REDUCTION OF CHROMIUM OXIDE IN STAINLESS STEEL SLAGS

N. Sano

Nippon Steel Corporation, 20-1, Shintomi, Futtu, Chiba, Japan. E-mail: sano@re.nsc.co.jp

ABSTRACT

The chromium oxide in stainless steel slags usually exists as Cr_2O_3*. However, there is a possibility that it is oxidized to hazardous* CrO_3 *after disposal or during use. Therefore, some technical developments to reduce chromium oxide by using a smelting reduction technique have been reported recently. This paper describes the fundamentals of the technique which have been applied to ferrochromium production and reviews the recent results in literature.*

1. INTRODUCTION

The stainless steel slag formed after premelting in an EF or LD before charging to AOD or VOD usually contains some Cr_2O_3. The typical slag composition is CaO 45-50, SiO_2 35-40, MgO 5-15, Al_2O_3 3-5, T Fe 1-3, Cr_2O_3 3-5 mass%. Although Cr_2O_3 is most stable among various chromium oxides at 298K in air, it is easily oxidized to CrO_3 or Cr^{6+} even at higher temperature when contained in molten slags or at ordinary temperatures in aqueous solutions. This means that when the slag is separated from metal and discharged in air, Cr_2O_3 in the slag may be oxidized to CrO_3. Since the solubility of Cr_2O_3 or $MgO\cdot Cr_2O_3$ in molten slags is limited, most chromium exists in slags as MgO Cr_2O_3 or Cr_2O_3. This is another reason why it is readily oxidized because the activity of Cr_2O_3 would be close to unity, although its content is not very high.

Although many means are proposed to avoid the oxidation, for example by surface treatment of slag particles, the present author believes that complete reduction of chromium oxide in slags is the safest approach and the way to minimize treatment cost should be sought. This paper is to review recent literature together with fundamental knowledges obtained for understanding the mechanism of smelting reduction of chrome ores.

2. THERMODYNAMIC BACKGROUND

Figure 1 shows the Cr^{6+}/Cr^{3+} ratio as a function of $XCaO/XSiO_2$ of the MgO-CaO-SiO_2-CrOx slag saturated with $MgO\cdot Cr_2O_3$ at 1873K [1]. Since Cr^{6+} in air exists as CrO_4^{2-} in slags the oxidation reaction may be expressed as Eq.(1).

$$MgO\cdot Cr_2O_3+20^{2-}+3/4O_2=2CrO_4^{2-}+MgO \qquad (1)$$

Therefore, as the slag is more basic the oxidation would proceed further. The same is true with an aqueous solution and with higher PH, more CrO_4^{2-} would form from chemical viewpoint and acid environment with acidic slags is desirable to avoid the Cr^{6+} formation. The solubility of $MgO\cdot Cr_2O_3$ in 20%MgO-20%Al_2O_S-30%SiO_2-30%CaO at 1873K is shown in Figure 2 as a function of oxygen partial pressure after Morita et al [2]. The solubility has a minimum. They observed a mixture of CrO and Cr_2O_3 at lower Po_2 and that of Cr_2O_3 and CrO_3 at higher Po_2 as stated above. When a molten slag is exposed to air, the remaining $MgO\cdot Cr_2O_3$ dissolves into bulk due to an increase in the solubility followed by oxidation to Cr^{6+}.

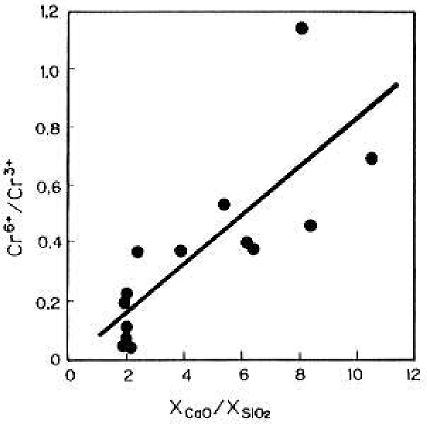


Figure 1. Dependence of Cr^{6+}/Cr^{3+} on CaO/SiO_2 ratio for the $MgO-SiO_2-CaO-CrOx$ system at 1873K in air [1].

