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EFFECT OF CHROMIUM CONTENT IN LIQUID IRON ON THE SMELTING REDUCTION OF CHROMITE ORE IN MOLTEN SLAG

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Synopsis: This work aims at clarifying the effect of chromium content in metal on the smelting reduction of chromite ore in slag. The reduction behavior of chromite ore, prereduced chromite and Cr_2O_3 powder by carbon in liquid Fe-Cr alloy held in graphite crucible was investigated at 1843 K mainly. During (FeO) (i.e.,oxygen concentration) was high, (CrO) was not reduced at metal-slag interface in metal contained 20 mass% chromium. In case of smelting reduction of chromite ore, (CrO) concentration dissolved in slag at an early stage of the reduction increased with an increase of [Cr]. Slag foaming height at early stage of the reduction was unchanged with time. The foaming height in the reduction of chromite ore was the highest of all. On the whole, the foaming height was not influenced by chromium concentration in metal.

Key words: smelting reduction, chromite ore, prereduced chromite ore, Cr_2O_3 powder, CO evolution rate, slag foaming height, partition ratio, reaction rate.

I Introduction

Smelting reduction of chromite ore has been extensively investigated in Japan. In previous works[1)~3)], the kinetic of the reduction in $CaO-SiO_2-Al_2O_3-MgO$ slags by the carbon in liquid iron held in graphite crucible was examined. The purpose of the smelting reduction of chromite ore is the production of ferrochromium and/or Fe-Cr alloy. In the previous experiments, chromium content in metal at the end of experiment was less than 2 mass% and its value was smaller than the value which the smelting reduction aimed. In this work, as a series of fundamental study of the smelting reduction, the influence of initial chromium concentration in metal, $[Cr]_0$, on the smelting reduction behaviors of chromite ore, prereduced chromite ore and Cr_2O_3 powder in $CaO-SiO_2-Al_2O_3-MgO$ slag was studied.

II Experimental

II-1 Chromite ore and flux

Chromium oxides used were South African chromite ore (ore A), prereduced chromite ore (ore B) and chemical reagent Cr_2O_3 powder (ore C). The chemical composition of the ore was shown in Table 1. The ore was ground and screened. The ore size was 53-105 μm. The ore B was prepared by the reduction of the ore A by H_2. Ninety mass% of FeO contained in the ore was reduced by the treatment of H_2 reduction.

The chemical composition of flux was shown in Table 2. The flux was premelted in graphite crucible before use.

Table 1 Chemical composition of South African chromite ore. (mass%)

Cr_2O_3	FeO	Al_2O_3	MgO	SiO_2	C	S	P_2O_5
44.8	25.3	14.5	10.3	3.0	0.019	0.007	0.007

Table 2 Chemical composition of flux. (mass%)

CaO	SiO_2	Al_2O_3	MgO
40	40	15	5

II-2 Experimental procedure

The experimental apparatus was schematically shown in Fig.1. The apparatus used was almost the same as the one used previously. But in the present work, the course of the smelting reduction was followed by measuring CO evolution rate mainly. Argon was introduced from the bottom of the reaction tube and exhaust gas flow rate was measured with soap film gas flow meter.

Raw material (electrolytic iron, electrolytic chromium and graphite powder) of 2.4×10^{-1} kg was charged into graphite crucible. They were melted to desired temperature in high purified Ar gas flow ($1\times10^{-5}\,m^3s^{-1}$) by using high frequency induction furnace and then the melt was kept at the constant temperature in order to be saturated with carbon. After Ar gas flow rate was measured accurately with the flow meter, both 1.5×10^{-2} kg of ore A or ore B (6.67×10^{-3} kg of ore C) and 1.5×10^{-2} kg of flux were added on the melt surface. Experiments were carried out at 1843 K mainly. Temperature of the metal on the inside of a submerged graphite tube was measured with two color eye. It was controlled within ± 10 K.

