Al_2O reaction gas products that contaminate the shop atmosphere. Al_2O_3 produced in the aluminum oxide reaction binds with CaO to form easily removable compounds.

A process of direct steel alloying with chrome is accomplished in the following fashion. A material containing non-metallic compounds of other elements in the form of chrome oxides is charged into a casting ladle together with manganese oxides and other non-metallic manganese compounds during tapping a molten metal from a steel-making vessel.

As chrome oxides have a high melting point, the presence of manganese oxide and other non-metallic manganese compounds in the charged material improves the heat balance and physical and chemical conditions of alloying element reduction owing to the lowered melting temperature of the charged material. The combined addition of the components into the casting ladle during tapping the metal is dictated by the necessity of accelerating the melting of the refractory component containing chrome oxides, this improving the slag phase homogenizing and the alloying element reduction process.

The consumption of oxides for increasing Mn and Cr content in the finished steel for each 0,1 percent by weight, selected from a manganese-chrome ratio of from 1,1 to 1,2 in the charged material containing non-metallic compounds of these elements, provides an optimal recovery (about 90%) of the alloying elements, chrome and manganese, in the metal, thereby improving chemical homogeneity of the steel, lowering the metal oxidation level, decreasing the amount of non-metallic inclusions and improving the steel quality. Reduction in the manganese-chrome ratio in the charged material below 1,1 aggravates the process parameters of chrome and manganese reduction due to degradation of the reduction process kinetic conditions caused by increased viscosity resulting from melting the liquid phase oxide materials and high heterogeneity of the formed slag. This impairs the performance of alloying element recovery from oxides, reduces the slag sorption capacity in respect of non-metallic inclusions, and raises contamination of the metal with

non-metallic inclusions. Increase in the manganese-to-chrome ratio in the charged material above 1,2 leads to dilution of the slag with the material containing chrome oxides, decreases the absolute amount of the materials containing non-metallic manganese compounds, hence lowers recovery of manganese and chrome by the metal, this resulting in lower chemical homogeneity of the alloying elements, manganese and chrome, in the metal body, and inferior quality of the steel.

Aluminum is added as a reducing agent into a casting ladle together with calcium carbide in the ratio of 1:(2,9-3,2). The selected ratio of the materials is dictated by the necessity of optimizing thermal and kinetic conditions of reduction of the alloying elements, chrome and manganese, from respective materials having different melting points. This improves recovery by the molten metal of alloying elements from the charged material owing to the provision of positive heat balance at the simultaneously occurring endothermic reactions between carbon of calcium carbide and oxygen of the melting material, and the exothermic reaction between aluminum and oxygen from the material and oxygen dissolved in the metal. In addition, the exothermic reaction takes place between calcium contained in calcium carbide and oxygen and sulfur dissolved in the metal with formation of CaO and CaS , respectively. This also contributes to heat balance stabilization in the reduction process. The reaction between carbon of calcium carbide and oxygen is accompanied by formation of carbon monoxide bubbles, which bubble the molten slag and improve the slag recovery

ability in respect of non-metallic inclusions, thereby decreasing their content in the metal and improving the quality of the steel.

Calcium contained in calcium carbide is not only the effective deoxidizing and desulfurizing agent, but also promotes globularization of aluminates that form in the metal surface layer as the result of metal deoxidation by aluminum in combination with the process of reduction of alloying elements from oxides thereof. The globularized aluminates are actively recovered by the surface slag, which contributes to decrease in the non-metallic inclusions and improving the steel quality. A portion of calcium added into the ladle reacts with sulfides formed in the metal, generally MnS and FeS , modifies their morphology and forms simple sulfides (CaS) and complex calcium-passivated manganese and silicon sulfides, thereby lowering the amount of non-metallic sulfide inclusions and sulfur content in the metal and improving the quality of the steel. Increase in the calcium carbide portion above 3,2 impairs process characteristics of reduction and refining of the metal from sulfur due to aggravated thermal conditions, and increases heterogeneity of the slag, decreases its sorption capacity in respect of non-metallic inclusions, increases chemical non-uniformity of metal in respect of alloying elements, chrome and manganese, and impairs the steel quality. Decrease in the carbide calcium portion below 2,9 increases the temperature of the reduction process zone and probably entails floating up of molten aluminum on the molten slag surface, reaction of aluminum

with atmospheric oxygen with formation of gas oxides due to incomplete oxidation of aluminum of AlO and Al_2O and after-oxidation thereof in the gas phase. This changes the heat balance, aggravates process characteristics of reduction of alloying elements from oxides thereof and refining of the metal from sulfur by calcium, and impairs the environment in the shop. Alteration of the ratio of reducing agent components in accordance with the present invention will aggravate kinetic conditions of the reduction and metal refining processes due to increased heterogeneity of the slag and reduced intensity of slag stirring by carbon monoxide bubbles, which impairs the slag recovery ability in respect of non-metallic inclusions and increases contamination of the metal with non-metallic inclusions. All these factors impair chemical uniformity of the steel in respect of content of the alloying elements, aggravate desulfurization, increase the content of non-metallic inclusions in the metal and impair the quality of the steel.

