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Nemoto et al.

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[54] **METHOD OF ADDING RARE EARTH METALS OR THEIR ALLOYS INTO LIQUID STEEL**

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[52] **U.S. Cl.** **75/58,** 75/53

[51] **Int. Cl.** **C21c 7/00**

[58] **Field of Search**.... 75/58, 53, 57, 123 E, 126 G, 75/51, 129, 152

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[57] **ABSTRACT**

When one or more rare earth metals or their alloys are added into liquid steel in an intermediate vessel disposed between a ladle and a mold, the resulting steel exhibits excellent impact property.

3 Claims, 4 Drawing Figures

FIG. 1

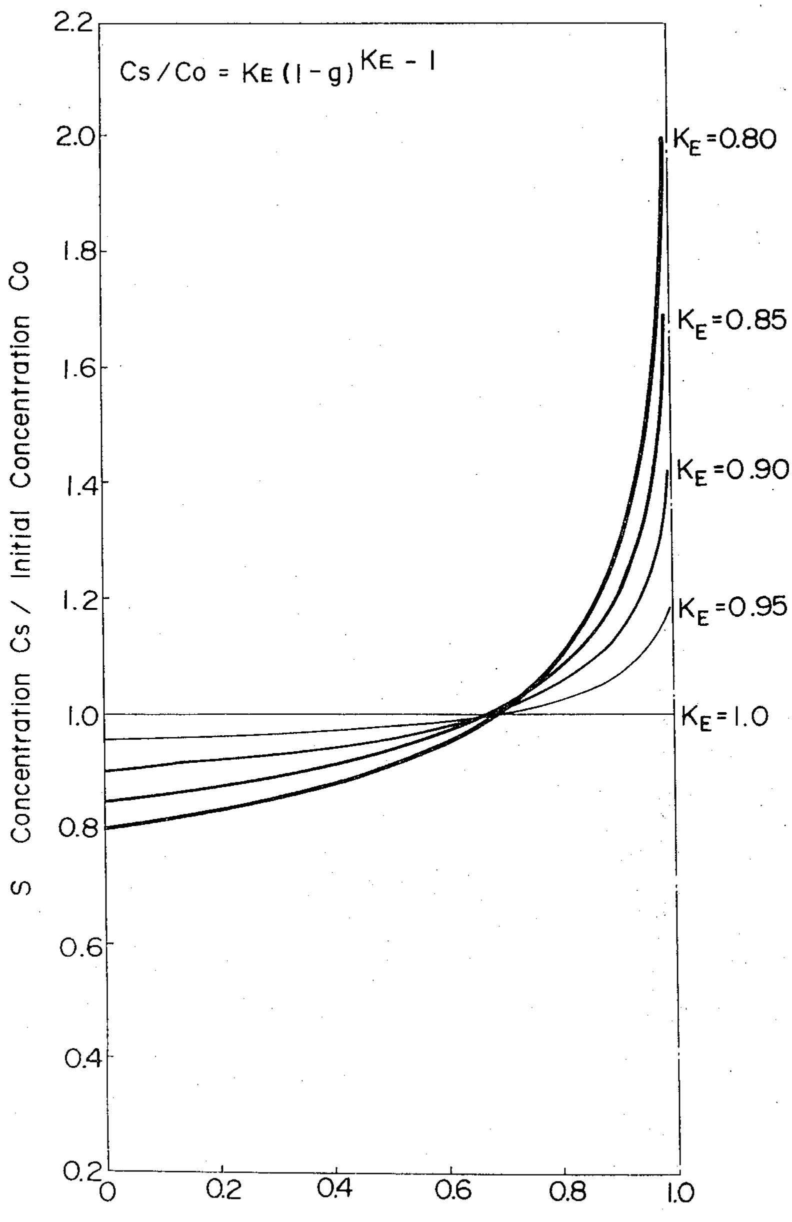

Cs / Co = KE (1 - g) KE - 1
KE = 0.80
KE = 0.85
KE = 0.90
KE = 0.95
KE = 1.0
Concentration Cs / Initial Concentration Co
Solidification Rate g
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0

