The separation of Cobalt in stainless steels with slags

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Abstract

The separation of cobalt in stainless steels was studied by different slags. The selections of slags were first made by calculation of activities of CoO and NiO with thermodynamics software F*A*C*T and binary phase diagrams. From the limited available thermodynamics data, the calculations have shown that the additions of SiO2, and TiO2 might change the activities of CoO and NiO significantly. The pre-selected slags of Fe2O3-SiO2-TiO2-CaF2 were melt with stainless steels in an 3000Hz 30 kW induction furnace, then different samples from the slags and ingots were analyzed by ICP spectrometer. The experimental results were compared with the thermodynamically calculations.

1.INTRODUCTION

The utilization of nuclear power have resulted large quantities of contaminated waste, the high cost of storage and ultimate disposal this waste has a strong incentive to reduce the volume requiring storage. Metals constitute about one third of the volume of such waste and can not be treated as combustible materials. Among them, stainless steel and nickel base alloys are few of major contaminated materials, especially the radio active cobalt behaves quite similarly in chemical and physical properties with nickel, it is very difficult to separate between them, if the radio active cobalt could be separate from nickel, the volume of waste would be reduced. Although cobalt could separate from nickel with hydrometallurgical technique, it has disadvantage of secondary contamination.

Melt refining has been considered as an alternative for decontamination and volume reduction of Low-level-contaminated metallic wastes. In a previous study[1], the separating of nickel from cobalt has been studied with alloy liquation, an similar works was also found by alloying of tin and lead[2], however the high cost of alloys is its drawback, hence other methods by slag refining were proposed. An investigating of the effect of slag treatment on the cobalt contained stainless steels is essential for effective treatment of future low level radio active waste metals. Variables such as slag type and composition, melting conditions will need to be identified before the real testing.

An analysis of complex heterogeneous equilibrium between the cobalt contained stainless steel and the multi-component slags is time exhausting and difficult, but the task could be achieved by use of themodynamical software. Recently such software[3-5] are commercial available, It is one of our objects to evaluate the values of calculations with comparison of experimental results which could be helpful for the future separation and reduction of radio active waste.

2.EXPERIMENTS

The selection of proper fluxes is important to the process of separation, the right refining slags should have a difference between the activities of nickel oxide and cobalt oxides in slags. If choice of fluxes are done by an try and error approach, it is too expansive to obtain the reasonable results. a thermodynamical analysis of the slag-metal equilibrium is necessary prior to experiments. F*A*C*T has been chosen as the analysis tools in this works, it could run in a normal PC, but the database is insufficient to the needed of this study.

The required data could be roughly built the by use of cobalt contained binary phase diagrams. The first step is to find the data of heat of fusion of CoO bearing binary alloys which are not available in literature, one methods of estimating the quantity would be given as follows:

At liquidus temperature in equilibrium of binary phase alloys, the solid solution of compositions $X_{i(s)}$ is equlibruated with liquid solution of compositions of $X_{i(l)}$, a relationship is held as follows:

$$RT \ln \left(\frac{a_{i(s)}}{a_{i(l)}?}\right) = \Delta G^o_{s \to l(i)} \quad (1)$$

By neglecting the small changes of heat capacities, equation (1) could be changed as

$$\Delta G^o_{s \to l(i)} \approx \Delta H^o_{mi}\left(1 - \frac{T}{T_{mi}}\right) \quad (2)$$

ΔH^o_{mi} = Standard heat of fusion at normal melting temperature T_{mi}

From equation (1) and (2), we have

$$\ln \left(\frac{X_{i(s)}}{X_{i(l)}}\right) + \ln \left(\frac{\gamma_{i(s)}}{\gamma_{i(l)}}\right) = \left(\frac{\Delta H^o_{mi}}{R}\right)\left(\frac{1}{T} - \frac{1}{T_{mi}}\right) \quad (3)$$

rearrange the equation

and assume that $\frac{\gamma_{i(s)}}{\gamma_{i(l)}}$ is constant, we get

$$\Delta H^o_{mi} = \frac{RTT_{mi}[\ln \left(\frac{X_{i(s)}}{X_{i(l)}}\right) + C}{T_{mi} - T} \quad (4)$$

By known the equilibrium compositions of solid and liquid phase at different temperatures from binary phase diagrams, the heat of fusion ΔH^o_{mi} and constant C could be obtained by regression analysis.

