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2,767,084

ALLOY FOR DEOXIDIZING STEEL

Filed Sept. 15, 1955

2 Sheets-Sheet 1

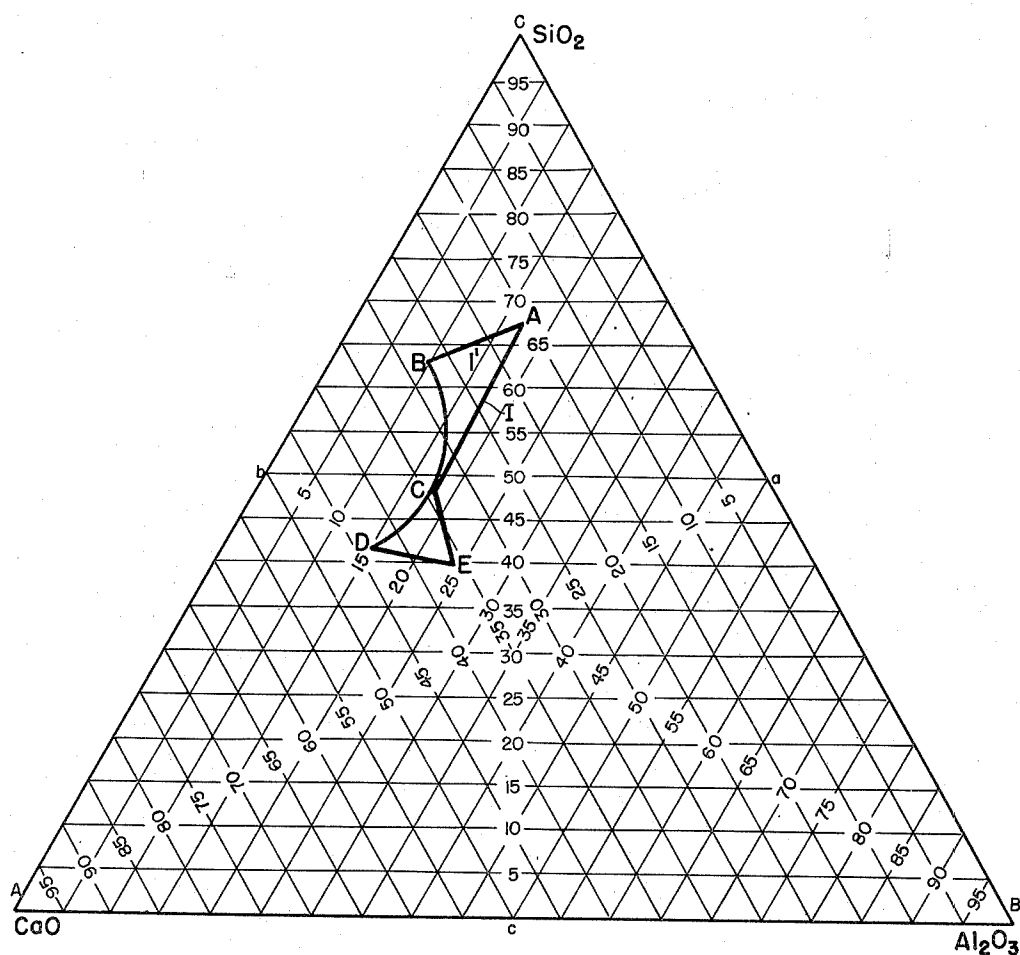


Fig. 1

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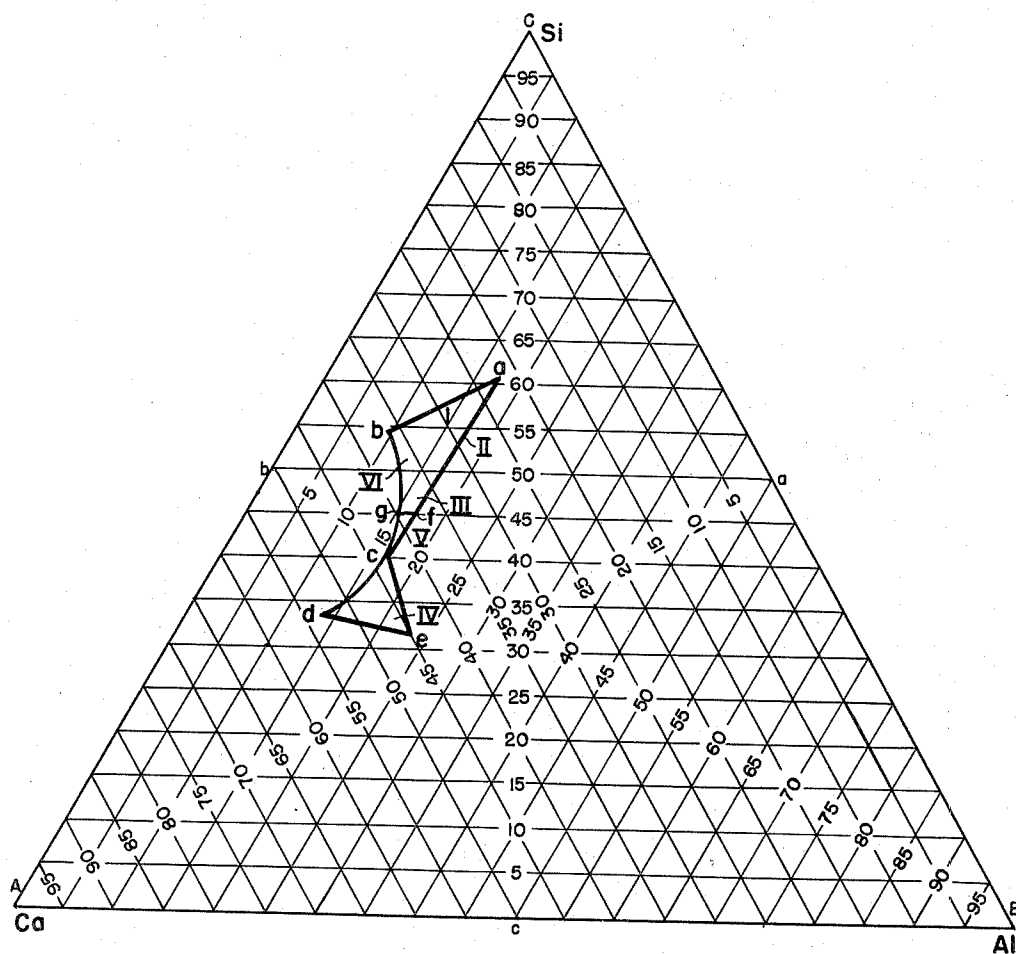


Fig. 2

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ALLOY FOR DEOXIDIZING STEEL

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1 Claim. (Cl. 75—134)

This invention relates to an alloy for deoxidizing steel. An object of the invention is to provide an alloy which, when added to liquid steel, minimizes residual contents of oxidic inclusions therein. Other objects will become evident in the course of the following description.

In the production of steel, the liquid metal contains oxygen in solution, the amount depending upon the particular steel composition and steel-making method. It can either be left therein to react with the carbon during solidification, resulting in the release from solution, but retention in the solidifying metal of carbon monoxide gas, to produce a so-called "rimming" steel, or the oxygen can partly or wholly be bound to solid deoxidizers. Among these solid deoxidizers, aluminum and silicon can, depending upon the extent of and/or time of the addition, deoxidize the steel fully or in part, resulting in so-called "killed" or "semi-killed" steels, respectively. Manganese is usually not added to the extent required fully to deoxidize a steel but if manganese is required, it is often added in combination with silicon and sometimes with aluminum. Vanadium is not added to steels alone to produce a "semi-killed" or "killed" product but is advantageously employed in "rimming" steels for deep drawing.

