

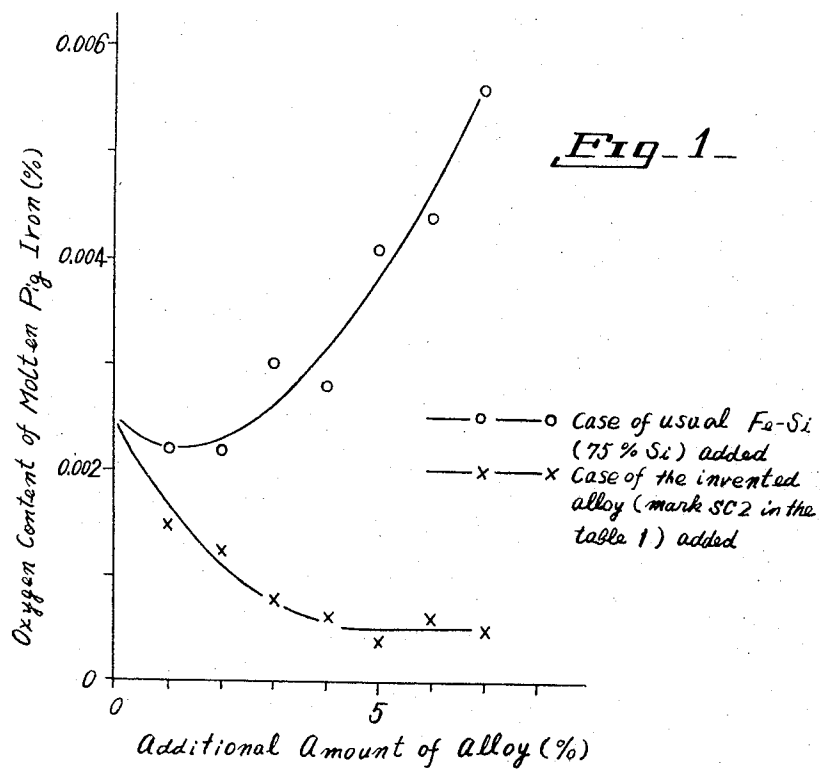
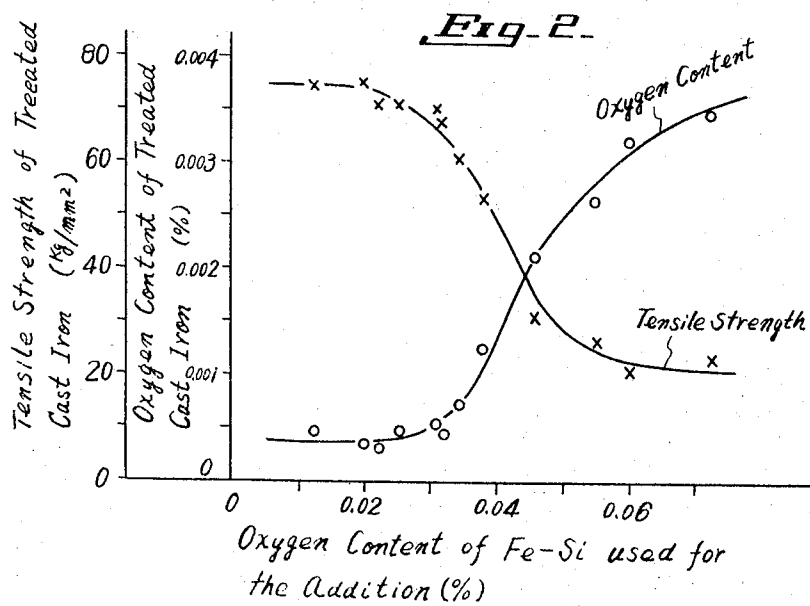
Feb. 14, 1967