The data are then substituted into the Fitbin programs and saved, then properties of multicomponent solutions are calculated with a polynomial model the in solution programs, the results were saved as a private database of system

$FeO - Fe_2O_3 - SiO_2 - CaF_2 - CoO - NiO$.

It will be used in latter equilibrium calculation with Equilib program, the computing schemes are given in Fig. 1. In the experimental study, stainless steel were melted approximately with 1% cobalt in an 30KW 3000Hz induction furnace.The weight of steels is 2 to 2.8 kg and the flux is 300 gram, the compositions of fluxes were shown in Table1,it will melt by the indirect heat from the steel melts.

Ramming refracories of magnesia were used as the lining of furnace.The temperature was measured with two color infra-red thermometer and was held at 1550,1750°C for 15 minutes after the charges were melted. Sample of melted ingots and slags were analyzed by ICP spectrometer.

Table 1 the compositions of fluxes

Flux No.	Fe_2O_3	TiO_2	SiO_2	CaF_2
SIO2S1	10	-	80	10
SIO2S2	20	-	70	10
SIO2S3	30	-	60	10
SIO2S4	40	-	50	10
SIO2S5	50	-	40	10
TIO2S1	10	80	-	10
TIO2S2	20	70	-	10
TIO2S3	30	60	-	10
TIO2S4	40	50	-	10
TIO2S5	50	40	-	10

3.RESULTS

The results of chemical analysis on the solidified metals are given in Table 2, it has also shown the separation coefficient and the nickel to cobalt ratio in steels, the separation coefficient was defined as

$$\alpha = \frac{Co_{i(M)}}{Co_{i(Slag)}} \bullet \frac{Ni_{i(Slag)}}{Ni_{i(M)}}$$

which $Co_{i(M)}$ *and* $Ni_{i(M)}$ are the concentration of cobalt and nickel in the steels,

$Co_{i(Slag)}$ *and* $Ni_{i(Slag)}$ are the contents of cobalt and nickel in the slags.

A good performance of separation would require a separation coefficient greater or less one , the nickel to cobalt ratio is measure of absolute of reduction in cobalt content.

The results have indicated quite good value in separation coefficient , a 3.02 in SIO2S4 slags and a 6.67 in TIO2S4 slags , but not so good in (Ni/Co) ratio, the reason is probably due to the oxidation of iron and chrome which will change the less active weight percentage or activities of nickel and cobalt. The separation effect is designed by a differential oxidation of cobalt and nickel with manipulation of its oxide activities in slag, the oxidation was conducted by addition of iron oxide in fluxes which would have the following reaction:

$$3Fe_2O_3 \Leftrightarrow 2Fe_3O_4 + 0.5O_2$$

$$Fe_3O_4 + Fe \Leftrightarrow 4FeO$$

$$Ni + FeO \Leftrightarrow NiO + Fe$$

$$Co + FeO \Leftrightarrow CoO + Fe$$

From Table2, it seems that a sufficient amount of iron oxide are necessary to have a good values in separation, however the separation coefficient will be worse when iron oxide contents were too high. A understanding of the behavior of such slags could only feasible by the analysis with solutions model,the results has been also compared with the computing values with F*A*C*T, it is shown in Figure 2.From the shown results, we found that the (Ni/Co) ratio of experimental and calculated values are very close each other,but the separation coefficient has a larger difference in the lower contents of iron oxide silica slags.It is known that a lower iron oxide contained silicate slags is viscous than a higher iron oxide slags, the slags could not reach a homogenous holding temperature due to the indirect heating, hence the thermodynamic properties of slags will different from the theoretical values. the activities of cobalt oxide and nickel oxide in different iron oxide silicate slags was also calculated with the software and are listed in table 3 and figure3., it could be seen that the cobalt oxide in slags is more close to ideal behavior, which shows that the mole fraction is quite close to the activities, on the other side, the nickel oxide, behave less ideal which enable a good value in separation coefficients.

