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UNDERSTANDING OF Cr-CONTAINING SLAGS BY SULPHIDE CAPACITY AND STRUCTURAL STUDY

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Abstract

The sulphide capacities of CaO-MgO-Al_2O_3-SiO_2-CrO_x slags with were measured by gas-slag equilibration method in the temperature range of 1823-1898K to reveal the effect of CrO_x on the sulphide capacities of slags. Both higher basicity and temperature enhanced sulphide capacities. The CrO_x additions in the range of 0-5 mass% increased the sulphide capacity, but, further increase of CrO_x contents to 7 % was found to lower the sulphide capacity. Utilizing the relationship for estimating the ratio of Cr^{2+}/Cr^{3+}put forward by the present authors, the influence of Cr(II) on the sulphide capacities of the slags studied is discussed.

Introduction

Chromium-containing slags play a predominant role in production of stainless steel and high alloy steels. It is important to understand the chemistry of chromium-containing slags with special reference to the phase equilibria[1-5], oxidation states of chromium in slag phase[6-11] and distribution of Cr between the steel melt and slag phases[6,12-14]. These studies provide invaluable information for the optimization of the processes for high alloy steels. However, experimental data on the properties of slags containing CrO_X are scarce in literature as the melting points of these slags are quite high. Drakaliysky et al. [15] reported sulfide capacities of CaO-MgO-SiO_2-Al_2O_3 slags containing small amounts of Cr_2O_3. Their results indicate that adding 5 wt% Cr_2O_3 to a high-MgO(25 wt%) slag could cause a 4-fold decrease in sulfide capacities. Wang et al. [16] studied sulfide capacities of CaO-SiO_2-CrO_x system in the temperature range 1823K - 1923K. These authors noticed that, when the SiO_2 content was fixed in the slag, the increasing content of CrO would initially decrease the sulfide capacity and increase it subsequently.

In the current study, experimental determinations of the sulphide capacities of chromium slags of 12 different compositions were carried out in the temperature range 1823K-1898K. CaO-MgO-Al_2O_3-SiO_2 was adopted as basic system and the chromium-oxide contents were varied.

Experimental work

The components after drying were mixed in required proportions and ground together in an agate mortar. The basicity, B, presented in Table 1 refers to the mass ratio of (CaO+MgO)/(Al_2O_3+SiO_2) and is valid for the entire manuscript. One gram of sample was used for each experimental run. The oxygen- and sulfur potentials of the CO-CO_2-SO_2-Ar mixture, as estimated by Gibbs energy minimization program (FACT SAGE), were controlled by suitably adjusting the flow rates of the component gases. The gas flow rates were accurately controlled by Brukes mass-flow meters. A horizontal furnace with $MoSi_2$ heating elements was used for the equilibration studies. In each run, the temperature was raised to the target temperature at the rate of 5K/min. During this process, purified argon gas with a flow rate of 200mL/min was kept flowing ensuring an inert atmosphere. When the temperature reached the targeted value, argon flow was replaced by the gas mixture according to the pre-set proportion. The gas-slag reaction took 6 hours to reach equilibration, as confirmed by the earlier work of the present authors[16]. After 6 hours, the alumina sample holder was drawn quickly to the cold end of the reaction tube under argon gas. Ocular examination showed that the slag samples were glassy. The samples were subjected to chemical analysis. The combustion method using carbon/sulfur analyzer (Horiba, EMIA-820V, Japan) was used to determine the mass percentage of sulfur in each sample. Raman spectra were collected in a Raman spectrometer (Horiba, LabRAM HR Evolution, Japan) with a resolution of $0.67cm^{-1}$.

Results and Discussion

3.1 Basicity dependence

The data obtained in the present work are listed in Table 1. In Fig.1, it can be seen clearly that, with increasing basicity, the sulphide capacity of the slag increases dramatically in the basicity range 0.7 – 0.8, irrespective of the chromium content. A similar trend was noticed even in the earlier work[16]. It is generally known that, with increasing basicity, the availability of O^{2-} for the sulphur exchange reaction would increase facilitating the desulphurization process.

