THERMODYNAMIC BEHAVIOR OF TRANSITION METAL (Cr, Ti, Nb, V) OXIDES IN MOLTEN SLAGS

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ABSTRACT

The industrial production of iron and steel contributes to a significant share of the global CO_2 *emissions. Electrochemical methods using an inert oxygen evolving anode can eliminate the* CO_2 *formation. The FFC Cambridge process approach was tried out for the reduction of hematite to produce iron at 915°C. The electrolyte consisted of pure molten* $CaCl_2$ *containing 0.5 mol% CaO. Different anodes were tested. Graphite anodes were found to halt the reduction of the inner parts of the cathode pellets. Also large amounts of carbon were found in the cathode product in these experiments. Nickel ferrite cermet with intergranular nickel and copper was tried as an inert oxygen evolving anode material. These anodes showed promising behaviour and also made the cathode pellet more active with respect to electroreduction. Iron was formed at the cathode during the process.*

INTRODUCTION

The thermodynamics of transition metals in molten slags is an importance aspect in process metallurgy. The activity coefficients of transition metal oxides are the essential information for metal extracting, and refining. For instance, to reduce the chromium loss in decarbonrization process of chromium stainless steel refining, it is necessary to optimize the slag composition based on the thermodynamic properties of chromium oxides in the slag. The role of titanium in the so-called oxide metallurgy has been well understood. In LAHS steels, micro amount of titanium can refine the grain size, and in tern enhance the strength of the steel. In some grades of steel, the titanium content has to be controlled below 0.002% (% denotes mass percent throughout this paper if *mol* does not appear in the front), indicating the necessity of the strict control of titanium content in slag.

A transition metal exists in slags often in two or more valency states. For instance, chromium in slags is present in Cr^{2+}, Cr^{3+} or Cr^{6+}, while titanium exists as Ti^{4+}, Ti^{3+} amd Ti^{2+}. Activity coefficients of transition metal oxides depend mainly on oxygen partial pressure, slag composition, especially basicity and total content of transition metal. Temperature is an influential factor to a certain extent. These, in turn, effect on the content proportion of different oxides of a transition metal in slags, and raise the complexity in the thermodynamics. As the complexity of thermodynamic behavior of transition metals, experimental study rather than theoretical prediction from first principle is the major approach for thermodynamic data attainments. The accumulation of the knowledge on this aspect is useful for optimizing the relevant process operation. In the present paper, the authors review thermodynamic studies on Cr, Ti, V and Nb in molten slags.

CHROMIUM IN MOLTEN SLAGS

Existing Forms of Chromium in Molten Slags

As mentioned, chromium in slags is present in Cr^{2+}, Cr^{3+} or Cr^{6+}, and CrO^{4+} is the stable form of Cr^{6+}. It was reported [1] that chromium exists as Cr^{6+} only in high basicity slags under highly oxidized atmosphere. The work [2] has conformed the existence of the equilibrium:

$$Cr^{3+} + \frac{5}{2} O^{2-} + \frac{3}{4} O_2 = CrO_4^{2-} \tag{1}$$

The results show that when basicity index X_{CaO}/X_{SiO_2} increases from 2 to 11, Cr^{6+}/Cr^{3+} raises fom 0.15 to 0. 95, which indicates the acidity of CrO_4^{2-}. As such high basicity slags are less applicable in ferrous or non-ferrous metallurgy, so Cr^{2+} and Cr^{3+} are main forms of Cr in slags.

It is considered that CrO in CaO or $CaO\text{-}SiO_2$ based slags behaves as weakly basic species [3, 4], while the basicity (or acidity) of Cr^{3+} is between Cr^{2+} and Cr^{6+}. Low basicity slags are more preferable for the existence of Cr^{2+}. For instance, an earlier investigation [5] reported that chromium mainly existed as Cr^{2+} in silica saturated slags. A similar conclusion was given earlier [6] from an equilibration study of $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}FeO\text{-}CrO_x$ with Fe-Cr-Si under moderate reductive atmosphere at 1873 K.

