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METHOD OF PRODUCING CAST STEELS

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The present invention relates to a method of producing steel and ferrous alloys possessing improved properties, and more particularly to a method of consistently producing sound cast steels possessing good ductility, impact resistance and yield ratio on an industrial scale in a practical and commercial manner.

It is well known that in the industrial production of cast steels of similar composition and heat treatment, successive castings were often defective because of excessive porosity, for example, when made in acid electric furnaces or basic open hearth furnaces, and/or because of low ductility. Heats of similar composition sometimes yielded cast steel which possessed poor fluidity in the molten state and low ductility when solid (and properly heat treated), while at other times the metal possessed good ductility but was excessively porous. This erratic production of cast steels resulted in products which were sometimes defective and sometimes satisfactory, but which could not be consistently duplicated. The production of good steel castings was an art requiring considerable skill and good fortune in order to obtain metal which did not possess the above mentioned shortcomings and which were characterized by freedom from porosity and by good ductility. The properties of the resulting castings appeared to be influenced by numerous variables, including the type of charge used, the type of furnace used, the amount of boil, the furnace conditions, the slag, the amount and kind of deoxidants used, and many others which those skilled in the art could not control to consistently produce castings which were sound and possessed good ductility and other satisfactory properties required by the trade.

In view of the erratic production of cast steels and in view of numerous productions of castings with low ductility and/or excessive porosity, those skilled in the art aware of the vexations nature of the problem facing the art and were diligently attempting to solve it. Numerous attempts and proposals have been made to solve the problem. Of these attempts a few of the pertinent ones will be referred to hereinbelow. Thus, in the United States Patent No. 765,932 to Meslans, a method of degasifying cast steel to decrease the amount of blowholes, is described in general terms. During the process, Meslans incorporates aluminum and calcium in the molten steel with a view of removing oxide of carbon, hydrogen and nitrogen. In commercial practice on an industrial scale this method did not consistently yield a product which combined high

ductility with freedom from porosity. Similarly, numerous other deoxidizers and degasifiers have been proposed for the production of sound metal, but it has been found in actual practice that the product had a tendency to be low in ductility, unsuitable for commercial practical applications, etc., when thoroughly degasified. Others who have attempted to solve the problem include Sims et al. who published their article in the Transactions of the American Institute of Mining and Metallurgical Engineers, 1932, vol. 100, page 154. Although Sims et al. were attempting to solve the problem, they found from their tests that steels deoxidized with aluminum possessed low ductility, and were not always free from porosity. When aluminum was used by Sims et al., they observed that there was a change in inclusions accompanied with a decrease in ductility, principally in the reduction of area. Occasionally the addition of aluminum did not affect the ductility, while on the other hand, the erratic behavior of the methods of producing steel would be further evidenced by steels which possessed low ductility even when not treated with aluminum. Other investigators have also published results showing that deoxidation with aluminum caused a decreased elongation and reduction of area of the cast steel. The aforesaid effects of aluminum have been described by McCrae et al. in their article in the U. S. Department of Commerce, Bureau of Standards Journal of Research, vol. 5, 1930, page 1123. Steels deoxidized with aluminum or other powerful deoxidizers and which exhibit this low ductility have been sometimes referred to as "over-reduced" steels. The art appreciated that a rather critical amount of oxygen was required for sound, ductile steel, but it was very difficult to control and very difficult to obtain the proper amount of oxygen in cast steel to yield a product free from porosity combined with good ductility, etc. Prior procedures in steel practice did not give assurance of the production of high quality steels which were consistently free from porosity combined with maximum physical properties, especially ductility. Although many attempts were made to remedy the aforementioned shortcoming, none, as far as I am aware, was entirely successful when put in commercial operation on an industrial scale in consistently producing satisfactory results and could be carried into practical and economic industrial scale operation.

I have discovered a method of producing steel and ferrous alloys free from the disadvantages and defects noted hereinabove which consist-

ently makes sound steel castings having improved physical properties, e. g., high ductility, high yield ratios, high impact resistance, etc., and devoid of porosity and which is capable of being carried into practice satisfactorily and economically when operated on an industrial scale for the manufacture of commercial steel castings.

It is an object of the present invention to provide a method of producing cast steel which is simple, practical and economical and which is capable of being operated consistently and successfully on an industrial scale to produce satisfactory and commercially acceptable products.

It is another object of the present invention to provide a method of manufacturing steel whereby castings can be consistently produced not only free from porosity but also with high physical properties especially high ductility.