The above embodiment of a method in accordance with the present invention does not exclude other embodiments within the scope of the claims and can be implemented in any vessel with molten metal, e.g. in an open-hearth furnace, a casting ladle, ladle furnace, etc.

Example 1

A method of direct alloying of steel with manganese and chrome was implemented in a converter with a capacity of 250 t. Molten iron comprising, in percent by weight: C - 4,42; Si - 0,82; S - 0,020; P - 0,095, iron - the balance, was charged into

the converter together with a slag-forming material, lime, comprising, in percent by weight: CaO - 92,0; Mg.O - 6,5; other side impurities (OSI) - the balance.

A material containing manganese oxides and other non-metallic compounds of manganese was a material having the total content of manganese, as net element, of 44,6 percent by weight. A material containing non-metallic compounds of other alloying elements was chrome oxide containing 70,81 percent by weight of Cr_2O_3 . Reducing agents were aluminum-containing and carbon-containing materials. The aluminum-containing material was undersized slag of aluminum production comprising, in percent by weight: Al_{metal} - 44,8; the volatile matter - the balance; the carbon-containing material was coal comprising, in percent by weight: C - 85,9; S - 0,47; the volatile matter - the balance. After charging the molten pig iron and slag-forming materials into the converter, oxygen was blown in the metal at the flow rate of $940 \text{ N m}^3/\text{min}$ for 8 minutes, and the oxidizing slag was removed. Then the material containing manganese oxides and other non-metallic manganese compounds, delivered at 14,0 kg/t (3500 kg) supply rate, and the material containing chrome oxide, delivered at 12 kg/t (3000 kg) supply rate, both with 10-20 mm fractions, were continuously charged into the converter on the molten metal surface. When the layer height of the supplied materials was 0,1-0,15 of the total height thereof, 1785 kg of a reducing agent, an undersized slag of aluminum production having 20-30 mm fractions, and 465 kg of coal having 10-20 mm fractions were added so that to provide the desired thermicity of the

mixed charged materials. Reduction of the alloying elements was carried out at the melting temperature of the mixed charged materials at the permanent contact between the molten part of the reducing agent and the molten part of the charged materials throughout the reduction process. To produce steel with a desired composition, the required alloying additives (copper and nickel) were charged into the converter, while the deoxidizing agent, ferrosilicon, was added into the ladle.

The finished steel was cast into 12,5 t ingots that were rolled to a sheet 10-20 mm thick and subjected to metallographic analysis.

The finished steel had the following composition, in percent by weight: C - 0,11; Si - 0,24; Mn - 0,57; S - 0,010; P - 0,007; Al - 0,025; Cr - 0,60; Ni - 0,70; Cu - 0,46; Fe - the balance.

Recovery of manganese by the molten metal was 92,7 percent and chrome - 89,8 percent. Contamination of the steel with non-metallic inclusions (in points) was as follows: oxides 1,4; sulfides 1,2; silicates 1,3.

Example 2 (conducted for comparison according to the closest prior art, (RU 2096491))

Melt was conducted in a 250 t converter with deoxidation and alloying of the metal in the converter. The metal tapped from the converter without slag at 1690°C contained aluminum and silicon. A mixture of manganese ore (Mn - 48,0%; SiO₂ - 3,5%; Fe - 3,4%; CaO - 1,5%; Al₂O₃ - 2,5%; P - 0,05%) and lime (CaO - 90%) at the ratio of CaO:Mn_xO_y = 1:1; carbon ferrochrome of ΦX-650

(FeCr 650) grade and ferrosilicon of Φ C-65 (FeSi 65) grade were simultaneously added into the ladle during the tapping. To produce steel with a required composition, nickel and copper were added into the converter, just as in the method in accordance with the present invention. Upon holding for 10 min and at the resulting slag basicity of $\text{CaO/SiO}_2 = 1,3$, the finished steel has the following composition, in percent by weight: C - 0,15; Mn - 0,51; Si - 0,27; Al - 0,003; Cr - 0,54; Ni - 0,72; Cu - 0,55; S - 0,017; P - 0,015; Fe - the balance.

The molten metal recovered 71,2 percent of manganese, 67,8 percent of chrome, and the steel contamination with non-metallic inclusions (in points) was: oxides 3,5; sulfides 2,8; silicates 2,0.

Use of the method in accordance with the present invention provided the high degree of recovery of alloying elements and decreased contamination of steel with non-metallic inclusions.