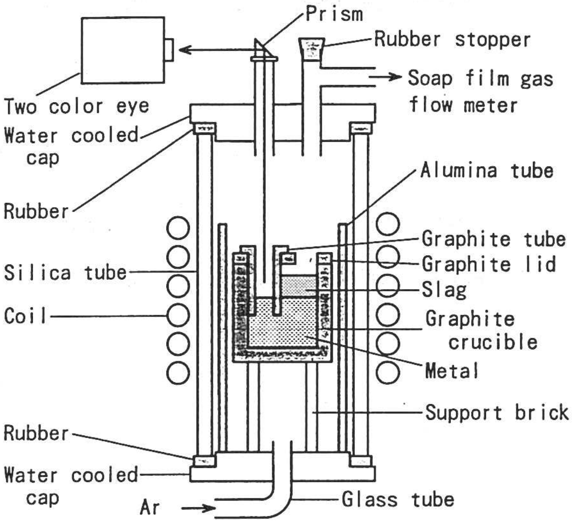

Fig. 1 Schematic diagram of experimental apparatus.

Exhaust gas flow rate was measured from the end of adding of them. As CO_2 was hardly detected, CO gas evolution rate was obtained by subtracting Ar gas flow rate from exhaust gas flow rate. The metal and slag samples were taken at predetermined time intervals by means of suction through silica tube and adding on tapered thin silica tube respectively. The compositions of metal and slag were analyzed by using conventional titration method and EPMA, respectively. The slag foaming height was estimated by detecting the position of slag surface with the tapered thin silica tube.

III Results

III-1 CO evolution rate

Fig.2 showed change of CO evolution rate with time in the reduction of ore A at 1843 K. Irrespective of $[Cr]_0$, CO evolution rate showed maximum value after flux fused and then decreased gradually. In particular, the rate in $[Cr]_0$=20 mass% decreased abruptly after 2 ks. In comparison among CO evolution rates till about 2 ks, CO evolution rate in $[Cr]_0$=40 mass% was the smallest and the rate in $[Cr]_0$=20 mass% was the largest.

Fig.3 showed change of CO evolution rate with time in the reduction of ore B at 1843 K. CO evolution rate in $[Cr]_0$=20 mass% was similar with the rate in $[Cr]_0$=40 mass% till about 1.2 ks. In the duration, CO evolution rate in $[Cr]_0$=0 mass% was the smallest.

Fig.4 showed change of CO evolution rate with time in the reduction of ore C at 1843 K. It seemed that there is no difference in the rate in each $[Cr]_0$.

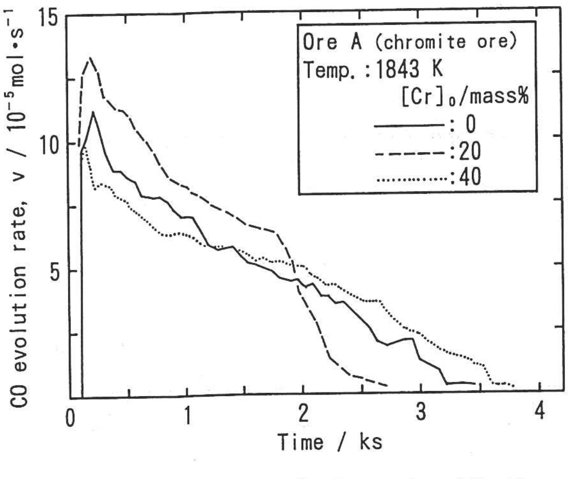

Fig. 2 Change in CO evolution rate with time.