It is a further object of the invention to provide a method of producing steel which consistently produces cast steels substantially free from porosity and intergranular distribution of inclusions, particularly sulfide inclusions, and which consistently produces sound cast steels wherein the sulfide inclusions are globular and randomly distributed.

The invention also provides a melting process for producing cast steels which involves a novel combination of operations which permits the use of strong deoxidizers, which thoroughly kills the steel, which produces random distribution of inclusions, including sulfides, and which consistently makes a sound cast steel having good ductility, impact resistance, high yield ratio, etc.

Other objects and advantages of the invention will become apparent to those skilled in the art from the following description.

In general, the invention involves a novel combination of operations which comprises establishing or producing a molten mass of steel or other ferrous alloy in a customary manner, oxidizing the molten mass in excess, i. e., over-oxidizing, partially deoxidizing with silicon, manganese or the like, adding a sulfide fixer from the group consisting of calcium, beryllium and zirconium to the bath containing excess oxygen, and adding aluminum thereby thoroughly killing the steel or ferrous alloy and producing random distribution of inclusions, including sulfides whereby a sound cast product is consistently made having improved physical properties, especially high ductility. One or more of the sulfide fixers may be added in any convenient form, e. g., metallic calcium, calcium silicon alloys, silicon zirconium alloys, beryllium copper alloys, etc., as will be apparent to those skilled in the art. The aluminum may be added with the sulfide fixer or afterwards, and may be added in either alloyed or unalloyed form. It is well known that low ductility is consistently associated with intergranular, chain-like sulfides while good ductility is obtained when the sulfides are globular and randomly dispersed. The type of sulfide inclusion is related to the oxygen or iron oxide content of steel, intergranular sulfides being obtained with low oxygen and iron oxide contents and randomly distributed sulfides being characteristic of high oxygen and iron oxide contents. A characteristic and consistent relationship exists between low ductility and intergranular sulfides, while steels too high in iron oxide are generally defective due to excessive porosity, etc. Intergranular sulfide condition may occur with any melting process, acid electric, basic electric, or basic open hearth. Steels subject to inter-

granular sulfides have poor fluidity in the molten state and low ductility, etc. when cast. Relatively high oxygen content is required for good fluidity and ductility thereby resulting often times in porosity. I have found that porosity will develop because of insufficient deoxidants, that low ductility will result because of insufficient oxygen content promoted by reducing conditions during melting, by the use of strong deoxidizers, etc., and that a narrow and critical balance must be adapted between the oxygen necessary for good ductility and the excess causing porosity. The desire for soundness, a primary requisite of good metal, has led to the use of strong deoxidizers such as aluminum, especially in converter and acid electric steel. It has been noted that aluminum killed steels possess low ductility. Aluminum is an excellent deoxidizer (0.93 to 0.08%) which assures soundness in cast steels but causes low oxygen content, poor fluidity and intergranular sulfides when cast. Its normal use is precluded in steels, particularly alloy steels, with high ductility requirements. In some instances, small amounts of aluminum are more detrimental than larger amounts. The present invention enables the art to use aluminum with none of its detrimental effects, such as low ductility. I have found that manganese appears to be a poor desulfurizer under reducing conditions, forming sulfides that appear on the grain boundaries, and that manganese is unable to disperse sulfides in a melt of low oxygen content. Silicon, another strong deoxidizer, also causes low ductility because of low oxygen content.

In carrying the present invention into practice, the new process contemplates over-oxidizing the molten steel by any of the methods known to those skilled in the art. This may be accomplished by introducing iron ore, iron oxide, mill scale, nickel oxide (when treating a molten nickel steel), by oxidation with the atmosphere and the like. In some instances, the melt may be in a sufficiently oxidizing condition without the need of further oxidation. The melt must contain sufficient excess oxygen, i. e., be over-oxidized, at the time the sulfide fixer, e. g., calcium, is added. The amount of oxidation necessary to produce a properly oxidized molten bath will vary the charge, furnace conditions, etc. For example, when adding iron ore, etc., the amount introduced will vary with the proportions of pig iron and scrap in the charge as will be apparent to those skilled in the art. However, the total amount added will include not only the normal amounts added for the conversion of the charge to the desired steel, but must include the additional amount required to produce sufficient excess oxygen in the molten steel at the time the sulfide fixer is added. It is preferred to over-oxidize the bath well beyond the minimum thereby assuring proper oxidation. Generally speaking, a spoon test is a satisfactory test which may be used to determine when sufficient excess oxygen is present. An operator using the spoon test will know that the molten bath contains more than the minimum required amount of oxygen if the metal effervesces slightly when cooling. Numerous other tests will also indicate when sufficient excess oxygen is present. As will be apparent to those skilled in the art, the various tests may easily be correlated with the spoon test and used to measure excess oxygen (or oxide) content or to check the spoon test. Thus, for example, the sparking of a molten test sample will indicate the presence of excess oxygen. The appearance of

