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1

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METHOD OF TREATING ALLOYS

David Valentine Atterton, Solihull, England, assignor to Foundry Services Limited, Birmingham, England, a British company

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The present invention relates to the treatment of metal alloys for the purpose of improving their physical properties. More particularly, the invention relates to the production of sodium modified aluminum-silicon alloys.

In common foundry practice additions of low melting point, highly reactive metals to metal alloys are made for the general purpose of improving the physical properties of the alloys. While these additions are desirable in that they serve to modify or refine the grain structure of the alloys, the addition of the modifying elements is difficult to accomplish in most cases because the low melting point metals being added are slow to dissolve and difficulties are experienced in bringing the additives into intimate contact with the molten alloy. Because the molten alloy is often at a much higher temperature than the melting point of the additive, there is a danger that the latter will boil and become oxidized at the surface of the molten alloy before an effective amount is added to the body of the alloy. The boiling and oxidation of the additives on the surfaces of the molten alloy causes splattering, fuming and burning which is dangerous and is desirably avoided. It has been found, too, that when salts, such as halides or oxides, of the above additive metals are used to avoid the hazardous reactions occurring when the pure metal additive is used, the efficiency of addition is extremely low and a large excess of salts must be used to accomplish the desired treatment.

In the production of aluminum-silicon alloys the properties of the alloy are considerably altered and improved by the introduction of small quantities of metallic sodium. Sodium, of course, is highly reactive at the temperature of its introduction to this particular alloy. Silicon, at room temperature, is almost insoluble in aluminum and, therefore, as the unmodified aluminum-silicon alloy solidifies, silicon is precipitated either as a primary constituent or in a eutectic alloy with aluminum. The excess silicon remaining over that forming the eutectic takes the form of coarse plates and needles, and this coarse structure, which is inherently brittle, gives the unmodified alloy poor mechanical properties.

The addition of sodium, either in the form of salts or metallic sodium, has been found to increase the possible silicon content of the aluminum-silicon eutectic to about 13% and, therefore, alloys containing less than this amount of silicon will not exhibit primary silicon crystals. In addition, the aluminum-silicon eutectic is considerably refined and the silicon in excess of that amount required to form the eutectic is precipitated in a fine globular form and not as coarse needles. It is this refinement of the microstructure which enhances the mechanical properties of the alloy. As a result of the treatment of the molten aluminum-silicon alloy with sodium, the physical properties of the alloy are considerably altered and improved. Such treatment is known to those skilled in foundry practices as "modification" and leads to a considerable refinement of the microstructure of the aluminum-silicon alloy with an improvement in both tensile strength and elongation of the alloy.

2

In accordance with the usual foundry practice, sodium is generally added either as metallic sodium or in the form of certain sodium salts, especially the halides such as sodium fluoride, which salts react with the metal alloy and lead to the introduction of sodium. The use of sodium salts has the disadvantage of being inefficient and consequently large quantities of salts must be added in order to effect satisfactory modification. Use of the salts has a further disadvantage in that the salts tend to corrode the crucibles in which treatment of the molten metal is carried out. Furthermore, the application of the salts is a laborious and time consuming operation inevitably causing a delay in casting of the modified alloy.

The use of metallic sodium, on the other hand, while more efficient with respect to the addition of sodium to the alloy, has the serious disadvantage of introducing an appreciable quantity of dissolved hydrogen into the molten aluminum-silicon alloy. The hydrogen gas results from the paraffin or oil which is generally used as a protective medium for the metallic sodium. The metallic sodium is also contaminated with moisture containing products which are violently driven off at the temperature of addition to the alloy causing splattering of both the molten alloy and sodium. All of these contaminants are sources of impurities and the metallic sodium used for modification purposes is often the cause of gas porosity problems in the cast aluminum-silicon alloy. Additions of sodium in the metallic form, in addition to having the above-mentioned disadvantages of carrying contaminants which are the source of hydrogen, is more expensive because it involves the additional steps of producing and refining metallic sodium of sufficient purity to avoid as much as possible the danger of contaminating the aluminum-silicon alloy with undesirable impurities.