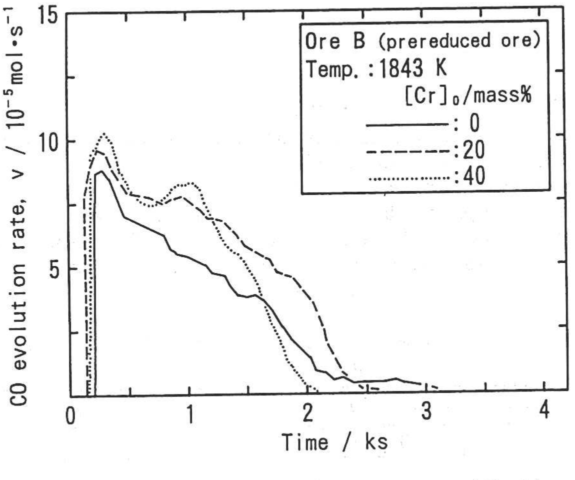

Fig. 3 Change in CO evolution rate with time.

In comparing the rate in each ore on the whole, the CO evolution rate in the reduction of ore A was the largest and the rate in the reduction of ore C was the smallest. With regard to influence of $[Cr]_0$ on the rate, it seemed that there is no systematical dependency of the rate on $[Cr]_0$. The analysis of the rate will be described later.

Ⅲ-2 Slag composition

In this report, behaviors of dissolved chromium oxide and iron oxide which were reducible constituents were described. The dissolved chromium oxide was regarded as CrO because slag color was blue at the end of experiment.

Fig.5 showed change in (CrO) and (FeO) with time in the reduction of ore A. (CrO) showed constant value at an early stage and then decreased. (CrO) at an early stage increased with an increase of $[Cr]_0$. (FeO) showed maximum value and then decreased.

Fig.6 showed relation between (CrO) and $[Cr]_0$ in each temperature. The dependency of (CrO) at an early stage of the reduction on $[Cr]_0$ increased with temperature.

Fig.7 showed change in (CrO) and (FeO) with time in the reduction of ore B. The behavior of (CrO) in the reduction of ore B was different from the behavior in ore A. (CrO) showed maximum value after flux fusion and then decreased. (CrO) immediately after flux fusion increased with an increase of [Cr]. It seemed that the behavior of (FeO) was similar with that in ore A.

Fig.8 showed change in (CrO) and (FeO) with time in the reduction of ore C. The behavior of (CrO) was similar with the behavior in ore B. Though ore C scarcely contained iron oxide, (FeO) was detected in the reduction of each $[Cr]_0$.

In comparison of (CrO) in the reduction of each ore immediately after flux fusion, (CrO) in the reduction of ore C was the highest and that in ore A was the lowest.

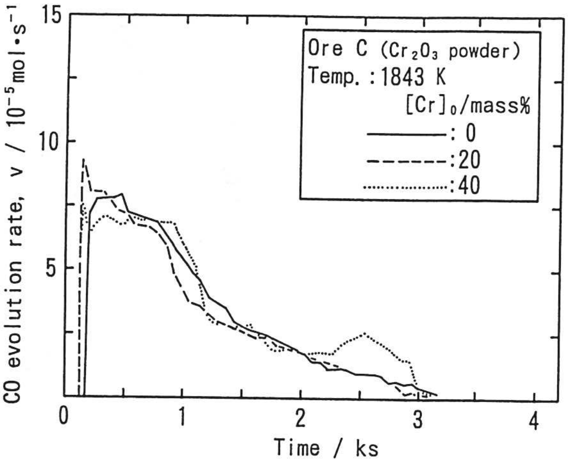

Fig. 4 Change in CO evolution rate with time.

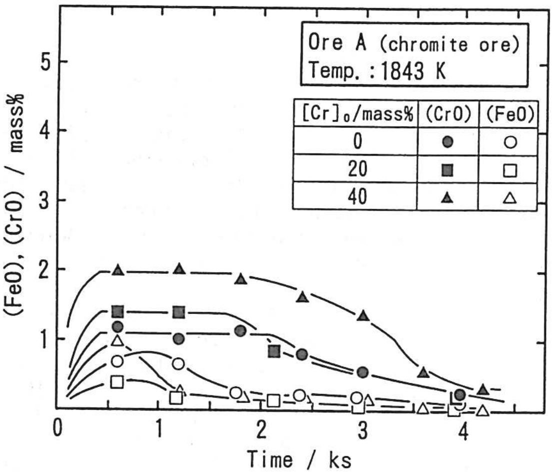

Fig. 5 Change in (FeO) and (CrO) dissolved in slag with time.

