



US 20080314199A1

(19) **United States**
(12) **Patent Application Publication**
Niemi et al.

(10) **Pub. No.: US 2008/0314199 A1**
(43) **Pub. Date: Dec. 25, 2008**

(54) **ENHANCED ALLOY RECOVERY IN MOLTEN STEEL BATHS UTILIZING CORED WIRES DOPED WITH DEOXIDANTS**

Publication Classification

(76) Inventors: **Leslie Wade Niemi**, Davenport, IA (US); **Gregory P. Marzec**, East Amherst, NY (US)

(51) **Int. Cl.**
C22C 29/04 (2006.01)
C22C 38/12 (2006.01)
C22C 38/14 (2006.01)
C22C 7/00 (2006.01)

Correspondence Address:
HODGSON RUSS LLP
THE GUARANTY BUILDING
140 PEARL STREET, SUITE 100
BUFFALO, NY 14202-4040 (US)

(52) **U.S. Cl. 75/238; 75/228; 75/246; 75/230; 75/526**

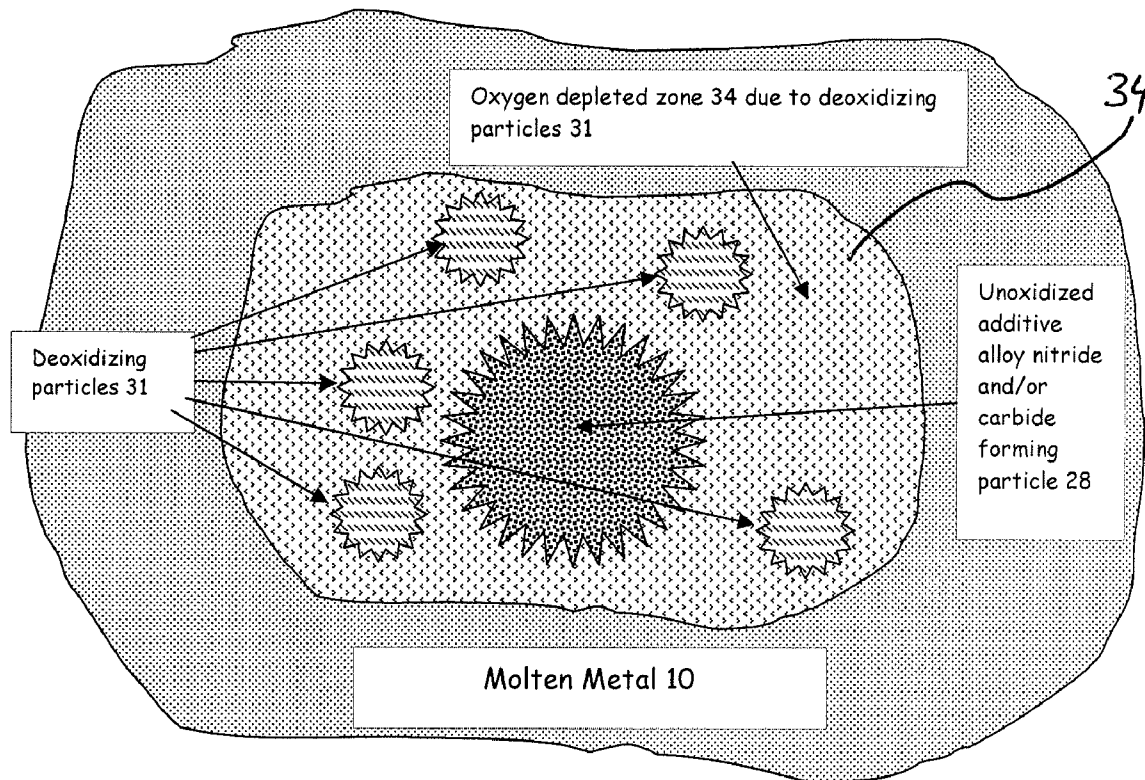
(21) Appl. No.: **12/122,889**
(22) Filed: **May 19, 2008**

Related U.S. Application Data

(60) Provisional application No. 60/938,671, filed on May 17, 2007.

(57) **ABSTRACT**

The present invention provides increased recovery in additive-enhanced or alloy-enhanced molten steel. This is accomplished by deoxidizing powders blended with the additive alloys. The deoxidizing powder reacts with the oxygen, thereby depleting the oxygen in this region. The alloy or additive region is enriched, thereby improving the recovery in the molten steel.



