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REMOVAL OF CHROMIUM FROM MOLTEN STEEL BY OXIDATION REFINING

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Synopsis: Removal of chromium from molten steel is investigated with $(CaO\text{-}MgO\text{-}MnO_2)\text{-}(SiO_2\text{-}Al_2O_3)\text{-}Fe_2O_3$ flux in a laboratory scale test. By using the flux of about 50 Kg/t, 60-75 weight% amount of chromium is removed from molten steel by oxidation refining, if

(1) FeO activity is high,
(2) slag basicity, $(CaO+MgO+MnO)/(SiO_2+Al_2O_3)$ is 1.5 - 2.0, and
(3) MgO is added to the flux as a component for accelerating removal of chromium.

In addition, manganese loss in this treatment is suppressed, if

(1) MnO_2 is added to the flux, and
(2) carbon is added to the slag after removal of chromium.

Key words: removal of chromium; tramp element; oxidation refining; secondary refining; scrap.

1. Introduction

Chromium in steel is considered to be a harmful impurity which affects property of cold working and deep drawing. For example, the level of chromium in steel is required to be reduced up to less than 0.03-0.05 % as for plain carbon steel,like cold-rolled plate for automobiles and so on.

On the other hand, in the refining process in an industrial electric furnace and in a converter furnace, an increase of chromium in molten steel is likely to occur, using scrap which includes chromium, for example, stainless steel, Cr-Mo steel, and so on. Recently, scrap on the market, especially low grade scrap, has tended to increase and the scrap is possibly available for raw materials in large amounts and at low cost. In that case, low grade scrap seems to be used more. In that situation, it is predicted that chromium in molten steel will exceed its specification by using scrap which includes chromium.

This paper reports on a fundamental study to remove chromium effectively from molten steel by means of slag which has high oxygen potential and low basicity.

2. Experimental Procedure

In a Tammann furnace, 2 kg molten steel whose typical composition is shown in Table 1, was melted in a MgO crucible under atmospheric pressure. After the molten steel was kept at a predetermined temperature (1600℃), the flux of 50 kg/t for removal of chromium was added onto the molten steel surface during Ar gas bubbling. Refining behaviours during removal of chromium were investigated.

Table 1. Composition (wt %) of molten steel

C	Si	Mn	P	Cr
0.05	tr.	0.15	0.015	0.10

Flux for removal of chromium consisted mainly of CaO, MgO, MnO_2, SiO_2, Al_2O_3, Fe_2O_3, and so on. In point of components of flux, CaO, SiO_2, and Al_2O_3 was used for controlling slag basicity. Fe_2O_3 was used as an oxidizing agent. MnO_2 was used for preventing manganese loss in molten steel. In addition, MgO was used for accelerating the reaction of removal of chromium and for protecting MgO-system refractory. On the other hand, the recovery of manganese and chromium in molten steel was investigated by adding carbon grains (1-2 mm in diameter) as a reducing agent in some experiments for preventing manganese loss during the treatment of removal of chromium.

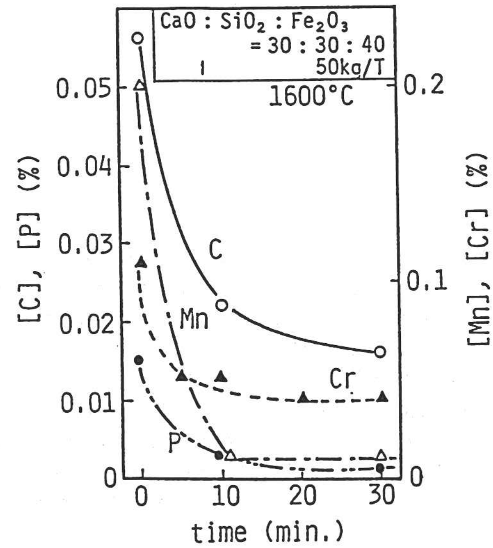

Fig. 1 Composition change of metal in treatment for removal of chromium

3. Experimental Results

3.1 Refining behaviours during a treatment for removal of chromium

Typical results for removal of chromium are shown in Fig.1. The figure illustrates that more than 60 % removal of chromium occured within only 10 minutes by adding the flux (50 kg/t) which contained a great amount of Fe_2O_3.

In addition, decarburization and removal of manganese proceeded at the same time. Furthermore, dephosphorization occurred when slag basicity (in this paper, $(CaO+MgO+MnO)/(SiO_2+Al_2O_3)$, was defined as slag basicity) was more than about 1.

