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Seya et al.

[11] **3,850,618**

[45] **Nov. 26, 1974**

[54] **DEMOLYBDENUM REFINING METHOD OF MOLYBDENUM CONTAINING ALLOY STEEL MATERIAL**

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[52] **U.S. Cl.** **75/51,** 75/52, 75/130.5

[51] **Int. Cl.** **C21c 7/04,** C22c 33/00

[58] **Field of Search** 75/51-55, 129, 75/84, 130.5

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Attorney, Agent, or Firm—Fred Philpitt; W. Robert Baylor

[57] **ABSTRACT**

A Mo reduction method of refining a melt of Mo alloy steel that includes Cr, Si, C, P and Mn comprises the steps of effecting oxidation of the molten steel to arrange that Cr is below 1%, and Si, C, P and Mn are below 0.1 percent respectively, arranging to contain oxygen above 0.02 percent in the molten steel, oxidizing Mo in the molten steel to produce Mo oxide by charging or blowing oxide of the alkali metal or alkali earth metal or salts of those metals and solid oxide (solid bond oxygen) or oxygen containing gas into the molten steel, and shifting the double salt formed by the Mo oxide and the oxide of the alkali metal or alkali earth metal into the slag.

6 Claims, 8 Drawing Figures

FIG. 1

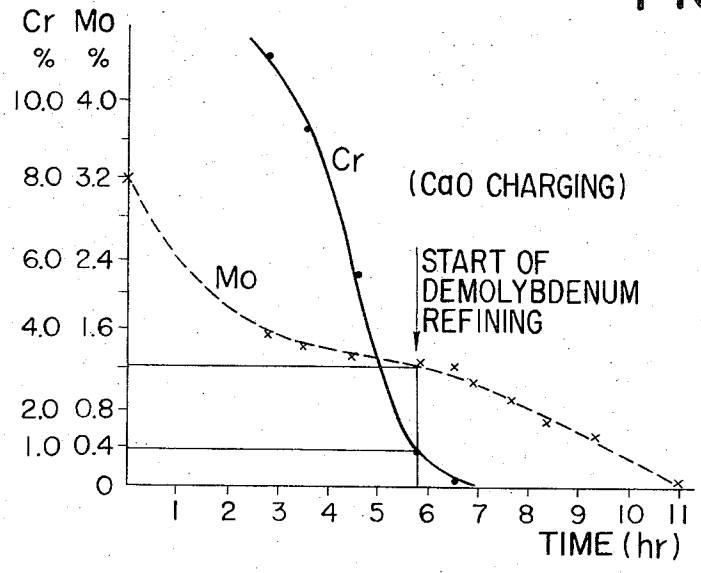

Cr Mo
% %
10.0 4.0
8.0 3.2
6.0 2.4
4.0 1.6
2.0 0.8
1.0 0.4
0
Cr
Mo
(CaO CHARGING)
START OF
DEMOLYBDENUM
REFINING
1 2 3 4 5 6 7 8 9 10 11
TIME (hr)

FIG. 2

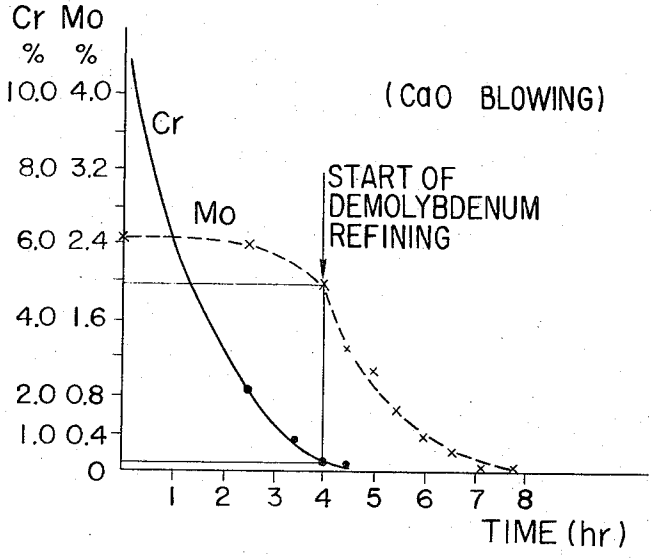

Cr Mo
% %
10.0 4.0
8.0 3.2
6.0 2.4
4.0 1.6
2.0 0.8
1.0 0.4
0
Cr
Mo
(CaO BLOWING)
START OF
DEMOLYBDENUM
REFINING
1 2 3 4 5 6 7 8
TIME (hr)