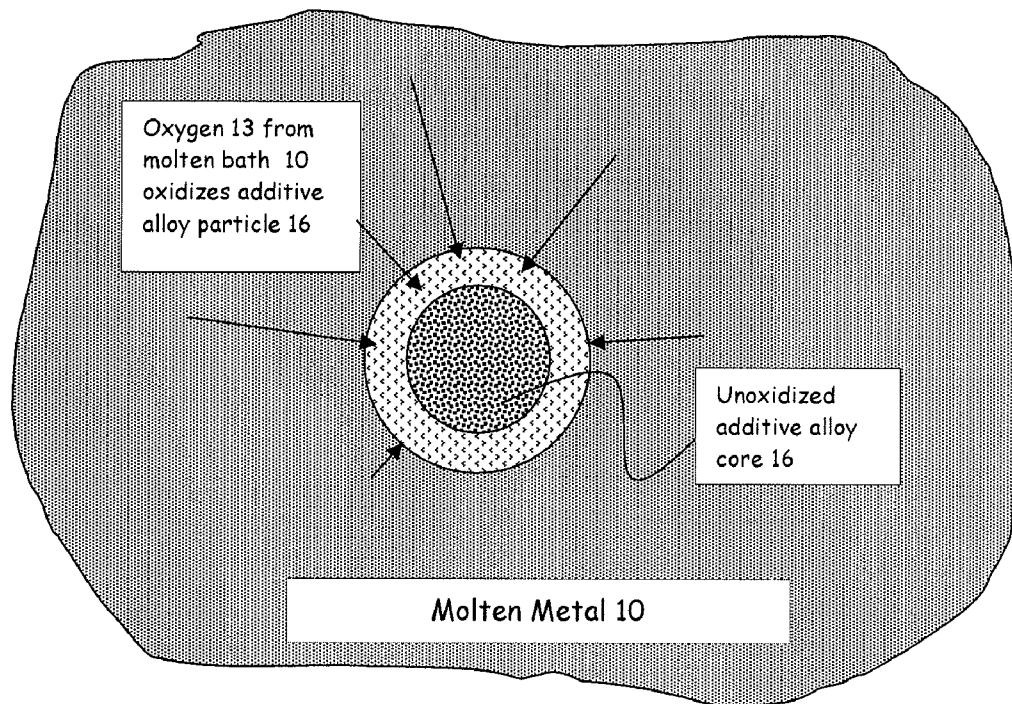


Fig. 1 - Prior Art

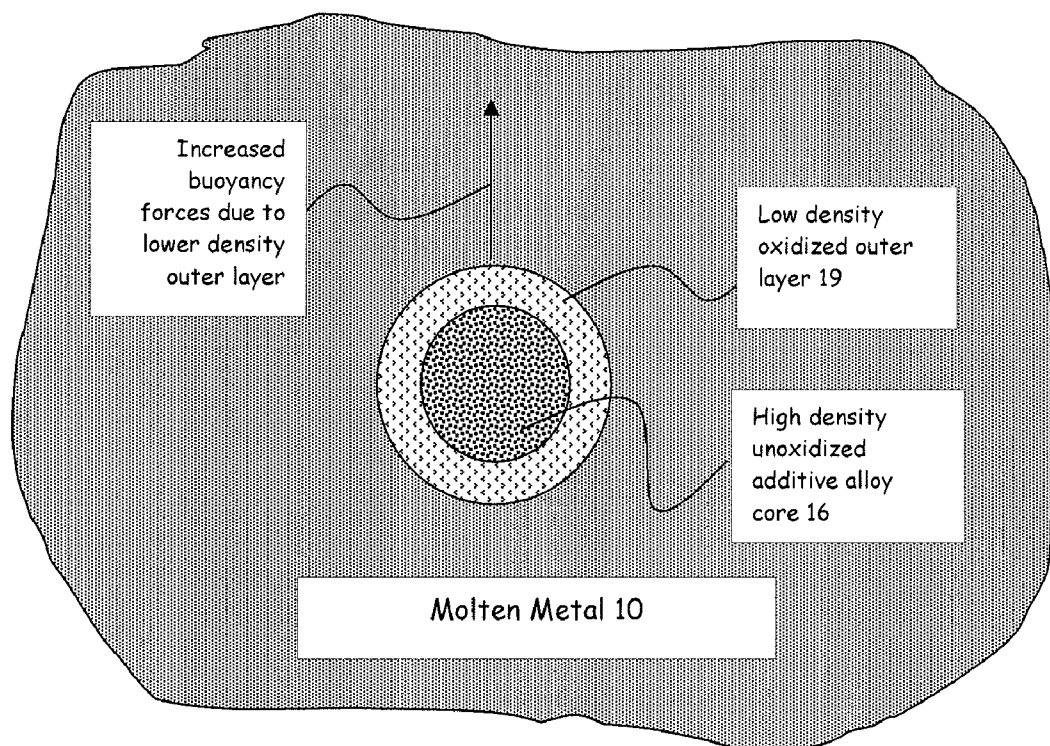


Fig. 2 - Prior Art

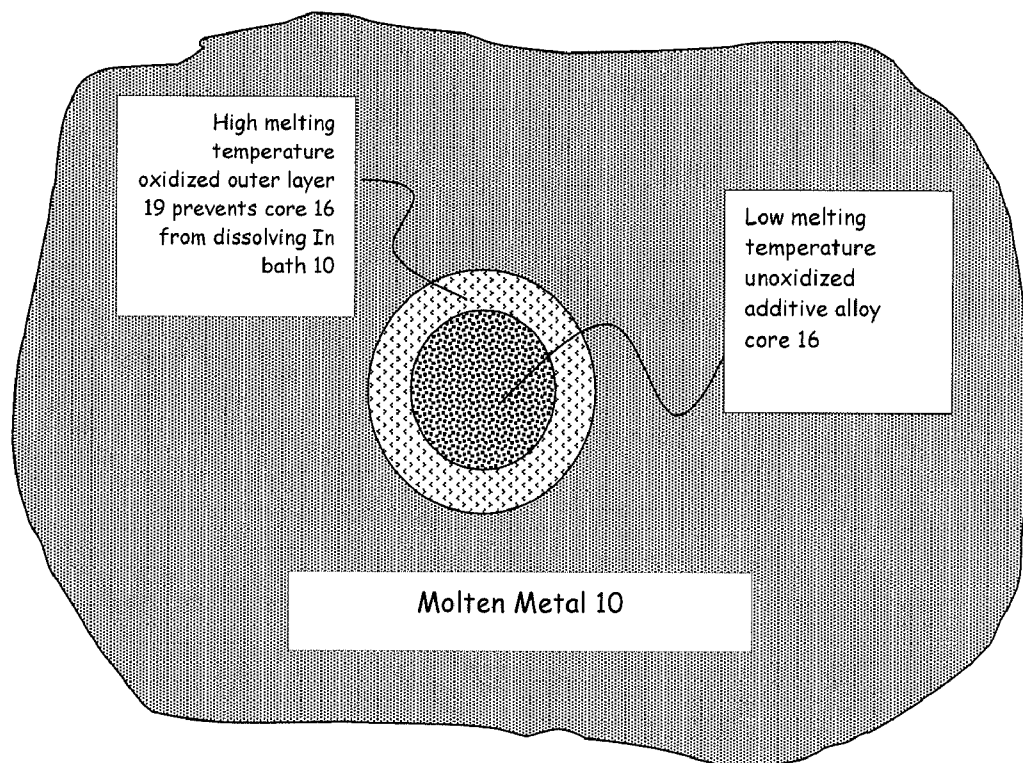


Fig. 3 - Prior Art

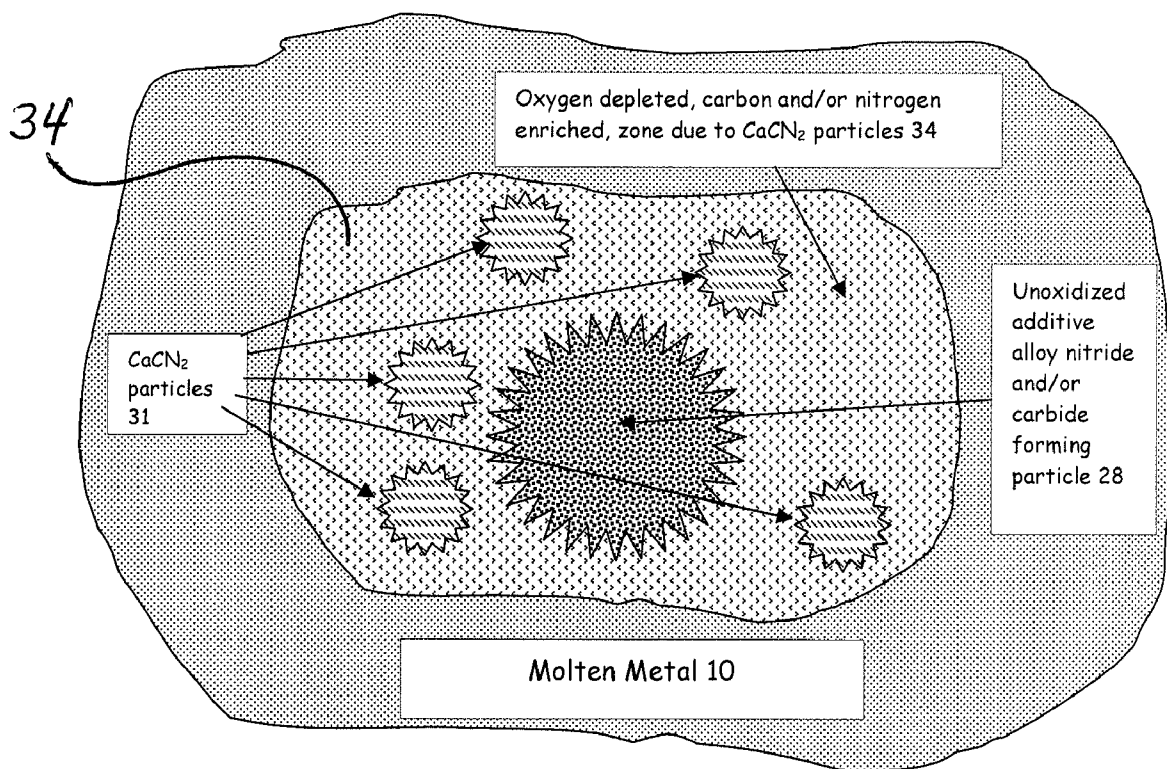


Fig. 4

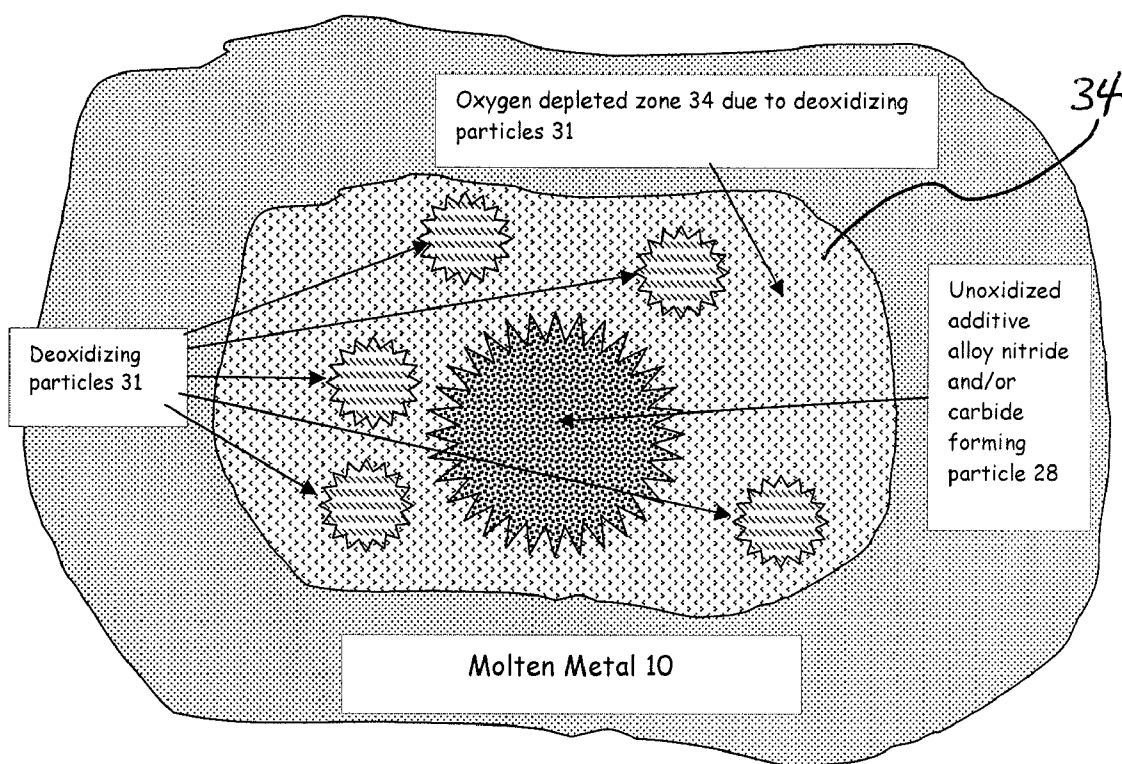


Fig. 5

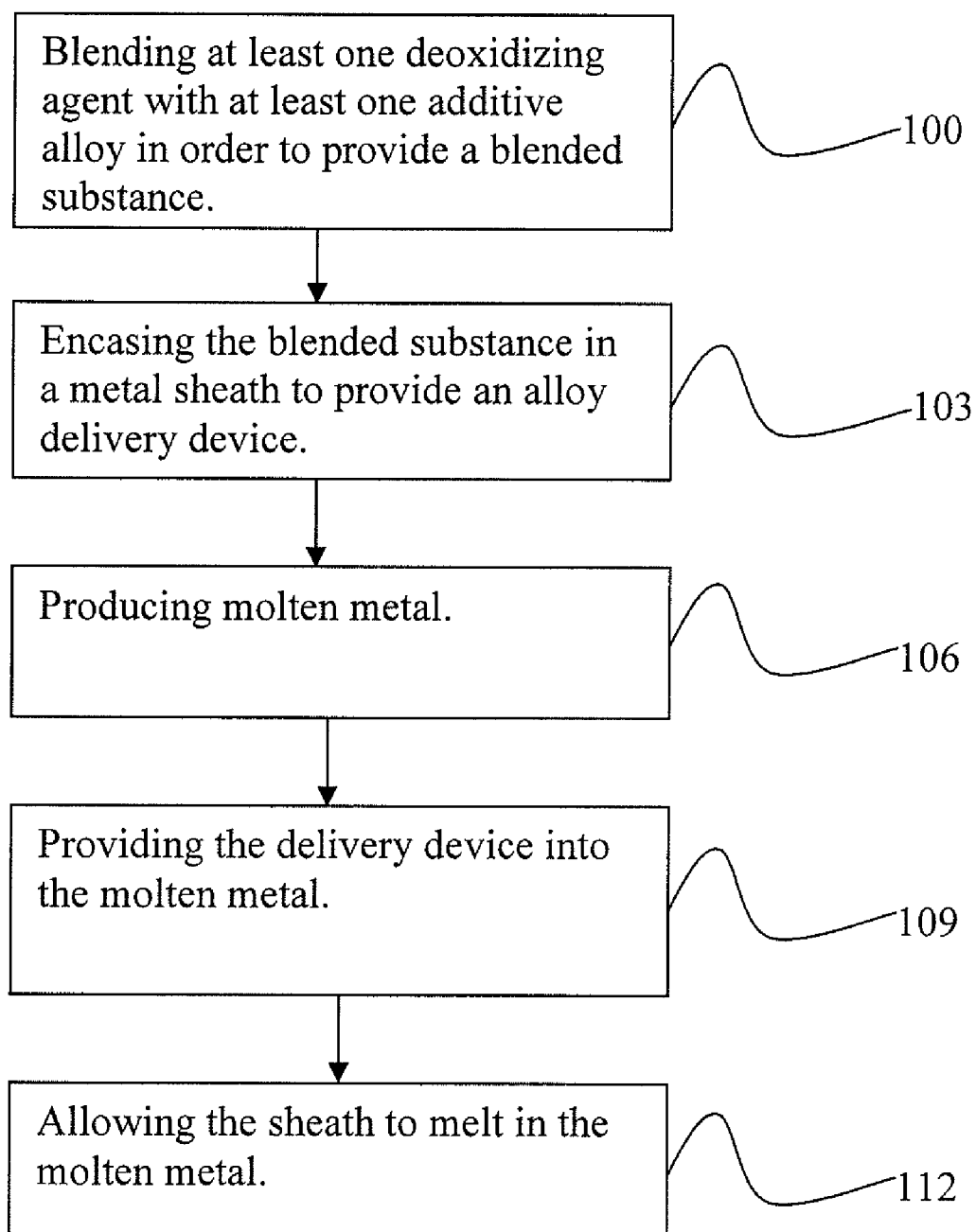


Fig. 6

**ENHANCED ALLOY RECOVERY IN MOLTEN
STEEL BATHS UTILIZING CORED WIRES
DOPED WITH DEOXIDANTS**

**CROSS-REFERENCE TO RELATED
APPLICATION**

[0001] This application claims priority to U.S. provisional application No. 60/938,671, filed on May 17, 2007, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to adding alloys to molten metal and steel in particular. More particularly, this invention relates to adding alloys and deoxidants to molten steel in order to increase recovery in the metal.

BACKGROUND OF THE INVENTION

[0003] It is well known to add alloys and other additives to molten steel in order to improve the material properties, including strength and toughness, of the final steel product.

