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SMELTING REDUCTION OF METAL OXIDES BY CARBOTHERMIC PROCESS

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Synopsis: Metal-oxide was melted by D.C plasma furnace to make the stoichiometric compounds of FeO or CrO to study the smelting reduction conditions in metal bath. It was melted in negative pressure in vessel, the reduction rate was increased linealy.

In the carbothermic reduction process, metal oxide reduction conditions were checked in state of alloy addition such as: Fe-M (M: C,Si,Mn,Cr,Ni,Cu etc), and activity of carbon "a_c" was calculated with the thermodynamic data by the equation of interaction parameter. The reduction rate was increased in the Fe-Ni,Cu system in the evidence of increasing "a_c" by thermodynamic calculation, but in the Fe-Cr,Mn system,the reaction time was increased by the decreasing "a_c" in the metal bath which has the same results in thermodynamic calculations.

Key words: D.C plasma, pressure vessel, carbothermic reduction, carbon activity, preliminary reduction rate, CO pressure

I . Introduction

Metal-oxide reduction process has been seperated into two stage by the several compulsory situations such as environmental contamination problems and the exhaustions of raw materials like a high bituminous coal etc. The smelting reduction process has been developed with the preliminary reduction at rotary furnace and smelting reduction in plasma furnace or oxy-converter. The development of smelting reduction has a long history; during the first world war, the rotary furnace (Krupp-Renn) [1] was developed, and after the second world war, new method was developed which was used both rotary furnace and electric furnace. The smelting reduction process has been studied continuously world wide by using an electric furnace after prereduction at rotary furnace. Just recently, many other processes such as , Elkem method [2], Plasma smelting method [3], Corex process [4], etc are developed.

In this study, to determining 1st stage (gas/solid) reduction to influence the burden of 2nd stage (slag/metal) reduction, FeO/Fe ratio was changed from 10 to 90 % and it was reduced in RF furnace. In the smelting reduction furnace,it must be studied exhaustive fundamental phenomena , because the process advanced by all kinds of the reactions. It was studied also of the mechanism of carbon materials/metal oxides, metal oxides/slag reactions, and the influence of the effects of the pressure to the carbon/metal oxides reduction.

The activity of carbon in Fe-Cr-C or Fe-Cr-M-C alloys, which was the most important ternary system of the chromium steel making, was calculated by the thermodynamic data to check of the behaviors of solute atoms such as C, Si, Mn, Cr, Ni, Cu, etc on the smelting reduction of metal oxides.

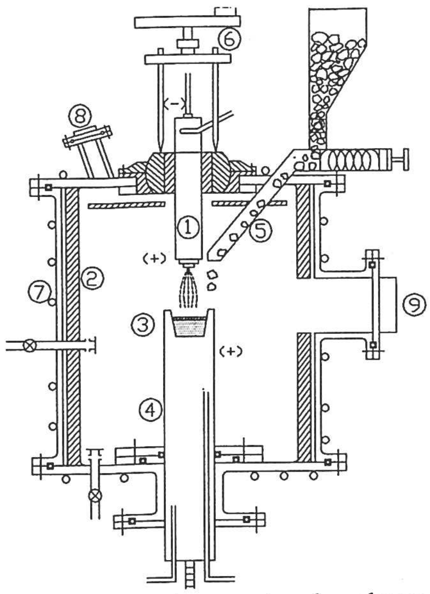

Fig.1 Experimental apparatus for plasma furnace.
① plasma torch ② shielding panel
③ Cu crucible ④ supporter
⑤ charging system ⑥ rotating device
⑦ vessel ⑧ peeping hole
⑨ side window