In the interface between metal and slag melts, the following equilibrium may exist:

$$2(CrO_{1.5})+[Cr]=3(CrO) \tag{2}$$

For convenience, a formula was proposed [7] to calculate the total content of chromium oxides:

$$\text{mol\% } CrO_x = \text{mol\% } CrO + \text{mol\% } CrO_{1.5} \tag{3}$$

where the activity of CrO_x is defined as follows:

$$a_{CrO_x} = a_{CrO_{1.5}}^{X_{CrO_{1.5}}/X_{CrOx}} \cdot a_{CrO}^{X_{CrO}/X_{CrOx}} \tag{4}$$

Regarding the thermodynamic behavior of the chromium oxides, it has been noted [5] that Cr^{2+}/ Cr^{3+} increases with the decreasing slag basicity and oxygen partial pressure, as well as the rising temperature. In a thermodynamic study [8] on CaO- Al_2O_3 -SiO_2 - MgO-CrO_x slags, CrO is reported to behave as bivalency metal oxides, like FeO, NiO and MnO. It is noted [9] that the Cr_2O_3 activity decreases with CaO content and Al_2O_3 addition in CaO-CaF_2-Cr_2O_3 slag at 1773K and CaF_2-Al_2O_3-Cr_2O_3 slag between 1723 and 1823K. More recent thermodynamic studies on chromium oxides in slags involved chemical equilibrium [4, 14] and EMS approaches [7].

Thermodynamic Behavior of (CrO) and ($CrO_{1.5}$) in Slag

The increase of activities and activity coefficients of (CrO) and ($CrO_{1.5}$) with the basicity of CaO-SiO_2- CrO_x slag at 1873 K was reported by Morita *et al.*; Xiao *et al.* [4, 7]. The former study was carried out in moderately reductive atmosphere, the partial oxygen pressure was 7.04×10^{-6} Pa, the total chromium content in slag was varied in three ranges: 3.5~4.9%, 9.1~9.9%, 15.0~16.6%. The results show that γ_{CrO} and $\gamma_{CrO_{1.5}}$ (All the activities for the oxides in molten slags in this paper are with respect to their corresponding solid oxides.) increase as many as 6~10 and 2~3 times respectively when $X_{CaO_{1.5}}/X_{SiO_2}$ is raised from 0.6 to 1.5. This leads to an increase of one to three times in Cr^{3+}/Cr^{+2}. The result also indicates that both Cr^{2+} and Cr^{3+} behave as basic species, and Cr^{2+} exhibits stronger basicity. The level of activity coefficient, γ_{CrO} or $\gamma_{CrO_{1.5}}$ is shown effected by total chromium content in the slags. In slags with the total chromium content ranging from 9.1 to 9.9%, γ_{CrO} values attained are higher. While $CrO_{1.5}$ in slags with low total chromium contents from 3.5 to 4.9% has higher activity coefficients. In the later study [7], an increasing tendency for a_{CrO} and $a_{CrO_{1.5}}$ in CaO-SiO_2-CrO_x is found when X_{CaO}/X_{SiO_2} increases from 0.2 to 1.5 under strongly reductive atmosphere with purified Ar at 1873K. It is also noted that $Cr^{2+}/(Cr^{2+}+Cr^{3+})$ decreases with the total chromium content increase.

The experimental study on CaO-SiO_2-CaF_2 system at 1623 K [10] indicates that CrO behaves as amphoteric oxide in higher basicity slags. A maximum in curve γ_{CrO} vs CaO% / SiO_2% at the basicity index value of 2 is the evidence of the amphoteric feature, which shows the behavior of CrO as basic or acidic oxide if CaO%/SiO_2% is less or greater than 2 respectively. At some specific slag compositions [11], the presence of strong interaction between Cr^{3+} and Cr^{2+} can lower the activity coefficient of $CrO_{1.5}$, indicating that Cr^{3+} behaves like acid.