TOHEI OTOTANI ETAL
LOW OXYGEN-SILICON BASE ADDITION ALLOYS FOR IRON AND
STEEL REFINING

3,304,174

Filed Aug. 17, 1964

2 Sheets-Sheet 1



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Fig. 3

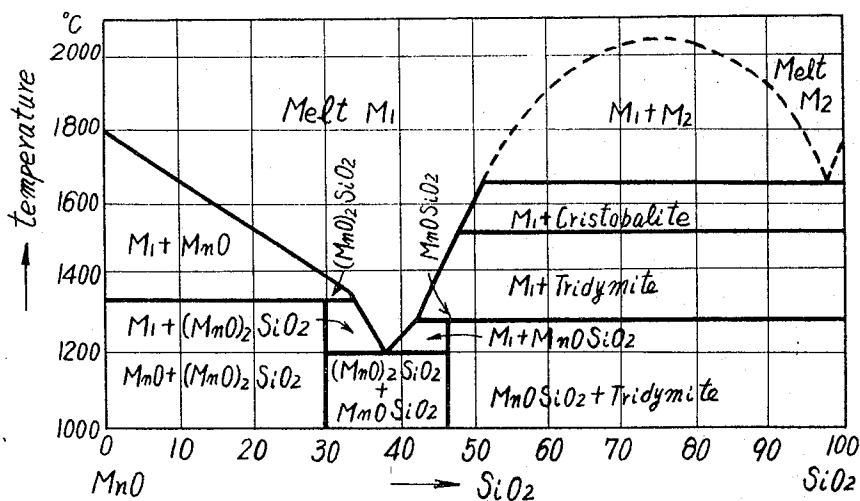
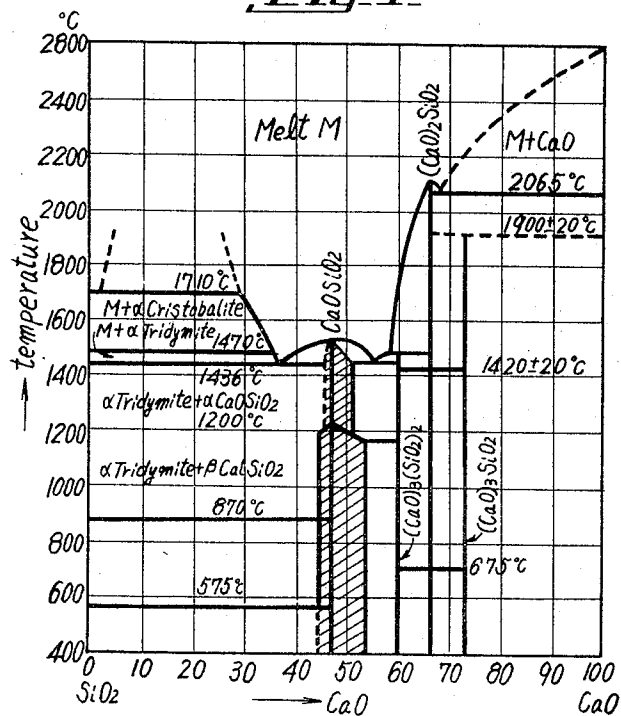


Fig. 4



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LOW OXYGEN-SILICON BASE ADDITION ALLOYS
FOR IRON AND STEEL REFINING

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The present invention relates to low oxygen-silicon
base addition alloys for iron and steel characterized in
that they contain 50 to 97% silicon, 0.1 to 30% manga-
nese, 0.1 to 10% calcium and the remainder iron, the
oxygen content being less than 0.04%.

The object of the invention is to improve the properties
of refining alloys such as the refining effect and economi-
cal problems as compared with those of conventional
Fe-Si, Ca-Si, Ca-Si-Mn, Fe-Si-Mg alloys and misch metal.

The refining alloys mentioned above have heretofore
been used for the removal of oxygen, sulfur and other
impurities in case of casting iron, steel and non-ferrous
alloys, or for the graphitization of high carbon steels
after elimination of impurities or for improvement of the
graphite form in cast iron.

The compositions of the refining alloys by the present
invention are shown in Table 1 as an example, wherein
the number is shown in weight percent.

TABLE 1

Mark	Si	Mn	Ca	O	Fe	Others
SC1-----	94.1	0.3	4.7	0.038	0.4	0.462
SC2-----	77.0	0.4	3.9	0.025	15.1	3.575
SC3-----	67.4	2.3	5.1	0.020	20.7	4.480
SC4-----	58.5	1.1	7.4	0.026	28.9	4.074
SMC1-----	68.9	5.7	8.1	0.029	15.1	2.171
SMC2-----	62.5	12.4	7.2	0.028	14.7	3.172
SMC3-----	56.6	18.6	5.9	0.032	17.2	1.668

As shown in Table 1, the oxygen content in the alloys
is less than 0.04%. On the other hand, the inventors have
found that the oxygen content in conventional Fe-Si al-
loys and other Si alloys is more than 0.04% in almost all
alloys. The oxygen content in such cases was ascertained
by the analysis of oxygen by a vacuum fusion method or
by calculation from the analysis value of oxide.