FIG. 3

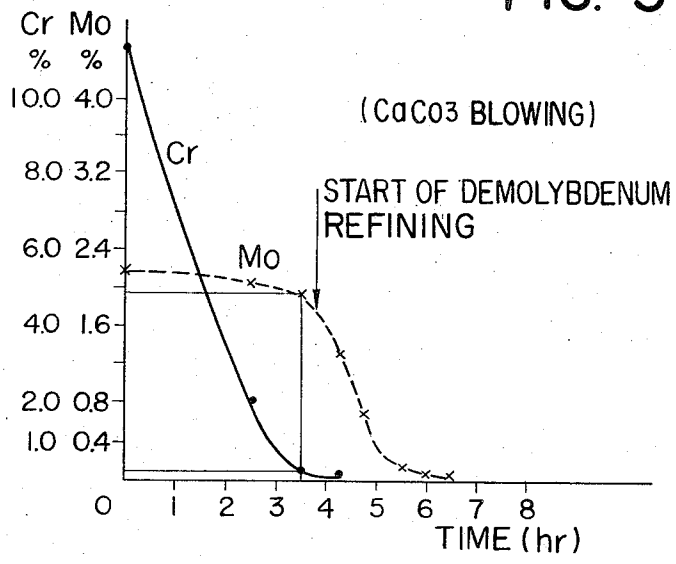

Cr Mo
% %
10.0 4.0
8.0 3.2
6.0 2.4
4.0 1.6
2.0 0.8
1.0 0.4
0 1 2 3 4 5 6 7 8
TIME (hr)
Cr
Mo
(CaCo3 BLOWING)
START OF DEMOLYBDENUM REFINING

FIG. 4

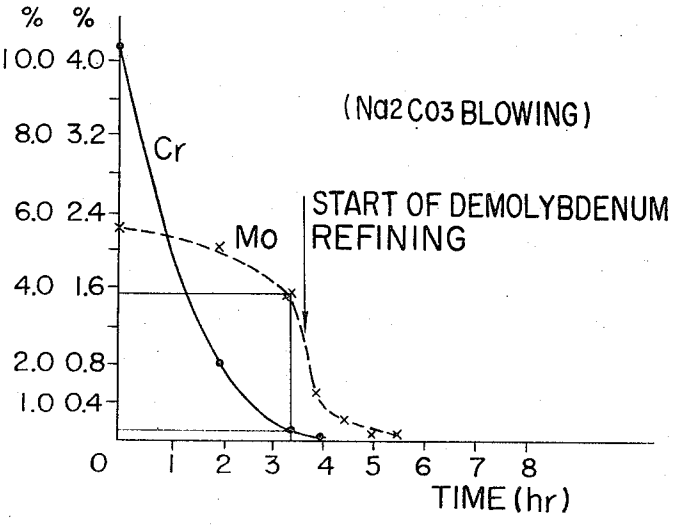

% %
10.0 4.0
8.0 3.2
6.0 2.4
4.0 1.6
2.0 0.8
1.0 0.4
0 1 2 3 4 5 6 7 8
TIME (hr)
Cr
Mo
(Na2Co3 BLOWING)
START OF DEMOLYBDENUM REFINING