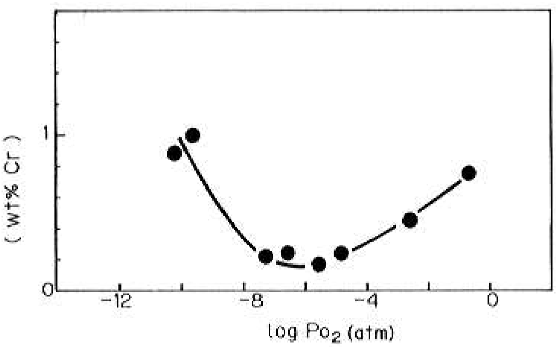


Figure 2. Dependence of the solubility of $MgO \cdot Cr_2O_3$ as mass% (Cr) in $20MgO-20Al_2O_3-30SiO_2-30$ mass% CaO melts at 1873K on oxygen partial pressure [2].

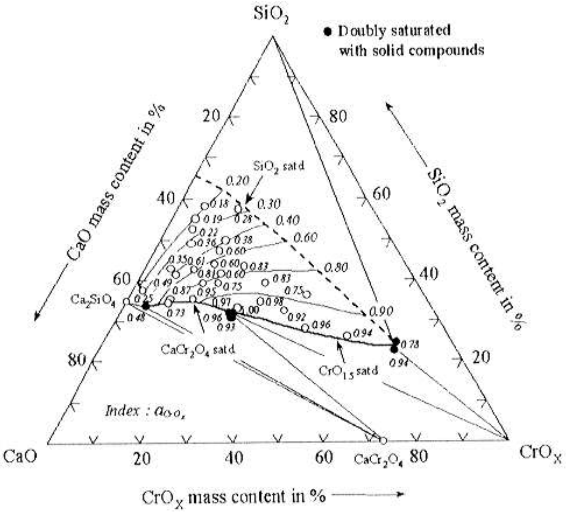


Figure 3. Iso-activity contours of CrOx and phaserelations for the $CaO-SiO_2-CrOx$ system at 1873K with $P_{O_2}=7 \cdot 10^{-6}$ Pa [3].

When MgO is not contained in slags, situation is much different and as Figure 3 shows, the $CaO-SiO_2-CrOx$ system at 1600 with $P_{O_2}=7\times10^{-6}$ Pa has a wide composition range of liquid, causing slag to be highly reactive. When chromium oxide is reduced into molten iron, practically we have three choices of reductant, namely carbon, silicon and aluminum.

2.1 Carbon

$$CrO_{1.5}+3/2C=Cr+3/2CO \tag{2}$$

$$\Delta G^{\circ} = 402{,}600-299\,T \text{ J/mol [4]}$$

Using following thermodynamic data, $\gamma\, CrO_{1.5}=7$ [3] and assuming CaO/SiO_2 ratio is unity and $e_{Cr}^{C}=-0.114$ [5], $aSiO_2=0.1$ [6], $\%(Cr^{3+})$ is calculated as 0.00043 when the slag with the composition described earlier is equilibrated with carbon saturated iron at 1773K. If metal contains 1 mass% C, $\%(Cr^{3+})$ is calculated as 0.35. Since carbon content significantly affects the degree of reduction, carbon saturation would be a necessary condition for reduction.

2.2 Silicon

Similarly,

$$CrO_{1.5}+0.75\underline{Si}=\underline{Cr}+0.75SiO_2 \qquad (3)$$

$$\Delta G^\circ = -6{,}440-29.3\,T \text{ J/mol [4]}$$

Suppose an iron melt contains 1 mass% Si and 1 mass%Cr after reduction, %(Cr^{3+}) is 0.057 at 1773K. If 3% of carbon coexists in the metal, (%Cr^{3+}) is lowered to 0.023 because of a strong interaction between carbon and silicon with e_{Si}^{C} =0.18 [5].