Table 1 Experimental sulphide capacities of $CaO-MgO-Al_2O_3-SiO_2-CrO_x$ system

Sample No.	Basicity	mass%CrO_x	Temp./K	$P_{O_2} \times 10^7$	wt%S	$Log_{10}C_S$	Log_{10}'Cs
A1	0.67	0	1873	1.05	0.0217	-4.074	-5.41
A2	0.67	3	1873	1.05	0.0232	-4.045	-5.38
A3	0.67	5	1873	1.05	0.0256	-4.001	-5.33
A4	0.67	7	1873	1.05	0.0256	-4.002	-5.32
B1	0.82	0	1873	1.05	0.0501	-3.697	-5.02
B2	0.82	3	1873	1.05	0.0580	-3.610	-4.95
B3	0.82	5	1873	1.05	0.0818	-3.477	-4.80
B4	0.82	7	1873	1.05	0.0575	-3.583	-4.94
C1	1	0	1873	1.05	0.0719	-3.553	-4.88
C2	1	3	1873	1.05	0.0846	-3.482	-4.80
C3	1	5	1873	1.05	0.1001	-3.410	-4.72
C4	1	7	1873	1.05	0.0885	-3.463	-4.77
B1	0.82	0	1823	1.0544	0.0196	-3.987	-5.43
B2	0.82	3	1823	1.0544	0.0187	-4.007	-5.44
B3	0.82	5	1823	1.0544	0.0222	-3.932	-5.36
B4	0.82	7	1823	1.0544	0.0189	-4.002	-5.43
B1	0.82	0	1848	0.80523	0.0719	-3.720	-4.87
B2	0.82	3	1848	0.80523	0.0886	-3.630	-4.77
B3	0.82	5	1848	0.80523	0.0939	-3.604	-4.74
B4	0.82	7	1848	0.80523	0.0913	-3.617	-4.74

Sample No.	Basicity	mass%CrO_x	Temp./K	$P_{O_2}\times10^7$	wt%S	$Log_{10}C_S$	Log_{10}'Cs
B1	0.82	0	1898	0.84918	0.1393	-0.856	-4.58
B2	0.82	3	1898	0.84918	0.1696	-0.771	-4.48
B3	0.82	5	1898	0.84918	0.1829	-0.738	-4.45
B4	0.82	7	1898	0.84918	0.1729	-0.762	-4.47

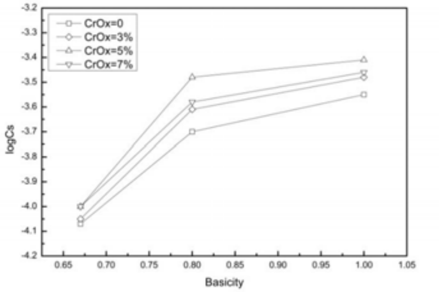

Figure 1 Basicity dependency of sulphide capacities on $CaO-MgO-Al_2O_3-SiO_2-CrO_x$ at 1873K,

$\log P_{O_2}$=-7

3.2 Temperature dependence

The effect of temperature on the sulphide capacity of chromium-containing slags is shown in Fig.2. The trend that higher temperature leads to higher sulphide capacity is consistent with literature and is attributed to the sulphur-oxygen exchange reaction, which is a thermally activated process and is endothermic.

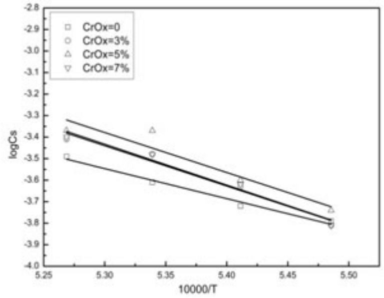

Figure 2 Dependence of $\log_{10}$ Cs with reciprocal of temperature

The slope of the plot of $\log_{10}$Cs as a function of 1/T is an Arrhenius-type of plot, the slope representing the enthalpy of the exchange reaction between oxygen in the slag and Sulphur in the gas phase. In the case of low basicity slags, it is well-known that the silicate chains are broken and oxygen ions are released for desulphurization. Thus, the slope of the above-mentioned plot is expected to be small. The present results as well as the earlier work reveal that, at constant basicity, addition of CrO_x to the slag would increase the absolute value of slope of the $\log_{10}Cs$ *vs* 1/T lines, *viz.* desulphurization enthalpy. The contributions to the slope are from the desulphurization reaction, Cr^{2+}- Cr^{3+} redox reaction as well as polymerization reaction.

On the basis of the earlier study [17], slag systems containing CrO_x should actually be considered as consisting CrO and $CrO_{1.5}$. The ratio between the two Cr-containing species has been shown to be a function of basicity and temperature. This leads to a certain degree of non-linearity in the $\log_{10}Cs$ *vs* 1/T plots if CrO_x is treated as a single species.