slag samples will also indicate the presence of sufficient excess oxygen, since a relationship exists between the oxygen in the slag and in the bath. For example, the coloring of the slag samples will indicate when sufficient excess oxygen is present. Under certain conditions a solidified slag sample will indicate proper oxygen content when the central portion of the surface has a silver-like appearance. This central portion decreases in size with decreasing oxygen content and takes on a black color with lower oxygen content. This and other tests should be correlated with the spoon test, particularly whenever conditions are varied, e. g., slag composition, composition of steel being produced, etc. Also, a porous test button will indicate the presence of excess oxygen. Still again, an operator will often note a slight activity in the molten metal in the furnace when the bath contains an amount of oxygen within the contemplation of the present invention. Steels in this condition are known to the trade as semi-killed or partially deoxidized steels. These and numerous other possible tests are available in determining when sufficient excess oxygen is present in the bath. An addition of silicon manganese or ferro silicon and ferro manganese is made to the oxidized bath to restrain active boiling thereby maintaining approximately a constant level of elements while the preliminary analysis is being run and to prevent further excessive loss of elements such as carbon, manganese, silicon, etc., which are then introduced in the desired amounts, but the amount of oxygen remaining in the bath must, after the additions, exceed the required minimum and can easily be determined as mentioned above, for example, by the spoon test or any other test. Even in the presence of about 0.30% to 0.40% of silicon and about 0.60% to 0.80% of manganese, the molten steel should effervesce slightly when a spoon test is taken. The oxidized bath is treated with at least one of the sulfide fixers, i. e., calcium, beryllium or zirconium, in an amount corresponding to the sulfur content of the bath. Normally, a steel bath will contain about 0.02% to about 0.05% sulfur, and, usually about 0.03% to 0.04%. When calcium is the sulfide fixer to be added to the oxidized bath of molten steel, it may be introduced in amounts varying between about 0.03% to 0.60% depending on the amount of sulfur present, etc. Generally about 0.05% to about 0.2% calcium, e. g., 0.1%, will give satisfactory results. Beryllium, more powerful than calcium, need only be added in amounts from 0.005% up to 0.02%, although larger amounts up to 0.25% are effective, and zirconium, not quite as effective as calcium, may be added in amounts from about 0.05% to about 0.60%. About 0.01% to about 0.04% of beryllium, e. g., 0.02%, and about 0.10% to about 0.20% of zirconium, e. g., 0.1%, will generally produce satisfactory results. The total amount of sulfide fixer, etc., added to the molten metal may not necessarily be present in the finished material. Should the sulfur content exceed the upper limit of the range normally found in steel, i. e., 0.05%, a larger amount of sulfide fixer should be added than is normally added, as will be apparent to those skilled in the art. Molten steels containing 0.08% sulfur have been successfully treated, and steels with 0.15% sulfur have responded in accordance with the present invention. However, steel baths containing about 0.01% sulfur apparently do not contain sufficient sulfur to result in low ductility and such steels are fairly