One of the most widely used deoxidizers in present practice is aluminum. However, aluminum forms a highly refractory hard oxide with a very high melting point. Therefore, in aluminum deoxidation, the resultant oxide or other alumina-rich inclusions remain in finely distributed form, disseminated throughout the solid steel. Occasionally, the oxidic inclusions aggregate to form clusters or stringers in, as well as surface defects on, the ingots or castings. These inclusions can lead to serious defects. In machining, they may cause tools to be worn rapidly or to break, owing to the hardness and the abrasive character of these inclusions. In the product itself, regions of weakness can be produced which have low resistance to impact and other stresses.

I have found that these difficulties can be overcome by adding to molten steel an alloy containing aluminum, calcium and silicon as active components and iron as a carrier metal. My alloys contain 15 to 35% iron. All percentages herein given are percentages by weight unless otherwise specified. The balance of the alloy consists of aluminum, calcium and silicon in the percentages of the balance of 9 to 18% aluminum, 22 to 40% calcium and 45 to 60% silicon, the percentages of aluminum, calcium and silicon in this balance falling within an area of a ternary diagram as more particularly specified hereinafter. Upon addition of the alloy to steel, the iron is absorbed, leaving the active components, aluminum, calcium and silicon, to combine with the oxygen in the steel to form a low-melting slag from the reaction products.