If ferrosilicon (70% Si), having a_{Si}=0.85, used as a reductant directly reacts with the slag, the remaining chromium content would be much less (0.83ppm).

2.3 Aluminum

$$CrO_{1.5}+\underline{Al}=\underline{Cr}+AlO_{1.5} \qquad (4)$$

$$\Delta G^\circ = -20{,}600+20.8\,T \text{ J/mol [4]}$$

When slag is reduced by the metal containing 1 mass% Al and 1 mass% Cr, the remaining Cr^{3+} content is calculated as 0.11ppm where $aAlO_{1.5}$ = 0.1 [6].

The above calculations demonstrate that aluminum is the best reductant. If carbon is chosen due to its lower cost, carbon saturation is preferable. Silicon is another choice and is widely used for reduction of a large content of chromium oxide such as 25～30 mass% in the slag for premelting stainless crude metal before charging to AOD, for example. Through those calculations the activity coefficient of $CrO_{1.5}$ was assumed to be 7 according to Morita. et al [3] who showed that this value increases with increasing basicity or CaO/SiO_2 ratio for the CaO-SiO_2-$CrOx$ system (Figure 4). This suggests that chromium oxide in basic slags is easily reduced. However, this is a mixed blessing in that the remaining Cr_2O_3 is more easily oxidized to Cr^{6+} after cooling as shown by Eq.(1). When MgO coexists as an actual case, the reducibility of CrOx would be decreased, because the activity coefficient of CrOx slightly decreases with an addition of MgO [7].

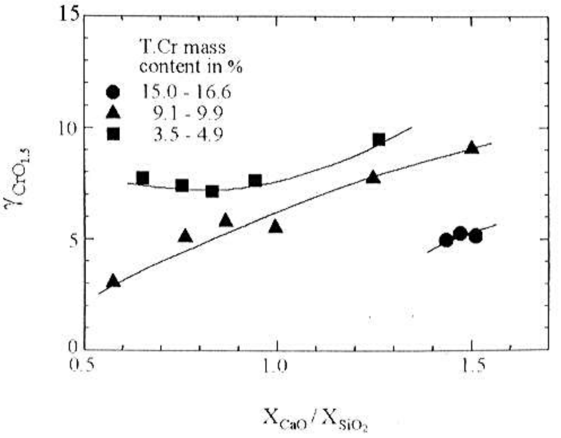


Figure 4. Effect of $XCaO/XSiO_2$ on the activity Coefficient of $CrO_{1.5}$ for the CaO-SiO_2-$CrOx$ system at 1873K with Po_2= $7\cdot10^{-6}$ Pa [3].

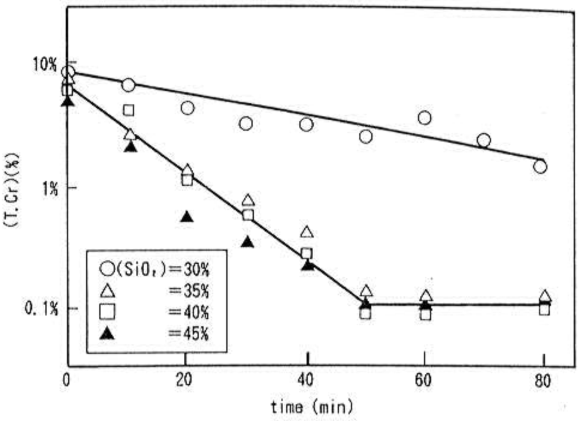


Figure 5. Influence of SiO_2 content on the reduction of Cr_2O_3 in high carbon ferrochromium slags by carbon saturated iron [8].