successfully treated by prior art methods, e. g., killing with aluminum, a treatment which cannot consistently produce satisfactory results with higher sulfur contents, although the present invention may also be used in treating such low sulfur steels. Molten steels containing about 0.01% sulfur are rare and are not met with in ordinary steel practice. Care must be taken that the sulfide fixer, contemplated by the present invention be added at a time when the molten bath is in an oxidized state predisposed for random distribution of the sulfides. This condition will be referred to as an over-oxidized condition. Any test used must indicate wherever or not the molten steel is in an oxidized state disposed to random distribution of sulfides when solid. The slight effervescence obtained in the spoon test is one indication that the molten steel is in this condition. The sulfur is apparently not removed from the molten bath by the sulfide fixer but is distributed randomly instead of intergranularly. Steel baths of normal sulfur still contain a substantial amounts of sulfur after treatment, e. g., 0.036%. The calcium, calcium silicon, etc. is wrapped in a container and plunged into the melt, to prevent losses at the surface. Any other suitable means may be used to introduce the sulfide fixer into the molten mass so long as care is taken to prevent the calcium, etc., from burning on the surface of the melt. Calcium silicon is readily added to acid electric and open hearth melts in carrying out the present invention by wrapping it in heavy paper bags which are tossed into the tapped stream of metal during pouring into the ladle and immediately carried beneath the surface of the melt. For small heats, screen containers can be attached to iron rods and used to plunge the calcium material into the bath. The sulfide fixer may be added either in the furnace or ladle, but is preferably added in the ladle when treating large heats. Aluminum, according to the invention, may be added along with the sulfide fixer or afterwards but not any appreciable time before. By "appreciable time" I mean any interval of time exceeding about 30 seconds to about one minute which usually appears to be the length of time necessary for the aluminum to exert deleterious effects on the condition of the bath that is required for the proper functioning of the calcium, beryllium, or zirconium. The addition of aluminum to an oxidized steel will alter the condition of the bath so that subsequent additions of the sulfide fixer will not prevent low ductility, etc., in the finished steels. While the time necessary for the aluminum to exert this deleterious effect will vary depending on conditions, e. g., condition of bath, the manner in which the aluminum is added, size of melt, etc., the length of time required for the aluminum to alter the condition of the bath may readily be determined for the particular conditions of the melts being treated. Under certain conditions an interval of two minutes after the addition of aluminum is sufficient to produce a bath which will be characterized by intergranular sulfide condition and low ductility when cast. It is preferred to add the aluminum along with or after the sulfide fixer rather than risk the possibility that the sulfide fixer be added too late, although, as pointed out hereinabove, a short time interval may exist within which it will be safe to add the aluminum first. If the bath is disposed to intergranular sulfide condition, e. g., when the aluminum is added more than an appreciable time before the calcium, it cannot be changed

without again subjecting the bath to oxidation. Aluminum, in accordance with the invention, may be added in amounts from about 0.01% to about 0.25% and about 0.04% to 0.10% will often be sufficient.

For the purpose of giving those skilled in the art a better understanding of the invention, I will now describe an illustrative method of producing cast steel free from porosity combined with maximum physical properties.

EXAMPLE

A normal charge of steel comprising about 60% scrap and 40% pig iron, some iron ore, and considerable lime is melted down in the usual manner in a basic open hearth, and followed by the customary boil. The slag is conditioned with fluorspar to increase the fluidity or lime to decrease it. High oxide contents should be maintained throughout the heat, planning to have the steel not quite killed even with 0.30 to 0.40% silicon present; any suitable test may be used to determine whether excess oxygen is present, e. g., the spoon test. Mill scale, iron oxide, iron ore, etc., should be added if necessary to supply excess oxygen. Basic open hearth steel slags usually contain 13 to 16% iron oxide but may run as low as 10% and as high as 20%. The slag should preferably run on the high side, e. g., 20% iron oxide. When the carbon is at 0.10-0.20%, an addition of silicon manganese or ferro manganese and ferro silicon is made to stop the boil and the carbon and manganese checked to determine the amounts required to attain the desired composition. When the desired analysis is attained, i. e., carbon, manganese, silicon and alloy content, with a slight excess of oxygen, the calcium and the aluminum are then added, e. g., in the ladle. The calcium is preferably added

poured two minutes after the aluminum addition. These steels were properly normalized and drawn (1600° to 1650° F. and 1200° to 1250° F., respectively). A cast low oxide steel deoxidized in the regular manner with silicon manganese and possessing low ductility, contained 0.0097% total oxygen, while a ductile high oxide steel, also deoxidized in the regular manner with silicon manganese, but susceptible to porosity, contained 0.0134% total oxygen. Cast steels prepared in accordance with the present invention consistently yield a product which is low in oxygen, free from porosity and superior in physical properties. Table II gives the results obtained from some properly oxidized heats treated in accordance with the present invention, using silicon manganese with proper oxygen and various amounts of calcium and about 0.06% aluminum. All heats were of usual sulfur content and were held two or three minutes before pouring. The cast steels, containing about 1½% nickel, 1½% manganese and 0.30% carbon, were all properly normalized and drawn before being subjected to tests. No. 4 to No. 8 inclusive represent steels treated simultaneously with calcium and aluminum while No. 9 is a steel treated with aluminum about 1 to 2 minutes after the calcium addition. The heats to which 0.05% calcium or more has been added have excellent ductility, high yield ratio, exceptional toughness, all in combination with very low oxygen contents ensuring freedom from porosity. A cast steel treated with calcium and aluminum in accordance with the present invention and characterized by high ductility had a total oxygen content of about 0.0065% after treatment. As little as about 0.03% calcium appears to have a beneficial effect; even when calcium is added in excess of about 0.60%, the resulting steels have satisfactory properties.

