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STEEL-LIKE ALLOY CONTAINING SPHEROIDAL GRAPHITE

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The present invention relates to graphitic ferrous alloys having carbon contents within the steel range, and, more particularly, to a graphitic steel-like alloy having a unique combination of properties and/or a special microstructure containing graphite or uncombined carbon in a spheroidal form, and to a process for producing the same.

It is an object of the invention to provide a steel-like alloy having high properties and containing spheroidal graphite in the as-cast condition.

Another object of the invention is to provide a novel graphitic steel-like alloy having a unique combination of properties including high strength, high wear resistance and good machinability.

A further object of the invention is to provide a practical method for producing a unique steel-like alloy containing small well-dispersed graphite, having high strength and having resistance to wear.

Generally speaking, the present invention contemplates a steel-like ferrous alloy having a unique combination of properties, containing spheroidal graphite in the as-cast condition and containing at least a small but effective amount up to about 0.5% retained magnesium to effect the occurrence of graphite in a spheroidal form. The alloy comprises at least about 1.2% but less than about 1.7% carbon, at least about 0.5% to about 5.0% or 6.0% silicon, up to about 2.5% manganese, up to about 36% nickel, up to about 3% copper, up to about 2.0% chromium, with the balance essentially iron, and the iron content being at least about 55% of the alloy. In alloys having a matrix of alpha iron at atmospheric temperatures, the iron content is at least about 85% or about 87% of the alloy. Usually the cast alloy will contain uncombined carbon or graphite in amounts of about 0.35% to about 1.0%, e. g., about 0.5% to about 0.8%, manganese in amounts from about 0.1% to about 1%, e. g., about 0.3% to about 0.8%, silicon in amounts from about 0.6% or about 0.7% to about 3%, etc. The presence of silicon in the aforesaid amounts in the composition is important and is required to insure the presence of uncombined carbon in the as-cast alloys provided by the invention. However, the silicon content ordinarily

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should not exceed about 3% as a pronounced hardening and embrittling effect is encountered at higher silicon levels. Nickel, when present, will usually be in amounts up to about 10%, e. g., about 0.1% to about 3% or about 5%. When chromium is present, it preferably does not exceed about 1% and more preferably does not exceed about 0.5% or 0.6%, e. g., about 0.1% to about 0.4%, as chromium has a pronounced whitening or carbide-stabilizing effect. Copper in large amounts interferes with the formation of spheroidal graphite. For this reason, it is preferred that copper not be employed in amounts exceeding about 2% without first determining the effect of copper on the graphite formation as certain alloying elements such as nickel may increase the tolerance for copper. The sulfur content is low, usually not exceeding about 0.02%, e. g., about 0.007% to 0.01% or 0.015%. Certain other elements not usually found in ferrous alloys interfere with the formation of spheroidal graphite and should be avoided or should be present only in very small amounts not subversive to the effect of magnesium or the formation of spheroidal graphite. These subversive elements include tin, lead, antimony, bismuth, arsenic, selenium, tellurium, etc. It may be possible to compensate for the presence of a small amount of these subversive elements preferably less than about 0.1% by increasing the amounts of magnesium introduced into the alloy during the production thereof and/or by the introduction into the alloy of specific elements to form compounds of high stability with the subversive elements. Phosphorus is usually considered an impurity which in the ordinary amounts does not materially interfere with the formation of spheroidal graphite and may be present in amounts as high as 0.5% or more. Preferably, the phosphorus content does not exceed about 0.25%, e. g., 0.02% to 0.06% or 0.15%. For special purposes, including strength improvement, matrix control, deoxidation, etc., the alloy may contain up to about 2% molybdenum, e. g., about 0.1% to about 0.75%; up to about 0.1% aluminum, e. g., about 0.02% to about 0.05%; up to about 0.05% calcium, e. g., about 0.01% to about 0.03%, etc.

The magnesium content of the special steel-like alloy containing spheroidal graphite provided in accordance with the present invention is usually

at least about 0.03% or about 0.035% or about 0.04% up to about 0.2% or about 0.3%. Very satisfactory results are obtained when the magnesium content is in the range of about 0.05% to about 0.1% or about 0.15%.