It is, therefore, the principal object of the present invention to provide a novel method for treating alloys with additions of low melting point additives which prevents the introduction of undesirable contaminants and which is efficient and economical to perform and can be easily and safely carried out to produce a metal alloy having improved physical properties.

A more detailed object of the present invention is to provide a method of the foregoing type for modifying an aluminum-silicon alloy with sodium without introducing hydrogen and other contaminants. A related object is to add sodium modifiers to aluminum-silicon alloys more efficiently and economically for producing an alloy having a refined microstructure and improved physical properties.

While the invention described herein is susceptible of various modifications, a certain illustrative method will be described in detail. It should be understood, however, that there is no intention to limit the invention to the specific form disclosed but, on the contrary, the intention is to cover all modifications, alternatives and equivalents falling within the spirit and scope of the invention as expressed in the appended claims.

In accordance with the present invention the desired treatment of a metal or metal alloy with a reactive metal additive is accomplished by the novel method which comprises contacting a molten bath of the alloy to be treated with a layer of fused salts, such as oxides or halides, of the metal additive, in a flux carrier and electrolyzing the salt layer or electrolyte with the molten alloy as one electrode. A second electrode, generally formed of carbon, is inserted in the molten supernatant layer of fused electrolyte and upon application of an electric current, the electrolyte salts are electrolyzed to discharge the desired metal as an ion into the molten alloy which is being treated. If the metal additive to be introduced is a cation, the molten alloy will be made the cathode. It is understood, however, that the polarity may be reversed and the molten alloy may be made the anode when the element to be introduced is contained in the anions of the electrolytic layer.

Upon application of an electric current and to the electrolyzing circuit, the fused salt in its flux carrier is electrolyzed so that the element to be introduced is discharged as a cation at the molten alloy surface and introduced into the molten alloy. In order to control the quantity of metal additive introduced into the molten alloy, the electrolyzing current, or alternatively the time for which a given current is applied, is varied. It is thus possible to control very accurately the amount of metal additive to be introduced for accomplishing a desired treatment.

In the production of aluminum-silicon alloys furnace charges of this alloy normally consist of a mixture of foundry returns and new ingot metal. The ratio of modified returns to new ingot is seldom constant over a number of consecutive melts and, therefore, the amount of sodium in any one furnace charge is difficult to estimate. The practice which is followed by the majority of light alloy founders is to destroy all existing traces of modification and then to remodify with a controlled amount of modifying agent. In this way the exact state of modification of the melt is known and can be varied at will to suit different casting sections.

Sodium modification is destroyed through degassing by the scavenging action of the degasser on the sodium contained in the melt. With aluminum-silicon alloys, therefore, degassing serves the dual purpose of removing small quantities of dissolved hydrogen which may have been absorbed during the melting of the alloy and destroying all traces of existing sodium modification.

For the purpose of adding sodium metal to the degassed aluminum-silicon alloy by the method embodying the present invention, a molten bath of the alloy is placed in a suitable container and in contact with an electrode. An electrolytic layer consisting of sodium chloride and potassium chloride carried in a flux is then floated on the molten alloy. The supernatant electrolytic layer is desirably a fused liquid and can be either prefused or fused after the salts have been placed on the molten alloy. An anode in the form of a carbon electrode is inserted into the fused electrolytic layer.

In order to introduce sodium into the molten alloy, an electrolyzing current is applied between the anode and the molten alloy as the cathode. The sodium cations are discharged at the alloy surface and are thereby introduced into the molten alloy. The anions produced by the electrolysis migrate towards the anode where they are discharged and collected, if desired, although the amount of such anions is ordinarily very small. When the desired amount of sodium has been deposited, as determined by the amount of current and the length of time the electrolyte is subject to electrolysis, the current is shut off and the container of modified alloy is tapped and the alloy cast into suitable molds.

To illustrate the above-described novel method, the following example is presented.