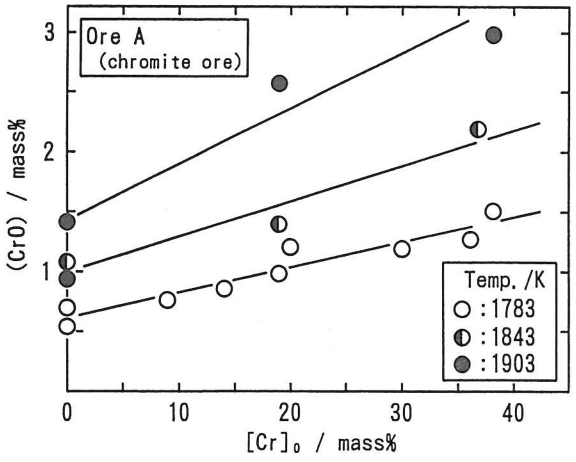

Fig. 6 Relation between (CrO) and $[Cr]_0$.

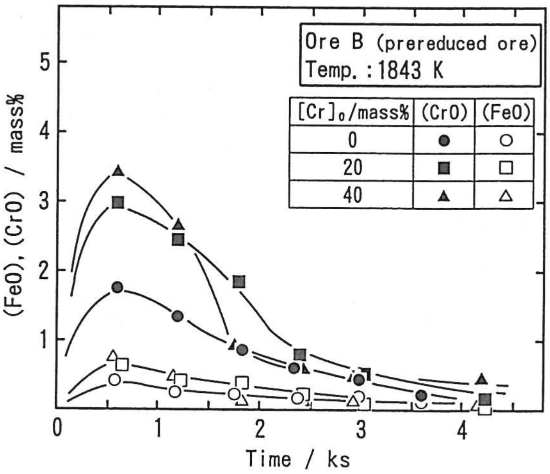

Fig. 7 Change in (FeO) and (CrO) dissolved in slag with time.

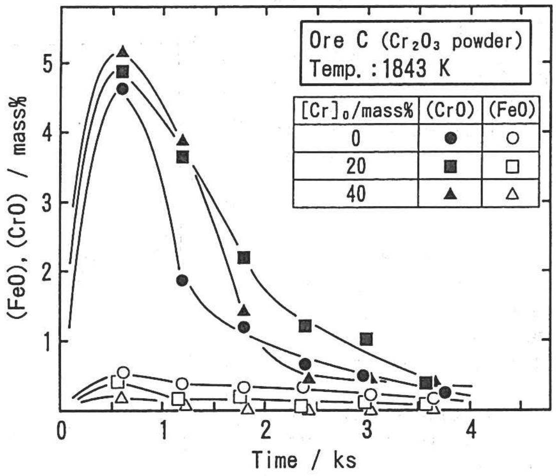

Fig. 8 Change in (FeO) and (CrO) dissolved in slag with time.

Ⅲ-3 Slag foaming height

Slag began to foam immediately after flux fusion. Except in the reduction of ore C in $[Cr]_0$=40 mass%, slag foaming height showed constant value and then decreased. The foaming height in ore C in $[Cr]_0$=40 mass% showed maximum value immediately after flux fusion and then showed constant value. When slag foaming calmed down, bare metal surface appeared.

Fig.9 showed relation between $[Cr]_0$ and slag foaming height which showed constant value at an early stage in the reduction of each ore (maximum value in ore C in $[Cr]_0$=40 mass%) at 1843 K . On the whole, the slag foaming height in the reduction of ore A was the largest of all and the foaming height in ore C was the smallest. Except in ore C in $[Cr]_0$=40 mass%, slag foaming height in the reduction of each ore didn't vary with $[Cr]_0$.

