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METHOD OF MANUFACTURING SILICON-IRON ALLOYS

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This invention relates to metallurgy and more particularly to an improved method for making silicon-iron alloys adapted for use in the manufacture of various electrical devices such as transformers, watt-meters, etc. In such devices, material of relatively low energy loss characteristics is desired, for example, in transformer cores. Heretofore in the art silicon-iron alloys containing silicon 3 to 5% have been proposed for use in these devices and various methods of rolling and heat-treatment have been proposed whereby the energy loss characteristics of the alloys are improved.

We have found, however, that the degree of purity of the silicon-iron alloy has a marked influence on the energy loss characteristics of this type of alloy, and that residual amounts of carbon, metal and metalloids oxides, dissolved and occluded gases, etc., should be eliminated from such alloys for best results and to obtain the lowest energy loss characteristics.

The present invention aims to provide a process whereby a substantially pure silicon-iron alloy may be obtained and to provide a substantially pure silicon-iron alloy having a relatively low energy loss characteristic for use in the manufacture of electrical devices. Other objects and advantages will be apparent as the invention is more fully disclosed.

The process of the present invention consists in first forming a molten iron bath substantially free from associated metal and metalloid impurities and of carbon and of dissolved and occluded gases; secondly, in adding to the said bath the desired amount of silicon or of silicon and a second desired alloying constituent each of which has similarly been freed from associated impurities; thirdly, in solidifying the resultant alloy in such manner and under such conditions as to avoid contamination of the same. The resultant solidified silicon-iron alloy thereafter may be mechanically deformed to desired size, shape and configuration for use in said electrical devices, by methods now known in the art, or preferably by the method described and claimed in a copending application hereinafter identified.

In the forming of a bath consisting of substantially pure iron, the following procedure is preferred:

Low carbon iron, previously purified by the best practices heretofore available, as for example, by the well known duplex processes, is melted in a substantially inert but slightly oxidizing atmosphere maintained at pressures less than atmospheric pressure. This melting is preferably ac-

complished in an electric induction furnace of the type described and claimed in either of the Patents Nos. 1,431,686, 1,983,242 and 2,085,450 and by methods as described and claimed in either of the Patents 1,555,313 and 1,555,314. The molten metal bath is thoroughly decarburized by introducing an oxidizing agent into or over the surface of the bath which agent does preferably not introduce into the bath any undesirable metallic or non-metallic constituent. We prefer to employ a solid oxidizing agent, such as iron oxide for this decarburizing step, in which case the molten bath containing the iron oxide in an amount in excess of that empirically necessary for the complete removal of the carbon is heated under gradually reducing pressures until no further gases can be exhausted therefrom.

The thus decarburized metal bath is then treated for the removal of dissolved and occluded or combined gases, particularly oxygen and nitrogen. The removal of oxygen and nitrogen is best accomplished by means of hydrogen which is itself of a high degree of purity. It is preferable to initially pass the gas into or over the surface of the molten metal bath in a relatively strong free flow, at atmospheric or slightly reduced pressures, and to subsequently heat the bath for a prolonged time interval at more elevated temperatures under gradually reducing pressures until the excess metal oxide has been completely removed and until the very lowest pressures have been obtained.

The residual oxygen and nitrogen may be eliminated instead of or after a treatment with hydrogen by incorporating a proportion of a metallic reducing agent preferably by a readily vaporizable one in the bath. The metallic reducing agents suitable for this purpose are metals of the alkali, alkaline earth and cerium groups, magnesium and beryllium. The most satisfactory one of these reducing agents appears to be calcium and perhaps cerium. The calcium may be used as pure metal or as calcium-silicon alloy and the cerium as "misch" metal, a mixture of metals of the cerium group.

After the addition of this reducing agent the heating of the bath is continued again under gradually reducing pressures until the excess of the metallic reducing agent has been effectively removed from the molten metal bath.

The substantially pure molten iron bath is now ready for the addition thereto of the desired amount of silicon or of the silicon and other desired alloying metal. It is preferable to employ substantially pure silicon prepared by any of the

available methods. Alternatively a ferro-silicon alloy which is substantially free from associated impurities may be employed. It is important that the silicon be substantially free from oxide and from adsorbed, dissolved or absorbed atmospheric gases, otherwise deleterious compounds of iron, silicon and oxygen, for example, will be formed in the alloy.