FIG. 3

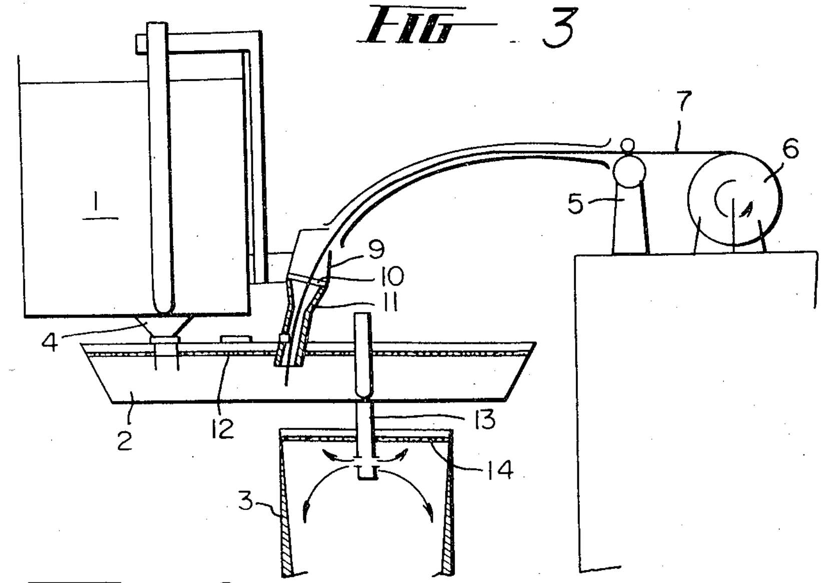


FIG. 2

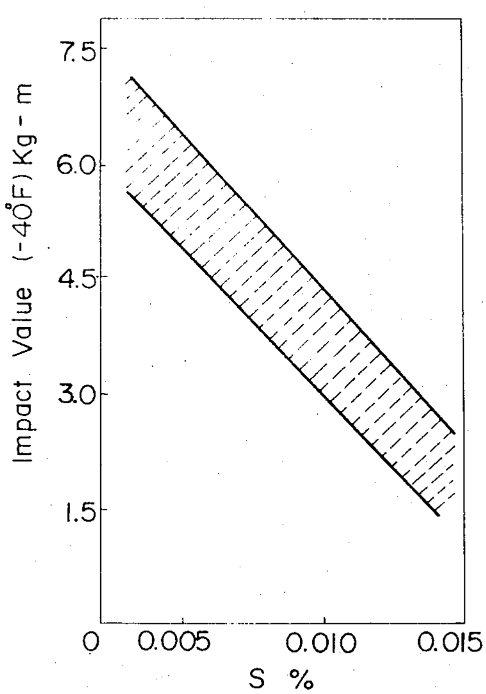
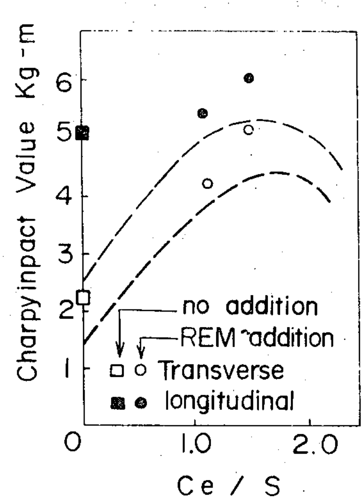


FIG. 4



METHOD OF ADDING RARE EARTH METALS OR THEIR ALLOYS INTO LIQUID STEEL

BACKGROUND OF THE INVENTION

This invention relates to a novel method of desulphurization to prevent center segregation of sulphur in casting of steel and more particularly to a method of adding continuously or otherwise rare earth metals or their alloys as desuphurization agents into liquid steel.

It is well known in the art that one effective means of improving mechanical properties of steel, particularly, impact strength, is to lower the sulphur content of steel. Various proposals for lower sulphur content in steel have been made and practiced besides desuphurization during steel refining, such as:

1. Adding desulphurization agent during blowing in of such gases as N_2 and Ar.
2. Stirring in molten steel in a rotary kiln type vessel, with desulphurization agent.
3. Utilizing pumping action caused by rotating means in a hot metal ladle.
4. To revolve slag into eddy current caused by the rotating means.
5. To give an eccentric motion to the vessel to cause hot metal swing movement and react same with desulphurization agent.
6. To utilize degassing facilities for desulphurization purposes.