The other elements listed in Table 1 are elements en-
tering mainly in the manufacturing steps, such as C, Cr,
Cu, Ni, P, S, Te, Na, Mg, K, Ti, Y, Li, Zn, Zr, lanthanum
series elements (rare earth elements).

The reason why the oxygen content is limited to be
less than 0.04% as one of the characteristics of the in-
vention is based on the fact that it limits the oxide con-
tent in the alloy and improves the activity of elements
having the refining action such as Si, Mn and Ca and also
increases their affinity with oxygen and other impurities
in the melt.

For a better understanding of the invention, reference
is taken to the accompanying drawing, in which,

FIG. 1 shows curves illustrating the test results of the
deoxidizing action taken for comparison of usual Fe-Si
alloy (75% Si) with the alloy of the invention having
similar composition thereto,

FIG. 2 shows curves illustrating the relation between
the oxygen content in the Fe-Si addition alloy and that in
the cast iron treated with the addition alloy and the tensile
strength of the cast iron at as-cast state, and

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FIGS. 3 and 4 are equilibrium diagrams of SiO₂-MnO
system (White-Howat-Hay) and SiO₂-CaO system (Shep-
herd-Rankin, Ferguson-Merwin) respectively illustrating
that the oxides produced by using the alloys of the inven-
tion are mainly complex system of SiO₂-MnO-CaO series.

After fundamental experiments the inventors have as-
certained as shown in FIG. 1 that there is a great differ-
ence between the deoxidizing action of conventional Fe-Si
alloy (75% Si) and the invented alloy which has a similar
composition except oxygen to conventional Fe-Si alloy.

In FIG. 1, the curves illustrate the relation between the
added amounts and the oxygen contents in cast irons after
the addition of these alloys. The composition of the cast
iron before the addition of the alloys was 3.2% C, 0.1%
Si, 0.2% Mn, 0.0025% O₂, and the remainder Fe. The
composition of the alloys used for the experiments is as
follows:

COMPOSITIONS OF TESTED ALLOYS

	Si	Mn	Ca	O	Fe	Others
Conventional Fe-Si alloy.	76.6	0.1	0.05	0.063	19.6	3.587
Alloy of the invention----	77.0	0.4	3.9	0.025	15.1	3.575

As shown in FIG. 1, when a conventional Fe-Si alloy
of high oxygen content is added in 1 to 2% to the molten
pig iron, the oxygen content in the cast iron is reduced
slightly, but the oxygen content in the cast iron increases
reversely with increase of the addition in excess of 3%.

This phenomenon is due to the fact that the oxide
(mainly SiO₂) in the Fe-Si alloy is brought into the cast
iron melt and a part of which is suspended in the melt
without flotation. Even if Fe-Si alloy containing a large
amount of oxide is added to the molten cast iron, the
quantity of the soluble oxygen should be reduced by
silicon. However, the oxygen content in cast iron is in-
creased due to the introduction of oxide is so much larger
than the reduced amount of soluble oxygen.

On the contrary, when the low oxygen content alloy
of the invention is added, the oxygen content in the cast
iron is reduced considerably as go with the addition in-
creases (FIG. 1).

As shall be mentioned later, the remarkable deoxidiz-
ing effect in the use of alloys of the invention is also
due to the formation of floatable oxides, chiefly, the
SiO₂-MnO-CaO system, in molten iron or molten steel
by addition of the alloy containing Mn and Ca besides Si.

The inventors have made experiments on 12 kinds of
the conventional and invented Fe-Si alloys which have
low contents of Mn, etc. elements except Fe and Si by
adding each 3.5% to the cast iron having a definite com-
position, and determined the relation between oxygen
content in the added Fe-Si alloy and the as-cast tensile
strength of the added cast iron. The reason why cast iron
was taken for the experiments is due to the fact that the
deoxidized extent is expressed as the variation in the shape
of graphite and it depends on the as-cast tensile strength.