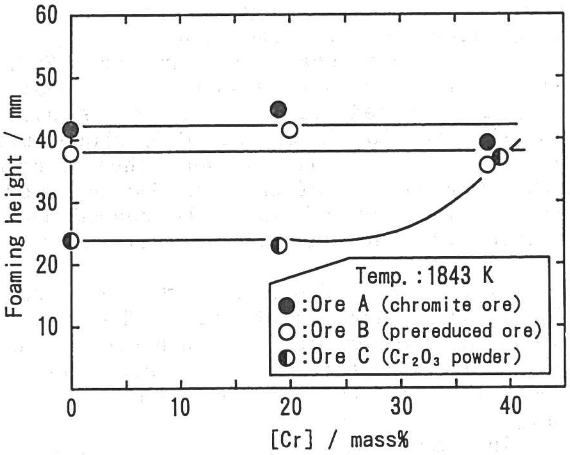

Fig. 9 Relation between slag foaming height and [Cr].

Ⅲ-4 Partition ratio

Fig.10 showed relation between $[Cr]_f$ and $(CrO)_f$ at 2 ks after stop of slag foaming. $(CrO)_f$ increased with $[Cr]_f$ and dependency of $(CrO)_f$ on $[Cr]_f$ decreased with temperature rise. In this experiment, slag contacted with both graphite and metal. Accordingly, it may be considered that (CrO) was equilibrated with graphite and metal. The former equilibrium relation between them was negligible because equilibrium (CrO) with C and Cr_3C_2 was less than 200 ppm[4]. Therefore (CrO) was apparently determined by the equilibrium between slag and metal. The gradient of straight line was regarded as apparent partition ratio, L, between (CrO) and [Cr].

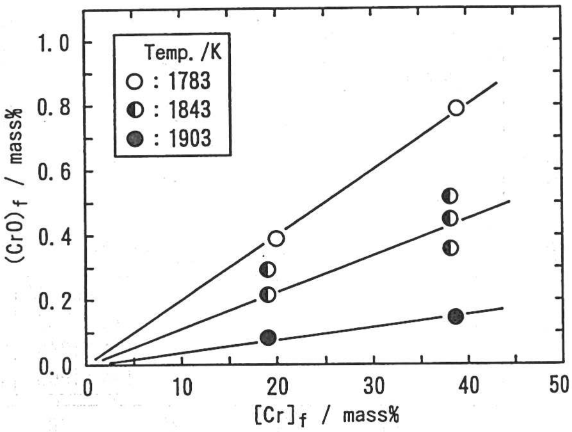

Fig. 10 Relation between $(CrO)_f$ and $[Cr]_f$.

IV Discussion

IV-1 Rate constant in the reductions of ore B and ore C.

In the reduction of ore A, CO is evolved by reduction of chromium oxide and iron oxide. Firstly, CO evolution rate in ore B and ore C will be analyzed because there is no need to consider the reduction of FeO.

In previous work, it has been clarified that the reduction rate is expressed by the sum of reaction rates at metal- and graphite-slag interfaces and that the rate at slag-metal interface was controlled by mass transport of (CrO). Assuming that CO evolution rate at graphite-slag interface is controlled by mass transport in slag, CO evolution rate, V[$\mathrm{mol \cdot s^{-1}}$], is expressed by

$$V = \frac{3}{2} k_{MS} \frac{\rho}{100 M_{CrO}} \{(\mathrm{mass\%CrO}) - L[\mathrm{Cr}]\} A_{MS} + \frac{3}{2} k_{GS} \frac{\rho}{100 M_{CrO}} (\mathrm{mass\%CrO}) A_{GS} \qquad (1)$$

where A is the interfacial area [$\mathrm{m^2}$]
k is the mass transfer coefficient [$\mathrm{m \cdot s^{-1}}$]
L is the apparent partition ratio
M is the molecular weight [$\mathrm{kg \cdot mol^{-1}}$]
ρ is the slag density [$\mathrm{kg \cdot m^{-3}}$]
subscript MS and GS indicate metal- and graphite-slag interfaces, respectively.

