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NODULAR GRAPHITE STEEL

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FIG. 1.

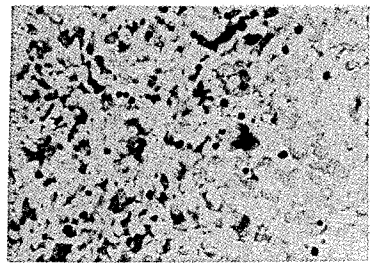
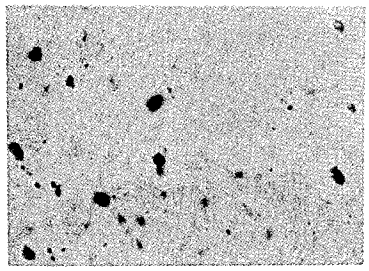


FIG. 2.



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NODULAR GRAPHITE STEEL

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This invention relates to a new high carbon steel in general containing nodular graphite, and to a new and improved method of producing such a steel.

The principal object of this invention is to obtain carbon steels and all kinds of alloy steels having nodular graphite structure having improved mechanical and physical properties.

A further object of this invention is to produce castings and ingots of carbon steels and of alloy steels having nodular graphite by treating chemically the molten bath of such steels.

The principle of the present invention is based on precipitating the nodular graphite by adding to the hyper-eutectoid steel a small amount of calcium and/or cerium together with a suitable flux if desired, thereby changing the primary free cementite into nodular graphite, in order to obtain a new material possessing the machining and wear-resistant properties ascribed to the presence of graphite as well as the responsiveness to various heat treatments and hot or cold-workability of steel.

Hyper-eutectoid steel contains primary cementite in a pearlite matrix, and so it has high hardness but is brittle. Accordingly, in order to improve its mechanical properties a method had been adopted to spheroidize or graphitize the cementite by suitable heat treatment.

It has now been found that the above precipitated free cementite can be avoided by adding a suitable amount of calcium and/or cerium to the molten bath of the hyper-eutectoid steel, and that the precipitated graphite can be nodularized. It has also been found that besides calcium and cerium, a suitable amount of either one or more elements from the group consisting of magnesium, lithium, strontium and barium may be added to the molten bath of said steel to produce a nodular graphite in the cast state. Calcium may be added in the form of Fe-Ca base alloy containing 10 to 80% of iron, 5 to 40% of calcium, and 5 to 55% of one or more of Ni, Si, Al or Mn or calcium silicide or any suitable calcium alloy. Usually 0.2 to 0.6% of Fe-Ca base alloy or 0.5 to 8% of calcium silicide is employed together with 0 to 2% of a flux containing calcium fluoride or magnesium fluoride as the main ingredient.

As an alternative, the amount of calcium to be added may be regulated to make the retained calcium in the casting of hyper-eutectoid steel less than 0.2%, and further cerium is added to maintain the remaining cerium at 0.005 to 0.15%.

This invention can be applied equally to eutectoid or hypo-eutectoid steels, i.e., to carbon steels containing less than 0.85% C and also to special alloy steels containing less than about 1.7% C together with one or more elements selected from the group consisting of Mn, Cr, W, Mo, V, Ti and similar elements forming carbides.

The phenomenon of precipitating nodular graphite by this invention even in eutectoid or hypo-eutectoid steels, in which primarily precipitated cementite is not produced, is difficult to illustrate diagrammatically, but it may be

assumed that nodular graphite is precipitated by considerably high atomic interaction at a high temperature between the atoms of the added elements such as cerium, calcium, magnesium and the like elements and the carbon atoms contained in the steel.

The accompanying illustration shows the microscopic structure of the steel produced by this invention. In the illustration:

Fig. 1 is a microscopic photograph showing a microstructure multiplied one hundred times of a hypo-eutectoid carbon steel (0.53% C, 0.74% Si, 0.28% Mn, 0.008% P, 0.008% S) treated with 1.0% of iron-calcium base alloy (22.7% Ca), annealed at 900° C. for 3 hours after casting, and

Fig. 2 is a similar microscopic photograph enlarged 400 times.

From Figs. 1 and 2, the distribution of precipitated nodular graphite in a matrix of pearlite and ferrite can be clearly recognized.

The standard structure of a common eutectoid steel consists mainly of pearlite matrix only, while that of hypo-eutectoid steel consists of ferrite and pearlite and is located on the side of iron from the eutectoid point as seen in the constitutional diagram. It is found, however, that according to this invention, by adding the above mentioned elements perfect nodular fine-grained graphite is precipitated even in eutectoid and hypo-eutectoid steels. The accompanying drawing illustrates the nodular graphite structure of hypo-eutectoid steel (about 0.6% C) obtained by this invention, showing that the graphite exists over the whole area of pearlite and ferrite matrix; it has precipitated at a high temperature, before primary ferrite and pearlite have been produced.

"Steel" means here an alloy consisting of iron and less than 1.7% of carbon as the main ingredients and containing in the matrix a small quantity of silicon and manganese as well as phosphor, sulfur, etc. as impurities.