3.3 Chromium oxides influence

The effect of chromium content on the sulphide capacity of the slag was not monotonous, which can be seen in Fig. 3. When the content of CrO_x increased from 0 to 5%, the sulphide capacity of slag increased gradually but when the chromium content reached 7%, C_S was found to decrease. In the present work, this effect is traced to the different valence of chromium ions. As reported by Wang and Seetharaman[16], Cr^{2+} acts dominantly as a basic ion while Cr^{3+} would be more amphoteric. At low Cr contents and moderate basicities, the predominant species in a silicate melt would be CrO, which, in turn, would act as a basic oxide. Thus, increasing chromium content would increase the sulphide capacity. However, as the CrO_x content increases, the acid effect would be more predominant hindering the reaction between sulfur and oxygen ion.

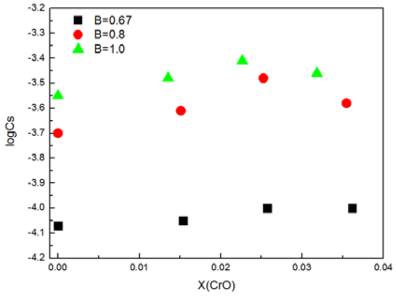

Figure 3 Effect of CrO on log Cs at 1873K, log P_{O2}= -7

In desulphuration process, the polymerization reaction involving different forms of oxygen in silicates is represented in Eqn.(1).

This reaction shows the charge balance required by the tetrahedral coordination of oxygen with silicon on the left-hand side of Eqn.(1) and the polymerization of two silicate units releasing a divalent oxygen ion. Although the effective refining agent is free oxygen ion, its amount is determined by the basicity of the slag or the degree of polymerization that would lead to the formation of free O^{2-}ions. Further, in a low basicity (metasilicate) environment, desulphurization reaction would be expected to lead continuously to the release of increased number free oxygen ions by the polymerization reaction.

The occurrence of reaction (1) in silicate systems containing transition metal cations is somewhat complicated by the presence of 3 d electrons. Apart from the variable valency exhibited by these cations, it has been shown in the earlier work [18] that the electron distribution in the silicate matrix is more even. From a thermodynamic point of view, the activity of O^- is raised. In the present discussion, the term "activity" is used to describe the thermodynamic situation and is not linked to any standard state. If O^{2-}can be replaced by S^{2-} continuously, the activity of O^{2-} is reduced, and consequently, the reaction of (1) will proceed further to the right side. This would, in turn, lead to an improvement of the desulphurization capacity. This effect is reflected in the trends shown by transition metal silicates with respect to molar sulphide capacities With the same amount of silicon, the value of molar sulphide capacity of $MnO.SiO_2$ and $FeO.SiO_2$ have high values; *viz.* -4.18 at 1973 K[19] for $MnSiO_2$, and -4.39 at 1773 K[20] for $FeOSiO_2$ and ca -5 for $CrOSiO_2$ [16]. The value is close to that of $CaO.SiO_2$ (-5.4 at 1923K).

The ratio of Cr^{2+}/Cr^{3+} would fixed (1.728、1.437 and 1.199 at 1873K) when temperature, oxygen partial pressure and the slag chemical environment (basicity, 0.67, 0.82 and 1.0 respectively) are kept constant. According to the relationship presented in the earlier work by the present authors for the ratio Cr^{2+} / Cr^{3+}, divalent Cr would be the dominant valence state at 1873K and basicity < 1. Thus, in the present case, the enhancement of sulphide capacity could be regarded as the contribution of CrO.

Meanwhile, it can be noted that the amount of CrO and $CrO_{1.5}$ were both increasing with the continuous addition of CrO_x. In a study of the crystalline Cr_2O_3, Tilley [21] had suggested that trivalent chromium would prefer the octahedral position just as Al^{3+}. As reported by Irmann, Cr(III) would exist as $[CrO_2]^-$ in basic slag phase[22] . It is known that Al^{3+} can fit into the Si polymeric chain but need to maintain charge balance. For Cr(III), such positive divalent ion could be Ca^{2+}, Mg^{2+} as well as Cr^{2+}. Assuming Cr^{2+} might act as charge compensator for Cr(III), it would cause a lessening of the effective amount of CrO involved in reaction (1). Thus, there will be a certain critical point at which more positive charge would be needed for the charge balance resulting in the lowering sulphide capacities in the system with 7% addition of CrO_x.

4.4 Raman spectrum for slag structure

Fig. 4 shows the deconvulsed Raman spectra for 3 different slag basicities. It is seen that, at basicity of 0.67, Q_2 is predominant in the whole slag. With more basic oxides(CaO and MgO) added, Q_2 and Q_3 both decreased while Q_0 and Q_1 both increased indicating depolymerization.