Table I

No.	Per-cent C	Per-cent Ni	Per-cent Mn	Per-cent Si	Treat-ment	Y. P.	El.	R. A.	Impact	Y. R.
1....	0.30	1.5	1.5	0.40	S. P.	50.0	15.0	18.7	21	43.6
2....	0.31	0	1.94	0.40	S. P.	56.0	19.2	29.5	21.5	61.4
3....	0.30	1.5	1.5	0.40	S. P. A..	67.7	21.0	36.0	28	72.5

Y. P.=Yield point in thousand pounds per square inch.
El.=Elongation in percent.
R. A.=Reduction in area in percent.
Impact=Charpy impact in foot pounds.
Y. R.=Yield ratio=ratio of yield point to tensile strength in percent.
S. P.=Treated in accordance with standard practice.
S. P. A.=Treated in accordance with standard practice and finished with 0.06% aluminum.

in an amount totaling about 0.05% to about 0.20%, for example, 0.1%, and the aluminum amounting from about 0.01% to about 0.25%, for example, 0.06%. This procedure results in the consistent production of steel castings of very low oxygen content substantially free from porosity and with random, globular sulfides and high ductility, etc.

Steels which have not been subjected to any special oxidation are often characterized by low ductility and a chain-like distribution of the light gray sulfide inclusions which appear to encircle the original grains of the cast metal and are sometimes called intergranular sulfides. The physical properties of three typical low oxide steels produced in the regular manner which contained usual amounts of sulfur and were sound but had inferior physical properties are given in Table I. No. 3 is a well oxidized heat

Table II

No.	Treatment after oxidation	Y. P.	El.	R. A.	Im-pact	Y. R.
4...	0.02% Ca and 0.06% Al.	69.8	21.0	35.7	32	69.2
5...	0.05% Ca and 0.06% Al.	67.3	26.7	53.1	39	68.6
6...	0.1% Ca and 0.06% Al.	71.0	26.0	62.2	---	71.0
7...	0.1% Ca and 0.06% Al.	65.0	28.8	56.0	47	74.5
8...	0.2% Ca and 0.06% Al.	67.2	30.7	58.1	47	71.6
9...	0.1% Ca then 0.06% Al.	69.7	28.0	55.5	60.5	76.8

Y. P.=Yield point in thousand pounds per square inch.
El.=Elongation in percent.
R. A.=Reduction in area in percent.
Impact=Charpy impact in foot pounds.
Y. R.=Yield ratio=ratio of yield point to tensile strength in percent.

A properly oxidized bath apparently has no disposition towards intergranular sulfide distribution and possesses excellent properties when cast after the addition of the sulfide fixer and

aluminum whereas heats treated with aluminum only, in amounts sufficient to assure freedom from porosity, will result in a product possessing poor ductility, etc. Heats treated with aluminum an appreciable time before the addition of calcium or other sulfide fixer will also possess poor properties when cast and must be subjected to sufficient oxidation to remove the aluminum before the molten bath can be properly treated in accordance with the present invention.

Zirconium or beryllium may be used instead of calcium as a sulfide fixer and some typical results in treating properly oxidized baths or molten steel are given in Table III. The physical properties are for normalized and drawn (tempered) cast steel containing 0.30% carbon, 1.5% nickel, 1.5% manganese, 0.40% silicon, and average sulfur. No. 10 to No. 12 inclusive were treated simultaneously with the sulfide fixer and aluminum; No. 11 was well oxidized before the addition of zirconium and aluminum. Table III shows that 0.02% beryllium is equivalent to about 0.1% calcium. Zirconium treated steels appear to possess excellent though slightly lower ductility than those treated with the same amount of calcium, but greater amounts will give equally good properties. Heats treated with titanium, molybdenum and tantalum, which are elements reported to have an affinity for sulfur, appear to

have nearly double the impact resistance, have better yield ratio, have a toughness that is hardly affected by increasing normalizing temperature whereas the impact resistance falls off rapidly for the other two types, have finer grain size, wider heat treating temperature ranges and are least susceptible to porosity. Steels produced in the regular manner with a silicon manganese deoxidation have a high susceptibility to porosity and a coarse grain size, while aluminum killed steels, i. e., steels to which more than about 0.02% aluminum have been added and with a low oxygen content, possess poor fluidity and poor ductility. Steels produced in accordance with the present invention consistently have lower oxide contents than regularly finished steels combined with good ductility, good fluidity, fine grain size, extremely low susceptibility to porosity, etc., thereby consistently assuring a cast steel characterized by soundness, always a fundamental requisite, and maximum physical properties.