3.2 Effect of oxygen potential on distribution of chromium

The effect of oxygen potential, (T.Fe) in slag, on the distribution ratio of chromium is shown in Fig.2. The distribution ratios of chromium increased with increasing (T.Fe) in slag. In other words, the oxidation reaction of chromium accelerated more with increasing (T.Fe) in slag ,simultaneously with an increase of oxygen concentration, according to Eq. (1).

$$Fe(l) + 2\underline{Cr} + 4\underline{O} = FeCr_2O_4(s) \quad \cdots (1)$$

3.3 Effect of slag basicity on distribution of chromium

The effect of slag basicity, $(CaO+MgO+MnO)/(SiO_2+Al_2O_3)$, after removal of chromium on the distribution ratios of chromium at various (T.Fe) level is shown in Fig.3. The distribution ratios of chromium were higher when slag basicity was 1.5-2.0, because of the following two hypotheses.

First, this is because the oxygen potential of slag is the highest when slag basicity is about 2 at the same (T.Fe). That is, the activity coefficient of FeO is the

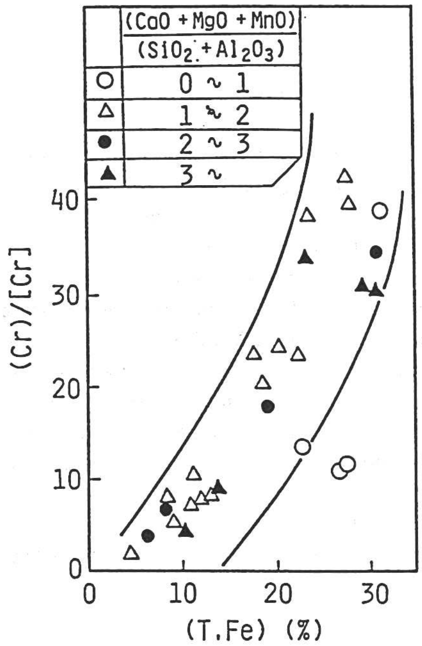

Fig. 2 Effect of (T.Fe) on chromium distribution ratio

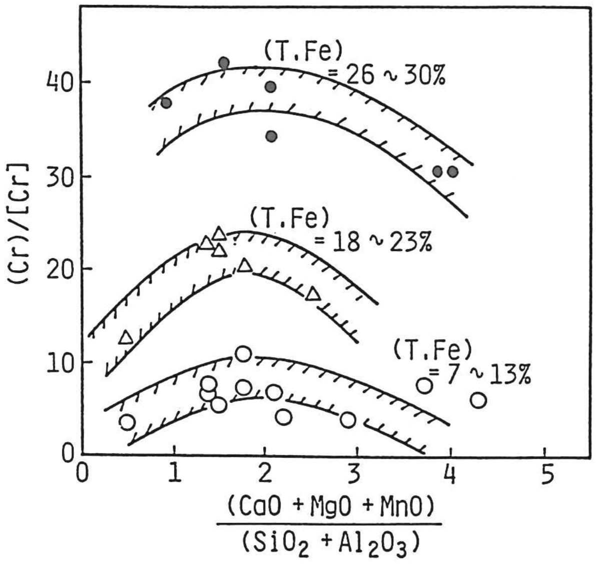

Fig. 3 Relation between chromium distribution ratio and slag basicity

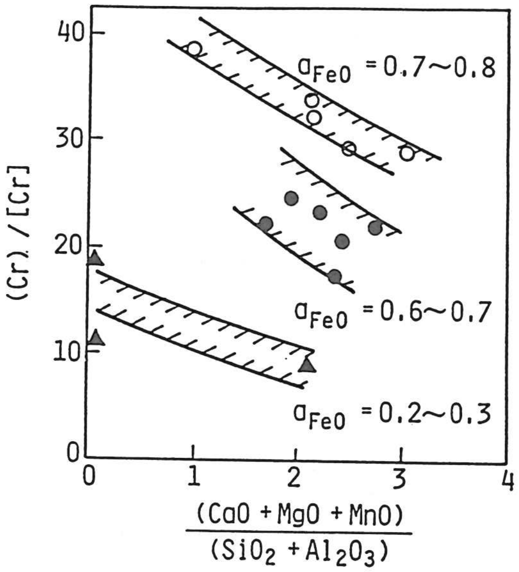

Fig. 4 Relation between chromium distribution ratio and slag basicity

highest when slag basicity is about 2, according to an iso-activity curve[1] of FeO by Turkdogan & Pearson.