FIG. 5

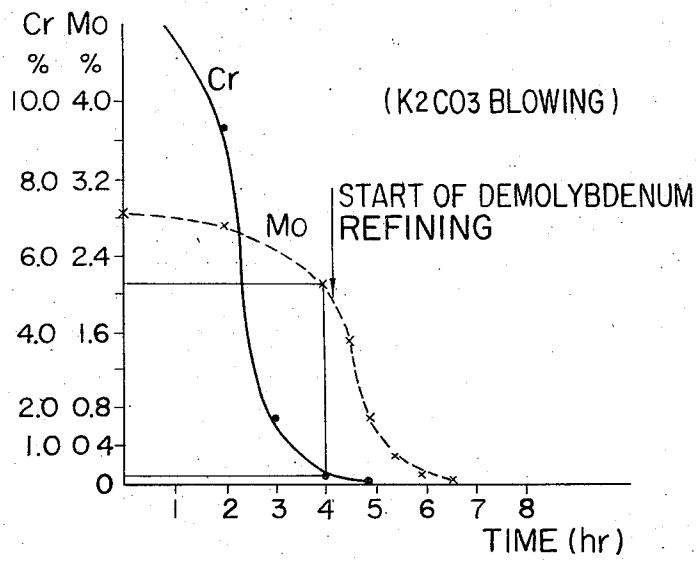

Cr Mo
% %
10.0 4.0
8.0 3.2
6.0 2.4
4.0 1.6
2.0 0.8
1.0 0.4
0
Cr
Mo
(K2CO3 BLOWING)
START OF DEMOLYBDENUM REFINING
1 2 3 4 5 6 7 8
TIME (hr)

FIG. 6

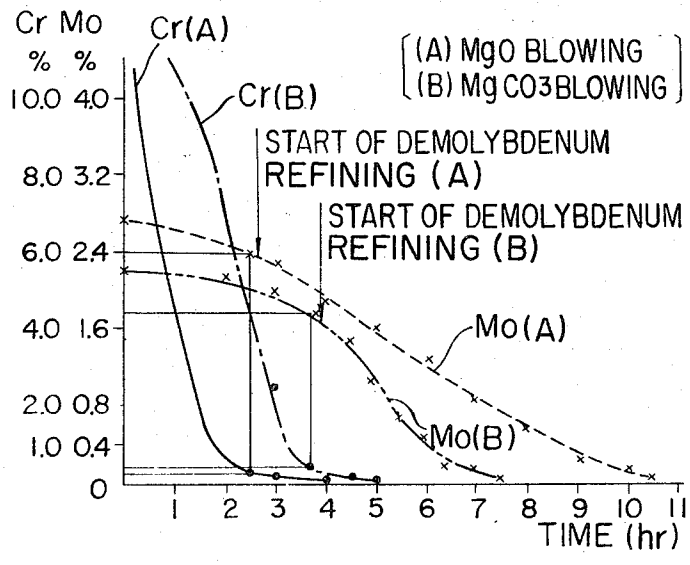

Cr Mo
% %
10.0 4.0
8.0 3.2
6.0 2.4
4.0 1.6
2.0 0.8
1.0 0.4
0
Cr(A)
Cr(B)
(A) MgO BLOWING
(B) MgCO3 BLOWING
START OF DEMOLYBDENUM REFINING (A)
START OF DEMOLYBDENUM REFINING (B)
Mo(A)
Mo(B)
1 2 3 4 5 6 7 8 9 10 11
TIME (hr)

