

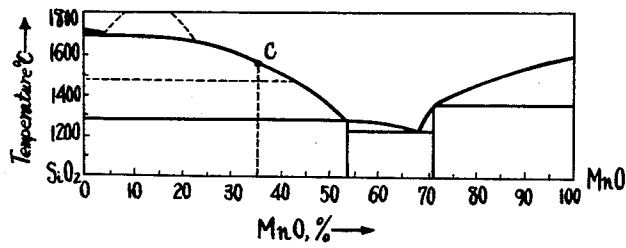
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METHOD OF MANUFACTURING FINE GRAINED AND CLEAN STEELS

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Binary diagram of MnO-SiO₂

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2 Claims. (Cl. 75-129)

The present invention relates to a method of manufacturing ordinary steels of eutectoid and hypo-eutectoid structures containing less than 0.85% carbon and alloy steels containing less than 2.0% carbon and also to such steels and alloy steels manufactured by the method.

The method of the invention is characterized in that ordinary steels of eutectoid and hypo-eutectoid structures containing less than 0.85% of C or an alloy steel containing less than 2.0% of C are made to contain 0.0001 to 0.05% of calcium by adding to the melt of the above steels a mixture of one or more elements of Al, Ti, V, Zr, Nb and N together with low carbon manganese-calcium base alloy.

The principal object of the invention is to produce ordinary steels and/or alloy steels having fine grained structure by reducing non-metallic inclusions and having improved toughness, fatigue limit and machinability.

It has heretofore been known in the art that the control of the size of the grain in steels is attained by adding a suitable quantity of one or more elements of Al, Ti, V, Zr and the like elements, and as the cleanliness of steel is effected by the deoxidation and the resultant oxides, a small quantity of Al was added after the deoxidation by means of Mn and Si.

The known Ca-Si-Mn alloys used for deoxidizing irons and steels have the following compositions:

	Ca, percent	Si, percent	Mn, percent
1.-----	12-16	55-65	18-22
2.-----	12-20	55-65	14-18
3.-----	20-24	55-65	10-14

On the other hand, in accordance with the invention use is made of the low carbon Mn-Al-Ca-Si addition alloys which contain 22 to 80% of Mn, 0.2 to 35% of Ca, 0.1 to 60% of Al, less than 10% of Fe and the balance substantially of Si, which is within the range of 2 to ¼ of Mn, and more particularly the alloys may contain in addition alkaline earth metals other than Ca and rare earth elements at an amount of about ¼ of the content of Ca. The above alloys manufactured for commercial purposes contain usually 5 to 6% of iron as impurities.

According to the invention, it has been found that Mn-Al-Ca-Si addition alloys containing higher amount of Mn than the heretofore known Ca-Si-Mn alloy can be manufactured easily. The new alloys have higher specific gravity due to the high Mn-content, the ratio of Mn to Si being 1:2 to 4:1, while it was 1:3 to 1:7 in the latter alloy and owing to low Si-content the new alloy serves as a very favorable addition agent for refining steels.

For a better understanding of the invention reference is taken to the accompanying drawing, a single figure of which illustrates the binary state diagram of MnO and SiO₂.

Referring to the drawing, the compositions which are in the molten state at a temperature below about 1,600° C. are limited to only those which contain more quantity of MnO than that as shown at the point C on the diagram, where the ratio MnO:SiO₂ is 35:65 (about 1:2). This ratio corresponds to 1:1.3 in the ratio Mn:Si.

It is apparent from the drawing that when an alloy in

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which the ratio of Mn to Si is more than 1:1.3 is added to a steel the resultant oxides, i.e., non-metallic inclusion in the steel produced by the alloy has the composition which should be in a molten state at a temperature below 1,600° C.

According to the invention, if compared with known Si-Mn-Ca alloys, the ratio Mn:Si is raised and defined to such an extent that all of the oxide products in the molten steel should be in the liquid state. Moreover, though the known Si-Mn alloys contain a large quantity of C as manganese carbide, yet the alloys of the invention have the specialty that they contain a very small amount of carbon as the alloys are decarbonized by the existence of 0.2 to 35% of Ca.

If, for instance, about 7.5% of Ca is added to a melt of Si-Mn alloy containing 1.2% of C, 20% of Si and 61% of Mn, the carbon content of the resulting alloy reduces to 0.25%. The carbon content of an ordinary Si-Mn alloy is 0.9 to 2.5%, whilst the carbon content of the present alloy is within the range of 0.1 to 1%.

In carrying out the method of the invention, a desired fine grained and clean steel can be obtained without effecting the perfect deoxidation and de-sulfurization to such an extent less than 0.001 to 0.005% of oxygen and 0.003 to 0.015% of sulfur, i.e., at more than 0.015% of sulfur content and more than 0.005% of oxygen content, if a suitable quantity of Al, Ti, V, Zr, Nb and nitrogen is retained and if the retained quantity of Ca is more than 0.0001% the casting or steel ingot has fine grained and clean structure so that it is not necessary to retain more than 0.05% of Ca. The purpose of previously containing Ce, V, Be, Li, Sr and Mg except Ca in the alloy is to expedite the de-sulfurization and deoxidation at the same time to raise the cleanliness of steel and in the manufacture of the addition alloy, it is more convenient to previously add these elements at an amount less than ¼ of the calcium content.