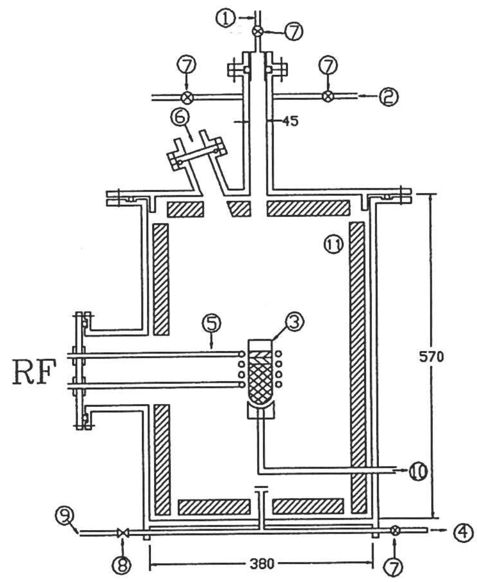

Fig.2 Schematic diagram of reaction chamber.
① Ar gas inlet ② H_2 gas inlet
③ melting crucible ④ gas outlet
⑤ working coil ⑥ peeping hole
⑦ needle valve ⑧ ball valve
⑨ to vacuum chamber

II. Experimental procedures

Fe-oxide or Cr-oxide was melted by the D.C plasma furnace as shown in Fig.1, which has a plasma torch with rotating device, D.C max 600 A power source, pellet charging devices, melting furnace with water cooled Cu crucible. Ar or N_2 flow rates are 12~18 ℓ/min for melting oxides. The plasma torch consisted with 6mmϕ water cooled Cu nozzle and 2 % thoriated 4~5ϕ W cathode [5]. After ignition by nontransferred plasma state, the charge was melted partly into a narrow pool to give enough electrical conductivity for transferred state, because oxides are very poor electrical conductivity and it has very high volatile characteristics. These materials are melted very rapidly with high power under positive chamber pressure.

Fe-M (M: C,Si,Mn,Cr,Ni,Cu etc) alloy was melted by RF power in 380 ϕ X 570 H pressure vessel as shown in Fig.2. Under the Ar or N_2 atmosphere, about 6g of FeO or CrO pellets were charged in the 30 or 60g Fe-M melt, and the reaction time was checked. The Fe-M alloy composition was changed by 1,3,12,20 %, four steps. In order to study of the influence of pressure on the reduction, vessel pressure was changed from positive to negative during tests.

III. Results and Discussion

A. D.C Plasma Melting

Iron oxide reduction was processed by two steps : $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$ and $FeO \rightarrow Fe$. The later reaction was processing by the smelting reduction stage in the high temperature zone on the BF. Chromium oxides are also reduced by two stage process : 1st gas/solid reduction in rotary-kiln and 2nd stage reduction in molten metal bath. In order to study later stage of reduction, the stoichiometric compound of FeO and CrO was going to make in the high temperature D.C. plasma furnace as shown in Fig.1. CrO compound was formed by melting Cr_2O_3 and Cr in D.C. plasma furnace twice and it was precipitated by cooling to room temperature into Cr_2O_3 and Cr. It was precipitated as about 5 or 6 μm fine blebs in the matrix of Cr-oxides. But, these materials are enough to use as a raw materials pellet "CrO" in 2nd stage smelting reduction. The metallic fine blebs were finely distributed and good coherent into the Cr-oxide matrix and they are easily absorbed into the oxide matrix when it was heated up to about reaction temperature 1620～1680℃, by the reaction of $Cr + Cr_2O_3 \equiv 3\ CrO$. In the reduction test, pseudo-CrO pellets are easily melted and made fluid slag form above metal bath,and its reaction was vigorously progressed by the graphite crucible wall and also on the boiled metal bath.

B. 1st and 2nd stage reduction ratio

In economics and production cost or technical points of view, it is important factor to determine how the 1 stage reduction degree would be influenced to the second stage smelting reduction periods. In order to study the influence of 1st stage (gas/solid) reduction degree to the 2nd stage (slag/metal) reduction, FeO:Fe ratio was changed from 10 to 90 % by increasing 10 %, and melted in D.C.plasma furnace as in Fig.1. Its product was pulverized under 150 mesh and pelletized again to use as the raw pellet in 2nd stage reduction.

These pellets are reduced in the RF reduction vessel as shown in Fig.2. Iron oxide reduction was more rapidly progressed than Cr-oxide pellets as shown in Fig. 3. By the tangential growth rate, 1st stage reduction ratio should be preferred with about above 40 %.