The experimental results are shown in FIG. 2.

Experimental conditions

(A) Composition of Fe-Si alloy samples:

(1) Conventional Fe-Si alloy—	Percent
Si content -----	74.2-74.8
O content -----	0.046-0.073
(2) Fe-Si alloy of the invention—	Percent
Si content -----	63.2-67.5
O content -----	0.012-0.038
Mn content -----	0.2-5.9
Ca content -----	0.5-4.3

(B) Composition (percent) of cast iron before addition of the Fe-Si alloy:

C	3.6
Si	0.6
Mn	0.2
S	0.009
O	0.0021

(C) Temperature of the cast iron melt in case of the Fe-Si alloy addition: 1,450° C.

As shown in FIG. 2 the oxygen content of the Fe-Si alloy was limited to 0.04% as the reference point and less than it the deoxidizing effect became more powerful and over than it the deoxidizing effect become reduced. Such effects influence the tensile strength: If the oxygen content of cast iron is lower, the tensile strength becomes higher, but with increase of the oxygen content, the tensile strength is reduced. In this test, the relation between the tensile strength of the cast iron and the shape of graphite was investigated with the following results:

Shape of graphite:	Tensile strength, kg./mm. ²
Spheroidal graphite only	>68
Spheroidal graphite and wormy flake graphite	53 to 61
Wormy flake graphite and flake graphite	27 to 31
Flake graphite only	21 to 23

From the results of the above experiments the inventors have confirmed the importance of the oxygen content in the silicon base alloys and further that the oxygen content in the alloy should be less than 0.04% in order to obtain a remarkable refining effect. Moreover, the large refining effect of the alloy of the invention is not only based on the oxygen content less than 0.04%, but also on the contents of Mn and Ca besides Si.

As already explained, the inventors have noticed that in molten steel or molten cast iron SiO₂ or silicate is suspended and hardly floatable. The oxides produced by the use of the alloy of the invention forms mainly a complex system of SiO₂-MnO-CaO, and as given in FIGS. 3 and 4, they have low melting points and make floatable. FIG. 3 represents an equilibrium diagram of the SiO₂-MnO system and FIG. 4 that of the SiO₂-CaO system.

The principal reason for addition of Mn and Ca besides Si to the alloy of the invention is to facilitate the flotation of the oxide produced and to exhibits the cooperating reaction in the refining activities of Si, Mn, Ca and Mg.

The reason why Si is made the chief component accounting for more than 50% in the composition of the alloy of the invention is based not only on the consideration of the refining effect of the alloy but also on the fact that Si is in the widest use in the iron and steel refining and is an inexpensive metal and also the alloy can be manufactured easily. The Si content of the alloy of the invention can further be increased when the contents of Mn, Ca, and Fe are low, but the upper limit is 97% since in the high silicon alloy of the invention, similar to the conventional metallic silicon, the refining effect requires the total sum of the contents of Mn and Ca to be more than about 3%. The Mn content was limited within the range of 0.1 to 30% preferably 0.1 to 10%.

The lower limit of the Mn content is fixed to be 0.1%, as it is the minimum quantity necessary for producing the oxide of the above-mentioned complex system. The upper limit of 30% is based on the fact that the addition of more than it reduces the refining effect due to the cooperating reaction with the other elements. This is probably due to the lower affinity of Mn with oxygen than Si and Ca. The Ca content was limited within the range of 0.1 to 10% preferably 0.1 to 7%.

The lower limit of Ca is selected to be 0.1% as it is the minimum quantity necessary for developing the refin-

ing effect due to having affinity with impurities and the formation of the floatable oxide.

The upper limit is determined to be 10%, since with the Ca content higher it only increases the manufacturing cost and no improvement is brought about in its refining effect. The alloy of the invention which is lower in the Ca content than conventional Ca-Si alloys and Ca-Si-Mn alloys, but it exhibits a more powerful refining effect than the latter alloys due mainly to its low oxygen content.