The lining of furnace were found moderately attacked by slags.,hence the slags would contain magnesia oxide which will influence the compositions and viscosity of slags.The slags will also changed by the oxidation of chromium oxide. In this experiments the slags actually contain NiO,CoO,Cr_2O_3 and magnesia other than the components of fluxes, this fact could make a discrepancy between the experimental and calculated values. Slag attack on lining has a significant factor and it will decreases the efficiency of the melt refining effect as in the case of calculation results. Higher temperature and fluid slags seem to be essential for better results.

4.CONCLUSION

From this study, it was found that titanium oxide and silicate slags could have good separation coefficient of 6.68 and 3.01 respectfully.

Thermodynamical simulation of the slag-metal reaction obtained good agreement in nickel to cobalt ratio in stainless steels , but partially discrepancy in separation coefficient and slag properties, the assuming a constant ratio of activities coefficient between cobalt oxide and other oxide in binary system could have a possible computing of the complex equilibrium between multicomponent cobalt oxide slags and steels.

5.ACKNOWLEDGEMENT

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Table 2 the compositions of fluxes and melt temperature

flux weight 300gFlux No.	Fe wt%	Cr wt %	Ni wt%	Co wt %	Temp. °C	(Ni/Co) ratio in steel	α
Blank	77.02	14.82	6.98	1.18	-	5.92	
SiO2S1	78.69	12.99	7.13	1.20	1500	5.92	1.49
SiO2S2	79.39	12.35	7.05	1.21	1600	5.83	1.12
SiO2S3	79.64	12.22	6.91	1.23	1700	5.62	0.841
SiO2S4	80.41	11.67	6.82	1.09	1650	6.24	3.018
SiO2S5	80.49	11.65	6.78	1.08	1750	6.30	2.32
TiO2S1	80.37	11.29	7.13	1.22	1650	5.86	1.07
TiO2S2	79.02	13.10	6.90	0.980	1650	7.04	2.86
TiO2S3	79.06	13.04	6.92	0.983	1650	7.05	1.12
TiO2S4	79.02	12.83	7.13	1.02	1650	6.99	6.67
TiO2S5	80.44	11.35	7.02	1.19	1600	5.89	0.893

Table 3 the calculated acivities of cobalt oxide nickel oxide in slags

Flux No	X_{CoO}	a_{CoO}	X_{NiO}	a_{NiO}
SIO2S1	1.0E-4	1.05E-4	5.5E-4	6.91E-4
SIO2S2	3.3E-5	3.73E-5	9.7E-5	1.28E-4
SIO2S3	1.1E-4	1.37E-4	6.2E-4	8.84E-4
SIO2S4	3.1E-5	4.3E-5	9.1E-5	1.42E-4
SIO2S5	7.0E-5	1.08E-4	4.0E-4	6.81E-4