3. LABORATORY TESTS OF CHROMIUM OXIDE REDUCTION

The author tested the reduction of chromium oxide in high carbon ferrochromium slags using a graphite lined rocking furnace with 4kg of carbon saturated iron and 1kg of slag (CaO 7.2, MgO 25.4, Al_2O_3 21.3, SiO_2 29.6, Cr 8.8 mass%) at 1873K The interfacial area between metal and slag was 240cm^2. The 3 mass% addition of SiO_2 to the original 30% SiO_2 drastically enhanced the reduction rate [8] (Figure 5). Undissolved $MgO\cdot Cr_2O_3$ was not observed microscopically in the slag with SiO_2 addition. This addition lowered the melting point of the slag by 100K, leading to an increase in its fluidity and mass transfer rate, since the dissolution of $MgO \cdot Cr_2Os$ into bulk slag is one of rate determining steps, where the solidity of $MgO \cdot Cr_2O_3$ at 1873K is approximately 1 to 2 as mass%(Cr) (Figure 2).

Fujita et al [9] investigated the smelting reduction behavior of prereduced chrome ore pellet using a 70kg carbon saturated Fe-40%Cr with the slag (CaO/SiO_2=1, Al_2O_3 17%, MgO 17 mass%) together with coke of 5-10 mm size.

Argon was blown through a porous plug at the furnace bottom. They found that at the first stage mass%(Cr) was reduced from 12 to 2 with a constant reduction rate, demonstrating that dissolution of $MgO \cdot Cr_2O_3$ into bulk slag is a rate determining step. After % (Cr) was lowered below 2, the first order reaction was observed, suggesting mass transfer control of (Cr) in slag (Figure 6). The rate constant was found to be constant up to mass% ($MgO+Al_2O_3$)>45 and as this parameter exceeds 45%, it significantly dropped (Figure 7). The Cr content of the last slag was 0.3 mass%.

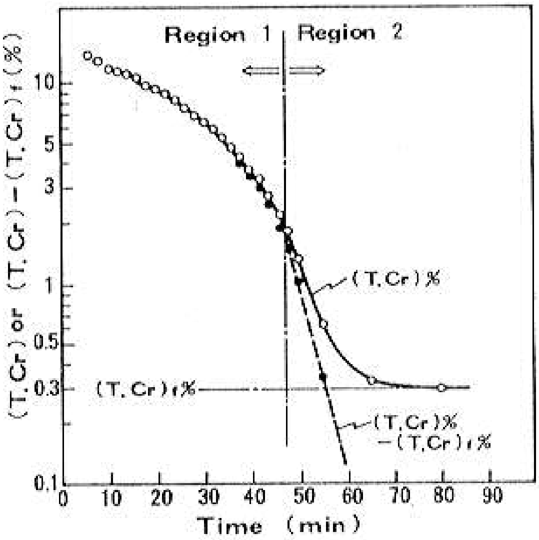


Figure 6. Change in chromium content of slag during smelting reduction of chromite ore with time [9].

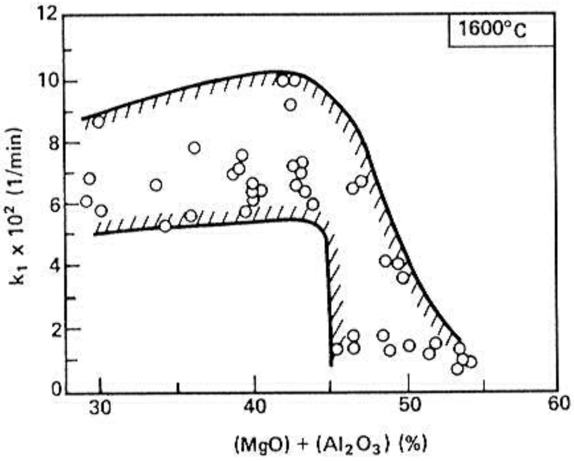


Figure 7. Effect of (MgO)+(Al_2O_3) content on the first order rate constant of reduction of Cr_2O_3 [9].