Second, this is because a stability of chromium oxide in slag increases with decreasing slag basicity. That is, it is estimated that Cr_2O_3 is a weak basic oxide as well as Fe_2O_3 according to Coulomb' s force[2], which correlates closely with the basicity of oxide. It is reported[3] that CrO increases relatively in an acidic slag. Therefore, CrO is more basic than Cr_2O_3. In addition, in the refining behaviour of molten stainless steel in industrial AOD furnace, it is necessary to keep slag basicity at higher level than some value[4], in order to reduce Cr_2O_3 and to recover chromium effectively at the reduction refining stage after the decarburization stage. Judging from this refining method, it is estimated that Cr_2O_3 is a basic oxide.

In conclusion, it is thought that chromium oxide, Cr_2O_3 or CrO, is stabilized more with a decrease in slag basicity

Next, the effect of slag basicity after removal of chromium on the distribution ratios of chromium, at various FeO activity instead of (FeO) as an indication of oxygen potential, is shown in Fig.3. In calculating FeO activity, a regular solution model by Banya[5] et al was adopted with the data of slag composition. Simple analysis of the results, i.e. the distribution ratio of chromium increased with decreasing slag basicity, can be obtained from Fig.4.

3.4 Effect of MgO addition on removal of chromium

In order to improve removal of chromium, it seems to be effective to add flux components which can stabilize Cr_2O_3 in slag, in other words, which can decrease the activity of Cr_2O_3, $a_{Cr_2O_3}$. The components to improve removal of chromium, oxide MO(s), are considered according to Eq.(2). $a_{Cr_2O_3}$ decrease in Eq (1) with decreasing $a_{Cr_2O_3 \cdot MO}$ in Eq.(2) in order to improve removal of chromium.

$$Cr_2O_3 \cdot MO(s) = Cr_2O_3(s) + MO(s) \quad \cdots (2)$$

After further consideration, the addition of MgO seems to be effective in order to improve removal of chromium. The effects of MgO addition in the flux, on removal of chromium and on manganese loss for oxidation was investigated. The results of substituting MgO addition for CaO addition in the flux are shown in Fig.5.

In this investigation, the total volume of (MgO) and (CaO) was constant in order to

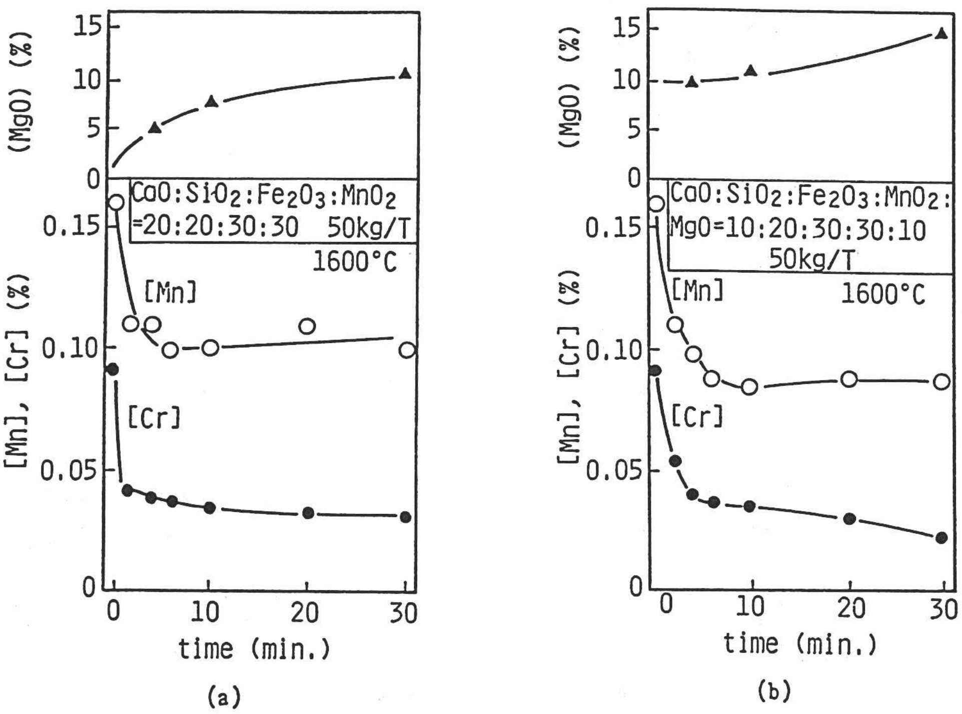

Fig. 5 Effect of MgO addition to flux on removal of chromium, [Mn] loss, and (MgO) increase from MgO crucible