As desulphurization agents in these processes, calcium, carbide, soda ash, lime, metallic magnesium, etc. are used, either singly or in combination of two or more. However, various experiments performed by the inventors hereof revealed that low sulphur steel obtained through the above mentioned prior processes were defective in precipitation and shape of the sulfide. As is clearly understood from FIG. **1**, explained hereinbelow in more detail, so long as S remains in the molten steel as a solute, its concentration gradually heightens as its solidification proceeds and precipitates in the form of MnS among dendrites and becomes concentrated segregation in the remaining molten steel. As is known in the art, the concentration of solute elements is obtained from the following formula: $C = CoK_E(1-g)^{K_E-1}$, wherein C= concentration at the solidification rate g; Co = concentration at an early stage; K_E = effective distribution coefficient and g = solidification ratio (0-1).

It is axiomatic and well known that this phenomenon is unavoidable from the fact that solubility of S in solidified stee is extremely small. Because of this extremely low sulfur content, even if S concentration on the whole is quite low, segregation of sulfide concentrated correspondingly which is often seen in high sulphur steel still aparently exists in the center part thereof. When such a slab is rolled and made into a product, its impact property, especially in the transverse direction, is unavoidably inferior. The MnS takes a comparatively round shape or of an eutectic crystal shape at the time of casting, but it is easily subjected to plastic formation during rolling. Thus, the resulting product is elongated excessively in the rolling direction. Such phenomenon, as shown in FIG. **2**, as explained further hereinbelow, cannot be eliminated simply by lowering the S content in steel.

For improvement of impact strength of steel, it is necessary to take the following points into consideration, besides merely lowering S content in steel. First, S in the molten steel should not be precipitated as MnS at the time of solidification. That is to say, S content in some way should be fixed prior to its precipitation as MnS. If this can be done, then its concentration will not occur and prevention of segregation at the final stage of solidification will be facilitated.

Second, it is desirable to change sulfide into something which will not be easily subjected to plastic deformation in the subsequent rolling step. This will enable prevention of elongation of MnS and improvement of mechanical properties, particularly impact strength. If the various problems mentioned above were to be resolved, then it will not be necessary to provide separate desulphurization process, but in fact, could be conducted during ordinary casting operation. This will contribute to improvement of productivity, lowering of manufacturing costs, and obtain an improved product.

However, as is known to workers in the art, all prior efforts to solve the above mentioned problems during the casting of liquid steel have been accompanied by extreme difficulties and have been quite unsatisfactory. Those solutions heretofore proposed have not been effective nor suitable.

SUMMARY OF THE INVENTION

This invention overcomes the aforementioned defects and problems, and advantageously enables increased productivity, lowering of manufacturing costs and production of an improved product. As explained hereinabove in the context of the prior art, the present invention enables desulphurization during ordinary casting and hence eliminates the prior art separate process of desulphurization.

Briefly, the invention encompasses addition of rare earth metals or their alloys or mixtures thereof substantially into liquid steel at a location between a ladle and a mold. The process is useful for continuous casting or other types of casting. An object of the invention is to provide a desulphurization method in which it is possible to fix S of solute in steel prior to precipitation of ordinary MnS, and thus to prevent S center segregation. Another object is to provide a desulphurization method which improves the impact properties in the transverse direction of a rolled steel.

Other objects, features and advantages of the invention will become more apparent from the following description and accompanying drawing.

BRIEF DESCRIPTION OF DRAWING

FIG. **1** is a graph depicting the manner of concentration of solute element S;

FIG. **2** is a graph depicting the relationship between S content in steel and its impact value;

FIG. **3** depicts a diagrammatic view of an illustrative embodiment of the invention; and

FIG. **4** is a graph depicting changes of Charpy impact value compared to Ce/S ratio.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The desulphurizing agent in the present invention desulphurizes and also plays an important part of fixing S content in steel before the S content is precipitated as MnS. The term "rare earth metal" is well known in the art. Any rare earth metal and/or their alloys or mixtures thereof may be used in this invention. Examples thereof may be Lanthanum (La), Cerium (Ce), Presodimium (Pr), Neodymium (Nd) and others. Alloys of rare earth metals are often called misch metals.