Table IV is illustrative of the physical properties of some of the plain and alloy cast steels containing usual amounts of sulfur treated in accordance with the present invention and produced by finishing a properly oxidized melt with about 0.1% calcium and about 0.06% aluminum; nickel, nickel-chromium, nickel-molybdenum, manganese, and carbon steels are used as examples.

Table IV

No.	Percent C	Percent Ni	Percent Cr	Percent Mo	Percent Mn	Percent Si	Y. P.	Y. R.	El.	R. A.	Impact
13.....	0.19	2			0.65	0.35	57.0	75.1	34.0	60.4	50
14.....	0.35	1.5	0.75		0.75	0.35	65.0	62.9	23.0	44.6	28.5
15.....	0.30	1.75		0.25	0.75	0.35	69.3	78.2	26.0	52.5	41
16.....	0.30				1.5	0.35	59.3	70.0	30.0	57.6	48
17.....	0.30				0.75	0.35	47.6	67.2	32.5	46.0	29

Y. P.=Yield point in thousand pounds per square inch.

El.=Elongation in percent.

R. A.=Reduction in area in percent.

Impact=Charpy impact in foot pounds.

Y. R.=Yield ratio=ratio of yield point to tensile strength in percent.

have no merit, the ductility being similar to that obtained with aluminum alone.

Table III

No.	Treatment after oxidation	Y. P.	El.	R. A.	Y. R.
10.....	0.1% Zr and 0.06% Al...	65.4	27.0	51.6	71.3
11.....	0.1% Zr and 0.06% Al...	64.0	28.0	52.0	70.8
12.....	0.02% Be and 0.06% Al...	67.0	26.7	50.3	68.4

Y. P.=Yield point in thousand pounds per square inch.

El.=Elongation in percent.

R. A.=Reduction in area in percent.

Y. R.=Yield ratio=ratio of yield point to tensile strength in percent.

Tables I, II and III clearly indicate some of the advantages of the present invention. Nickel-manganese steels finished in the regular manner showed a reduction of area below 40% and as low as about 18%, although they sometimes have a reduction of area up to 55% but are coarse grained and susceptible to porosity, while similar steels properly oxidized and finished with proper amounts of the sulfide fixer and aluminum consistently have high reduction of area, generally exceeding 50%, while possessing low oxygen content, absolute freedom from porosity, and fine grained structures.

Steels treated with calcium and aluminum consistently possess superior properties to sound steels treated only with calcium or only with silicon manganese. The calcium aluminum steels

In all cases the calcium-aluminum treatment results in steels consistently having a yield ratio at least as high as for regularly finished steels and in most cases decidedly superior while maintaining a high ductility. The toughness is increased wherever comparative values are available and all steels finished with the calcium-aluminum addition are free from porosity while regularly finished steels have a rather high susceptibility to porosity. Calcium-aluminum treated steels while somewhat susceptible to temper brittleness, have greater toughness than regularly produced steels even in the embrittled state; they also possess superior toughness and impact resistance at low temperatures to regularly produced steels.

While the invention has been described with particular reference to cast steels, it is applicable to cast steels and products whose properties depend on the properties of the steel as cast. It is also to be understood that when I refer to steel in the description and the accompanying claims I include therein plain carbon steels, alloy steels, and other iron base alloys subject to the difficulties and disadvantages mentioned hereinabove. These cast steels may have various carbon contents, say about 0.08% to about 0.75% or more, and various alloy contents, say from an effective percentage to about 7% or 8% or more and usually may have various elements present, 75

such as phosphorus, manganese, silicon, etc., as those skilled in the art will readily understand.

Although the present invention has been described in conjunction with preferred embodiments, it is 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 readily understand.