Example 3

Steel was melted in a 160 t converter. The specification requirements were: the melt tapping temperature of 1630°C; the content of carbon of 0,03-0,05 percent, and manganese of 0,055 percent. Pig iron was poured into the converter in the amount of 146 t. The charged pig iron had the temperature of 1410° and comprised, in percent by weight: C - 4,2; Si - 0,85; Mn - 0,57; S - 0,016; P - 0,021. The melt was blown with oxygen at 120 Nm₃/min flow rate for 22 min until the melt temperature reached the temperature exceeding the tapping temperature according to the specification by a value determined from the

expression: $\Delta t = 33[Mn]$, where: Δt is the value in excess of the tapping temperature, °C; $[Mn]$ is the amount of manganese reduced from the materials containing non-metallic manganese compounds, percent by weight; 33 is the empirical coefficient. The $[Mn]$ value in the expression $\Delta t = 33[Mn]$ was determined based on the melt specification. In the example the manganese content prior to tapping should be 0,55 percent at the carbon content of 0,03-0,05 percent. At such carbon content at the end of blowing the manganese content was generally 0,05-0,07% (taken as 0,05%). Then the $[Mn]$ value was determined as $0,55 - 0,05 = 0,05\%$. The Δt value from the expression $\Delta t = 33[Mn]$ was determined as 16,5%. For this reason, the blowing was conducted until the melt temperature was 1647°C. Then the oxidizing slag was removed from the converter, and a mixture comprising manganese oxides, a material containing other non-metallic inclusions, lime and coke, as a carbon-containing reducing agent, added in the amount chosen from the ratio of $1 : (0,18 - 0,20) : (0,10 - 0,12)$, respectively, the weight of each batch comprising all the supplied materials was 0,01-0,02 of the molten metal weight. The molten metal temperature upon termination of the direct alloying process before tapping was 1630°C. Before tapping the metal comprised, in percent by weight: C - 0,05; Mn - 0,54; P - 0,006; S - 0,005.

Table 1 shows process characteristics and results of the method.

The molten metal tapped into the casting ladle exhibited

low oxidation factors and low sulfur and phosphorus content, which resulted in the low contamination of steel with non-metallic inclusions and contributed to the finished metal quality improvement. Manganese recovery by the molten metal was 81,7 percent.

Table 1

Melt No.	Consumption, kg/t			Ratio	Weight, kg	Content of elements, wt. %				Non-metallic inclusions, points			
	Mn _x O _y	CaO	C			Oxygen	Sulfur	Phosphor		Oxides	Sulfides	Silicates	
1	10,0	1,8	1,0	1:0,18:0,10	150	0,004	0,004	0,005		1,0	0,5	0,5	
2	10,0	1,9	1,1	1:0,19:0,11	220	0,004	0,004	0,005		1,0	0,5	0,5	
3	10,0	2,0	1,2	1:0,20:0,12	300	0,005	0,005	0,006		1,0	1,0	0,5	

Example 4

A steel was melted with the following composition, in percent by weight: C - 0,09-0,12; Mn - 0,40-0,65; Si - 0,17-0,34; S - 0,20; P - 0,20. The molten metal produced in a steel-making vessel was tapped in the non-oxidized form into a casting ladle with a capacity of 5 t. A carbon-containing material; coke; a material containing manganese oxides, and a material containing other non-metallic manganese compounds, at the total manganese content, as net element, in the materials of 44 percent by weight; aluminum as a reducing agent and lime were charged into the casting ladle during tapping the molten metal; the materials were fed into the ladle in the proportion in accordance with the present invention. The metal was cast in ingots of 1 t. Samples of the metal were taken for chemical analysis before and after addition of the materials into the ladle. Samples were also taken from the rolled product produced from the ingots to determine points of non-metallic inclusions.

The steel produced by a direct alloying method in accordance with the present invention exhibited a high degree (95,4%) of recovery of the alloying element, manganese, by the metal, and low contamination by non-metallic inclusions.

Example 5

Melts were performed in 100 t electric steel-making furnace using a method of direct alloying of steel with chrome in accordance with the present invention.

The molten metal was tapped from the furnace into a casting ladle at the temperature of 1650°C, and during the tapping a

material containing non-metallic compounds of an alloying element, chrome, was added in the form of a converter slag of medium-carbon ferrochrome production, having the chrome content, as net element, of 48,99 percent by weight, in the amount of 1200 kg, and materials containing manganese oxides and other non-metallic manganese compounds, having the total manganese content, as net element, of 44 percent by weight, in the amount of 1400 kg. 370 kg of a secondary aluminum of AB-86 grade and 1100 kg of calcium carbide were also added to the casting ladle in the ratio of 1:3.