The influence of oxygen partial pressure on Cr^{2+}/Cr^{3+} in CaO-SiO_2-CrO_x and CaO-Al_2O_3-CrO_x-SiO_2 melts at 1773 K has been investigated [12]. The decrease of Cr^{2+} content in the two slags was about 30% with the oxygen partial pressure decrease from $1.01\times10^{-4.56}$ to $1.01\times10^{-7.50}$ Pa.

It was reported [4] that the effect of temperature on the chromium partition between Cu-Cr alloy and CaO-SiO_2-CrO_x slag can be neglected in X_{CaO}/X_{SiO_2} range from 1.26 to 1.51 between 1803 and 1923 K with total Cr content from 11.1% to 17.4%. However, slight γ_{CrO} increase and $\gamma_{CrO_{1.5}}$ decrease can be found with the rising temperature, these changes raise the content ratio of Cr^{3+}/Cr^{2+}. It is found [7] that the activities of CrO and $CrO_{1.5}$ are slightly decreased with the temperature rising from 1773 to 1873 K at X_{CaO}/X_{SiO_2} of unity. The proportion of Cr^{2+} in total chromium content slightly increases with the temperature rising.

At the high temperature for steel making, some amount of MgO in refractory can be dissolved in the molten slag, Al_2O_3 as a deoxidation product existing in slag may affect the temperature of liquidus. MgO and Al_2O_3 addition would alter the thermodynamic properties of the slags. Investigations [2, 4, 7, 12, 13] were carried out on effects of MgO and/or Al_2O_3 addition. The investigation [13] was carried out on 41% CaO- 41% SiO_2-10% Al_2O_3-8% CrO_x (X_{CaO}/X_{SiO_2}=1.47) slag at 1873 K and under oxygen partial pressure of 7.04×10^{-6} Pa. The results show a continuous Cr^{3+}/Cr^{2+} decrease from 26 to 14 with MgO content rising up to 15% due to the change of activity coefficients of CrO and $CrO_{1.5}$. As a consequence, the activity coefficient increases at 2.5% MgO addition, and levels off up to 10 % MgO. For effects of Al_2O_3 addition, Cr^{3+}/Cr^{2} ratio in 43%CaO-43% SiO_2-5% MgO-9%CrO_x slag maintains constant in Al_2O_3 content up to 7%, then gradually increases due to the change in activity coefficients of CrO and $CrO_{1.5}$. On contrary to MgO addition, the activity coefficient of CrO_x slightly decreases with the Al_2O_3 addition. MgO and Al_2O_3 addition change the effect of slag basicity on activity coefficients of CrO and $CrO_{1.5}$. For CaO-SiO_2-5% MgO-10% Al_2O_3 slag, maximum values for γ_{CrO} and $\gamma_{CrO_{1.5}}$ are reached around X_{CaO}/X_{SiO_2} value of 1.1 and then slowly lowered with X_{CaO}/X_{SiO_2} rising from 0.5 to 1.3.

The result from a study [7] on CaO-SiO_2-Al_2O_3-CrO_x system shows a slight increase for $CrO_{1.5}$ and CrO activities with Al_2O_3 addition increase up to 20 % and at X_{CaO}/X_{SiO_2} of unity.

An experimental study [14] was carried out on 22.5~30.0%CaO-37.5~30.0% SiO_2 -20% Al_2O_3-10% MgO -10%Na_2O slag with Cr_2O_3 addition under oxygen partial pressure ranging from 10^{-4} to 10^{-8} Pa at 1673 and 1773 K. The results show 10% NaO does not obviously change effects of slag basicity, total chromium content, oxygen partial pressure and temperature.

