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METHOD OF REFINING MOLTEN METALS BY ELECTROLYZING
MOLTEN SLAG UNDER ARC DISCHARGE
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3,203,883

Fig-1- PRIOR ART

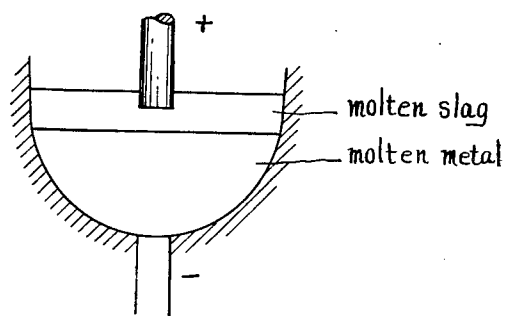
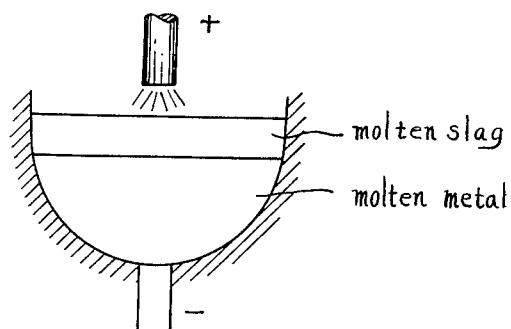


Fig-2-



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METHOD OF REFINING MOLTEN METALS BY ELECTROLYZING MOLTEN SLAG UNDER ARC DISCHARGE

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2 Claims. (Cl. 204—140)

The present invention relates to a method of refining molten metals by electrolyzing molten slag under arc discharge at ambient pressure characterized in that molten slag consisting of calcium silicate containing one or more of halides of alkaline earth metals, or in addition therewith aluminum oxides or aluminum halides is used as the electrolyte and electrolyzed by applying direct current high potential between the molten metal as a cathode and an anode suspended above the electrolyte, thereby effecting deoxidation of the molten metal.

The principal object of the invention is to effect strong refining of steels, pig irons, ferro-alloys and non-ferrous metals in the molten state and more particularly to effect intensive deoxidizing refining.

The electrolytic refining by high potential arc discharge of the invention has the following specialities if compared with an ordinary electrolysis using dipped electrode wherein an anode is dipped into the electrolyte and the electrolysis is carried out at a comparatively low voltage.

(1) The temperature of molten slag, molten metal or alloy during the electrolytic refining can be easily maintained by the heat of arc.

(2) The fluidity of the molten slag can be maintained at a suitable degree.

(3) Even if the anodic current density becomes large the phenomenon of lowering the efficiency of electrolysis such as an anode effect does not absolutely occur.

(4) Since the carbon electrode is not dipped in the molten metal or alloy the electrolytic refining of low carbon metals and alloys is possible. Contrary to the present method it is difficult in the former electrolytic refining with dipped electrode, for instance, in steels to obtain the product of less than 0.15% carbon due to the carburizing phenomena.

(5) The more intensive deoxidation refining can be effected if compared with the electrolysis using dipped electrodes since the load voltage is high and a high basicity slag having higher resistance may be used as electrolyte.

As above described, according to the electrolytic refining using arc discharge of the invention the temperature of the molten metal can be easily maintained by the heat of arc and the powerful reduction refining which has heretofore been considered difficult is rendered possible so that it can be applied to the production of steel, and moreover, the time required for the reduction is made substantially equal to that of ordinary processes or can be shortened even less than that. Accordingly, the cost of melting refining in the electrolytic refining under high potential arc discharge is substantially same as that of melting refining in ordinary refining method and the cost

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of the direct current electrolyzing device can be compensated by the improvement in the yield of the product.

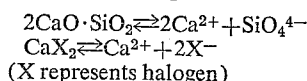
A large merit obtainable in carrying out the method of the invention is to produce a melt of refined metals due to the extreme deoxidation and desulfurization for eliminating impurities and improving the yield of the product and its limit varies according to the kinds of metals, yet the deoxidation as described hereafter by an example results in 20 to 60% improvement compared with ordinary refining and the yield is improved for 1 to 4%.

The deoxidation and desulfurization mechanism of the electrolytic refining using arc discharge is as follows:

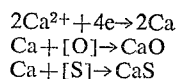
The reaction of electrolytic refining of the molten slag proceeds (1) by the electrochemical reaction and (2) thermo-dynamic reaction.

(1) *Electrochemical reaction.*— $2\text{CaO} \cdot \text{SiO}_2$ and CaX_2 are taken as a slag to be deoxidized and desulfurized for example.