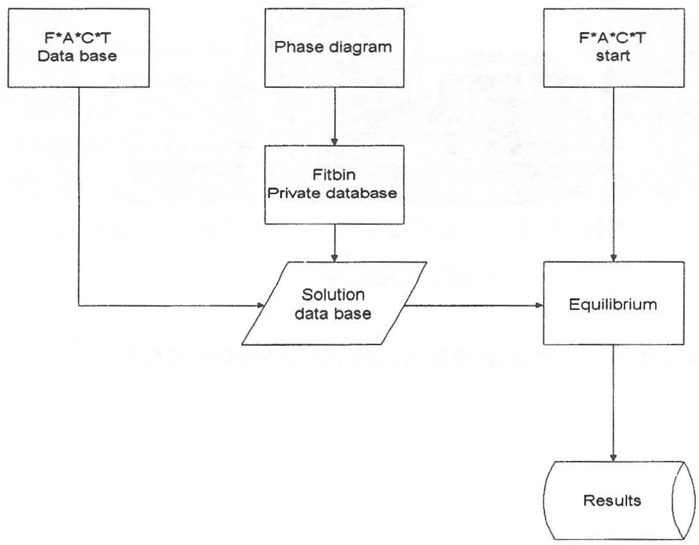

Fig.1 Scheme of thermodynamical calculation with F*A*C*T program

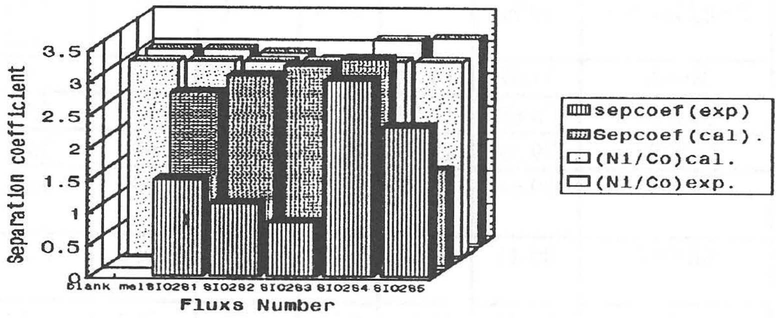

Fig.2 The comparision of the effects of slag refining between caculate and experimental results

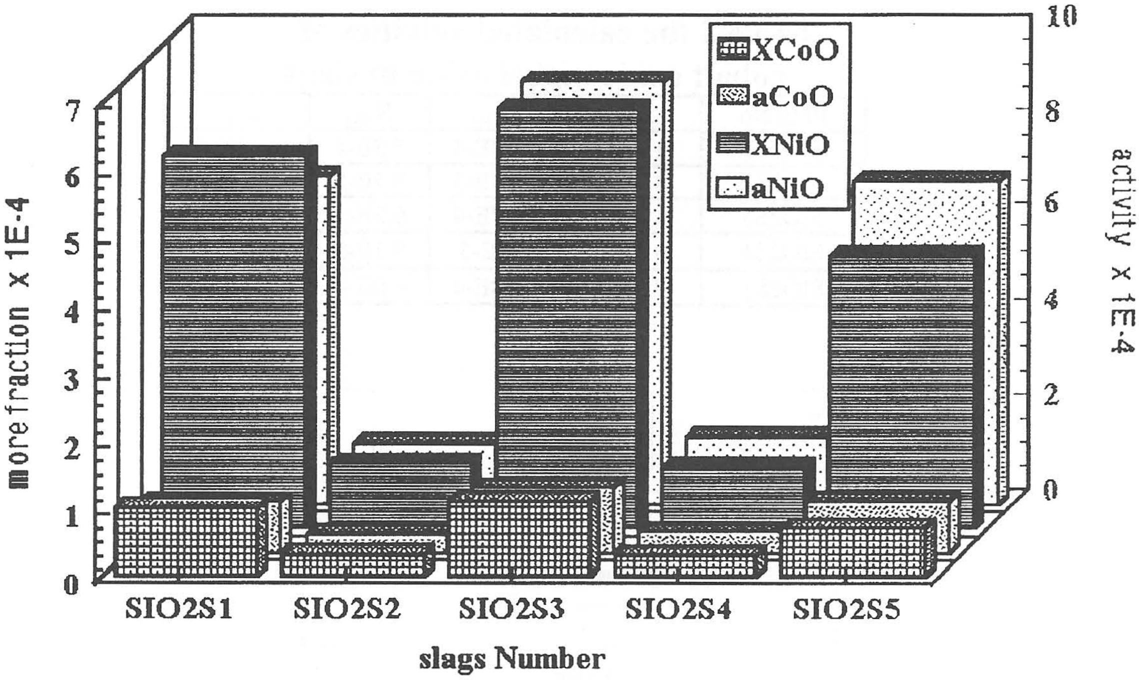

Fig.3 The comparision of calculated activities between CoO and NiO in different slags