Miyamoto et al [10] recently investigated the smelting reduction behavior of Cr_2O_3 in the slag to simulate chromium recovery from the slag to produce stainless crude metal before decarburization. They melted 70kg of Fe-C(-Cr) together with 3kg of the $CaO\text{-}SiO_2\text{-}Cr_2O_3\text{-}FeO\text{-}MgO\text{-}Al_2O_3$ slag with CaO/SiO_2=2.5 at 1873K and measured the reduction rate of Cr_2O_3 as functions of initial (Cr_2O_3), (Al_2O_3), $\underline{C}$ and $\underline{Cr}$ contents. All slags contained some solid oxide phases such as $MgO \cdot Cr_2O_3$, $FeO \cdot Cr_2O_3$, $2CaO \cdot SiO_2$ etc. depending on slag composition. Their typical initial slag composition was CaO 39.3, SiO_2 15.7, Cr_2O_3 35, FeO 5.0, MgO 5.0 mass %.

Their findings are summarized as follows:

The additions of Al_2O_3 and CaF_2 and lower CaO/SiO_2 ratio enhance the reduction of Cr_2O_3 due to increased mass transfer rate of chromium in slag through increased proportions of molten phase or less solid phase. As the reduction progressed, the proportion of solid phase decreased as shown in Figure 8. However, those procedures lead to excessive erosion of MgO refractory so that they claim that the optimum slag composition is CaO/SiO2=2.5 and mass%Al_2O_3≒15 without CaF_2. They also found the carbon content up to 1 mass% increases the reduction rate but beyond this content the rate leveled off. Increase in initial chromium of content of the metal decreased the reduction rate and that of the slag increased the rate. They concluded the reduction is mix-controlled by the rate of dissolution of solid oxide ($MgO \cdot Cr_2O_3$ etc.) and that of mass transfer of chromium in metal.