The oxygen content was limited below 0.04% due to the reason that more than it the oxides of Fe, Si and Ca are not only increased as described above but also the activities of these elements are reduced so that the refining effect as desired by the invention can not be attained. The impurities which enter unavoidably during the manufacturing process of the alloy of the invention are C, Cr, Cu, Ni, P, S, Te, Na, Mg, K, Ti, Y, Li, B, Zn, Zr, lanthanum elements, H₂ and N₂. Among these elements there are two metallurgically known classes of elements which act positively for the refining action of iron and steel such as Te, Na, Mg, K, Ti, Y, Li, B, Zn, Zr, and lanthanum elements (rare earth elements) and also the elements acting negatively such as H₂, P and S. The rate of entering these elements differs according to the method of manufacturing their alloys, but in any process the quantity of elements positively acting for the refining action is in most cases equal to or larger than that the quantity of elements acting negatively. It has been found that even if the refining effects of both of these elements are compensated, the total sum of these elements up to maximum 6% does not disturb the refining action attainable by the alloy of the invention. In the manufacture of the alloy of the invention, the lowering of the oxygen content necessitates higher temperature smelting than in the case of manufacturing conventional Fe-Si alloys. The high temperature smelting is not only to make the reduction of oxides in raw material easier but also it makes more perfect separation of molten alloy and slag. It is also usual in manufacturing the alloy of the invention to add lime stone besides silica as the raw material. Moreover, in manufacturing alloy of the invention these is a method of heating or remelting the Fe-Si alloy manufactured by a conventional process and adding Mn and Ca during its step. In adding Mn and Ca there are two different methods: (1) The direct addition of these metals or alloys; (2) The addition of these metals by the reduction of oxides of such elements in slag. The refining alloys of the invention can be used for the melting of various kinds of metals and alloys, among which a remarkable refining effect has been obtained for steel for construction, high silicon steel, stainless steel, tool steel, graphitic steel, stainless cast steel, graphite cast steel, tough cast iron and spheroidal graphite cast iron. The invention will be explained in detail by examples in use.

Example 1

In casting 18-8 stainless steels, the following two kinds of alloys were separately added to the melt in the ladle as the refining agent under the same condition and their refining effects were compared. The addition of the alloys was 0.5% to the weight of the molten steel.

(1) Composition of refining alloy samples (percent):

No.	Nomenclature	Si	Mn	Ca	O	Fe	Others
1.	Ca-Si-Mn	61.1	15.2	20.8	0.52	1.4	0.98
2.	Alloy of the invention.	62.5	12.4	7.2	0.028	14.7	3.172

(2) Refining effect (test results of stainless steel products):

No.	Name of addition alloy for refining	Analyzed composition (percent)		Non-metallic inclusion by JIS-Standard (Percent)			
		S	O	Sulfide and silicate	Alumina	Granular oxide	Total
1-----	Ca-Si-Mn	0.012	0.0049	0.014	0.008	0.0044	0.0066
2-----	Alloy of the invention.	0.004	0.0019	tr.	tr.	0.0020	0.0020

NOTE.—In the table, JIS means Japanese Industrial Standard.

As shown in Table 2, the allowable maximum S-content in the molten cast iron increases as the contents of Mn and Ca in the addition alloy increase. This depends on the desulfurization effects of Mn and Ca in the alloy.

Example 3

60% steel scrap and 40% returned scrap were melted as the raw material iron in a 500 kg. basic high frequency induction furnace, and then 3.0% alloy of the invention (SC No. 3 in Table 1) was added to the melt in a ladle. It was compared with the product of spheroidal graphite cast iron obtained by adding 3.0% of No. 1 alloy in Table 2 to the melt in another ladle under the same condition. The results are shown in the following:

Kinds of addition alloys for refining	Analyzed compositions (percent)					Tensile strength (kg./mm. ²)	Elongation (percent)	Duration of spheroidal graphitization
	C	Si	Mn	S	O			
No. 1 alloy in Table 2-----	3.54	2.83	0.27	0.011	0.0008	65.9	2.4	12
Alloy of the invention SC No. 3 in Table 1.	3.41	2.78	0.35	0.005	0.0004	74.8	4.8	25

As compared the compositions of the above two alloys, the invented one is about 3% and 14% lower in the Mn and Ca contents respectively than those of Ca-Si-Mn alloys, notwithstanding the refining action of the alloy of the invention which is more powerful.