[0004] In the prior art, adding alloys and additives to molten steel is often accomplished by encasing powdered alloys and additives in a metal sheath to form a "cored wire" which is subsequently "injected" into the molten steel contained in a ladle at the steel refining facility of most steel mills. U.S. Pat. No. 4,128,414 describes such an injection process. Some of the material injected into the steel does not stay in the steel. In order to efficiently produce additive-enhanced or alloy-enhanced molten steel, it is desirable to increase the "recovery" in molten steel.

[0005] "Recovery" is a measure of the amount of alloys and additives contained in the molten steel after injection. Recovery is expressed as the percent of alloy or additive injected in the steel that is contained in the steel after injection. The greater the percentage contained in the steel after injection, the greater the recovery will be. Greater recoveries mean lower cost to the steel maker because less cored wire is injected. Also, greater recovery usually means the final steel chemistry will be more predictable and repeatable.

[0006] It has been well known that additive alloys (typically ground to powders under one millimeter in diameter) encased in a steel jacketed cored wire that is injected deep into molten baths results in a significant improvement in recovery. But it is also well known that the recovery of certain additive alloys is negatively affected by the oxygen contents of both the molten bath and the molten slag on top of the molten bath. Reducing the oxygen content of the molten bath and slag is possible; however, at no time can it be brought to zero. Most generally, there is always an amount of oxygen remaining in the molten metal and the slag that negatively affects the additive alloy recovery. The greater the oxygen level, the more negative the effect.