C. Effects of the slag composition

In order to reduce melting points of slag, CaO and SiO_2 were melted in the D.C plasma furnace, but Na_2O and $CaCl_2$ slag systems could not be melted by the D.C plasma furnace, because of its volatilization characteristics. Four different kinds of slags were made: ① $CaO-SiO_2$, ② $CaO-SiO_2-Na_2O$, ③ $CaO-SiO_2-CaF_2$, ④ $CaO-SiO_2-CaCl_2$. 3 grams of the above slags were added into the 30 or 60g of iron melt and 6g of FeO, or CrO pellets were charged into the crucible. Reduction conditions were checked, but $CaO-SiO_2-CaCl_2$ and $CaO-SiO_2-Na_2O$ systems were very difficult to check, because of the crust formation and volatilization. $CaO-SiO_2-CaF_2$ slag systems were easily melted and fluid condition, and much increased reduction rate of metal oxides.

D. Effect of the vessel pressure.

Metal-oxides were reduced by C̲ or CO reducing gas by the equation of (1) or (2), and reaction products were CO↑or CO_2↑ gases in the carbothermic reduction systems [6]. In order to study the influence of pressure on the reduction of metal-oxides, pressure vessel were prepared as shown in Fig.2, which has the positive and negative pressure controlling systems.

$$FeO + C \rightarrow Fe + CO\uparrow \quad \cdots\cdots\cdots\cdots (1)$$

$$CrO + C \rightarrow Cr + CO\uparrow \quad \cdots\cdots\cdots\cdots (2)$$

$$7(CrO) + 10\ C \rightarrow Cr_7C_3 + 7\ CO\uparrow \quad \cdots\cdots\cdots\cdots (3)$$

In the reduction of metal oxides in the graphite crucible, it was found that the reactions are progressing by two different mechanism, the first reaction is occured in the rim of the graphite/oxide-slags/metal interface by the equation (1) or (2) , and the other reaction is occured in which whole surface of smelted metal oxide/metal bath by the equation of (1) or (2). Especially in the negative pressure, reduction rate was linely increased as shown in Fig.4. On the contrary, when the vessel pressure was in the state of positive, the reduction rate was decreased, but its effect was not much as in the negative pressure.

Cr-oxides will be reduced to carbide forms [7] by the reaction of (3) with the more available free energy, if there are another alloying metals such as Fe, Fe-Cr is formed because of the more less active Cr atoms.

E. Activity of carbon in Fe-Cr-M-C system

In this study, the object was to search the influence of carbon activity (a_c) in metal bath by the addition of several elements : such as C,Si,Mn,Cr,Ni,Cu etc in carbothermic reduction.

The interaction coefficients in dilute solution which contains i,j,k... adopted as first by Wagner [8] and Chipman [9], and later by Lupis and Elliott[10]. It is expressed in the Mclaurin series form. If the concentration is expressed in the mole fraction, the activity coefficients are expressed by the following equation (4).

$$\ln \gamma_i = \ln \gamma_i^o + \sum_{j=2}^{n} \varepsilon_i^j . N_j + \sum_{j=2}^{n} \rho_i^j . N_j^2 + \sum_{\substack{j=2 \\ j<k}}^{n} \sum_{k=2}^{n} \rho_i^{j,k} . N_j . N_k + .. \quad \cdots\cdots (4)$$

$$\varepsilon_i^j = \left(\frac{\partial \ln \gamma_i}{\partial N_j} \right)_{N_i, N_j \to 0} \quad \cdots\cdots (5)$$

Generally, ε_i^j is the interaction coefficient of j element in the Fe-i-j-k system. γ_i^o is activity coefficients in the Fe-i infinite dilute solution, and $\gamma_i^o \equiv 0.57$ was adopted in this calculation [11]. Standard activity [12] of carbon ($a_c \equiv 1$) is adapted at $N_c \fallingdotseq 0.203$. In the Fig.5 in Fe-Cr-Si-C alloy system, $a_c>1$ value was appeared, but it is only relative values. Carbon activity "a_c" was calculated by equation (4) by the thermodynamic data of J.F.Elliot [10], K.Sanbongi [12], Schenk [11], and ploted in part of it a_c data in Fig.5.