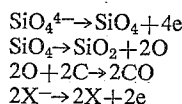
The reaction between two poles is as follows:



Cathode reaction:



Anode reaction:

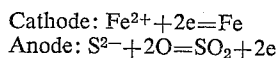


As seen from the above the deoxidation and desulfurization refining proceed by the cathode reaction of the active element produced by the electrolysis.

(2) *Thermo-dynamic reaction.*—Assuming the activities of S and Fe in the molten iron be expressed by $a\text{S}$ and $a\text{Fe}$ respectively and the activities of S^{2-} and Fe^{2+} in the molten slag be $a\text{S}^{2-}$ and $a\text{Fe}^{2+}$ respectively and the equilibrium constant between them be L_{FeS} , then the following thermo-dynamic relation is established.

$$L_{\text{FeS}} = \frac{a\text{S}^{2-} \cdot a\text{Fe}^{2+}}{a\text{S} \cdot a\text{Fe}}$$

When D.C. potential is applied to molten iron-molten slag which are in such condition of equilibrium the following relation proceeds between two poles.



That is, both of $a\text{S}^{2-}$ and $a\text{Fe}^{2+}$ are reduced by the reaction between two poles and accordingly, in order to maintain the equilibrium, FeS in the molten iron must proceed into the molten slag to effect the deoxidation refining reaction simultaneously to the desulfurization.

Even though the reaction of electrolytic refining proceeds by either of the above mechanisms oxygen or halogen gases are produced at the anode which controls the speeds of reaction of the electrolytic refining.

When the anode is dipped into the molten slag the generated gases are attracted by the anode surface to form non-conductive monomolecular film and multi-molecular film which interrupt the flow of electric cur-

rents and considerably reduce a speed of electrolytic reaction.

On the contrary, in case of high potential arc discharge the anode is suspended above the molten slag so that the generated gases are not attracted by the anode surface and even though there might form a gaseous film on the surface of the molten slag it is broken at a high temperature of arc and ion or electron bombardment so that the speed of anode reaction is considerably accelerated to highly advance the desulfurization reaction. When aluminum oxides and halides are contained in the molten slag which is the electrolyte in the present method the aluminum electrolytically reduced by the high voltage arc discharge and precipitates under the active condition on the interface of molten metal and molten slag to cause strong deoxidizing reaction. In this case, since the reaction occurs on the surface of the molten metal (interface between the molten slag) the reaction product (alumina) is consumed by the molten slag at once so that it cannot be retained in the molten metal as non-metallic inclusions and refined metal may be obtained.

Moreover, the excessive precipitated aluminum serves to produce fine grained structure and to toughen the steel entering into the steel in case of refining.

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

FIG. 1 is a diagrammatic sectional view of low voltage dipped electrode electrolytic device, and

FIG. 2 is a similar diagrammatic sectional view to FIG. 1 illustrating the location of an anode in a high potential arc discharge electrolytic refining device.

The method of the invention will be explained further in detail by the examples:

Example 1

In stainless steels containing 0.16% C and 13% Cr, the comparison of ordinary refining, low potential dipped electrode electrolysis and arc discharge electrolysis is shown in the following table:

The furnace used is 1 ton Héroult type electrolytic furnace.

	Ordinary refining	Low voltage dipped electrode electrolytic refining	Arc discharge electrolytic refining
Condition of electrolysis:			
Composition of slag (percent)—			
CaO	67.27	70.29	69.30
SiO ₂	25.99	23.58	24.62
MgO	1.22	1.06	1.43
Al ₂ O ₃	2.08	0.98	0.45
FeO	1.24	0.69	0.40
D.C. load voltage (V)		17.8	55.3
D.C. load current (A)		2,900	2,500
Duration of electrolysis (minutes)		25	25
Test results of products:			
Impurities (percent)—			
S	0.009	0.006	0.004
O	0.0077	0.0057	0.0045
Purity by point counting process (percent)—			
Sulfides, silicates	0.004	0	0
Alumina	0.006	0	0
Granular oxide	0.072	0.041	0.029
Yield of product in weight to the weight of steel ingot (percent) ..	73.0	73.9	74.3

Example 2

In low carbon steels, such as stainless steel containing less than 0.12% C and 13% Cr, even if very low carbon materials are used as charging raw material the carbon content of the molten steel becomes higher than 0.15% in the low voltage dipped electrode electrolysis so that the electrolysis under high voltage arc discharge must be used necessarily and the result is as shown in the following:

The furnace used is 1 ton Héroult type electrolytic furnace.