I claim:

1. A method of consistently producing cast steels possessing freedom from porosity combined with high ductility which comprises establishing a bath of molten steel containing about 0.02% to about 0.05% sulfur, over-oxidizing said bath by adding iron oxide in such amounts that when a spoon test is made the molten steel of the test sample will effervesce slightly upon cooling, adding silicon and manganese to said bath and adjusting the composition of said molten steel while maintaining excess oxygen in said molten steel in such amounts that when a spoon test is made the molten steel of the test sample will effervesce upon cooling, transferring a portion of said molten steel to a ladle, adding to said portion of molten steel containing excess oxygen about 0.1% calcium and about 0.06% aluminum in such a manner that said aluminum is not added an appreciable time before said calcium, and casting the molten steel thus treated whereby low oxygen cast steels are consistently produced which combine freedom from porosity with high ductility.

2. A method of consistently producing fine grained cast steels substantially devoid of porosity and possessing high ductility which comprises establishing a molten steel bath containing about 0.02% to about 0.05% sulfur, maintaining high oxide content throughout the heat, adding silicon and manganese and adjusting the composition to the desired amounts while maintaining excess oxygen in said molten bath in such amount that when a spoon test is made the molten steel of the test sample will effervesce upon cooling, adding to said molten steel containing excess oxygen about 0.1% calcium and about 0.06% aluminum in such a manner that said aluminum is not added an appreciable time before said calcium and casting the metal thus treated whereby fine grained steels are consistently produced which combine freedom from porosity with high ductility.

3. A method of consistently producing fine-grained cast steels substantially devoid of porosity and possessing high physical properties, including high ductility, which comprises establishing a bath of molten steel containing about 0.02% to about 0.05% sulfur, excessively oxidizing said bath of molten steel to introduce excess oxygen in the molten steel in such amount that when a spoon test is made the molten steel of the test sample will effervesce upon cooling, adding desired amounts of silicon and manganese to said bath while maintaining excess oxygen in said molten steel in such amount that when a spoon test is made the molten steel in the test sample will effervesce upon cooling, adding to said molten steel containing excess oxygen about 0.1% calcium and about 0.06% aluminum in such manner that said aluminum is not added an appreciable time before said calcium, and casting the molten steel thus treated whereby low oxygen cast steels are consistently produced which possess freedom from porosity combined with high physical properties, especially high ductility.

4. A method of consistently producing fine grained, low oxygen cast steels which possess freedom from porosity combined with high ductility which comprises establishing a bath of molten steel containing about 0.2% to about 0.08% sulfur and desired amounts of carbon, manganese, silicon, and alloying elements; conditioning said bath by regulating the oxygen content of the molten steel so that said steel contains excess oxygen in such amount that when a spoon test is made the molten steel in the test sample will effervesce upon cooling after the desired amounts of manganese and silicon have been introduced; treating said molten steel containing excess oxygen with about 0.1% calcium and about 0.06% aluminum, said aluminum being added in such a manner that it is not added an appreciable time before said calcium; and casting the molten steel thus treated whereby fine grained, low oxygen cast steels are consistently produced which possess freedom from porosity combined with high ductility.

5. A method of consistently producing low oxygen cast steels possessing freedom from porosity combined with high ductility which comprises establishing a bath of molten steel containing about 0.02% to about 0.08% sulfur; over-oxidizing said bath to such extent that when a spoon test is made the molten steel in the test sample will effervesce upon cooling; adding silicon and manganese to said bath to adjust the composition thereof while maintaining said bath in an over-oxidized condition such that when a spoon test is made the molten steel of the test sample will effervesce; treating said over-oxidized molten steel with at least one sulfide fixer from the group consisting of calcium, beryllium and zirconium in amounts of about 0.05% to about 0.2%, about 0.01% to about 0.04%, and about 0.1% to about 0.2%, respectively; adding about 0.4% to about 0.1% of aluminum along with or subsequent to said sulfide fixer treatment but not an appreciable time before; and casting the molten steel thus treated whereby low oxygen cast steels are consistently produced which combine freedom from porosity with high ductility.