[0007] It is believed that oxygen **13** in the molten metal **10** causes the surface of the additive alloy **16** to become oxidized before the additive alloy powder particle **16** can become dissolved in the molten metal **10**. This is depicted in FIG. 1. In this case, the oxidized layer **19** covers the additive alloy powder particle **16** and thereby reduces the overall density of the particle **16**, making it more buoyant than the steel **10**. For example, Nb has a density of 8.57 gm/m³ and the density of Nb₂O₅ is 4.47 gm/m³, but the density of steel is 7.6 gm/m³. FIG. 2 depicts an oxidized alloy having a lower density rising toward the surface of the molten steel **10**. In other cases, the

oxide layer **19** becomes a barrier to the molten additive alloy core **16**. For example, 70% FeTi has a melting temperature of 1085 C, whereas, TiO₂ has a melting temperature of 1850 C, but the molten steel **10** temperature is usually about 1600 C. This problem is illustrated in FIG. 3. These mechanisms have the affect of not allowing the additive alloy particle **16** to be fully dissolved in the metal molten **10** before the particle **16** rises to the slag surface where it is absorbed.

[0008] In other known methods, the purpose of the additive alloy **16** being injected into the molten bath **10** is to form nitrides and/or carbides beneficial to the final product. For years steel producers have used Calcium Cyanamid (CaCN₂) for the purpose of increasing the nitrogen content in their molten bath **10**. See, for example, U.S. Pat. No. 3,322,530. Further, the recovery of nitrogen is found to be greatly improved when the CaCN₂ is added to the molten bath **10** using cored wire injection as described in U.S. Pat. No. 4,897,114.

[0009] Despite the improvements in the prior art, there remains a need to improve upon the recovery in the molten metals, and steel in particular.