The special steel-like alloy containing spheroidal graphite in the as-cast condition is preferably made by a process which involves establishing a molten iron bath containing up to about 5% silicon, e. g., about 0.2% or about 0.4% to about 2.7%, and containing carbon and other alloying elements in amounts within the aforesaid ranges with the balance essentially iron, adjusting the temperature of the bath to a proper temperature for casting, incorporating into said bath magnesium in an amount sufficient to provide a retained magnesium content of about 0.03% to about 0.3% or 0.35% in castings made from said bath, inoculating the bath at least once and casting the inoculated bath to obtain steel-like castings containing the aforesaid amounts of magnesium and containing spheroidal graphite in the as-cast condition. Inoculation of the magnesium-treated molten iron baths preferably is effected by means of a late addition of a graphitizing inoculant, such as silicon, which may be incorporated in the bath along with or subsequent to the magnesium introduction. For example, ferrosilicon, i. e., an iron alloy containing a major portion up to about 95% silicon, gives very satisfactory results. Other silicon-containing agents such as calcium silicide, nickel silicide, silicon metal, etc., and various proprietary inoculants commonly used for reducing dendriticism and reducing chill may be employed as inoculants. As those skilled in the art know, commercial ferrosilicon and other commercial inoculants frequently contain calcium in amounts up to about 1% or so and the presence of calcium is considered to improve the inoculating effect of such inoculants. It is preferred to employ silicon as the inoculant in amounts between about 0.3% and 2.5%, preferably between about 0.4% and about 1.2%. Preferably, magnesium is introduced into the baths in the form of a magnesium-containing addition agent such as an alloy or mixture, e. g., briquette. It is preferred to introduce magnesium as an alloy of magnesium with nickel, copper, and/or silicon and containing about 4% to 20% magnesium. Nickel-base alloys containing about 4% to about 20% magnesium give satisfactory results, e. g., an alloy containing about 90% nickel and about 10% magnesium. Other satisfactory alloys include nickel-magnesium-carbon alloys containing about 10% to about 20% magnesium and about 1% to about 4% carbon (as described in our co-pending application, Serial No. 88,494, now U. S. Patent No. 2,529,346), and nickel-magnesium-silicon alloys containing about 12% to about 20% magnesium and about 25% to about 50% silicon (such as described in our co-pending application, Serial No. 108,424, now U. S. Patent No. 2,563,859). Nickel-magnesium-silicon alloys provide the added advantage that magnesium introduction and inoculation can be performed simultaneously. Inoculation is an essential feature of the preferred process embodying the invention which produces the novel steel-like product containing spheroidal graphite in the as-cast condition as it has been found that magnesium of itself exerts a very powerful carbide-stabilizing effect, and if inoculation is not employed, substantially no uncombined carbon or graphite will be present in the solidified magnesium-containing casting.

It is not sufficient merely to add the magnesium-containing agent to the molten metal bath. It is essential in carrying out the process embodying the invention that magnesium be incorporated in the molten iron bath and be retained in the final product in the aforesaid required amounts. Because of its high reactivity when added to molten iron, its low solubility in iron-base melts, its low boiling point, etc., it is difficult to introduce magnesium into molten iron and high losses of magnesium are encountered by way of addition reactions, etc., when it is attempted to incorporate magnesium into iron-base melts. It has been found that in many cases, particularly when the less preferred addition agents are employed, no magnesium can be recovered from the addition agent or only a small amount can be recovered, e. g., 3% of the amount added. A further loss of magnesium can be encountered after incorporation of magnesium into the molten metal, possibly due to oxidation of magnesium contained in the melt, etc. These losses must be compensated for in making the magnesium additions to iron-base melts required to provide the retained magesium contents in the steel-like alloys contemplated by the invention. Since the molten baths to be treated in accordance with the invention, particularly baths containing less than about 3% silicon, have relatively high melting points, the magnesium-containing agents must be added to the molten baths when the baths are at temperatures of about 2800° F. to about 2900° F. and this factor contributes to substantial addition losses of magnesium in carrying out the invention. If any undesirable elements, which tend to combine with and/or counteract the effect of magnesium, for example, sulfur, oxygen, etc., are present or subsequently combine with the magnesium, the amount of magnesium introduced in the molten metal should be increased by the amount required to counteract the effect of the presence of these elements in consuming magnesium by removing the elements or by otherwise overcoming their effects. Sulfur is the magnesium-counteracting element which is most likely to be present in the bath. It has been found that in all baths treated in accordance with the present invention, all the magnesium-containing agents which produced this spheroidal form of uncombined carbon or graphite introduced the magnesium in a form which combined with sulfur present in the baths with the result that the sulfur content was reduced to 0.02% or less, for example, about 0.010% to 0.015%. Sulfur may be present in the baths to be treated in accordance with the invention in various amounts as high as even 0.15% or more and it is therefore necessary to add an amount of magnesium sufficient to combine with the sulfur present and to provide an excess sufficient to give the retained magnesium content required by the invention. Preferably, the sulfur content of the bath does not exceed about 0.05%. The introduction of about three parts by weight of magnesium is required to react with about four parts by weight of sulfur. In actual practice, about one part by weight of magnesium is introduced for each part by weight of sulfur to be removed. Thus, sufficient magnesium must be added to the molten iron bath to compensate for the losses encountered in addition reactions, to reduce the sulfur content of the bath to a low level, to overcome the losses of magnesium after its incorporation in the melt, and to provide the required retained magnesium