F. Effects of alloying elements

Fe-M alloy was melted in the D.C plasma furnace in the composition of Fe-40% M as the mother alloys. It was melted about 30 or 60g Fe-M alloy in the pressure vessel by RF power, and about 6g of FeO, or CrO pellets was charged by lowering of the pellet's basket which was hanged by hook in the vessel, and in the case of addition of slags, it was charged just after melt down of base metal or just before adding of oxide pellets. The reaction time and condition were observed and checked.

Without addition of slags, the reaction time was taken in the FeNi, FeCu alloy systems by 1.50 and 2.55 min, and it was retarded in the FeCr,FeMn alloy system by 4.10 and 3.30 min respectively. But, in the Fe-Si alloy system, $FeO.SiO_2$ slag was formed, and the definite reaction time and condition could not be checked. In the high alloy content about >15%, slag formation tendency was increased such as : $FeO.Cr_2O_3$ chromite was formed, and the reaction time is increased.

By the summarizing of the above experiments and with the calculation of activity of carbon "a_c", as the increase of a_c in Fe-M alloy as Fig.5, the reduction rate is increased, on the contray as the decrease of a_c in Fe-M alloy in Fig.5, the reduction rate is retarded by the comparison to the another systems.

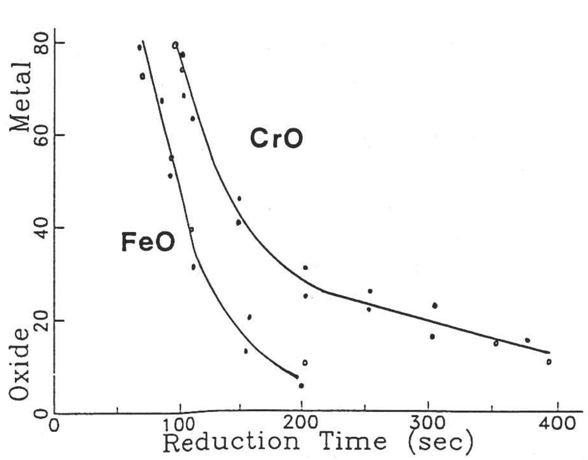

Fig.3 Reduction time by 1st stage reduction degree.

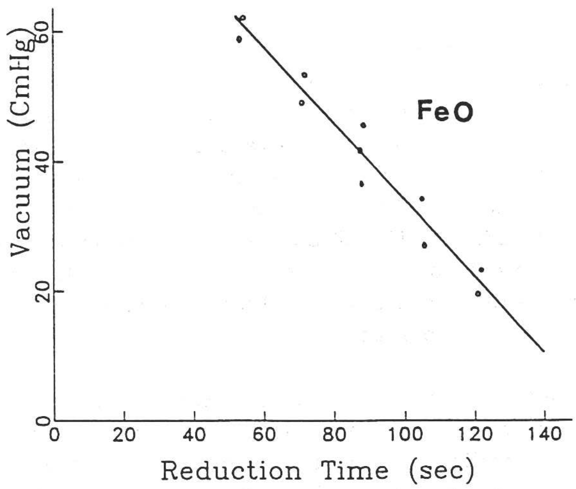

Fig.4 Reaction time and vessel pressure.