keep the condition: $(CaO+MgO+MnO)/(SiO_2+Al_2O_3)$ nearly equal to 2. As reported by Banya[5], the effect of CaO on a_{FeO} is different from that of MgO on a_{FeO}. However, a_{FeO} was 0.77 in Fig.5(a) and 0.79 in Fig.5(b) when calculated by the regular solution model. Fig.5 illustrates the following;

① Removal of chromium
The ratios of removal of chromium increased slightly, that is, from 65% to 75%, substituting MgO for CaO.

② Manganese loss for oxidation
The amount of manganese loss for oxidation increased slightly, substituting MgO for CaO.

③ MgO increase in slag from MgO crucible
The amount of MgO increase in slag from MgO crucible decreased up to half of the level, that is, from 11% to 5%, substituting MgO for CaO. It is expected that the addition of MgO to the flux protects MgO-based refractory.

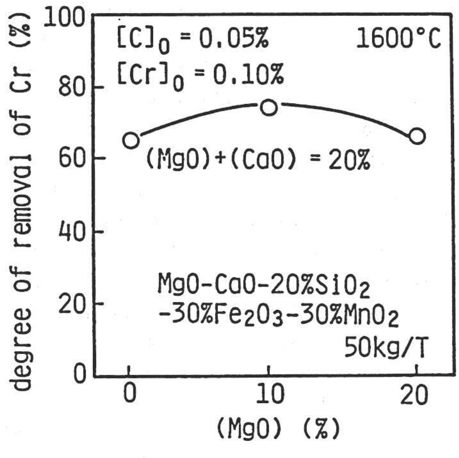

Fig. 6 Effect of (MgO) on degree of removal of chromium

The relation between removal of chromium and MgO addition is shown in Fig.6. The ratios of removal of chromium increased with 10 wt% MgO addition. However, the ratios of removal of chromium decreased when more than 10 wt% MgO was added.

3.5 Prevention of manganese loss during removal of chromium

Manganese in molten steel decreased for oxidation during removal of chromium because of using the flux which had high oxygen potential. Therefore, for some kinds of steel, it is necessary to add expensive manganese alloy after removal of chromium. The