FIG. 7

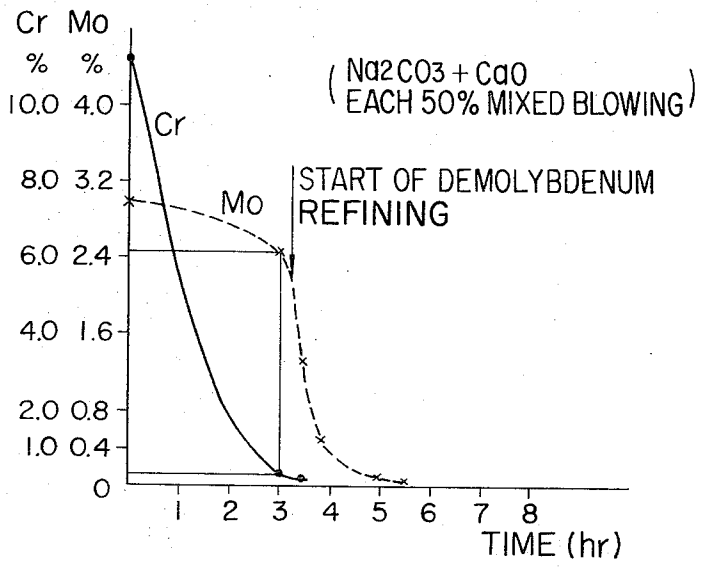
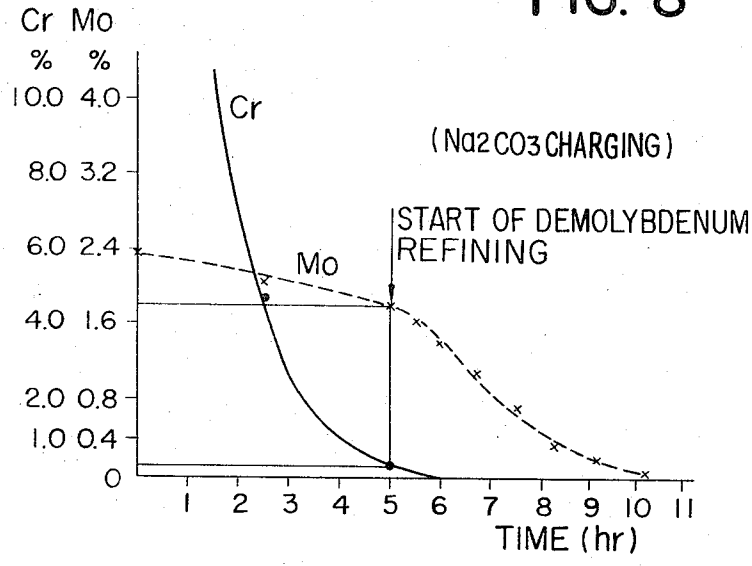

Cr Mo
% %
10.0 4.0
8.0 3.2
6.0 2.4
4.0 1.6
2.0 0.8
1.0 0.4
0
Cr
Mo
(Na2CO3 + CaO
EACH 50% MIXED BLOWING)
START OF DEMOLYBDENUM
REFINING
1 2 3 4 5 6 7 8
TIME (hr)

FIG. 8


Cr Mo
% %
10.0 4.0
8.0 3.2
6.0 2.4
4.0 1.6
2.0 0.8
1.0 0.4
0
Cr
Mo
(Na2CO3 CHARGING)
START OF DEMOLYBDENUM
REFINING
1 2 3 4 5 6 7 8 9 10 11
TIME (hr)

DEMOLYBDENUM REFINING METHOD OF MOLYBDENUM CONTAINING ALLOY STEEL MATERIAL

SUMMARY OF THE INVENTION:

The present invention relates to a method of eliminating a substantial part of the contained molybdenum through the refining of the alloy steel material containing the molybdenum. Heretofore, the elimination of molybdenum from the molybdenum alloy steel has been regarded as extremely difficult. The reason for this is based on the premise in steel making that the affinity molybdenum to oxygen is small as compared with iron. In an oxidation refining method in which the elements are oxidized and the slag-off is effected, the elements whose stability are smaller than that of FeO and whose dissociation constants are greater than that of FeO are not actually oxidized in normal molten bath conditions.

Notwithstanding the foregoing premise of steel making wherein the molten steel is in an oxidized condition, molybdenum reacts with oxygen in the form of MoO though in a small amount and thus it does exist in the molten steel. However, this solubility is extremely small and the transfer of the MoO to the slag is regarded also as extremely small in general oxidation refining, therefore, as a result of studies relating to methods of making the transfer of MoO to slag easier, it has been confirmed experimentally that oxides of alkali metal or alkali earth metal or salts of these metals are directly caused to react with the MoO in the molten steel, that they form a double salt with the alkali metal or alkali earth metal, and that MoO in the molten steel is consumed in order to deposit it from the molten steel. For this reason, the reaction in which in the molten steel reacts with O_2 newly is regarded to advance until the temperature of O_2 is reduced to a fixed value. Furthermore as result of numerous experiments, the present inventors have invented the most effective demolybdenum refining method.

More particularly, the present invention relates to a molybdenum reduction method of refining a melt of molybdenum alloy steel that includes chromium, silicon, carbon, phosphorous and manganese and comprises the following steps: effecting oxidation of the molten steel whereby chromium is oxidized below 1 percent and silicon, carbon, phosphorus and manganese are oxidized below 0.1 percent and the molten steel contains more than 0.02 percent of oxygen; effecting introduction of a charging material of a stream of an oxidizing gas rich in oxygen and at least one compound selected from the group consisting of an oxide of an alkali metal, alkali earth metal and salts of the alkali metal and alkali earth metal, to produce an oxide of molybdenum; and effecting the transfer of the oxide of the alkali metal and alkali earth metal and the formed double salt of the oxide of molybdenum from the molten bath into the slag.