Figure 1 is a portion of the phase diagram of the ternary system Al_2O_3 — CaO — SiO_2 , presenting the isothermals of

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incipient solidification of slags at 1300° C. All compositions within the area enclosed by these isothermals have melting points of 1300° C. or lower.

Figure 2 shows a portion of the phase diagram of the ternary system Al — Ca — Si , on which have been plotted Al — Ca — Si alloys, which when fully oxidized would correspond to the slags shown in Figure 1.

The oxidation product, i. e., slag of a properly balanced Al — Ca — Si composition can be made to have a melting point that is adequately low to permit it to coagulate in the liquid steel and to rise out of the molten metal, either in the ladle or ingot mold or both. The melting range of such an oxide mixture or compound should be well below the temperature of liquid steel. To function in this manner, the maximum temperature of the melting range of these oxidic materials should be less than 1300° C.

Such melting points provide an adequate differential between the temperature of the liquid steel in the ladle or in the ingot mold when the deoxidizer is added thereto, and the temperature of solidification of the steel itself. The time elapsing during the cooling of the steel from the moment of addition of the deoxidizer to the time when solidification is substantially completed thus will suffice for the liquid deoxidation products to coagulate in, rise out of, and separate from the steel. A physical separation of these oxidic compounds from the metal is thereby made possible.

While the above description provides an explanation of the functioning of my alloy, based upon equilibrium data, it has not been possible to reach the conclusion that these equilibria would govern in the practical conduct of a steel-making operation. The discovery of the possibility of this particular and critical alloy combination functioning in a novel manner, to overcome difficulties previously encountered, was based upon the belief that these results would be obtained. In practice, it was later determined that such results could be achieved. The known equilibria thus served solely as a means of explaining the observed performance of the alloy of my invention.

It must be understood that the rate of reaction is important and it is conceivable that with such rates differing from three elements of different character, it would be entirely possible for oxides formed by one of these elements to move out of the range of combination with oxides of the other forming later. This can readily occur when the elements are added singly or in partial combination with each other. When, however, the three elements are associated as a three-component alloy, these deleterious effects are not observed as the low-melting slags are formed and then readily clear themselves from the molten steel.

Referring more particularly to Figure 1, the lines connecting the points A, B, C, D, E, C and A, enclose an area designated by reference I, in which the melting points of slags of the compositions shown are 1300° C. or less. The compositions of the slags represented by these points are given in the following table:

Table 1

Slag	Al_2O_3	CaO	SiO_2
A	17	16	67
B	10	27	63
C	18	34	48
D	15	43	42
E	24	36	40

When the compositions of these oxides are translated into the alloys, which when fully oxidized result in these oxides, the following corresponding alloys result:

Table 2

Alloy	Al	Ca	Si
a	17.4	22.1	60.5
b	9.8	35.8	54.4
c	16.9	43.3	39.8
d	13.6	52.7	33.7
e	22.2	45.1	32.7

Referring to Figure 2, the lines connecting the points a, b, c, d, e, c and a, enclose an area designated by reference numeral II. All alloys within area II, when fully oxidized, result in slags whose melting points are 1300° C. or less. The area II may be considered as constituted by an upper, generally triangular area III and a lower, generally triangular area IV, these two areas III and IV being connected by a narrow neck at the point c.

However, considerable difficulties are encountered in manufacturing alloys of the Ca—Al—Si—Fe type having compositions that with respect to their proportions of Ca—Al and Si, fall within the area IV and which contain more than about 45% calcium and more than about 15% aluminum. The lower narrow part of area III has been cut off in Figure 2 by a line connecting point f and point g, the area defined by the points c, f and g being designated by reference numeral V. If it were attempted to produce alloys having compositions falling within this very confined area V, it would be necessary to maintain the calcium-aluminum-silicon within narrow limits and, more particularly, it would be necessary to maintain the calcium and aluminum within very narrow limits. It is not possible commercially to repetitively produce alloys within these abnormally narrow limits. Accordingly, the actual alloys of my invention, which can readily and consistently be manufactured, and which when oxidized result in slags having a melting point below 1300° C., are those falling within the area VI defined by the points a, b, g, f and a. It is thus seen that the active components of my alloy when considered as representing 100%, are in the proportions of 9 to 18% aluminum, 22 to 40% calcium and 45 to 60% silicon.

Reference numeral 1 on Figure 2 indicates a composition containing 13.9% aluminum, 32.0% calcium and 54.1% silicon. Such composition, when fully oxidized, results in a slag 1' having a melting point of 1170° C. as shown in Figure 1.