TITANIUM IN MOLTEN SLAGS

Existing Forms in Molten Slags

Titanium exists in molten slags as Ti^{4+}, Ti^{3+} and Ti^{+2}. The concentration ratio of different titanium oxides depends on oxygen partial pressure, the slag basicity, composition and temperature. Ti^{4+} is considered as network forming ion, it is known that Ti^{4+} and Ti^{3+} are stable forms in molten slags, and have a glass-forming tendency. It is noticed that TiO_2 appears to have a trend to weak the structure network in silicate melts, therefore, influence on viscosity, conductivity and sulphide capacity of the slag. The existence of Ti_3O_5 is found in some slags [15, 16]. The order of basicity of titanium oxides can be listed as: $TiO_2<Ti_3O_5<Ti_2O_3<TiO$. TiO_2 is considered as amphoteric oxide in slags, the others are basic ones. A review was made [17] for activity coefficients of $TiO_{1.5}$, $TiO_{1.67}$ and TiO_2 of some CaO-SiO_2 based slags from previous publications [18, 19, 20, 21, 22]. For a clarified understanding, analyses are still desirable.

In CaO-SiO_2 Based Slags

A study on equilibrium of Ti^{3+} and Ti^{4+} in molten CaO-SiO_2-Al_2O_3-MgO system with TiC and C in carbon monoxide was carried out between 1673 and 1823 K [18]. Ti^{4+} in slags is found to behave amphoterically with a critical X_{CaO}/X_{SiO_2} of unity. When alumina content is fixed, the activity coefficient of TiO_2 has a maximum at X_{CaO}/X_{SiO_2} of unity. Ti^{3+} generally exhibits basic feature in slags, except in very high basicity slags such as CaO-Al_2O_3 based slags.

The equilibrium between Ti^{3+} and Ti^{4+} in blast furnace typed slag 35~50 % CaO -7~22% Al_2O_3-25~45% SiO_2- 10% with Fe-C_{sat}-Ti melt was investigated in pure CO atmosphere at 1773 K [19]. It is found that the TiO_x content does not show remarkable effect on its activity coefficient. $TiO_{1.5}$ and TiO_2 activity coefficients are found ranging from 2.3 to 8.6 and 0.1 to 0.3 respectively. The value of [Ti%]/("TiO_2"%) is ranging from 0.1 to 0.2.

The redox behavior of titanium in CaO-SiO_2- TiO_x was investigated between 1783 and 1903 K under oxygen partial pressure from 1.01×10^{-10} to 1.01×10^{-5} kPa in TiO_x content range from 7% to 50%, and X_{CaO}/X_{SiO_2} value from 0.55 to 1.35 [20]. The results show that the ratio of Ti^{3+}/Ti^{4+} increases with the decreasing oxygen partial pressure, and decreases with the increasing bacisity and decreasing temperature. The amphoteric feature for Ti^{4+} is not seen from variations of $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ and Ti^{3+}/Ti^{4+} with basicity.

An equilibrium investigation [17] was carried out under oxygen partial pressure of 4.1×10^{-7} Pa at 1873 K for 25~53%CaO~27~46% SiO_2- 10~55% TiO_x slag. Basicity index CaO%/SiO_2% was ranging from 1.0 to 2.1. The results show a minimum in curve of Ti^{3+}/Ti^{4+} vs TiO_x content at a TiO_x content of 25%, and ranging from 7.9 to 91.2. Similar with attained earlier [20], $\log(Ti^{3+}/Ti^{4+})$ shows a linear relationship with $\log P_{O_2}$, the slope of the straight line is -0.25 at the basicity, CaO%/SiO_2% of 1.36.

The equilibrium between [Ti] and [O] in liquild iron saturated with solid TiO_x from 1823 to 1923 K was investigated [16]. It is found that in the range of 0.25 %<[Ti]<4.7 %, the deoxidation product in liquid iron is solid Ti_2O_3, while it is solid Ti_3O_5 if [Ti]<0.25%.

The equilibrium between 25~44%CaO-30~46%SiO_2-10~39%$TiO_{1.67}$ slag and Fe-O-Ti melt at 1873 K under strongly reductive atmosphere was investigated using EMF [22]. The titanium content in liquid iron was ranging from 0.013% to 0.25%. The results show that the activity coefficient of $TiO_{1.67}$ increases from 0.39 to 1.68 with the increase of slag basicity. The highest $\gamma_{TiO_{1.67}}$ value is obtained in high basicity region in CaO-SiO_2-$TiO_{1.67}$ phase diagram.