Rare earth metals, as is known, have an extremely strong affinity for oxygen, and hence, require extraordinary care for their use. The degree any type of care required for heir use is different from those required for ordinary and conventionally known desulphurizing agents such as calcium. For example, it is possible to fill an iron pipe with the rare earth metal and fix the pipe within a casting mold, which may gradually be dissolved by bottom blowing in the ordinary ingot making process. However, this is practically not feasible because of the strong affinity of rare earth metals with oxygen. Accordingly, optimum conditions for the location where the rare earth metal is added, the shape or form thereof, the rate of addition and amount thereof should be provided for as discussed hereinbelow.

The rare earth metals, their alloys or mixtures thereof, may be added into liquid steel in a vessel which is disposed betweeen a ladle and a mold. Ordinarily, the liquid steel is poured directly from the ladle into the mold. We have discovered that an intermediate vessel should be provided between the ladle and mold for addition of the rare earth metal to the liquid steel, in order to obtain highest yield of additives, to employ the purest steel available and to easily control additive amounts. If, for instance, the rare earth metals were to be added to the ladle, they would unavoidably react with the slag in the ladle either before or after pouring. The yield would then be unavoidably lowered due to oxidation. Undesirable reaction of the rare earth metals with refractories in the ladle also occur since the casting takes considerably long periods of time, regardless of whether ordinary or continuous casting is used. Thus, there is no merit in adding the rare earth metals to the ladle. When addition of the rare earth metals to the casting mold was studied, an excessively undesirable influence to the steel was confirmed to exist. This is because, it is thought, of the usual presence of a covering agent on the bath surface which will react with the added rare earth metal, which in turn deteriorates the purity of the surface layer of the cast pieces. Even if oxidation of rare earth metals was to be prevented, sulfide with rare earth metal tends to gather toward the surface layer, and since such sulfides have a larger density (e.g. 6–7 g/cm^3) compared to other non-metallic inclusions, their ability to float and separate within the casting mold is quite inferior. This inferiority causes deterioration of cleanliness of the slabs and materials. This drawback is much too great to offset the utility of raising yield of addition. There is no reason to recommend such an addition to the casting mold.

Addition of rare earth metals (it is to be understood that use of such term herein means also their alloys and mixtures thereof) in accordance with the present invention may be made to the intermediate vessel. Generally, concentration of C, P, and S in the final stage of solidification is seen due to the behaviour of solute elements. Concentrated segregation of S having small distribution coefficient appears in the center part and causes deterioration of the material as mentioned above. Thus, it is desirable to provide certain conditions for optimal results, including the use of the intermediately located vessel.

Liquid steel to be poured to the vessel to which the the rare earth metal is added, should be substantially

completely deoxidized for preferred effects. If there is any free oxygen remaining in the steel, for example

$$Ce + O \rightarrow CeO_2 \text{ or } Ce_2O_3;\ La + O \rightarrow La_2O_3,$$

added rare earth metal will tend to be wasted and lower the yield of desulphurization agent. For the same reason, rare earth metals to be added should be substantially completely sealed until they enter into the liquid molten steel. As will be described later, this can be easily done, for example, by such means as an immersion type nozzle using inert gasses. Rare earth metal to be added in this manner may preferably be in the form of a wire. Particle, granular or mass forms may be employed with desired effects.