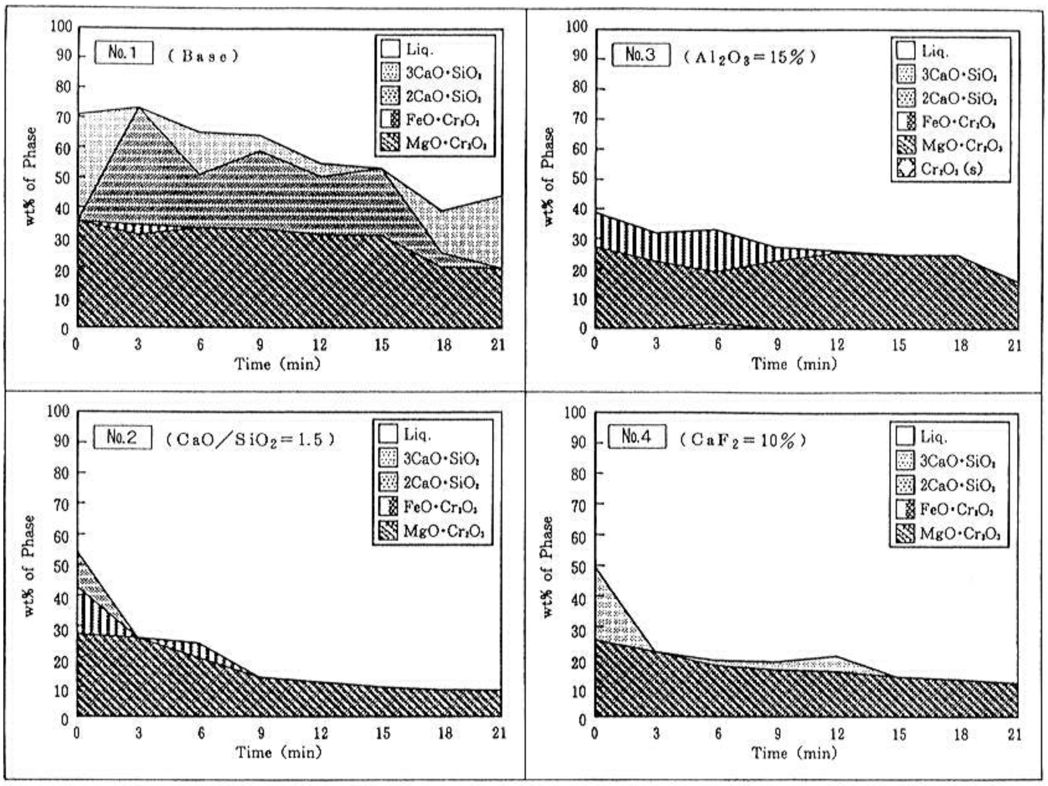


Figure 8. Change in calculated proportions of phases in weight during reduction [10].

Shibata et al [11] reduced the CaO-SiO_2-FeO-Al_2O_3 slag containing 0.4%Cr by aluminum, ferrosilicon and graphite. The 0.2g of Al or Fe-Si was added every 60 second with a total addition of 1.0g to 20g of the slag melted in an alumina crucible at 1823K. Simultaneously they oveserved the reduction by X ray fluoroscopy. In the course of aluminum reduction the formed Al_2O_3 disturbed further reduction and an intense stirring was needed.

The lowest Cr content of 0.01 mass% was attained. However, this is still one order of magnitude higher than thermodynamic estimation. Higher temperatures and CaO/SiO_2 ratios enhanced reduction because of increase in fluidity of the slags. Metal droplets containing Fe and Cr as reduction product were observed at the bottom of the crucible (Figure 9). When Fe-Si was used, unreacted Fe-Si metal remained at the upper part of the slag.

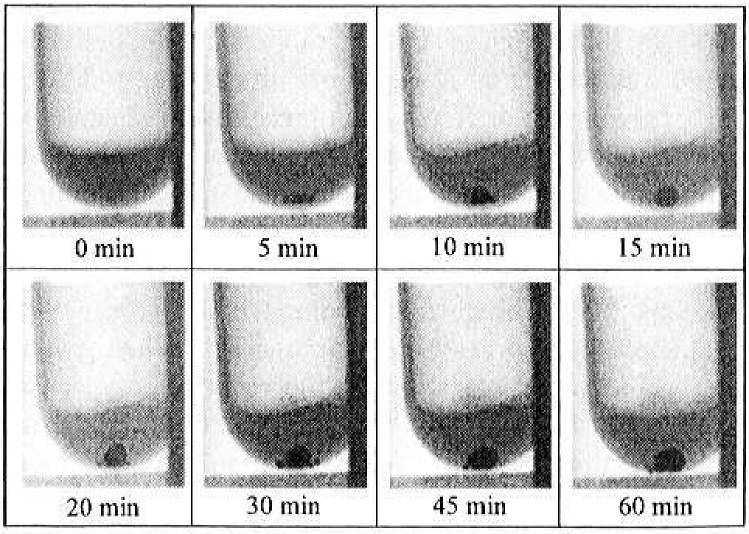


Figure 9. Formation behavior of metal drop during reduction by aluminum [11].

4. PILOT AND COMMERCIAL SCALE TESTS

Kawasaki Steel [12] developed a dust treating process (STAR process), utilizing the coke packed bed type smelting reduction. In this process tuyeres are provided at two stages. The powdery stainless steel sludge (daily consumption is 140t) and dust is injected through the upper tuyere and heated by the fuel supplied from the lower tuyere (Figure 10).