The West Panzhihua area, Sichuan Province, China is rich in magnetoilmenite deposit. In the slag with sintered magnetoilmenite concentrate as raw material for blast furnace smelting, the content of TiO_2 can reach as much as 25~30 % [23]. For effective slag utilization, it is necessary to study the thermodynamic properties of slags with higher TiO_2 content. The equilibrium between Ti^{3+} and Ti^{4+} in CaO- SiO_2-Al_2O_3- MgO- 11~ 40%TiO_2 slag was carried out at 1823 and 1873 K under oxygen partial pressure from 4.3×10^{-3} to 9.3×10^{-3} Pa [24]. Results show that the molar ratio of $Ti^{4+}/(Ti^{4+})+(Ti^{3+})$ increases linearly in a range of $CaO\%/SiO_2\%$ less than 2. Ti^{3+}/Ti^{4+} increases with the increasing total titanium oxide content.

In High Basicity CaO-SiO_2 Based Slags for Ladle Treatment

The thermodynamic behavior of titanium oxides in ladle typed slags with high basicity around 3.5 was investigated [21]. In order to control the titanium content in carbon steel, ferrite stainless and aluminum deoxidized steel, experiments of three series were carried out for the equilibrium of the molten slags with different metallic melts under pure CO atmosphere at 1873 K.

For carbon steel, experiments were carried out between Fe-C_{sat}-Ti and CaO-SiO_2-30% Al_2O_3 -MgO -TiO_x melts. The slag composition was 43.3~56.2%CaO-6.67~16.0%SiO_2 -29.2~32.4% Al_2O_3- 1.96 ~6.61%MgO-1.23~3.52%TiO_x. The results show that $TiO_{1.5}$ activity exhibits negative deviation to ideal behavior, while TiO_2 activity shows positive deviation. The activity coefficient of TiO_2 reaches a maximum of 2.3. The ratio $TiO_{1.5}/TiO_{2.0}$ is ranging from 0.4 to 2.8, and increasing with titanium content in liquid iron.

For ferrite stainless steel, experiments were carried out between Fe-C_{sat}-(16~18)%Cr-Si-Ti and 44.7~55.8%CaO-13.2~16.0% SiO_2-17.6~21.2% Al_2O_3 -1.62~3.95%MgO-1.23~3.52%TiO_x melts. The results show that $TiO_{1.5}$ activity exhibits negative deviation to ideal behavior. γ_{TiO_2} is ranging from 0.6 to 3.5. Its activity has positive or negative deviation to ideal behavior if the TiO_2 content is less or greater than 2.7%. $TiO_{1.5}/TiO_{2.0}$ varies from 0.4 to 2.5.

For steel using aluminum as deoxidizer, the experiments were carried out between Fe-Al-Ti and 34.3~44.6%CaO-2.9~9.80% SiO_2-27.9~32.9% Al_2O_3-13.2~16.4% MgO-6.1~8.8%TiO_x melts. The results show that TiO_2 in total titanium oxides can reach about 80%, its activity is ranging from 2 to 7. The $\gamma_{TiO_{1.5}}$ values are ranging from 54 to 132, showing its positive deviation to ideal behavior.

In MnO-SiO_2-TiO_x System

Deoxidation products using Mn, Si or Ti as reagents in liquid steel can become the nuclei of MnS precipitations during the steel solidification. MnS precipitations exist as nuclei in the transformation of austenite to inner crystal ferrite. Fine sized ferrite crystal grains can enhance the strength of the steel. Fine and dispersed oxide impuritiss can facilitate the precipitation of nitride, carbide and sulfide on oxide particles, therefore to improve the mechanical properties of the steel.