content in the bath and in the final castings. However, the total addition of the magnesium-containing agent must not be too large or difficulties are encountered due to chilling of the molten metal, etc. To conform with good foundry practice, the amount of the magnesium-containing addition agent employed ordinarily should not exceed about 3%, e. g., about 1.5% or 2% to about 2.5%. Magnesium-containing alloys which will accomplish the foregoing objectives include nickel-magnesium alloys such as binary nickel-magnesium alloys, nickel-magnesium-carbon alloys, and nickel-magnesium-silicon alloys referred to hereinbefore containing about 10% to about 20% magnesium, e. g., about 12% to about 15% magnesium. Of course, those skilled in the art will appreciate that alloying elements such as copper, nickel, silicon, etc., present in the magnesium-containing agents or in other agents added to the bath will be incorporated in the bath to a large extent when the agents are added thereto and the alloy content of the initial bath should be controlled accordingly. Improved results by way of magnesium recovery in the bath, etc., are obtained by adding the magnesium-containing agent to the molten stream of metal running into a container or the like.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given:

Example 1

A molten iron bath containing about 1.27% carbon and about 0.05% manganese was established and adjusted to a proper temperature for casting. Magnesium as a 95% nickel-5% magnesium alloy was incorporated into one portion of the bath, an inoculating addition of about 0.5% silicon (as ferrosilicon containing about 85% silicon) was made and metal from said portion was cast to obtain a casting produced in accordance with the present invention containing about 0.07% magnesium, about 1.9% silicon, and containing graphite in a spheroidal form. Another portion of the bath which had not been treated with magnesium was inoculated with a similar silicon inoculation and was cast to produce a magnesium-free casting not made in accordance with the present invention and containing about 2% silicon. The magnesium-containing casting had a tensile strength of about 87,000 pounds per square inch and a hardness of about 334 Brinell while the magnesium-free casting tested under similar conditions had a tensile strength of only about 64,000 pounds per square inch and a hardness of about 332 Brinell. In addition, the magnesium-containing casting resisted a transverse breaking load of 11,600 pounds and had a deflection of about 0.29 inch when tested over 12-inch centers whereas the magnesium-free casting tested under similar conditions broke under a transverse load of only 6900 pounds and had a deflection of only about 0.11 inch. The impact resistance of the magnesium-containing casting was about three times that of the magnesium-free casting.

Example 2

A molten iron bath containing about 1.5% carbon and about 0.07% manganese was established and adjusted to a proper temperature for casting. One portion of the bath was treated by incorporating therein magnesium as a 95% nickel-5% magnesium alloy in an amount sufficient to provide a retained magnesium content of about 0.07% in castings made therefrom, was

then inoculated with an addition of 0.5% silicon (as ferrosilicon containing about 85% silicon) and metal from the magnesium-treated inoculated portion was cast to provide a casting made in accordance with the present invention containing about 0.07% magnesium, about 1.8% silicon, and containing graphite in a spheroidal form. Another portion of the bath which had not been treated with magnesium was inoculated in a similar manner to the magnesium-treated portion and was cast to provide a magnesium-free inoculated casting not made in accordance with the present invention and containing about 1.9% silicon. It was found that the magnesium-containing casting had a tensile strength of about 85,000 pounds per square inch and a hardness of about 364 Brinell, while the magnesium-free casting had a tensile strength of only about 45,000 pounds per square inch and a hardness of 330 Brinell.