Example

A melt of aluminum-silicon alloy, after degassing, was analyzed and contained 0.0005% by weight of sodium. This alloy was placed in a crucible and an electrolyte containing sodium chloride, potassium chloride, and a flux was floated on its surface. A carbon electrode was then inserted into the molten metal, being insulated from the electrolyte. A carbon anode was inserted into the supernatant electrolyte and a potential of 5 volts was applied between the anode and the molten metal cathode. With this arrangement a current of approximately 45 amperes was applied for a period of about 10 minutes. After the electrolytic treatment, the alloy, now modified with sodium, showed a sodium content of 0.0293% and exhibited the physical properties characteristic of a well modified aluminum silicon alloy.

In order to illustrate the effect of sodium modification on aluminum-silicon alloys, the following table presents a comparison of average physical properties of modified and unmodified sand cast alloys:

Average mechanical properties	Unmodified alloy	Modified alloy
Ultimate tensile strength (ton/sq. in.)	7.0	11.5
Elongation (percent on 2 in.)	3.0	8.0

By using the above described electrolytic method for modifying an aluminum-silicon alloy with sodium, it can be seen that the efficiency of the addition of sodium has been substantially increased over the older methods of adding sodium, such as by reacting sodium salts with the alloy or by adding sodium metal, in which it was possible to add an amount of sodium only to the extent of about 0.020% of the weight of the alloy. The efficiency of conversion of the available sodium is thus quite high with the present invention as compared with older methods, making the herein described novel method particularly desirable for use with alloys having a high silicon content. It is to be further noted that by carrying out the sodium modification electrolytically, it is unnecessary to purify or otherwise treat the sodium metal or salt to be added. The electrolytic method is selective for sodium ions and the introduction of impurities into the alloy is thereby prevented.

A novel and improved method for the production of sodium modified aluminum-silicon alloys has been described. According to this method, a supernatant electrolyte containing sodium ions is electrolyzed with a cathode of molten aluminum-silicon alloy into which the sodium is to be introduced for purposes of modification. An efficient and economical method for such treatment is thus attained, which method eliminates the necessity of procuring and purifying a sodium metal additive and further eliminates any undesirable reactions of the additive with the molten alloy at the temperature at which the addition must be made. In addition, the novel method, by ionizing the sodium, affords a more intimate contact of the modifying element with the alloy. It thus becomes possible to modify alloys having a high silicon content to form a silicon-aluminum eutectic and cause the excess silicon to precipitate in fine globules instead of brittle needles and plates.

I claim as my invention:

1. The method of modifying an aluminum-silicon alloy with sodium which comprises the steps of forming a molten bath of aluminum-silicon alloy, adding an alkaline chloride electrolyte as a source of sodium ions, inserting an electrode into said electrolyte, and electrolyzing said electrolyte with said electrode as an anode and said molten alloy as a cathode to remove sodium ions from said electrolyte and introduce sodium ions into said alloy for modifying the same.

2. The method of claim 1 wherein an electrolyzing current of about 45 amperes is applied for a period of about ten minutes.

3. The method of claim 1 wherein the molten electrolyte comprises sodium chloride and potassium chloride.

4. The method of claim 1 wherein the electrolysis is stopped when the cathode metal acquires a sodium content of about 0.0293%.

5. The method of modifying an aluminum-silicon alloy by additions of sodium which comprises electrolyzing a molten alkaline chloride electrolyte containing sodium ions with an anode inserted in said electrolyte and with

a cathode consisting of the aluminum-silicon alloy in a molten state.

6. The method of claim 5 wherein the electrolysis is stopped when the cathode metal has acquired enough sodium to be well modified.

7. The method of claim 5 wherein the molten electrolyte comprises sodium chloride and potassium chloride.

8. The method of modifying the microstructure of an aluminum-silicon alloy with additions of sodium metal which comprises the steps of forming a molten bath of the alloy, adding a supernatant alkaline chloride electrolyte as a source of sodium ions, inserting a carbon electrode into said electrolyte and electrolyzing said electrolyte with said carbon electrode as an anode and said molten alloy as a cathode to remove sodium ions from said electrolyte and introduce said sodium ions into the alloy for modifying the same.

9. The method of claim 8 wherein the electrolyte comprises sodium chloride and potassium chloride.

References Cited in the file of this patent

UNITED STATES PATENTS

1,464,625	Pacz	Aug. 14, 1923
1,910,017	Hulin	May 23, 1933
2,013,926	Pacz	Sept. 10, 1935