The rare earth metal may be fed deeply into the liquid steel in the intermediate vessel under suitable conditions of shape, size and initial speed of addition. If the rare earth is in powder form, it has been found that such is difficult to feed deeply into the liquid steel. Experiments performed by the inventors showed that the diameter of the metal particles, or other forms, should preferably be at least **2** mm or more in order to physically feed same into liquid steel with a suitable desired speed. A diameter of at least **2** mm or more is thus preferred as a minimum size. Any size above this may also be used. The size may be selected dependent upon the amount to be added continuously corresponding to the casting speed. Such size, amount and speed can be readily calculated by the worker by observing such factors as rate of full utilization and entry into the liquid. A significant factor is the amount which is continuously added. The amount depends upon the s content in the liquid steel to a large degree. However, a different type of care is required in continuous casting operation where one charge of molten metal is continuously case and drawn as a slab or predetermined dimensions. The most suitable addition speed and hence amount corresponds to the casting speed in order to provide sufficient rare earth metals for reaction with the S content. If the amount to be added continuously was not suitable for the casting speed, then various defects, such as above mentioned become unavoidable. Such an amount may be determined as just mentioned from the casting speed of the liquid steel which corresponds to the drawing speed of slab in known continuous casting processes. The invention is not to be construed to be limited to speed, amount of addition, although such factors as size and speed are specific features of the invention. The use of rare earth metals has heretofore not been known in the process of this application.

FIG. **3** shows one illustrative embodiment by which the invention process may be practiced. One feature of the invention lies in arrangement of an intermediate vessel **2** between ladle **1** and mold **3.** First, tapped liquid steel from refining furnace (not shown) is substantially completely deoxidized by Al, Si and Mn in ladle **1.** It is recommended that an inert gas such as N_2, Ar and the like be blown through a nozzle (not shown) made of porous bricks or the like provided at the bottom part of ladle **1** for making clean molten steel and producing uniform temperature of the steel. The liquid steel is then poured into an intermediate vessel, such as a tundish **2.** A teeming stream is prevent from air-oxizing by an enclosing device **4.** Covering **12** on the bath surface is used to prevent oxidation of the liquid steel and to keep the temperature high. Immersion type nozzle **13** is used for casting purposes. A covering agent

14 is also used on the bath surface of casting mold 3. Thus, the liquid steel which is substantially completely deoxidized, made clean and of uniform temperature, does not come into contact with the atmosphere again. In this manner, addition of rare earth metal brings about highest effects. The rare earth metals are also substantially prevent from coming into contact with the atmosphere.

The rare earth metal or alloy thereof may be fed deeply into the liquid steel by an arrangement such as shown in FIG. 3. This arrangement comprises a hood 9, a feed ring 10 for inert gas feed, refractory pipe 11 immersed deeply into the liquid steel in vessel 2. There is no substantial possibility of the added rare earth metal becoming oxidized by the air. When the metal is in the form of a wire, a suitable arrangement such a shown in FIG. 3 may be used. The arrangement may comprise a wire feeder 5, a reel 6 for the wire 7 which is shown being uncoiled and guide pipe 8 for the wire. The arrangement for adding the rare earth metal to the liquid steel may be similarly constructed for metals having the form of particles, granules, or massive. The liquid steel is thus desulpherized efficiently without being subjected to air pollution and may hence be continuously finished as a product. It will be readily understood from the above that there are no factors present which would reduce the productivity.

The above combination, i.e. a ladle, an intermediate vessel and a mold, may be most efficiently and effectively put into practice for known continuous casting processes. In such case, the intermediate vessel may be a tundish of the process.

The following specific example of the present invention, which is applied to continuous casting process, is set forth for illustrative and not limiting purposes.

Manufacturing conditions:
- Steel making furnace used: 100t LD converter.
- Deoxidation agent: Al, Si, Mn
- Composition of liquid steel (taken from teeming stream)

0.12% C	0.22% Si	0.69% Mn
0.024% P	0.012% S	0.038% Sol.Al

  remainder iron and unavoidable elements.
- Treatment in the ladle: Making clean liquid metal and uniform temperature achieved by N_2 gas blown through porous bricks provided at bottom of ladle.
- Desulphurization process:
  - Processing Apparatus: as shown in FIG. 3.
  - Rare earth metals used: misch metal of Ce 45%, La 30%, Nd 15% and others.
  - Conditions for addition: wire of 4 mm diameter is continuously added to the tundish at speed of 0.10 m/sec at the rate of 0.03% per ton of liquid steel.
  - Casting speed: Continuous casting at rate of 1.24 t/min.
- Casting effects:
  - desulphurizing effect: The 0.012% S content is lowered to 0.008%. No segration in steel.
  - Impact value: FIG. 4 shows the values as compared to that which has not been subjected to desulphurization with rare earth metals.