As k_{MS} has been obtained in previous work, k_{GS} is calculated herein. A_{MS} was calculated from the shape of crucible, and both (mass%CrO) and A_{GS} were regarded as functions of time.

The obtained k_{GS} unchanged with time at an early stage of the reduction and then increased with time. In the reduction of ore C, the k_{GS} at an early stage in $[\mathrm{Cr}]_0$=0, 20, 40 mass% were 6.4, 2.6, 2.5 $\times 10^{-6} \mathrm{m \cdot s^{-1}}$, respectively. In ore B, the k_{GS} in $[\mathrm{Cr}]_0$=0, 20, 40 mass% was 9.5, 6.2, 7.6 $\times 10^{-6} \mathrm{m \cdot s^{-1}}$, respectively. However, it is not acceptable that the reduction rates at graphite-slag interface in $[\mathrm{Cr}]_0$ = 20 ,40 mass% are smaller than the rate in $[\mathrm{Cr}]_0$=0 mass% because there is no difference in reaction product adhered on graphite in each $[\mathrm{Cr}]_0$.

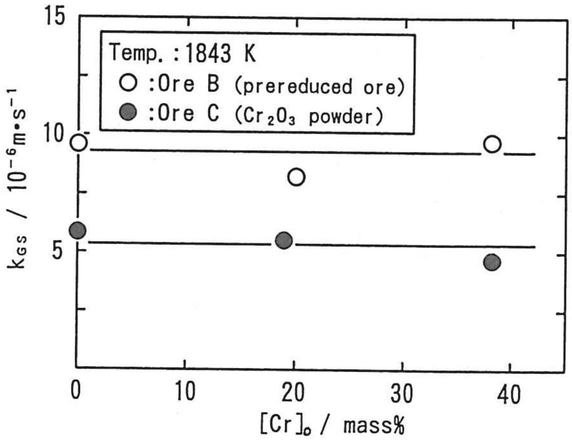

Fig. 11 Relation between rate constant, k_{GS}, and $[\mathrm{Cr}]_0$.

The k_{GS} in $[\mathrm{Cr}]_0 \geqq 20$ mass% is recalculated on assumption that (CrO) is not reduced at metal-slag interface. As above mentioned, the k_{GS} also unchanged with time at an early stage of the reduction and then increased with time. The k_{GS} at an early stage were shown in Fig.11. The k_{GS} in $[\mathrm{Cr}]_0 \geqq 20$ mass% showed good agreement with the k_{GS} in $[\mathrm{Cr}]_0$=0 mass%. The k_{GS} in the reduction of each ore was not influenced by [Cr]. Accordingly, it was found that the reduction at metal-slag interface didn't occur.

The reason is explained as follows. As described in III-2, (FeO) existed in slag even in the reduction of ore C. It was estimated that oxygen concentration was higher than the one equilibrated with (CrO) and $\underline{\mathrm{C}}$. Accordingly, due to the high oxygen concentration at metal-slag interface, chromium in metal was oxidized as

$$(\mathrm{FeO}) + \underline{\mathrm{Cr}} = (\mathrm{CrO}) + \underline{\mathrm{Fe}} \qquad (2)$$

The explanation was supported by that (CrO) immediately after flux fusion increased with an increase of [Cr].

Next, the behavior of the increase of k_{GS} with time is discussed. It is anticipated that oxygen concentration decrease at a later stage of the reduction. Therefore k_{MS} is calculated from eq.(1) using k_{GS} shown in Fig.11. k_{MS} obtained was 9.9 $\times 10^{-6} \mathrm{m \cdot s^{-1}}$ and its value was the similar value (k_{MS} = 11.2 $\times 10^{-6} \mathrm{m \cdot s^{-1}}$) obtained in previous work.