BRIEF DESCRIPTION OF DRAWINGS

FIGS. 1 through 8 show refining curves of chromium and molybdenum of examples which are practiced in accordance with the refining method of the present invention.

DETAILED DESCRIPTION OF INVENTION

The fundamental essential conditions of the demolybdenum refining method of the present invention are as follows:

a. Oxide the molten steel and maintain the melting oxygen concentration sufficient to generate a molten oxide of Mo in the molten steel.

b. React the compound of an alkali metal or alkali earth metal directly with the molten oxide of Mo in the molten steel to deposit the oxide of Mo of the alkali metal or alkali earth metal and materialize the continuous reaction whereby the oxide of Mo is easily transferred to the slag.

Furthermore, in order to perform effective industrialization of the demolybdenum process, it is necessary a perfect process that not only satisfies the essential conditions of (a) but also overcomes the the obstacle of only oxidizing Mo in case there is present an element whose affinity to oxygen is greater than those of Mo and Fe coexist with the greater part of steel such as a molybdenum containing alloy steel material since the majority of such steel material contains Si, Mn, C, P and Cr.

The present invention proposes that a molybdenum containing alloy steel material be melted in order to satisfy the essential condition (a), first of all. Thereby Cr, Si, C and Mn and the like are subjected to oxidation and elimination thereof to make such elements below certain limits. As the molten steel is partially subjected to oxidation, Mo is also oxidized. An extremely small amount of Mo is thereby transferred to the slag, and also as the loss of Fe and other alloy constituting elements is substantial. Such effects, however, are small even if the demolybdenum refining is carried out at this time. When the majority of Si, C, P, Mn is oxidized, even if Cr exists substantially, the molybdenum can be transferred to the slag. It has been confirmed as a result of experimentation that the demolybdenum effect is most effective when the content of Cr is below 1 % and those of Si, C, P, Mn below 0.1 percent and the content of oxygen in the molten steel is at least about 0.02 percent.

Attention is directed to a molten steel situation in which the residue of Cr is 1 percent. It is possible to eliminate more than 50 percent of the contained Mo by one refining reaction. The oxygen concentration of such molten steel is considerably high and Si, C, P and Mn can be greatly reduced from 0.1 percent (0.02 – 0.03 percent). The supply of oxygen in this case seems to be partially carried out by CO_2—CO + O by decomposition of carbonate of alkali metal or alkali earth metal that is charged or blown into the molten steel. However, the operation can be effective by directly blowing the gas oxygen into the molten steel.

Next, when the amount of molybdenum in the molten steel is reduced, the concentration of the molybdenum compound in the slag that is generated by the initial demolybdenum refining becomes higher. Further demolybdenum refining reaction becomes difficult because of the equibrium relation of the slag and the molybdenum in the molten steel. Accordingly, it is necessary to repeat several times the demolybdenum refining step that produces the slag newly by effecting the slag off. The number of times that this action is repeated depends on the type of molybdenum that is required. As a general rule, a desired finish can be obtained with two or three actions by having the demolybdenum at below 2 to 0.05 percent. The cause of performance of the operation is attributable to temperature of the molten

steel, the degree of oxidation, and the element compositions that are contained in the alloy. In general, the temperature at which the demolybdenum method is performed is preferably a low temperature. Further amount of activity of the oxygen which is an element of the alloy also exerts a substantial influence. Many of the alkali metal and alkali earth metal have extremely strong affinity with oxygen as compared with Fe, Ni, Co and the like. Also if these oxides or salts are charged or blown into the molten steel, they are reduced in the molten steel. There is almost no reason to be concerned that they are contained in the product as an alloy of the metals. It has been known that the oxides of the majority of alkali metal and alkali earth metal are bonded with the oxide of Mo to form a double salt. The following are principal compounds thereof.