	Air discharge electrolytic refining	Ordinary refining
5 Condition of electrolysis:		
Composition of slag (percent)—		
CaO	67.40	66.53
SiO ₂	25.00	25.09
MgO	2.84	2.56
Al ₂ O ₃	1.54	2.92
FeO	0.69	1.05
10 D.C. load voltage (V)	58.5	
D.C. load current (A)	2,500	
Duration of electrolysis (minutes)	25	
Test results of products:		
Carbon content (percent)	0.09	0.09
Impurities (percent)—		
S	0.004	0.008
O	0.0029	0.0058
15 Purity by point counting process (percent)—		
Sulfide, silicate	0	0.008
Alumina	0	0
Granular oxide	0.0035	0.0045

As seen from the above example the effect of deoxidation refining of steels by the high potential arc discharge electrolysis is very large.

Example 3

From the results of test carried out similarly to cast iron, high voltage arc discharge electrolysis is not only smoothly carried out its operation if compared with low voltage dipped electrode electrolysis but also the effect of deoxidation and desulfurization are increased. So that the nodularization of graphite due to inoculation can be made easy. The furnace used is 1 ton Héroult type electrolytic furnace.

	Low voltage dipped electrode electrolytic refining	Arc discharge electrolytic refining
35 Condition of electrolysis:		
Composition of slag (percent)—		
CaO	67.18	68.90
SiO ₂	22.61	24.53
MgO	5.98	2.74
Al ₂ O ₃	1.42	1.79
FeO	0.88	0.61
40 D.C. load voltage (V)	12.5	52.0
D.C. load current (A)	2,050	2,030
Duration of electrolysis (minutes)	20	20
Test results of product:		
Main ingredient (percent)—		
C	3.61	3.59
Si	1.99	1.95
Mn	0.58	0.55
Impurities (percent)—		
S	0.004	0.003
O	0.0008	0.0005

Example 4

The next table illustrates an example of the method of the invention as applied to pure copper. It is apparent that the pure copper of very high quality (oxygen free copper) was obtained.

The furnace used was 100 kg. high frequency electrolytic furnace.

Condition of electrolysis:	Arc discharge electrolytic refining
Composition of slag (percent)—	
CaO	59.41
NaCl	10.08
CaF ₂	28.43
D.C. load voltage (V)	60.4
D.C. load current (A)	1,250
Duration of electrolysis (minutes)	22

Product:

Impurities, percent (the value in bracket shows that before electrolysis)—	
O	0.0008 (0.0015)
S	0.002 (0.006)
As	0.001 (0.004)

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Example 5

Iron-chromium alloys and Fe-Si alloy are subjected to the high potential arc discharge electrolytic refining and as its results the oxygen content in the alloy was reduced to $\frac{1}{2}$ to $\frac{1}{3}$ and when the refined alloy is used for the melting of iron and steel, refined steel and iron containing less oxygen was obtained.

The extent of the deoxidation refining according to the method of the invention depends on the kinds of metals and in higher alloy steels it is sometimes better than vacuum smelting.

As above described the present method has advantages that if compared with ordinary method of smelting the products of high purity can be obtained at the same or less costs owing to the extremely strong deoxidation.

What we claim is:

1. A method of arc-discharge, electrolytic refining of a molten metal, wherein said metal is selected from the group consisting of steel, cast iron, ferroalloys, and copper, which comprises covering said metal to be refined with a molten calcium silicate slag containing a compound selected from the group consisting of compounds of alkali metals, alkaline earth metals, iron and aluminum as an electrolyte, above the surface of said slag, suspending an anode and applying a D.C. voltage between said anode and said metal to be refined to electrolyze the molten

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slag by arc discharge and to effect electro-chemical deoxidation and desulphurization refining.

2. A method of arc-discharge electrolytic refining of a molten metal, wherein said metal is selected from the group consisting of steel, cast iron, ferro-alloys, and copper, which comprises covering said metal to be refined with a molten calcium silicate slag containing a compound selected from the group consisting of compounds of alkali metals, alkaline earth metals, iron and aluminum as an electrolyte, above the surface of said slag suspending an anode and applying a D.C. voltage between said anode and said metal to be refined at ambient pressure to electrolyze the molten slag by arc discharge and to effect electrochemical deoxidation and desulphurization refining.

References Cited by the Examiner

UNITED STATES PATENTS

800,984	10/05	Chance	204—140
2,787,592	4/57	Burkhardt	204—140

FOREIGN PATENTS

741,567	12/55	Great Britain.
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25 JOHN H. MACK, *Primary Examiner.*
JOHN R. SPECK, *Examiner.*