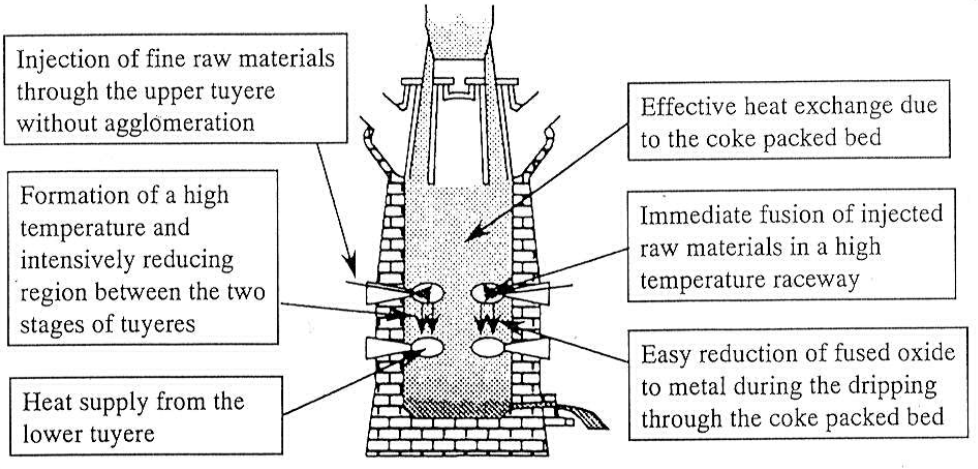
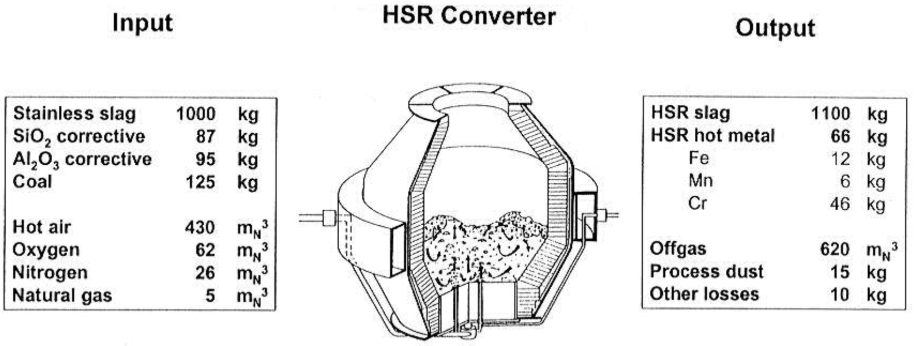


Figure 10. Principle of STAR Process [12].

They are recovering iron containing C 3.9-4.2, Cr 7.7-8.5, Al 1.4-1.8 mass% and slag composition is T. Fe 0.18-0.27, Cr 0.12-0.18, CaO 37-38, SiO_2 36-37, Al_2O_3 14 mass% with chromium yield of 98%. This is commercial equipment which greatly contributes to establish their environment conscious production of stainless steel.

Tschudin and Brotzmann [13] developed the HSR (Holsim Smelting Radix) process, which essentially reduces chromium oxide in stainless steel slags in a BOF type furnace with blowing oxygen and powdery coal through bottom and top blowing of air (Figure 11). Typically, 3t of premelted slag was charged onto 10t of Fe-Cr-Cr metal from the previous heat. The chromium content of the slag was lowered from 4.7 to 0.2 mass% with 96.5% yield. If needed, further reduction by Fe-Si (0.4kg Si per kg Cr in slag) lowered the chromium content down to 0.02 mass%. This 0.4kg of Si is in accord with stoichiometic calculation excluding the one needed to keep the silicon content at 2 mass% which is the calculated silicon content to attain 0.02 (% Cr) by slag-metal equilibration under their conditions. This again suggests that ferrosilicon reacts directly with chromium oxide in slag before dissolving into a metal bulk. They could adjust the slag composition with CaO/SiO_2=1.2～1.3 and mass%Al_2O_3=13 for use as a cement material. Leachability of Cr^{6+} from a cement containing 50% of this type slag was tested and they found that its leachability was 50% less than for ordinary portland cement. The existence of (Cr^{3+})after reduction under strongly reducing conditions is the reason for this finding in accordance of blast furnace slags.