(Alkali metals)

Li_2MoO_4, Na_2MoO_4, $Na_2O_33MoO_3$,
$Na_20.5MoO_3$, K_3MoO_4, $K_20.2Na_2O_3$,
MoO_3, Cs_2MoO_4

(Alkali earth metals)

$BeMoO_4$, $MgMoO_4$,
$CaMoO_4$, SrMoO4,
$BaMoO_4$

As will be obvious from the foregoing, when oxides or salts of majority of the alkali metals and alkali earth metals are charged or directly blown into the molten steel which has been oxidized, the demolybdenum refining can be expected in which Mo in the molten steel is transformed to the slag as double salts of the alkali metal and the alkali earth metal and the oxide of Mo. By and by making actual experiments on the various kinds of metals, this phenomenon may be proved. By the way, the actual demolybdenum refining methods are roughly classified into the following three groups.

1. Where a compound of alkali metal or alkali earth metal and other solid oxide (solid bond oxygen) are charged into the molten steel;
2. Where a compound of alkali metal or alkali earth metal is suspended in a gas containing oxygen (when the molten steel is in oxidized condition, nitrogen gas may be used) and it is blown into the molten steel; and
3. Where the steps of charging of a compound of alkali metal or alkali earth metal to the molten steel and the blowing of an oxygen containing gas are separately carried out.

Three examples of the present invention will be described in the following.

Example 1

Where the demolybdenum refining method of the foregoing (1) was employed:

Two tons of an alloy steel material having the following composition and containing Mo was charged into an Heroult electric arc furnace and 300 kg of mill scales (Feo) and 100 kg of CaO were added thereto and the mixed materials were melted. The composition of the steel material was as follows:
Ni 20.7 %, Co 21.3 %, Cr 20.3 %, Mo 3.2 %, C 0.07 %, Si 1.2 %, P 0.02 %, and Mn 1.3 %.

In the melt down, the composition was such that Mo was 1.6 % and Cr was 11.28 %, and considerable demolybdenum and dechromium were carried out but this phenomenon was due to the fact that the temperature was low at the time of melting and that the partial oxidation was taken place by the mill scales and direct contact by CaO. However, after the effect of the slag off, as a slag forming material, 25 kg of CaO and 200 kg of iron ore and 40 kg of siliceous sand were added thereto. Oxygen was blown thereinto and the dechromium step was repeated and eight times of slag off was conducted. Then 100 kg of CaO and 30 kg of iron ore were charged per one demolybdenum refining step and eight times of the demolybdenum refining step was carried out, and results shown in the first refining curve of FIG. 1 were obtained. Chromium was reduced to a trace in the third demolybdenum refining step but it took 8.5 hours from the melt down until Mo became 0.09 percent as the demolybdenum reaction speed was extremely slow. The composition at the time of tapping was as follows:

Ni 23.1 %, Co 22.6 %, Cr trace, Mo 0.09 %, C 0.02 %. Si trace, P 0.02 % and Mn trace.

Example 2

Where the demolybdenum refining method of the foregoing (2) was employed in which Na_2Co_3 (soda ash) was blown with a mixed gas of 1 oxygen and 4 nitrogen.

Similar to the foregoing example, the steel material was melted and the steel having a composition of the melt down of Ni 29.55%, Co 17.64 %, Cr 10.45 %, Mo 2.20 %, was subjected to the dechromium step as described in the foregoing. Na_2CO_3 powder consisted of Cr 0.10 %, Mo 1.55 %, C 0.04 %, Si 0.04 %, P 0.025 %, Mn 0.05 %, O_2 0.035 % was blown into the molten steel with a mixed gas of oxygen and nitrogen having the foregoing ratio to perform the demolybdenum refining step. Results shown in the refining curve of FIG. 4 were obtained. The slag off was carried out twice until Mo became 0.06 %, and the rate of the demolybdenum was the highest among the examples. The composition at the time of the tapping was as follows:

Ni 33.57 %, CO 20.15 %, Cr trace, Mo. 0.06 %, C 0.025 %, Si trace, P 0.02 %. Mn trace.