The steel to be produced by this invention contains very little oxygen and sulfur, such as 0.001 to 0.005% of oxygen and 0.005 to 0.015% of sulfur.

Further, in carrying out this invention, the molten bath to be treated should be previously de-oxidized and de-sulfurized as perfectly as possible because this procedure is effective in retaining the above described addition elements in the product. That is, the above mentioned addition elements, cerium, calcium, lithium, strontium, barium and magnesium are added to the molten steel, so that they react rapidly with the oxygen and sulfur in the bath to form their oxides and sulfides which float upon the surface of the bath. Accordingly, when such elements are to be added, the loss of the additional elements due to de-oxidation and de-sulfurization in the molten bath and the loss of the additional elements during the maintenance of the bath after the addition should be compensated so that a sufficient quantity to hold the necessary amount of elements retained in the final casting or steel ingot should be added.

This invention can widely be applied to all kinds of steels such as carbon steels and alloy steels; that is, it includes ordinary steels with nodular graphite and alloy steels having nodular graphite together with one or more special elements selected from the group consisting of silicon, manganese, nickel, chromium, copper, tungsten, molybdenum, titanium, cobalt and zirconium, and their castings and ingots, which are forgeable. The specific physical properties of such steels having nodular graphite structure show a remarkable improvement in the strength, a reduction of notch-effect, an increase in damping capacity, a reduction of coefficient of expansion, an increase of abrasion and oxidation resistances, and a reduction of thermal distortion.

Example I

A molten bath of hyper-eutectoid steel containing about 1.5% of carbon, about 0.8% of silicon, about 0.4% of manganese, and about 0.03% of phosphor was made and to this molten bath was added about 0.3% of calcium, 0.04% of cerium and 0.1% of barium. For the addition of calcium, Fe-Ca-Si alloy (33.5% Fe, 29.5% Ca and 35% Si) was used and for cerium "misch" metal was used and for barium the metallic barium was used.

Such a casting produced by this invention was a hyper-eutectoid steel having very fine nodular graphite structure, and showed a tensile strength of 65.4 kg./mm.^{2}, an elongation of 3.5% (gauge length 50 mm.) and a Brinell hardness number of 241.

Example II

A molten bath of hypo-eutectoid steel containing 0.6% of carbon, 0.8% of silicon, 0.04% of manganese, and 0.02% of phosphor was prepared and to this molten bath was added 0.2% of calcium. The calcium was added as the Fe-Ca-Si alloy (33.5% Fe, 39.5% Ca and 36% Si) mixed with some calcium fluoride (flux).

A steel ingot produced by this invention is of hypo-eutectoid steel consisting of very fine nodular graphite dispersed in a matrix of ferrite and pearlite, and showed a tensile strength of 66.2 kg./mm.^{2}, an elongation of 14% (gauge length 50 mm.) and a Brinell hardness number of 187.

Example III

A molten bath of Hadfield steel containing 1.25% of carbon, 0.5% of silicon, 13.5% of manganese, and 0.02% of phosphor was prepared and to this bath was added 0.31% of calcium using Fe-Ca-Si alloy (25.0% Fe, 31.6% Ca and 42.7% Si) mixed with 0.4% of calcium fluoride (flux).

A casting prepared by the above method of this invention was a steel having very fine nodular graphite and cementite structure, and when it was quenched in water at a high temperature it showed austenite structure containing very fine nodular graphite and was stronger than ordinary Hadfield steel, and could be easily machined. The tensile strength of the hardened cast steel was 54 kg./mm.^{2}, the elongation 12% (gauge length 50 mm.), the reduction of area 27% and Brinell hardness number of 206.

Example IV

A molten bath of chromium-tungsten steel containing 0.7% of carbon, 0.5% of silicon, about 0.5% of chromium, about 2% of tungsten and 0.03% of phosphor was made and to this bath was added 0.31% of calcium as Fe-Ca-Si alloy (25.7% Fe, 31.6% Ca and 42.7% Si) mixed with 0.7% of calcium fluoride as flux and 0.04% of cerium as misch metal.

The forged product made by the above method of this invention was a very strong chromium-tungsten steel containing fine nodular graphite and cementite, without acicular carbide which usually precipitates in the crystal grains; the steel showed very good machinability.

What I claim is:

1. A method of manufacturing steel castings, which comprises adding to a molten bath of steel containing less than 1.7% of carbon, 0.2 to 6.0% of iron-calcium-silicon alloy and 0.005 to 0.15% of cerium so as to obtain a casting containing about 0.001 to 0.5% of calcium and less than 0.15% of cerium.

2. A nodular graphite steel containing calcium and cerium in the amount of 0.001 to 0.5% of calcium and 0.005 to 0.15% of cerium and the balance a steel composition with less than about 1.7% of carbon, said casting being characterized in the as-cast condition by a microstructure comprised of soft, gray-colored, substantially spherical graphite particles dispersed in ferrite and pearlite.

3. A nodular graphite steel having the characteristic, in the as-cast condition, of a microstructure containing substantially spherical particles of uncombined carbon dispersed in ferrite and pearlite and being comprised of about 0.001 to 0.5% of calcium with the balance steel composition with less than about 1.7% of carbon.

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