Input

Stainless slag	1000	kg
SiO_2 corrective	87	kg
Al_2O_3 corrective	95	kg
Coal	125	kg
Hot air	430	m_N^3
Oxygen	62	m_N^3
Nitrogen	26	m_N^3
Natural gas	5	m_N^3

Output

HSR slag	1100	kg
HSR hot metal	66	kg
Fe	12	kg
Mn	6	kg
Cr	46	kg
Offgas	620	m_N^3
Process dust	15	kg
Other losses	10	kg

Figure 11. Consumption figures for treatment of 1t liquid input of stainless steel slags (HSR process) [13].

Burstron and Ye [13] tested the reduction for of chromium oxide in a 5t DC furnace at MEFOS (The IPBM process).

Their typical slag composition is as follows. Fe 0.35, CaO 56.6, SiO_2 19.6, MnO 1.18, P_2O_5 0.2, Al_2O_3 21.9, MgO 2.85, Cr_2O_3 0.03 mass% and slag temperature was 1953K.

5. DISCUSSIONS

As reviewed above, carbon is the most realistic choice as a reductant of chromium oxide when iron is used as an absorber of reduced chromium. Thermodynamically as carbon content decreases, its reducting power significantly drops. The metal after reduction may be recycled as long as the reduction furnace is located near a stainless steel making furnace. Since heat resource is the most important factor for treating slags, this is an indispensable condition.

When silicon is used as a reductant, two different mechanisms are possible, whether (1) ferrosilicon directly reacts with slag or (2) it dissolves into the metal and then silicon in metal reacts with slag or a mixture of (1) and (2).

Thermodynamically, the former case has a much higher silicon activity than the latter. In the former case, formation of silica film on ferrosilicon particle during reduction would leave it undissolved, resulting in loss of efficiency . In both cases, the necessary amount of ferrosilicon is the sum of (a) that used for reduction and (b) that to keep the silicon content high enough to keep the oxygen potential low. For example, slag containing 25 mass% Cr_2O_3 is reduced to 3% at 1923K, (a)12.2 and (b) 0.5kg/t of silicon (total 12.7kg/t) are required, respectively, where the coexisting metal contains C 0.7%, Cr 16%, and Si 0.05 mass%. Actually 12～13kg of silicon as ferrosilicon(70～75%Si) is fed onto the slag [14]. Thermodynamically the equilibrium Cr_2O_3 content is calculated as 14 mass%, which is far higher than the obtained content of 3 mass%. In this case sufficient mixing is desirable for effective reduction between Fe-Si and slag. When 1t of the slag containing 3% Cr_2O_3 is completely reduced to harmless level of 0.05 as % (Cr) with 1 %Si in the metal, 44kg of silicon is needed, if the weight ratio of slag to metal is 0.3. If the ratio can be increased to 1, the needed silicon amount would decrease to 20kg. Therefore the treatment should be done with a small amount of metal.

As a result, the best process would be reduction by carbon saturated iron with a small addition of silicon at the end. In this case the slag is treated after separation from stainless crude metal where the method of heat supply is most important. Therefore reduction should be carried out near a stainless steel making furnace before the slag solidifies. As in the HSR process, oxygen on air blowing with some carbonaceous fuel would be a solution.

Thermodynamically aluminum is the best reductant except for cost. Industrial waste such as aluminum dross may be used if it is available near location of a stainless steel plant.

6. CONCLUSIONS

In this paper the reduction of chromium oxide stainless steel slags was shown to be technically feasible by reviewing fundamental knowledges for smelting reduction of chrome ore in the past and the results of recent pilot plant tests.

The only problem to be solved is how to supply heat for treatment after separation of the bulk metal. Since the price of treated slag is not expected to be high, a large investment may not be possible. However, the author believes that in order to continue to produce stainless steel without much concern in future an introduction of the slag treatment process is compulsory and some investment may be worthy to establish an environment conscious process.

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