According to Frantz and Mysen, the mole fractions of different structure units are proportional to the band areas in Raman spectra. Table 2 gave fitting results along with each band area. The average number of bridging oxygen of each sample is used to explain the contributions of each unit to depolymerization. Because Q_0~Q_3 could reveal the bridge oxygen in different Si-O structure, the average bridge oxygen content could be represented by Equation (1).

$$BO = 0\times Q_0 + 1\times Q_1 + 2\times Q_2 + 3\times Q_3 \quad (1)$$

Fig. 5 shows the relationship between basicity and average bridge oxygen in the slag. It can be seen that with increasing slag basicity, the average bridge oxygen decreases dramatically. It is well-known that a higher basicity would lead to a greater depolymerization degree in the slag, which could also be confirmed by the decreasing average bridge oxygen.

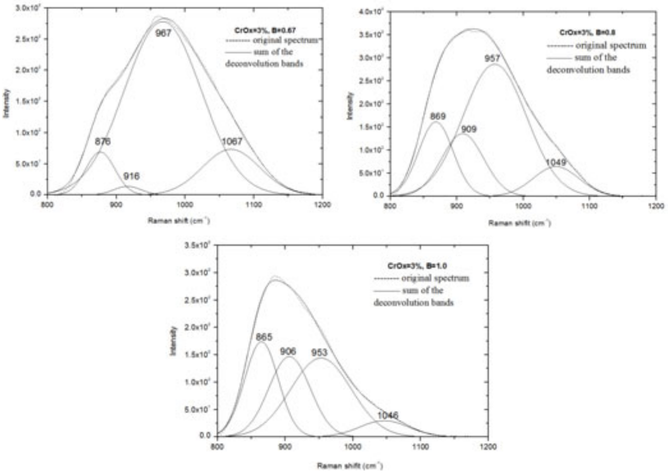

Figure 4 Effects of basicity on Raman Spectrum of CAMS-CrO$_x$(CrOx=3%)

3.2 Effect of chromium oxide addition on structure

Fig. 5 shows the deconvolution results of Raman spectra of slags with different chromium contents. Generally, Q_2 is found to be predominant in the set composition ratio (B=0.8). When content of CrO$_x$ increased to 5%, the amount of Q_2 decreased gradually and the amounts of Q_0 and Q_1 exhibited a corresponding increase. The present results lead to the conclusion that the depolymerization degree of the slag decreases with increase of Cr content upto 5 %. Higher degree of depolymerization of the slag would increase the number of oxygen ion available for sulphur exchange with a consequent increase in the sulphide capacity.

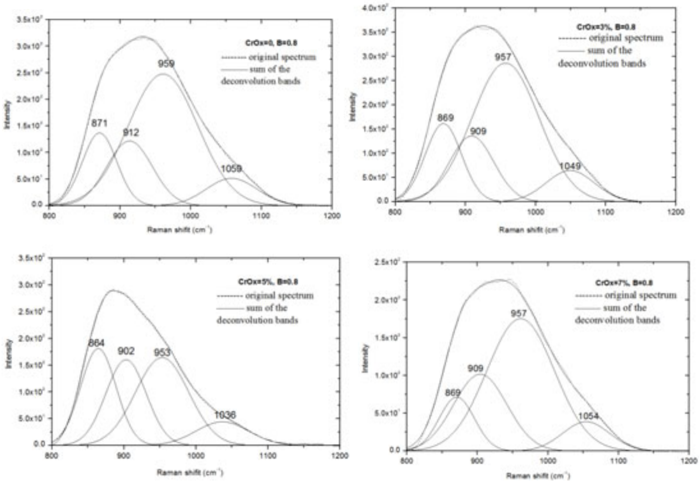

Figure 5 Effects of CrOx on the Raman spectrums of CAMS-CrOx(B=0.8)

It is interesting to note that, when the content of CrO_x was increased to 7%, the fraction of Q_0 decreased but Q_1 was nearly the same. Comparing the sulphide capacities of slags with 7% CrO_x and 3% CrO_x, it can be inferred that both Q_0 and Q_1 had positive effects on the desulphurization of slag. This is in conformity with the results corresponding to different basicities.

Conclusion

Gas/slag equilibrium technique was used in the investigation of the effects of chromium oxides on the desulphurization process in the temperature range of 1823-1898K. It was found that the sulphide capacity of $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$ with the basicity from 0.67-1.0 can be enhanced by the addition of chromium oxide. By employing the formula of the Cr^{2+}/Cr^{3+} ratio to evaluate the distribution of Cr(II) and Cr(III) in the slag phase, the contribution of CrO on desulphurization has been proposed. With relatively high content of CrO_x (7%), Cr(II) also will take a charge compensation role for Cr(III), which resulted in the lowering of sulphide capacity of the system.

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