SUMMARY OF THE INVENTION

[0010] The present invention may be embodied as an alloy delivery device. The delivery device may include a blended substance having at least one additive alloy and at least one deoxidizing agent. The blended substance may be covered by an elongated sheath. The sheath may be a substantially hollow wire in which the blended substance resides.

[0011] The at least one additive alloy may be FeNb, FeV, or FeTi. The at least one deoxidizing agent may be Ca, CaSi, Si, Al, or CaCN₂. The deoxidizing agent may be a powder typically comprised of particles having a diameter of less than one millimeter. The additive alloy may be ground powder particles typically having a diameter of less than one millimeter. The deoxidizing agent may be present in an amount of typically 5% to 50% of the mixture by weight or volume.

[0012] The present invention may be embodied as a method for providing an additive alloy to molten metal, wherein at least one deoxidizing agent is blended with at least one additive alloy to provide a blended substance. The blended substance may be encased in a metal sheath to provide an alloy delivery device. Molten metal may be produced and the alloy delivery device may be provided into the molten metal. The delivery device may be fed into the molten metal and the sheath may be allowed to melt in the molten metal. Once melted, the blended substance is allowed to mix with the molten metal and thereby results in dispersing the blended substance into the molten metal.

[0013] In one embodiment of the present invention, the recovery of the alloying additive in the molten steel is enhanced by blending deoxidizing powders with the additive alloys, such as, but not limited to, Ca, CaSi, Si, Al, CaCN₂, etc., in varying amounts (typically, but not limited to, 5% to 50% of the mixture by weight or volume). Without intending to be bounded by theory, it is believed that when blended with additive alloying agents and contained within a cored wire that is injected into the molten bath, the deoxidizing powders are released in close proximity to the additive alloy powders. The deoxidizing powders react with the dissolved oxygen content of the molten metal creating an oxygen depleted zone in the same area as the additive alloy particles. Likewise, in the case of blending CaCN₂ powders with nitride and/or carbide forming additive alloys in cored wires, the zone where the

powders are released in the molten bath is both depleted in oxygen and enriched with carbon and nitrogen. Thus, the present invention provides an additive-enhanced or alloy-enhanced molten steel with improved recovery.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] For a fuller understanding of the nature and objects of the invention, reference should be made to the accompanying drawings and the subsequent description. Briefly, the drawings are:

[0015] FIG. 1 depicts a prior art method, wherein an oxygen enriched molten bath reacts with an additive alloy, thereby forming an oxide layer over an additive alloy core.

[0016] FIG. 2 demonstrates that, in the prior art methods an oxide layer will reduce the density, thus increasing the buoyancy of the additive alloy in the molten steel bath.

[0017] FIG. 3 depicts a high melting temperature oxide layer that acts as a barrier to dissolution of the low melting temperature additive alloy core.

[0018] FIG. 4 depicts an embodiment of the present invention, wherein CaCN_2 particles reacting with oxygen in the bath cause an oxygen-depleted zone. At the same time carbon and nitrogen are released into the molten bath, causing enrichment in the oxygen-depleted zone.

[0019] FIG. 5 depicts an embodiment of the present invention in which the deoxidizing agent does not release carbon or nitrogen into the molten bath.

[0020] FIG. 6 is a flow chart of a method according to the invention.

FURTHER DESCRIPTION OF THE INVENTION

[0021] The present invention may be used to provide increased recovery in additive-enhanced or alloy-enhanced molten steel. Without intending to be bound by theory, it is believed that the addition of deoxidizing powders **31** to additive alloy powders **28** in cored wires for the injection into molten baths causes a chemical reaction between the deoxidizing powder **31** and the oxygen atoms contained in the molten bath **10**. This reaction reduces the oxygen content in the localized zone **34** in which the additive alloy powders **28** are released. This can be seen in FIG. 4 and FIG. 5. By reducing the oxygen content of the bath in zone **34** in which the additive alloy powders **28** are released, the amount by which these additive alloy powders **28** are oxidized is greatly reduced, thereby increasing the recovery of the additive alloy **28**. By increasing the recovery of the additive alloy **28**, the amount required to be injected into the molten metal **10** is reduced, thus saving time and money for the metal producer. Further, by increasing the recovery, the final chemistry of the molten steel becomes more predictable and repeatable—both being desired process traits.