Example 2

The inventors ascertained several years ago that when Fe-Si alloys of low oxygen content were used, spheroidal graphite cast iron could be manufactured by the addition of Fe-Si alloy only, but in the method of adding Fe-Si alloy only, if the sulfur content in the molten cast iron before addition of the alloy was considerably high, the spheroidal graphitization was not perfect. On the other hand, if the alloy of the invention is used, satisfactory spheroidal graphite cast iron can be obtained even from molten cast iron having unfavorable conditions by the effective refining effect of a small quantity of Mn and Ca.

As apparent from the above results, the alloy of the invention has not only a powerful effect of graphite spheroidization but is also very effective to elongate the duration of graphite spheroidization. In the melting of spheroidal graphite cast iron, the longer the time from the addition, of the refining alloy to the casting in a mold beyond a certain limit, the lower is the rate of graphite spheroidization. The duration time of graphite spheroidization represents the interval from the instant when the alloy is added into the ladle to the time when graphite spheroidization begins to decrease.

Example 4

60% steel scrap and 50% returned scrap were used as the raw material and melted in a 1.5 ton basic Héroult arc furnace, to which 1.2% alloy (SC3 in Table 1) of the invention was added. The spheroidal graphite cast steel thus produced shows the following composition and properties.

Analyzed compositions (percent) as-cast condition					Properties after annealed		
T.C.	G.C.	Si	S	O	G.C.	Tensile strength (kg./mm. ²)	Elongation (percent)
1.24	0.48	1.09	0.006	0.0018	0.62	94.2	6.4

NOTE.—In the table, T.C. means total carbon; G.C., graphite carbon; the S-content before the addition of the alloy, 0.022%; the O-content, 0.0048%.

Table 2 illustrates the relation between Mn and Ca contents in the addition alloy when graphite can be perfectly spheroidized and the allowable maximum sulfur content in the molten cast iron to which the alloy is added. The values of the S-content shown in Table 2 are those obtained from the experimental results with 3.0% addition of the alloy.

TABLE 2

No.	Compositions percent of addition alloys						Allowable max. content of S in molten pig iron
	Si	Mn	Ca	O	Fe	Others	
1-----	65.5	0.05	0.08	0.039	30.7	3.631	0.020
2-----	67.4	2.3	5.1	0.020	20.7	4.480	0.040
3-----	68.9	5.7	8.1	0.029	15.1	2.171	0.050
4-----	62.5	12.4	7.2	0.028	14.7	3.172	0.055

NOTE.—In the table, No. 1 alloy does not belong to the invention.

The deposition of 0.48% graphite carbon under the as-cast state is due to the refining activity of strong de-oxidation and desulfurization effects of the addition alloy of the invention.

Example 5

It is generally known that in the manufacture of tough cast irons, oxygen and sulfur are extensively dispersed in lots and the oxygen content in the inoculation alloy is high so that it is difficult to obtain the product having a definite quality.

However, even under the worst condition when molten cast iron in an acidic cupola is used, it becomes possible to manufacture the product of a definite quality by the use of the alloy of the invention. 35% pig iron, 35% returned scrap and 30% steel scrap were used as the raw material and melted in a 2 tons cupola, to which 0.6% alloy of the invention (SMC1 in Table 1) was inoculated.

ANALYSIS OF THE PRODUCTS AND TEST RESULTS

Blow No.	Analyzed composition (percent)			Tensile strength (kg./mm. ²)
	C	Si	O	
PC 1.....	30.2	2.12	0.0036	32.8
PC 2.....	3.28	2.09	0.0025	33.4
PC 3.....	3.16	2.16	0.0030	32.5
PC 4.....	3.33	2.06	0.0022	35.6
PC 5.....	3.20	1.97	0.0019	33.6

What we claim is:

1. Low oxygen-silicon base addition alloys for refining iron and steel consisting essentially of 50 to 97% silicon, 0.1 to 30% manganese, 0.1 to 10% calcium and the remainder iron, the oxygen content being less than 0.04%.

2. A low oxygen-silicon base addition alloy for refining iron and steel according to claim 1, wherein the manganese content is 0.1 to 10%.

3. A low oxygen-silicon base addition alloy for refining iron and steel according to claim 1, wherein the calcium content is 0.1 to 7%.

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