Example 3

Where the demolybdenum refining method of the foregoing (2) was employed in which K_2CO_3 was blown by means of a mixed gas of 1 oxygen and 3 nitrogen:

Similar to the foregoing example, the steel material was melted and steel having a composition of melt down of Ni 28.42 %, Co 22.07 %, Cr 12.57 %, and Mo 2.86 % was subjected to the dechromium step similar to the one in the foregoing example. K_2CO_3 consisting of Cr 0.04 %, Mo 2.12 %, C 0.05 %, Si 0.05 %, P 0.032 %, Mn 0.04 %, and O_2 0.02 % was blown into the molten steel by means of a mixed gas containing oxygen and nitrogen of the foregoing ratio to perform the demolybdenum refining step and results shown in the refining curve of FIG. 5 were obtained.

The slag off was carried out three times until Mo became 0.052 percent, and judging from the result, the effect of demolybdenum similar to that of Na_2Co_3 (soda ash) of the foregoing example 2 was obtain. However, the composition at the time of tapping was as follows: Ni 33.62 %, Co 26.6 %, Cr trace, Mo 0.052 %, C 0.015%, Si trace, P 0.02 %, and Mn trace.

As the foregoing three examples and other refining curves in the drawings show, the oxide of a alkali metal and alkali earth metal was of strongly basic type while the oxide of Mo was of an acidic type and both oxides easily became double salts as they bond to each other very easily.

The refining step in which Mo was eliminated from the alloy containing Mo was carried out by directly contacting and reacting the oxide of alkali metal and alkali earth metal or salts with the molten metal of the alloy containing Mo which had been oxidized whereby they become a double salt compound of the oxide of Mo and alkali metal and alkali earth metal, and thus the practicing of the refining of eliminating the Mo from the molten steel was extremely useful in achieving the object of the present invention.

Furthermore, the present invention may be performed by employing only one metallic compound among the alkali metal and the alkali earth metal, group. It is possible to enhance the efficiency and workability of the operation at a much higher degree by combining the characteristics through the simultaneous employment of more than two compounds. As a method step of directly contacting the molten steel with a compound of the alkali metal group and the alkali earth metal, there is a method step in which the compound is directly charged into the molten steel as shown in the examples. Besides the method step of direct blowing, there is a method step in which the molten steel is transferred to the rotary furnace or rocking ladle. Then like and then a compound of the alkali metal group or alkali earth metal is added to the molten steel. The molten steel and the compound are directly in contact by the rotating or rocking motion, whereby such a method step makes it possible to be useful to the higher enhancement of the demolybdenum effect. The method of the present invention has a minimum of loss of Co, Ni, etc., and also it is possible to recover the molybdenum from the slag from which the demolybdenum is effected, and thus the method of the present invention has a great economical effect and also is extremely excellent in using the demolybdenum alloy steel material as magnet steel, etc.

What is claimed is:

1. A molybdenum reduction method of refining a melt of molybdenum alloy steel that includes chromium, silicon, carbon, phosphorus and manganese comprising the following steps:

effecting oxidation of said molten steel whereby chromium is oxidized below 1 percent and silicon, carbon, phosphorus and manganese are oxidized below 0.1 percent and said molten steel contains more than 0.02 percent of oxygen;

effecting introduction of a charging material of a stream of an oxidizing gas rich in oxygen and at least one compound selected from the group consisting of an oxide of an alkali metal, alkali earth metal and salts of said alkali metal and alkali earth metal, to produce an oxide of molybdenum; and

effecting the transfer of said oxide of the alkali metal and alkali earth metal and the formed double salt of the oxide of molybdenum from the molten bath.

2. A method as claimed in claim **1,** in which the oxygen in said oxidizing gas is at least 0.02 percent.

3. A method as claimed in claim **1,** wherein said oxidizing gas includes a nitrogen gas.

4. A method as claimed in claim **1,** wherein said oxygen containing gas stream is blown into said molten steel in a separate and distinct step from the charging of the selected compound.

5. A method as claimed in claim **1,** in which the alkali earth metal group includes $BeMoO_4$, $MgMoO_4$, $CaMoO_4$, $SrMoO_4$, and $BaMoO_4$.

6. A method as claimed in claim **1,** in which the alkali metal group includes Li_2MoO_4, Na_2MoO_4, $Na_2O_33MoO_3$, $Na_20.5MoO_3$, K_3MoO_4, $K_20.2Na_2O_3$, MoO_3, Cs_2MoO_4.

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