The present invention differs from U.S. Patent 3,000,731 in that the alloy is added together with one or more elements of Al, Ti, Va, Zr, Nb and the like forced deoxidizing agent and nitrogen. One or more of the above elements may be previously alloyed with Mn-Ca base alloy.

After deoxidation by means of manganese and silicon in the final refining period of molten steel, 0.001 to 0.3% of N₂ and Al, Ti, Va, Zr and the like elements to be added as a small quantity of forced deoxidizing agent combines with oxygen in the melt and a part forms a compound and another part forms nitride and the remaining is alloyed with the melt. If, however, the elements of these forced deoxidizing agents are contained in the Mn-Al-Ca-Si addition alloy such elements act more effectively on the melt so that it is sufficient to use ½ to ⅓ the quantity of the former deoxidizing agent if used alone. Only in this case Mn-Al-Ca-Si addition alloy is added without said forced deoxidizing elements.

According to the invention, it has been found that if the method of the invention using the Mn-Al-Ca-Si addition alloy is used together with the known process, for instance, if it is used in parallel to the aluminum process the calcium in the said addition alloy reduces alumina in the melt to produce metallic aluminum and aluminum nitride. Accordingly, by the increase of metallic aluminum and aluminum nitride the grains of steel become considerably refined so that it is more effective if compared with the case when using Mn-Ca base alloy alone.

Further, according to the invention, the calcium accelerates the reducing action of alumina in the melt and the deoxidizing action, and simultaneously improves the cleanliness of steel.

The method of the invention can be applied to ordi-

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nary steels containing less than 0.85% of C and alloy steels containing less than 2.0% of C, that is, the invention can be effectively applied to ordinary steels of eutectoid and hypo-eutectoid structure naturally and also the alloy steels containing less than 2.0% of C and one or more of special elements, such as, Si, Mn, Ni, Co, Cr, Cu, Al, W, Mo, V, Ti and Zr.

The steel subjected to the above treatment has fine grained and clean structure and its elongation and the reduction of area increase without substantial change in the strength and also the notched impact value increases considerably and at the same time the machinability is improved and the remarkable improvement in mechanical properties is recognized especially in quenched and tempered steels.

The invention will be explained further in detail with examples.

Example 1

A steel containing 0.6% of carbon was melted in a basic high frequency electric furnace and deoxidized at a temperature of 1,630° C. with 0.5% ferro-manganese, 0.2% Si and 0.06% Al. The steel ingot treated with 0.8% of Mn-Ca base alloy (Ca 24.1%) and untreated one were taken as samples and after forged the grain size and grain coarsening temperature were studied, and the following results were obtained:

Treatment of Steel	A.S.T.M. Grain size number, 960° C. × 3 hrs.	Grain coarsening temperature, ° C.
(1) Addition of 0.05% of Al only-----	5.0	920
(2) Addition of 0.05% of Al+0.8% of Mn-Ca base alloy-----	7.5	1,050

Example 2

Steel containing 0.82% was melted in a basic high frequency electric furnace and after deoxidation with 0.5% Mn and 0.2% Si at 1,620° C. the molten steel was divided into 2 portions, to one of which was added

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0.8% of Mn-Ca base alloy (Ca 24.8%, Al 3.2%) and to the other 0.05% of Al and after casting the samples were forged and the grain size was tested and obtained the following results:

Treatment of Steel	A.S.T.M. Grain size number 960° C. × 3 hrs.	Grain coarsening temperature, ° C.
(1) Addition of 0.05% of Al-----	4.0	960
(2) Addition of 0.8% of the addition alloy of the invention-----	8.0	1,040

What I claim is:

1. A process for producing fine grained and clean steels from steels having the composition of carbon steels with less than 0.85% carbon and having upon solidification eutectoid and hypoeutectoid structures and alloy steels containing up to 2% carbon, the steps which comprise adding to a melt of the steels which contain after preliminary deoxidation with manganese and silicon 0.001-0.3% of the elements selected from the group consisting of Ti, V, Zr, and Nb together with N in an amount of 0.001 to 0.3% and then adding an alloy consisting essentially of 22%-80% Mn, 0.2 to 35% Ca, 0.1 to 60% Al, less than 10% Fe and the balance substantially Si, wherein Si is within the range of 2 to 1/4 of Mn, said alloy being in an amount sufficient to leave 0.001-0.05 Ca in the steel, thereby forming a nitride of said group and producing said clean and fine grained steel.

2. A method of manufacturing fine grained and clean steels according to claim 1, which comprises using said Mn-Al, Ca-Si addition alloy containing rare earth metals and alkaline earth metals other than calcium at an amount less than 1/4 of the calcium content.

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