After the addition of the silicon to the molten iron bath, the bath should again be heated under gradually reducing pressures for a time interval adapted to thoroughly distribute the silicon throughout the bath and then should be cast and solidified under conditions calculated to prevent the absorbing therein of deleterious impurities. Preferably the alloy should be cast in vacuo.

The resulting solidified ingot of silicon-iron alloy should preferably be mechanically deformed to sheets of the thickness desired by the process disclosed and claimed in Hiemenz application Serial No. 88683, filed July 2, 1936, assigned to the same assignee as the present invention, care being taken in the heating and rolling of the same to avoid the introduction into the alloy of deleterious amounts of oxygen and carbon and other impurities, f. i., sulphur. To this end the hydrogen utilized in the heating furnaces should be substantially free from water vapor and of nitrogen and prior to such heating the surface of the metal should be cleaned to remove surface scale and carbon lubricants.

In the manufacture of silicon-iron alloys in accordance with the present invention we have been able to make material which is characterized by an energy loss measurement as low as $V_{10}=0.48$ W/kg, and frequently obtain material having energy losses ranging between 0.48 and 0.60 W/kg. The lowest energy loss measurements for the same material heretofore obtainable by prior methods approximates about 1.0 and the usual range is between 1.2 and 1.3. The maximum permeability for material with the same treatment is about 40,000-45,000.

We attribute the improvement as a result of the present invention to the removal of associated metal, and metalloid impurities from the alloy together with the substantially complete degasification of the alloy.

We have found that the addition of relatively small amounts of alloying constituents such as copper, aluminium, zirconium and titanium may have a beneficial effect on the properties of the alloy. The added copper or other alloying constituent may be added just prior to the addition of the silicon or simultaneously therewith and also must be substantially pure and free from associated metal and metalloid impurities and gases. It is undesirable to add the copper after the silicon has been added for the reason that from the time the silicon is added to the bath until the alloy is solidified the greatest care must be exercised to prevent oxygen from having access to the molten bath, and during the addition of the silicon the silicon and the bath must be carefully protected from oxidation.

Having broadly and specifically disclosed the present invention, it is apparent that many modifications and adaptations may be made therein and all such are contemplated as may fall within the scope of the accompanying claims.

What we claim is:

1. The method of manufacturing silicon-iron alloys which comprises forming a molten bath comprised of low carbon iron, heating said bath under oxidizing conditions and under conditions

of reduced pressures until the carbon is entirely removed from the bath, deoxidizing the bath with a vaporizable reducing agent, heating the bath under conditions of gradually reducing pressures and at temperatures effective to vaporize the excess of said reducing agent, adding the desired proportion of substantially pure silicon to the bath, heating the bath in an inert atmosphere to thoroughly distribute the silicon throughout the bath, and casting and solidifying the resultant alloy under conditions preventing the contamination of the said alloy.

2. The method of manufacturing silicon-iron alloys which comprises forming a molten bath comprised of low carbon iron, heating said bath under oxidizing conditions and under conditions of reduced pressures until the carbon is entirely removed from the bath, deoxidizing the bath with substantially pure hydrogen, heating the bath under conditions of gradually reducing pressures and at temperatures effective to remove the excess of said hydrogen, adding the desired proportion of substantially pure silicon to the bath, heating the bath in an inert atmosphere to thoroughly distribute the silicon throughout the bath, and casting and solidifying the resultant alloy under conditions preventing the contamination of the said alloy.

3. The method of manufacturing silicon-iron alloys which comprises forming a molten bath comprised of low carbon iron, heating said bath under oxidizing conditions and under conditions of reduced pressures until the carbon is entirely removed from the bath, deoxidizing the bath with substantially pure hydrogen, adding to the bath a proportion of a readily vaporizable metallic reducing agent, heating the bath under conditions of gradually reducing pressures and at temperatures effective to vaporize the excess of said reducing agent, adding the desired proportion of substantially pure silicon to the bath, heating the bath in an inert atmosphere to thoroughly distribute the silicon throughout the bath, and casting and solidifying the resultant alloy under conditions preventing the contamination of the said alloy.

4. The method of manufacturing silicon-iron alloys which comprises forming a molten bath comprised of low carbon iron, heating said bath under oxidizing conditions and under conditions of reduced pressures until the carbon is entirely removed from the bath, deoxidizing the bath by adding to the bath a proportion of a readily vaporizable metallic reducing agent, heating the bath under conditions of gradually reducing pressures and at temperatures effective to vaporize the excess of said reducing agent, adding the desired proportion of substantially pure silicon to the bath, heating the bath in an inert atmosphere to thoroughly distribute the silicon throughout the bath, and casting and solidifying the resultant alloy under conditions preventing the contamination of the said alloy.