As previously pointed out, the iron in my alloy amounts to 15 to 35% of the alloy. An alloy containing less than 15% of iron does not have a high enough specific gravity so that it may be readily introduced below the surface of the steel being treated, and thus incurs losses of active components. Moreover, the normal difficulties encountered in producing, especially by direct smelting, alloys so rich in calcium and aluminum, are greatly alleviated if this lower limit of iron content is observed. On the other hand, if the iron exceeds 35%, the active ingredients are so diluted that it requires a relatively large addition of the alloy which may produce excessive cooling of the steel being treated, thus adversely effecting the results.

Alloys of this invention can be produced in a number of ways, which may be related to the delivered cost of raw materials and the availability of operating equipment. One method is the direct alloying by melting of ferro-silicon, calcium silicide and aluminum. All of these materials are commercially available and may be fused in an induction furnace or other suitable melting equipment.

The deoxidation capacity of the three active metals in

the alloy of my invention can be gauged by their respective heats of oxide formation, as follows:

	Per formula gm. weight, cals.	Per gm. weight of metal, cals.	Per gm. weight of O ₂ , cals.
Al ₂ O ₃	380,000	7,045	7,920
CaO.....	151,000	3,790	9,430
SiO ₂	201,000	7,160	6,280

These heats of formation, especially on the oxygen basis, are substantially above those for iron, manganese, chromium, molybdenum and vanadium, i. e., of iron and its common alloying elements.

In addition, substantial heat is developed in the formation of silicates from aluminum and calcium oxides. Against this heat output there must be offset the heat absorbed in melting the iron of the alloy.

An alloy of this invention which contains 11% Al, 22% Ca, 44% Si and 23% iron, when oxidized, results in a slag containing 14% Al₂O₃, 21% CaO and 65% SiO₂. Here 21 parts of lime bind 21 parts of silica leaving more than enough silica to form aluminum disilicate. Heat of formation of these silicates above the heat of formation of the constituent oxides, is as follows:

[Heat developed in cals.]

	Per gm. weight of for- mula	Per gm. of metal oxide	Per gm. of silica
Al ₂ O ₃ .2SiO ₂	8,500	84	71
CaO.SiO ₂	25,000	449	420

Iron contained in the alloy requires 334 cals. per gm. to fuse and thus be absorbed in the steel bath. On the basis of these data, it is found that the removal of 1 lb. of oxygen from the steel bath by the alloy containing 11% Al, 22% Ca, 44% Si and 23% Fe develops 3,200,000 cals. net, compared with 3,600,000 cals produced in the oxidation of the requisite amount of aluminum. In neither case has allowance been made for the heat required for raising the active components to the reaction temperature, but the difference is not appreciable. It will be seen that the alloy of this invention approaches aluminum in efficiency of oxygen removal, in respect to the amount of heat generated, the difference being only about 10%, although it carries a cargo of almost one quarter its weight of iron. To this feature must be added the much cleaner performance of the alloy in the deoxidation of steel.

These calculations largely explain the observations made during the production of many commercial heats of steel to which these alloys have been added, combined with the study of the properties and performance of the steel products into which these heats have been converted.

In connection with the study of the steel heats just mentioned, it has been noted that there is some lowering of the sulphur content of the steel, thus adding another benefit that is derived from the application of the alloy of my invention. Additionally, there is an influence upon the nitrogen content of the steel. Nitrogen is present in appreciable amounts in all steels produced by present steel-making practices, the amount depending in part upon the steel composition, but in larger part upon the method of production. For most uses, improvement of steel properties results by effectively combining this nitrogen, producing a form commonly referred to as "acid-insoluble." The alloy of my invention has a definite effect in this direction.

The small amounts of sulphur and nitrogen which will combine in this manner with the active components of the alloy of my invention therefore remove corresponding amounts of alloy from functioning as deoxidizers. These

amounts are extremely small and do not interfere with the functioning of my alloy as described; this action, however, also points to the desirability, hereinbefore expressed, of having the alloy composition maintained within the wide area VI previously noted.

Among the steels included in these studies, there may be mentioned sheets made from "killed" and "semi-killed" steels, carbon steel bars of low and medium carbon content and low alloy steels in bar and sheet form. Examination of these steels showed substantial improvement in 10 internal cleanliness and surface quality.

I claim:

An alloy for deoxidizing steel, said alloy containing 15 to 35% iron, the balance consisting of aluminum, calcium and silicon in the percentages of the balance of 9 to 18% aluminum, 22 to 40% calcium and 45 to 60% silicon, the percentage of aluminum, calcium and silicon in the balance falling within area VI of Figure 2.

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