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RARE EARTH MASTER ALLOYS

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1 Claim. (Cl. 75—170)

This invention relates to a new and improved method of preparing rare earth master alloys and to the rare earth master alloys produced thereby.

In the manufacture of steel, the introduction of rare earth metals into the molten metal, either molten iron or alloys thereof, is practiced for deoxidizing purposes or to alloy the rare earth metal with base metal, or metals, to impart desired characteristics thereto.

The rare earth metals individually and in the form of Misch metal, oxidize with great rapidity in the atmosphere and accordingly stocks of the same must be protected at considerable expense against this reaction until the metal is desired for use. If no such protection is provided heavy oxide coatings form which must be fully removed at considerable expense before the metal can be used.

Accordingly, it is an object of the present invention to provide a new method of producing rare earth metal master alloys in which the rare earth metal, or metals, will remain unoxidized and will be available as such for direct addition to a melt of another metal, or alloy without having to first remove an oxide coating.

The rare earth metals when combined with low carbon steels, or with alloys, such as stainless steel containing nickel, have the effect of improving the working properties of the same. However, in such prior art additions, a very appreciable oxidation and evaporation loss occurs during the additions of the rare earth to the melts as a result of which the desired ultimate percentage content is not always attained according to calculation due to the oxidation and evaporation losses.

Accordingly, a further object of the invention is to provide a new rare earth master alloy and method of making the same, by which oxidation losses will be materially minimized in alloying the metal to steel, making possible a considerable saving in the actual amount of rare earth metal, or metals to be used per ton of steel.

Prior to my invention rare earth metal alloys were prepared by reduction of the rare earth metal halide to the elemental metal by electrolysis in a fused salt bath and then subsequently alloying the thus obtained rare earth metal with the base metal or alloy by melting the rare earth metal and the base metal together. As a consequence of this process as heretofore practiced, there is a considerable oxidation and evaporation loss.

It is, therefore, a further object of the present invention to prepare a rare earth master alloy by direct chemical reduction of the rare earth halide in the presence of the base metal without the attendant disadvantages of the prior art.

Another object of the invention is to provide a rare earth master alloy and method of producing the same wherein the master alloy has included therein a protective agent which materially minimizes oxidation during storage and upon its addition to a molten metal bath.

More specific objects and advantages are apparent from the description, which merely discloses and illustrates and is not intended to limit the scope of the invention.

Prior methods of preparing rare earth alloys such as by the electrolysis process previously referred to result in considerable loss by oxidation. I have now discovered that this oxidation can be avoided without the use of protective atmospheres and the like by producing the rare earth metal addition in the form of a rare earth master alloy by the direct chemical reduction of a rare earth metal halide by a reducing agent which is preferably magnesium in the presence of the base metal with which it is desired to alloy the rare earth.

Generally the method comprises melting together an excess of magnesium and a base metal and then adding thereto the rare earth metal halide thereby resulting in the production of a rare earth master alloy comprised of the rare earth metal, the base metal, and a percentage of magnesium. The magnesium content of the molten bath not only serves as the reducing agent but additionally due to its presence in excess, alloys with the rare earth base metal alloy and serves as a protective agent for the rare earth metal thus protecting the same against oxidation during storage and upon its addition to a molten metal bath. Since the rare earth master alloy has been produced in situ oxidation is materially minimized. Furthermore, since the rare earth metal is intimately associated with the base metal, it is further protected from any likelihood of oxidation. The base metal is selected dependent upon the metal to which the rare earth master alloy is to be added.

For example, nickel is a metal common to most steels, in which rare earth additions are made. Since nickel is readily dissolved in molten iron, it has been found that the rare earth metals can be added to steel with a minimum of oxidation losses in the form of a rare earth-nickel master alloy. Such alloys would include lanthanum-nickel; didyminum-nickel; cerium-nickel; Misch metal-nickel, etc., and successful preparation of such alloys has been accomplished in which the rare earth content has been as much as 30%. In each of these rare earth master alloys there is included a percentage of magnesium which serves as a protective agent as previously set forth.