5. The method of manufacturing silicon-iron alloys which comprises forming a molten bath comprised of low carbon iron substantially free from associated metal and metalloid impurities, adding thereto a proportion of iron oxide substantially in excess of that empirically necessary to combine with the carbon content of the bath enclosing the surface of the bath from the atmosphere, heating the bath under gradually reducing pressures to effectively bring about the removal of the carbon as carbon oxides by reaction with said oxide, introducing an atmosphere of

substantially pure hydrogen over the surface of the bath, continuing the heating of the bath under gradually reducing pressures while maintaining a circulation of said hydrogen over the bath until the excess iron oxide is substantially reduced to a residual percentage, adding the desired proportion of substantially pure silicon to the bath and again heating under gradually reducing pressures of an inert and non-reactive gas until the silicon is thoroughly distributed throughout the bath, and then casting and solidifying the resultant alloy under conditions inhibiting contamination of the said alloy.

6. The method of manufacturing silicon-iron alloys which comprises forming a molten bath comprised of low carbon iron substantially free from associated metal and metalloid impurities, adding thereto a proportion of iron oxide substantially in excess of that empirically necessary to combine with the carbon content of the bath, enclosing the surface of the bath from the atmosphere, heating the bath under gradually reducing pressures to effectively bring about the removal of the carbon as carbon oxides by reaction with said oxide, adding a proportion of a readily vaporizable metallic reducing agent to said bath, again heating said bath under gradually reducing pressures of an inert and non-reactive gas until the excess of said reducing agent is removed from the bath, adding the desired proportion of substantially pure silicon to the bath and again heating under gradually reducing pressures of an inert and non-reactive gas until the silicon is thoroughly distributed throughout the bath, and then casting and solidifying the resultant alloy under conditions inhibiting contamination of the said alloy.

7. The method of manufacturing silicon-iron alloys which comprises forming a molten bath comprised of low carbon iron substantially free from associated metal and metalloid impurities, adding thereto a proportion of iron oxide substantially in excess of that empirically necessary to combine with the carbon content of the bath, enclosing the surface of the bath from the atmosphere, heating the bath under gradually reducing pressures to effectively bring about the removal of the carbon as carbon oxides by reaction with said oxide, introducing an atmosphere of substantially pure hydrogen over the surface of the bath, continuing the heating of the bath under gradually reducing pressures while maintaining a circulation of said hydrogen over the bath

until the excess iron oxide is substantially reduced to a residual percentage, adding a proportion of a readily vaporizable metallic reducing agent to said bath, again heating said bath under gradually reducing pressures of an inert and non-reactive gas until the excess of said reducing agent is removed from the bath, adding the desired proportion of substantially pure silicon to the bath and again heating under gradually reducing pressures of an inert and non-reactive gas until the silicon is thoroughly distributed throughout the bath, and then casting and solidifying the resultant alloy under conditions inhibiting contamination of the said alloy.

8. The method of claim 1, the reducing agent comprising at least one of the metals of the alkali alkaline earth, and cerium groups, and magnesium and beryllium.

9. The method of claim 1, the reducing agent comprising at least one of the metals of the cerium group.

10. The method of claim 1, the reducing agent comprising cerium.

11. The method of claim 1, the reducing agent comprising calcium.

12. The method of claim 1, the reducing agent comprising a calcium-silicon alloy.

13. The method of claim 1, said casting and solidifying being made under reduced pressures in a substantially inert and non-reactive atmosphere.

14. The method of claim 1, adding a proportion of a desired alloy constituent other than silicon to the purified bath prior to or simultaneously with the addition of the said silicon.

15. The method of claim 1, adding copper from a small but effective amount up to about 0.8% to the purified iron bath prior to or simultaneously with the addition of the said silicon.

16. The method of claim 1, adding aluminium from a small but effective amount up to about 0.2% to the purified iron bath prior to or simultaneously with the addition of the said silicon.

17. The method of claim 1, adding zirconium from a small but effective amount up to about 0.2% to the purified iron bath prior to or simultaneously with the addition of the said silicon.

18. The method of claim 1, adding titanium from a small but effective amount up to about 0.2% to the purified iron bath prior to or simultaneously with the addition of the said silicon.

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