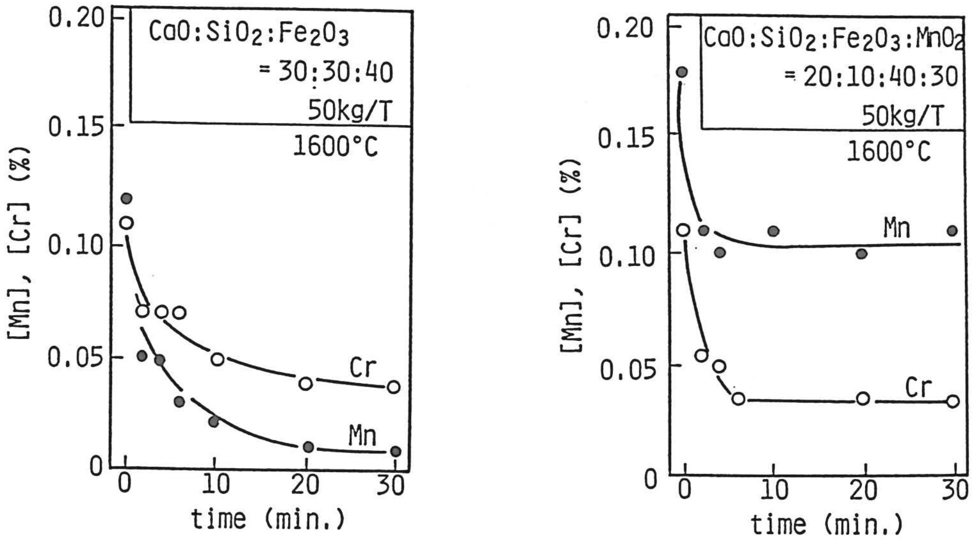

Fig. 7 Decrease of [Mn] loss by MnO_2 addition to flux

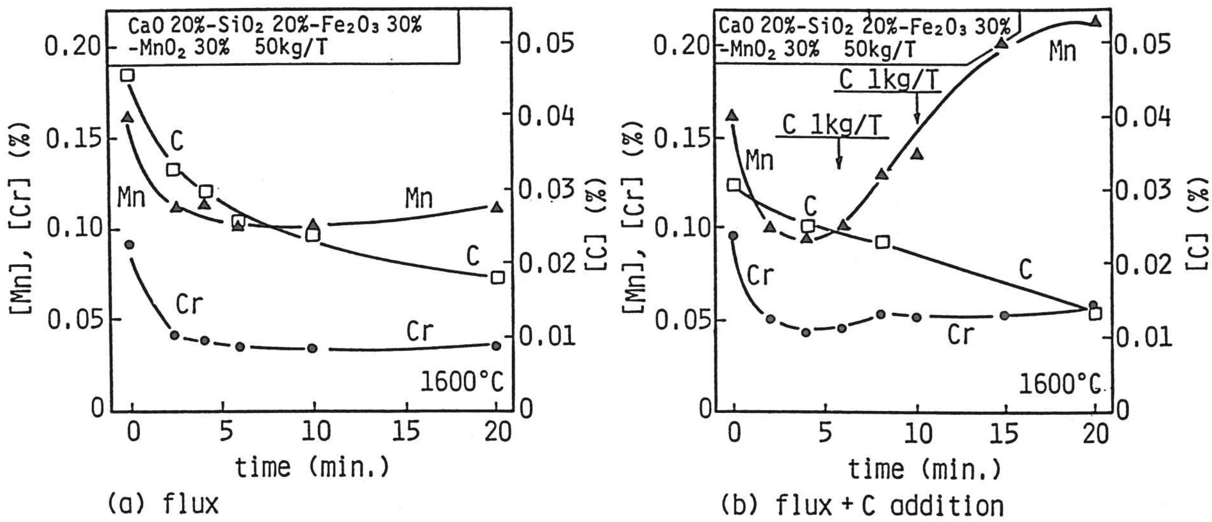

Fig. 8 Effect of carbon addition on [Mn] loss

methods of preventing manganese loss during removal of chromium are investigated as follows;

① MnO_2 addition to the flux

② carbon addition into the slag after removal of chromium

3.5.1 Effect of MnO_2 addition to the flux

The results of investigating the effect on preventing manganese loss with the flux, which included MnO_2, are shown in Fig.7. Chromium in molten steel was removed, maintaining manganese in molten steel, that is, manganese kept at about 0.10 %, with 20-30 wt% MnO in slag.

3.5.2 Effect of carbon addition into the slag after removal of chromium

It proved to be necessary to add more than 30 wt% MnO in slag for manganese in molten steel to maintain more than 0.10 %, for example, 0.15 %. In that case, the problems occured because of the following three points;

① Removal of chromium decreased, because the relative volume of Fe_2O_3, CaO, SiO_2, and so on decreased.
② The fluidity of the slag decreased.
③ The damage against the refractory increased.

(MnO) in slag after removal of chromium was 20-30 wt%. On the other hand, (Cr_2O_3) in slag after that was 1.0-1.5 wt%. Therefore, the method of increasing manganese by adding carbon grains as a reducing agent was investigated. In this treatment, (MnO) in slag rather than (Cr_2O_3) seems to be reduced by physical contacts with carbon grains in non-equilibrium.

The results of carbon grain addition are shown in Fig.8. Manganese in molten steel decreased from 0.16 % to 0.10 % during the first 5 minutes. After carbon grain addition at 5-10 minutes, manganese in molten steel increased. On the other hand, there was no problem about chromium because chromium in molten steel increased by 0.005 % after carbon grains addition.

4. Conclusions

Removal of chromium from molten steel was investigated with slag, which has high oxygen potential and low basicity, when chromium exceeds its specification by using scrap, which include chromium, after refining in a converter furnace or melting in a electric furnace.

(1) 60 - 75 weight% amount of chromium is removed from molten steel by using (CaO-MgO-MnO_2)-(SiO_2-Al_2O_3)-Fe_2O_3 flux of about 50 Kg/t

(2) The optimum conditions for removal of chromium are as follows;
① Oxygen potential of slag, (T.Fe) in slag, is high.
② Slag basicity is 1.5-2.0.
③ (MgO) in slag is about 10 wt%.

(3) The method of preventing manganese loss for oxidation are as follows;
① MnO_2 is added to the flux.
② Carbon is added into the slag after removal of chromium.

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