6. A method of consistently producing low oxygen steels possessing freedom from porosity combined with high physical properties which comprises establishing a bath of molten steel containing about 0.01% to about 0.15% of sulfur and desired amounts of carbon, manganese, silicon and alloying elements; regulating the oxygen content of the molten steel so that said steel is sufficiently oxidized after the desired amounts of silicon and manganese have been introduced that when a spoon test is made the molten steel of the test sample will effervesce upon cooling; treating said oxidized molten steel containing desired amounts of silicon and manganese with at least one sulfide fixer from the group consisting of calcium, beryllium and zirconium in amounts of about 0.03% to about 0.6%, about 0.005% to about 0.25%, and about 0.03% to about 0.6%, respectively; adding about 0.01% to about 0.25% of aluminum along with or subsequent to said sulfide fixer treatment but not any appreciable time before; and casting the molten steel thus treated whereby low oxygen cast steels are consistently produced which combine freedom from porosity with high physical properties, especially high ductility.

7. A method of consistently producing low oxygen steels possessing freedom from porosity combined with high physical properties which

comprises establishing a bath of molten steel containing about 0.02% to about 0.08% sulfur and desired amounts of carbon, manganese, silicon and alloying elements; regulating the oxygen

5 content of the molten steel so that said steel is oxidized after the desired amounts of silicon and manganese have been introduced to such extent that when a spoon test is made the molten steel of the test sample will effervesce upon cooling; treating said oxidized molten steel contain-
10 ing desired amounts of silicon and manganese with at least one sulfide fixer from the group consisting of calcium, beryllium and zirconium in amounts of about 0.05% to about 0.2%, about 0.01% to about 0.04% and about 0.1% to about 0.2%, respectively; adding about 0.04% to about 0.1% of aluminum along with or subsequent to said sulfide fixer treatment but not any appreciable time before; and casting the molten steel
20 thus treated whereby low oxygen cast steels are consistently produced which combine freedom from porosity with high physical properties, especially high ductility.

8. A method of consistently producing low oxygen cast steels possessing freedom from porosity combined with high ductility which comprises establishing a bath of molten steel containing about 0.02% to about 0.15% sulfur; over-oxidizing said bath to such extent that when
30 a spoon test is made the molten steel of the test sample will effervesce; adding silicon and manganese to said bath while maintaining said bath in an over-oxidized condition such that when a spoon test is made the molten steel of the test sample will effervesce; treating said over-oxidized molten steel with at least one sulfide fixer from the group consisting of calcium, beryllium and zirconium in amounts of about 0.03% to about 0.6%, about 0.005% to about 0.25%, and about 0.03% to about 0.6%, respectively; adding about 0.01% to about 0.25% of aluminum along with or subsequent to said sulfide fixer treatment

but not any appreciable time before; and casting the molten steel thus treated whereby low oxygen cast steels are consistently produced which combine freedom from porosity with high ductility.

9. A process for consistently producing sound, ductile steel castings containing randomly distributed globular sulfide inclusions which comprises establishing a bath of molten steel containing about 0.02% to about 0.15% sulfur and desired amounts of carbon, manganese and silicon; conditioning the bath of molten steel by regulating the oxygen and oxide content therein to that amount corresponding to the oxygen and oxide content which will cause effervescence in a molten test sample when a spoon test is made
15 after manganese and silicon have been added; subsequently treating the oxidized molten steel containing desired amounts of manganese and silicon and having an oxygen and oxide content corresponding to the oxygen and oxide content 20 which will cause effervescence in a molten test sample when a spoon test is made with at least one sulfide-fixer from the group consisting of calcium, beryllium and zirconium within the range of about 0.03% to about 0.6%, about 0.005% to about 0.25%, and about 0.03% to about 0.6%, respectively, thereby producing a molten steel bath disposed to randomly distributed sulfide inclusions; and treating said molten steel with about 0.01% to about 0.25% of aluminum
30 thereby completely deoxidizing said molten steel bath, said aluminum being added along with or subsequent to said sulfide-fixer treatment but not an appreciable time before; and casting the thus-treated molten steel whereby sound, fine-grained steel castings are consistently produced which are characterized by randomly distributed globular sulfide inclusions and high ductility compared to a similar aluminum-killed steel not subjected to the aforesaid operations.

ALBERT P. GAGNEBIN.

CERTIFICATE OF CORRECTION.

Patent No. 2,204,585.

June 18, 1940.

ALBERT P. GAGNEBIN.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 41, after "art" insert --were--; and for "vexations" read --vexatious--; same page, second column, line 25, for "inverstigators" read --investigators--; page 3, first column, line 37, for "spon" read --spoon--; and second column, line 14, for "wherever" read --whether--; page 4, second column, line 8, for "deoxodized" read --deoxidized--; page 6, second column, line 41, claim 5, for "0.4%" read --0.04%--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of September, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.