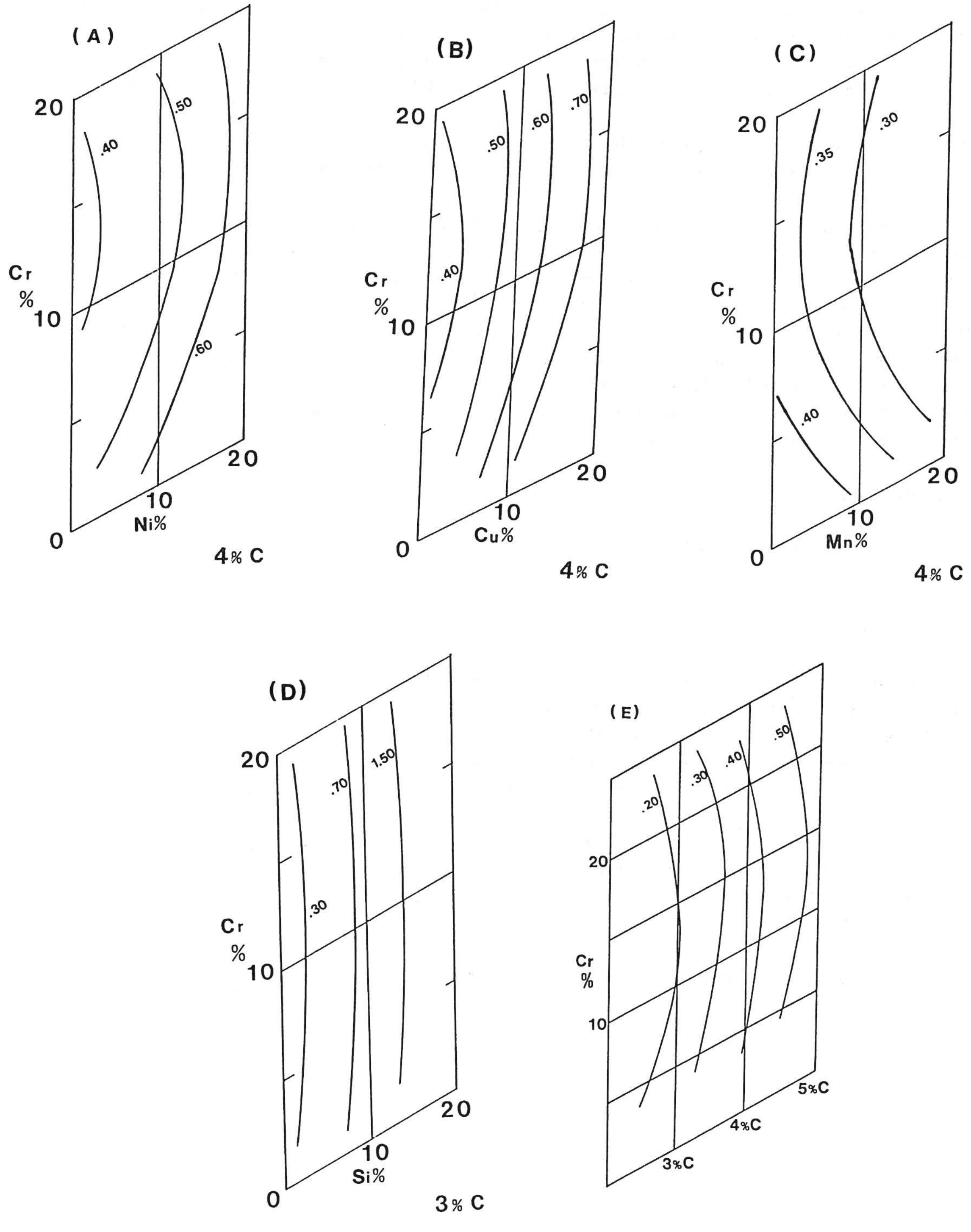

Fig. 5 Carbon activity lines (a_c) in Fe-Cr-M-C system.
(A) Ni, (B) Cu, (C) Mn, (D) Si, (E) C.

IV. Conclusions

The various conditions of metal oxides in the carbothermic reductions were studied by melting in the 1st stage at D.C plasma furnace and the 2nd stage at RF furnace in the pressure vessel. The obtained results can be summarized as follows.

- To determining how the 1st stage reduction degree would be influenced to the 2nd stage, 1st stage smelting reduction, by the experimental, should be preferred with about above 40% in the reduction.
- In the reduction of metal oxides in the graphite crucible, it was found that reduction time was linearly decreased by the negative pressure, because of the evolution of CO gas in the carbothermic reduction.
- In the smelting reduction of metal oxides, $CaO-SiO_2-CaF_2$ slag systems are easily melted and hold in the fluid conditions and it was assisted to increase the reduction of metal oxides.
- The effect of the addition of various allying elements such as C, Si, Mn,Cr, Ni, Cu etc in Fe-M system were studied also on the smelting reduction of metal oxides.
- The activity of carbon "a_c" calculated by the thermodynamic data and compared with the experimetal results. The reduction rate was increased in the system of Fe-Ni,Cu in the evidence with increasing "a_c" by thermodynamic calculation, but in the Fe-Cr,Fe-Mn systems, the reduction time was increased by the decreasing "a_c" in the metal bath which has the same results in the thermodynamic calculation.

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