The preferred steel-like alloy provided by the present invention containing uncombined carbon or graphite in a spheroidal form in the as-cast condition is characterized by a unique combination of properties, including strength, resistance to the effects of galling and wear, machinability, etc. It has been found that the spheroidal graphite ar uncombined carbon present in the steel-like alloy castings in the as-cast condition is present in the form of small, well-dispersed particles which do not materially interfere with the continuity of the structure and which do not materially reduce the strength of the matrix. This desirable characteristic contributes to wear-resistance, machinability, etc. When it is desired to enhance certain particular properties or to modify the combination of properties, the steel-like alloys provided by the invention, particularly those having alpha-iron matrices, can be subjected to known heat treatments, including induction hardening, flame hardening, and similar surface treatments, to affect particular properties or combinations of properties of various alloys. Thus, the alloy provided by the invention having an alpha-iron matrix can be subjected to known heat treatments for stress relief, strengthening, hardening, toughening, etc., including isothermal treatments or austempering treatments. Illustrative heat treatments which may be employed include quenching and drawing, normalizing and drawing, etc. For example, the steel-like alloy can be re-heated above the critical transformation temperature, then cooled in air or quenched in oil and water, and then drawn at about 400° F. to about 1250° F.

As pointed out hereinbefore, magnesium exerts a powerful whitening or carbide-stabilizing effect in the steel-like alloy castings provided by the invention. Accordingly, the castings may in some cases contain excessive amounts of free massive carbides; for example, in cases where inoculation has been ineffective, etc. It has been found that free massive carbides can be removed by heat treatment above the critical temperature to decompose the free massive carbides and to produce, or to increase the amount of, uncombined carbon or graphite in the form of spheroidal bodies without the development of graphite in flake form. For example, a heat treatment at about 1400° F. to about 1800° F., more preferably within the range of about 1500° F. to 1750° F., for at least about one-half hour, more preferably at least two hours, will decrease the amount of carbon present in the form of free carbides.

When it is desired to hot work the steel-like

alloy provided by the invention, the alloy can be cast into ingots or the like containing a large amount of free massive carbides and substantially no uncombined carbon, the ingots can be hot worked, e. g., as by rolling, forging, etc., and the hot-worked products can subsequently be graphitized by the aforementioned heat treatment between about 1400° F. and about 1800° F. for periods of time of about one-half hour or more. When the foregoing procedures are employed, the presence of magnesium in the alloy contributes to a markedly more rapid rate of graphitization than that which characterizes similar products devoid of magnesium.

The present application is a continuation-in-part of our co-pending application, U. S. Serial No. 787,420, filed November 21, 1947, now U. S. Patent No. 2.485,760.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will understand. Such modifications and variations are considered to be within the purview and scope of the invention and of the appended claims.

We claim:

1. As a new article of manufacture, a steel-like alloy containing spheroidal graphite in the as-cast condition, about 0.03% up to about 0.3% magnesium to control the occurrence of the aforesaid spheroidal graphite, about 1.2% to about 1.6% total carbon, about 0.5% to about 6% silicon, with the balance essentially iron and the iron content being at least about 85% of the alloy composition.

2. As a new article of manufacture, a cast steel-like alloy containing about 1.2% to 1.6% total carbon, with at least about 0.35% of the alloy being uncombined carbon present in a spheroidal form, about 0.03% to about 0.5% magnesium to effect the occurrence of uncombined carbon is a substantially spheroidal form in the as-cast condition, about 0.5% to about 6% silicon, up to about 36% nickel, up to about 3% copper, up to about 2.5% magnanese, with the balance essentially iron and the iron content being at least about 55% of the alloy, said alloy being characterized by a high combination of strength, wear resistance and machinability.