As specific examples of rare earth master alloys and methods of preparing the same, the following are given, it being understood, however, that these are only illustrative and are not intended to in any way limit the invention as to materials employed or proportions thereof.

EXAMPLE 1

Rare earth—nickel

500 parts by weight magnesium (in excess)
2000 parts by weight nickel
1313 parts by weight rare earth fluoride

After the magnesium was melted, the nickle was added to it until the whole became fluid to form a magnesium-nickel alloy. The rare earth fluoride was then added portionwise with stirring into the liquid magnesium-nickel alloy which was maintained at 2250–2450° F. (1233–1343° C.). The resulting rare earth alloy was poured into standard pig molds. Pig weight was 2940 parts by weight and the salt weight was 670 parts by weight. The rare earth alloy pigs were found to contain 26.5% rare earth metal, or an overall recovery of 86% based on the equivalent of rare earth metal contained in the rare earth fluoride charged.

EXAMPLE 2

Rare earth-manganese-aluminum alloy

2500 parts by weight aluminum
4000 parts by weight fused $MnCl_2$
500 parts by weight magnesium (in excess)
900 parts by weight rare earth fluoride

The 50–50 manganese-aluminum alloy was prepared by

reducing the manganese chloride in molten aluminum. The magnesium was then gradually added to the molten aluminum alloy until it was all in solution. The liquid magnesium-manganese-aluminum alloy was maintained at 2300–2500° F. (1260–1370° C.) while the rare earth fluoride was added portionwise with stirring, and the resulting rare earth alloy was poured into pig molds. The pigs weighed 3825 parts by weight and contained 11.6% rare earth metal for an overall recovery of 69%.

The present invention has been described using the rare earth fluorides as an example. It is to be understood, however, that any of the rare earth halides, namely the rare earth chlorides, bromides, or the iodides may be used. It has been found, however, that the fluorides are more satisfactory than the other halides and their use is preferred.

As previously stated different base metals can be utilized according to the present invention. Preparation of lanthanum-copper master alloys has been successfully accomplished according to the herein set forth process, containing as high as 14% lanthanum and it is found that the lanthanum content is quantatively recovered in the preparation of copper alloys containing 0.5 to 4% lanthanum.

The rare earth master alloys prepared according to the present invention may be used for addition to metals not heretofore susceptible to the alloying of rare earths therewith. Titanium possesses the highest strength to weight ratio of any common metal and has excellent corrosion resistance, but it is seriously limited in its applications by the fact that it successfully withstands temperatures only to from 800° to 1000° F., without becoming seriously oxidized. Improvement in the temperature resistance of this metal may be brought about by the alloying of rare earths therewith. This has not been done heretofore for the reason that the rare earth metals are highly volatile at the extremely high temperatures encountered in the arc melting of titanium.

By introducing the rare earth metals into the titanium in the form of a master alloy, the alloying efficiency

of the rare earth metals is improved probably for the reason that the rare earth metal is so intimately associated with or surrounded by the base metal of the master alloy and thus volatilization of the rare earth is minimized. For this purpose there has been prepared a lanthanum-aluminum-manganese master alloy; a cerium-aluminum-manganese master alloy; a Misch metal-aluminum-manganese master alloy; a Misch metal-aluminum master alloy; and an aluminum-titanium-Misch metal master alloy, according to the process of the present invention. Master alloys of other rare earth metals may be similarly prepared. In instances where the magnesium is not in excess of that required for reduction it is apparent that the magnesium will perform only as a reducing agent.

Having described the invention, I claim:

The method of preparing a master alloy suitable for subsequent alloying with other metal or metals, wherein the master alloy contains a rare earth, magnesium and nickel, which comprises melting approximately 500 parts by weight of magnesium and adding thereto approximately 2000 parts by weight of nickel, maintaining the nickel-magnesium alloy at a temperature in the range of approximately 1233° C. to 1343° C. while adding thereto approximately 1313 parts by weight of a rare earth fluoride.

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