From an analysis of the above factory scale experiment, it was found that there was disappearance of S segregation which was seen in the center part of the slab (such as by sulphur print, not shown in the drawing) and that desulphurization had been performed in an excellent manner. This further revealed that addition of misch metals, and rare earth metals, fixes C content in steel as sulfide of the added rare earth metals and leaves no room for precipitation as MnS. Accordingly, there is no concentration in the solidification stage, nor is there segregation. Such a situation, as shown more clearly in FIG. 4, brings about improved impact properties.

FIG. 4 is a graph showing the results of the above factory scale experiment in which the Ce/S ratio was varied, and the resulting impact values. Specifically, the results of ⅔ V notch Charpy test at 0°C and performed on a 9 mm thickness of plate are shown. According to this graph, there appears to be no significant difference in the rolling direction caused by addition of said rare earth metal, but surprisingly, the impact value in the transverse direction is remarkably improved, in contrast to prior art steels, to an extent that Ce/S is at its maximum value of about 1.5 (1.2 to 2.0). Such remarkable improvement is caused, it is thought, by no other reason than the S content in the steel being fixed as sulfide with CeS, LaS or as compound sulfide thereof or as oxysulfide. Thus, there is no substantial elongation in the longitudinal direction at the rolling stage, as would be the case for prior art steels in which MnS is present. Hence, control of the shape was successfully achieved. Sulfides of rare earth metals exceeded our expectations in eliminating substantially completely all of the drawbacks caused by the sulfides of the conventional art, such as MnS.

In the above mentioned experiment, a wire of about 4 mm in diameter in an amount of about 0.03% per ton of liquid steel was added continuously at the speed of 0.10 m/sec. as against a casting speed of 1.24 t/min. This is one illustration of a continuous adding speed corresponding to the casting speed as discussed before. Numerous variations of S content in the ladle, diameter of wire and adding speed employed corresponding to one casting speed are foreseeable and the present invention is intended to cover all such variations.

According to another experiment by the inventors, it was confirmed that a wire, such as above mentioned may be preferably effectively fed deeply into the liquid steel when the adding speed was 0.05 m/sec as above. Thus, the rare earth metals or misch metals or any combination thereof may preferably be used in the present invention in the following ranges when used in the form of a wire: diameter: 2mm or above; adding speed: 0.05 m/sec. or above.

The inventors then performed an ultrasonic flaw detection test for cleanliness of the resulting steel and confirmed that there was no difference in the defective echos in the steel to which addition of rare earth metals had been made and in the steel to which no addition had been made. This confirmed that there was no deterioration of cleanliness of steel caused by the addition of rare earth metals or misch metals.

The present inventive process is also very effective in other casting processes. For example, the known bottom pouring process is one of the embodiments wherein the mold of the combination of ladle, intermediate vessel and mold may be replaced with a teeming pipe.

The foregoing description is intended to be illustrative of the principles of the invention. Numerous variations and modifications thereof would be apparent to the worker skilled in the art. All such variations and modifications are to be considered to be within the spirit and scope of the invention.

What is claimed is:

1. In a continuous casting process using a succession of separate ladle, tundish and mold, the steps comprising

substantially completely deoxidizing molten steel in said ladle by addition of aluminum, silicon, manganese or any combination thereof;

thereafter pouring said molten steel into said separate tundish having means for preventing oxidation of said steel therein;

adding a rare earth metal selected from the group consisting of La, Ce, Pr and Nd, any alloy thereof or any combination thereof, in the ratio of rare earth metal to sulfur of between 1.2 and 2.0 and in the form of a wire of a diameter of at least 2.0 to 4.0 mm, deeply into said substantially completely deoxidized steel contained in said tundish, without being exposed to oxidation, said adding being at the rate of at least 0.05 m/sec; and

thereafter passing said molten steel to said separate mold having means for preventing oxidation thereof, thereby to produce a steel having improved impact strength.

2. Process of claim 1, wherein said wire is added at the rate of 0.03% per ton of said molten steel and at the speed of addition of 0.10 m/sec with the rate of casting being at about 1.24 t/min.

3. Process of claim 1, wherein cerium is used and the cerium/sulfur ratio is 1.5.

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