The finished steel was cast to 12,5 t ingots which were rolled to a sheet 10-20 mm thick and subjected to metallographic analysis.

The finished steel had the following composition, in percent by weight: C - 0,11; Si - 0,17; Mn - 0,54; S - 0,006; P - 0,007; Al - 0,023; Cr - 0,61; Ni - 0,70; Cu - 0,53; Fe - the balance.

Compositions of the materials added to the ladle and results of testing the produced steels are shown in Table 2.

Table 2

Melt No.	1	2	3
Material composition, wt. %:			
Material containing non-metallic compounds of alloying elements	56,0	60,0	65,0
Coke	5,0	6,0	7,0
Aluminium	12,0	14,0	12,0

Lime	27,0	20,0	12,0
Manganese recovery, %	96,8	97,0	98,0
Desulfurization degree, %	64,2	58,4	61,0
Maximum point of non-metallic inclusions:			
Oxides in the form of inclusion lines	1,9	1,8	1,8
Spotted oxides	1,4	1,6	1,5
Sulfides	2,3	2,5	2,4

In this example, the recovery by the molten metal was: 91,2 percent of chrome and 93,2 percent of manganese.

The use of a method of direct steel alloying at the chrome oxide consumption in accordance with the invention provided high chemical homogeneity of the steel in respect of the main alloying elements, high desulfurization degree and low contamination of steel with non-metallic inclusions.

What is claimed is:

1. A method of direct alloying of steel, comprising: melting a steel in a steel-making vessel; alloying the steel with manganese reduced from oxides during addition of a material containing manganese oxides and a reducing agent and reaction therebetween, said method characterized in that the manganese reduction is carried out in association with reduction of other alloying elements from a material containing non-metallic compounds of the alloying elements and charged on the molten metal surface, and/or with reduction of manganese from a charged material containing other non-metallic manganese compounds; the addition of a reducing agent starts when the layer height of the charged material is from 0,1 to 0,15 of the total layer height; the reduction temperature is maintained at the level of the melting temperature of the charged material and the reducing agent; constant contact is provided between the molten part of the reducing agent and the molten part of the charged material containing non-metallic compounds of alloying elements, the reducing agent being delivered in the amount ensuring required thermal characteristics of the mixture of the charged material and the reducing agent.

2. The method according to claim 1, wherein the material containing non-metallic compounds of alloying elements comprises oxides or carbonates of alloying elements, or combination thereof.

3. The method according to claim 1, wherein the reducing agent is an aluminum-containing, or silicon-containing, or

carbon-containing material, or a material comprising a group of alkaline-earth metals, or combinations thereof.

4. The method according to claim 1, wherein the charging of a material containing non-metallic compounds of alloying elements is performed continuously or in batches, each batch being no less than 0,1 of the total consumption.

5. The method according to claims 1,2,3,4, wherein in a direct steel alloying process carried out in a steel-making vessel, a slag-forming material and a carbon-containing material used as a reducing agent are further charged into the vessel in the amount selected from the ratio of $1:(0,18-0,20):(0,10-0,12)$ of the material containing non-metallic compounds of alloying elements, the slag-forming material and the carbon-containing material, respectively, when the molten metal reaches a temperature that exceeds the tapping temperature by a value determined from the expression: $\Delta t = 33[Mn]$, where Δt is the value in excess of the tapping temperature, °C; $[Mn]$ is the amount of reduced manganese, percent by weight; 33 is the empirical coefficient; and the oxidizing slag is withdrawn from the steel-making vessel.

6. The method according to claim 5, wherein the material containing non-metallic compounds of alloying elements, the slag-forming material and the carbon-containing material are charged in batches, each batch comprised of all the charged materials having the weight of 0,01-0,02 of the molten metal weight.

7. The method according to claims 1,2,3, wherein in a

direct steel alloying process carried out in a casting ladle, a carbon-containing material is additionally added into the ladle; the charged reducing agent is aluminum; and lime is additionally added as a slag-forming agent in the alloying process; the components being taken in following ratio, in percent by weight: the material containing non-metallic compounds of alloying elements 56-65; aluminum 12-16; carbon-containing material 5-7; lime - the balance.

8. The method according to claims 1,3, wherein when alloying steel with chrome in a casting ladle, the non-metallic compounds of other elements are chrome oxides that are added to the ladle during tapping the molten metal; to increase manganese and chrome content in the finished steel for each 0,1 percent the chrome oxides are charged in the amount selected from a manganese-chrome ratio of from 1,1 to 1,2 in the material containing non-metallic compounds of these elements, and aluminum added as a reducing agent is charged together with calcium carbide in the ratio of 1:(2,9-3,2).

9. The method according to claim 8, wherein the material containing chrome oxides is a converter slag of medium-carbon ferrochrome production.