[0022] In one embodiment of the present invention, an alloy delivery device is provided. The alloy delivery device may include a blend of an additive alloy such as FeNb, FeV, or FeTi, and a deoxidizing agent of Ca, CaSi, Si, Al, or CaCN_2 . This blend may be housed in an elongated metal sheath.

[0023] Unlike the prior art, the present invention has recognized the deoxidizing and/or the carburizing and nitriding potential if CaCN_2 is combined with certain oxidizable nitride and/or carbide formers (e.g., FeNb, FeV, FeTi) and is then introduced into the molten bath by cored wire injection. FIG. 4 illustrates that when CaCN_2 particles **31** are blended with nitride and/or carbide forming additive alloys **28** in

cored wires, the CaCN_2 particles **31** established a zone **34** around the additive alloy particle **28**, wherein the oxygen content is reduced and the carbon and nitrogen contents are enriched.

[0024] In a preferred embodiment, the deoxidizing agent is in the form of a powder with particles that typically have a diameter of less than one millimeter, while the additive alloy is in the form of a ground powder with particles that typically have a diameter of less than one millimeter. In another preferred embodiment, the deoxidizing agent is present in an amount typically of 5% to 50% of the mixture by weight or volume.

[0025] FIG. 6 depicts a method according to the invention. In one such method, a deoxidizing agent of Ca, CaSi, Si, Al, or CaCN_2 is blended **100** with an additive alloy, which may be FeNb, FeV, or FeTi. The blended material may be encased **103** in a metal sheath in order to provide an alloy delivery device. Then, once a bath of molten metal, such as molten steel, is produced **106**, the alloy delivery device is provided **109** into the molten metal. The sheath is allowed **112** to melt, and the blended substance is disbursed into the molten metal. FIG. 6 depicts such a method.

[0026] It is believed that, by blending a compound that both deoxidizes and enriches the molten metal with nitrogen and carbon (e.g., CaCN_2) with oxidizable nitride and/or carbide forming powders in cored wires, the zone in which the blend is released will show oxygen depletion and enrichment of both nitrogen and carbon. The result is improved recovery of the additive alloy, as previously described, with the benefit of producing more nitrides and/or carbides in the final product. In this case, the amount of nitride and/or carbide forming additive alloys injected into the molten bath can be reduced at the same time the final product will show the enhanced benefit of increased nitrides and/or carbides. Thus, production costs can be reduced and product properties can be improved.

[0027] Although the present invention has been described with respect to one or more particular embodiments, it will be understood that other embodiments of the present invention may be made without departing from the spirit and scope of the present invention. Hence, the present invention is deemed limited only by the appended claims and the reasonable interpretation thereof.

What is claimed is:

1. An alloy delivery device, comprising:
at least one additive alloy; and
at least one deoxidizing agent, the deoxidizing agent being blended with the alloy to provide a blended substance; and
an elongated sheath around the blended substance.
2. The alloy delivery device of claim 1, wherein the at least one additive alloy is selected from the group consisting of: FeNb, FeV, and FeTi.
3. The alloy delivery device of claim 1, wherein the deoxidizing agent is selected from the group consisting of: Ca, CaSi, Si, Al, and CaCN_2 .
4. The alloy delivery device of claim 1, wherein the at least one deoxidizing agent is a powder comprised of particles having a diameter of less than one millimeter.
5. The alloy delivery device of claim 1, wherein the at least one additive alloy is comprised of ground powder particles having a diameter of less than one millimeter.
6. The alloy delivery device of claim 1, wherein the at least one deoxidizing agent is present in an amount of 5 to 50% of the mixture by weight or volume.
7. A method of providing an additive alloy to molten metal comprising:

blending at least one deoxidizing agent with at least one additive alloy to provide a blended substance;
encasing the deoxidizing agent and additive alloy blend in a metal sheath to provide an alloy delivery device;
producing molten metal;
providing the alloy delivery device into the molten metal.

8. The method of claim 7, wherein the molten metal is steel.

9. The method of claim 7, wherein the at least one deoxidizing agent is selected from the group consisting of: Ca, CaSi, Si, Al, and CaCN₂.

10. The method of claim 7, wherein the at least one additive alloy is selected from the group consisting of: FeNb, FeV, and FeTi.

11. The method of claim 7, wherein the method further comprises the step of allowing the casing to melt.

12. The method of claim 7, wherein the method further comprises the step of dispersing the blended substance.

* * * * *