3. As a new article of manufacture, a steel-like alloy containing about 0.03% to about 0.4% magnesium, about 1.2% to about 1.6% total carbon, with at least about 0.35% of the alloy being uncombined carbon, about 0.5% to about 3% silicon, up to about 36% nickel, with the balance essentially iron, said alloy being characterized by an improved combination of strength, wear resistance and machinability and by the presence of uncombined carbon in a spheroidal form.

4. As a new article of manufacture, a steel-like alloy containing graphite in a spheroidal form in the as-cast condition, about 0.04% to about 0.2% magnesium to control the occurrence of graphite in said spheroidal form, about 1.2% to about 1.6% total carbon, about 0.6% to about 5% silicon, up to about 36% nickel, with the balance essentially iron, and the iron content being at least about 55% of the alloy composition.

5. As a new article of manufacture, a steel-like alloy containing graphite predominantly in a spheroidal form in the as-cast condition, about 0.05% to 0.1% magnesium to control the occurrence of graphite in said spheroidal form, about 1.2% to about 1.6% total carbon, about 0.6% to about 3% silicon, with the balance essentially iron, and the iron content being at least about 85% of the alloy composition.

6. As a new article of manufacture, a steel-like alloy containing about 0.04% to about 0.2% magnesium, about 1.2% to about 1.6% total carbon, with at least about 0.35% of the alloy being present as fine, well-distributed spheroids of uncombined carbon, about 0.6% to about 3% silicon, with the balance essentially iron, said alloy being characterized by an improved combination of strength, wear resistance and machinability.

7. As a new article of manufacture, a steel-like alloy containing graphite in a spheroidal form in the as-cast condition, about 0.04% to 0.15% magnesium to control the occurrence of graphite in said spheroidal form, about 1.2% to about 1.6% total carbon, about 0.7% to about 3% silicon, about 0.1% to about 0.8% manganese, with the balance essentially iron and the iron content being at least about 85% of the alloy composition.

8. The improved method for producing a steel-like alloy containing spheroidal graphite in the as-cast condition which comprises incorporating magnesium into a ferrous bath containing more than about 1.2% but less than about 1.7% carbon, up to about 5% silicon, with the balance essentially iron, inoculating the magnesium-treated bath with at least about 0.3% silicon, and casting metal from the magnesium-containing inoculated bath to obtain a steel-like casting containing spheroidal graphite and containing at least about 0.03% magnesium to control the occurrence of graphite in a spheroidal form.

9. The improved method for producing a steel-like alloy containing spheroidal graphite in the as-cast condition which comprises establishing a molten ferrous bath containing about 1.2% to about 1.6% carbon and about 0.4% to about 5% silicon, introducing into said bath a quantity of magnesium sufficient to provide a retained magnesium content of about 0.03% to about 0.3% in a casting made from said bath, inoculating the bath containing said amount of retained magnesium with about 0.3% to about 2.5% silicon as a silicon-containing agent, casting the inoculated bath to produce a steel-like alloy casting containing about 0.03% to about 0.3% magnesium, about 1.2% to about 1.6% carbon, about 0.5% to about 6% silicon, up to about 36% nickel, up to about 2% copper, up to about 2.5% manganese, up to about 1% chromium with the balance essentially iron, and having a microstructure containing graphite in a spheroidal form.

10. The improved method for producing a steel-like alloy containing spheroidal graphite which comprises establishing a molten ferrous bath having a temperature of about 2800° F. to about 2900° F., containing about 1.2% to about 1.6% carbon and about 0.2% to about 2.7% silicon, incorporating into said molten bath about 1.5% to about 3% of an alloy containing about 10% to about 20% magnesium selected from the group consisting of nickel-magnesium alloys, nickel-magnesium-carbon alloys and nickel-magnesium-silicon alloys, thereafter inoculating said bath with about 0.3% to about 2.5% silicon as ferrosilicon and casting metal from said bath to obtain a steel-like alloy casting containing about 1,2% to about 1,6% carbon, about 0.5% to about 3% silicon, containing graphite in a spheroidal form and containing about 0.04%

to about 0.5% retained magnesium to control the occurrence of graphite in said spheroidal form.

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