It can be seen from these that (CrO) in $[\mathrm{Cr}]_0 \geqq 20$ mass% cannot be reduced at metal-slag interface until oxygen concentration was low enough. The result obtained accords with the one obtained by Fujita et al..⁵⁾

As shown in Fig.11, the k_{GS} in the reduction of ore B was larger than the one in ore C. The reason is explained by whether ore contains iron oxide or not. As ore B contained small amount of FeO, it was considered that k_{GS} was enlarged by only CO evolution rate due to reduction of FeO.

IV-2 Rate in the reduction of ore A.

As ore A contains FeO more than ore B, it is considered that the reduction of (CrO) cannot occur at metal-slag interface. On the assumptions that (FeO) isn't reduced at metal-slag interface and rate constant in the reduction of (FeO) is the same as the one in the reduction of (CrO), the CO evolution rate was

$$v = k'_{GS} A_{GS} \left\{ \frac{3\rho}{200 M_{CrO}} (\text{mass\%CrO}) + \frac{\rho}{100 M_{FeO}} (\text{mass\%FeO}) \right\} \qquad (3)$$

The k'_{GS} calculated from the eq.(3) was shown in Fig.12. As [Cr] increased at an early stage of the reduction in $[Cr]_0$=0 mass%, CO evolution rate in that case was excluded from the calculation. The k'_{GS} obtained at 1783 K was independent on $[Cr]_0$ and the k'_{GS} obtained at 1843 K and 1903 K decreased with an increase of $[Cr]_0$. The k'_{GS} at 1783 K was the smallest of all and the k'_{GS} at 1843 K was almost the same as the one at 1903 K.

These behaviors were explained qualitatively as follows. The reduction didn't occur at metal-slag interface at 1783 K. At higher temperature, it seemed that (FeO) was reduced at metal-slag interface in relatively lower [Cr]. Therefore k'_{GS} was apparently enlarged by only the CO evolution rate at metal-slag interface due to the reduction of (FeO).

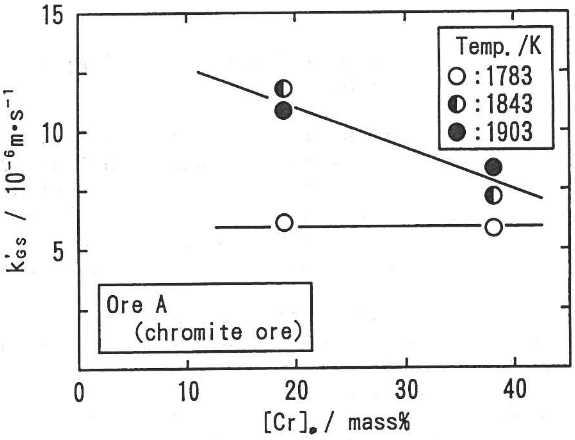

Fig.12 Relation between rate constant, k'_{GS}, and $[Cr]_0$.

V Conclusion

The courses of the smelting reduction of chromite ore (ore A), prereduced chromite ore (ore B) and Cr_2O_3 powder (ore C) were followed by measuring CO evolution rate, slag composition and slag foaming height.

The results obtained were as follows:

(1) During (FeO) concentration in slag was high, (CrO) was not reduced at metal-slag interface in metal contained more than 20 mass% chromium.

(2) In case of smelting reduction of ore A, (CrO) content in slag at an early stage of the reduction was unchanged with time. (CrO) increased with an increase of [Cr]. In case of smelting reduction of ore B and ore C, (CrO) showed a maximum value immediately after flux fusion and then decreased gradually.

(3) Slag foaming height at an early stage of the reduction was unchanged with time. The foaming height in the reduction of ore A was the largest and the foaming height in ore C was the smallest. On the whole, the foaming height was not influenced by chromium concentration in metal.

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