The phase relations in MnO-SiO_2-TiO_2 system at 1673 K was investigated, and the activities of TiO_2 and SiO_2 were calculated using the measured MnO activity data in the melt [18]. The results show that the iso-activity lines of each component are roughly parallel to the relevant liquidus, the TiO_2 activity increases with the increasing TiO_2/MnO ratio if the TiO_2 content is fixed.

The equilibrium between MnO-SiO_2-TiO_x and Mn-Si-Ti melts was investigated at 1673 K [26]. The results show the TiO_x content increase up to 25% with [Ti] content in metallic melt up to 11%. TiO_x content dramatically increases with [Ti] content increase if [Ti]> 11%. A thermodynamic study on MnO-TiO_2 slag [27] shows that both oxides have negative deviations to ideal behavior. A concept of relative ion characteristic was proposed [16] for MnO containing binaries along with an order: MnO• SiO_2 > MnO•TiO_2> MnO • Al_2O_3. From this order, it is noted that the acidity of TiO_2 is between that of SiO_2 and Al_2O_3.

NIOBIUM AND VANADIUM IN MOLTEN SLAGS

In Na_2O-SiO_2 and CaO-CaF_2-SiO_2 Systems

The equilibrium for Nb, V (and Sb) between Na_2O-SiO_2 and carbon saturated liquid iron from 1473 to 1623K was investigated [28] under oxygen partial pressure of 8.59×10^{-8} Pa. The results show the change in valencies of transition metals with X_{Na_2O}/X_{SiO_2}. The average valency increases from +4.8 to 5.0 with X_{Na_2O}/X_{SiO_2} increase from 0.5 to 1.3 indicating Nb existing mainly as Nb^{5+}, the rest as Nb^{4+}. The activity coefficients of NbO_2 and $NbO_{2.5}$ vary from 10^{-2} to $10^{-2.3}$ and from 10^{-3} to 10^{-4} respectively. V exits in molten slag as V^{2+},V^{3+}, V^{4+} and V^{5+}. The content ratio of these ions varies with slag basicity. The results of the investigation show an average valency increase from +2.2 to +4.8 with X_{Na_2O}/X_{SiO_2} increase from 0.5 to 1.3. γ_{VO_2} and $\gamma_{VO_{2.5}}$ decrease from 10^{-4} to 10^{-6} and from 10^{-7} to 10^{-10} respectively when X_{Na_2O}/X_{SiO_2} increases from 1.0 to 1.7. The content distributions for Nb and V between molten slag and carbon saturated iron increase remarkably with X_{Na_2O}/X_{SiO_2} increase, and decrease slightly with temperature rising.

A similar study was carried out [28] on the equilibrium between CaO-Na_2O- CaF_2-SiO_2 and carbon saturated liquid iron at 1573K for investigating the effect of Na_2O addition on the slag dephosphorization. The slag used was saturated with CaO and $3CaO \cdot SiO_2$, which were previously found possessing high phosphate capacity. It is noted that small Na_2O addition of 2% can considerably increase the partition of Nb, V between molten slag and carbon saturated liquid iron, and decrease the manganese partition between the two phases. This can be attributed to decrease of activity coefficients, γ_{VO_2} and $\gamma_{VO_{2.5}}$, γ_{NbO_2} and $\gamma_{NbO_{2.5}}$ about 1 to 1.5 order of magnitude caused by Na_2O addition. On contrary to the behavior of Nb, V and Ti in the slag, γ_{MnO} is slightly increased by Na_2O addition. The differences indicate that V^{4+}, V^{5+}, Nb^{4+} and Nb^{5+} are more acidic.

In Nb_2O_5-MnO-SiO_2 Systems

The iron ore in Inner Mongolia, China, contains some amount of niobium. Nb in iron ore is extracted into hot metal in blast furnace smelting. Nb in hot metal is then oxidized by converting in BOF and dissolved in the slag. Nb exists in BOF slag mainly as Nb^{5+}, the rest as Nb^{4+}. The BOF slag can be utilized to produce Nb-Fe. For optimizing Nb-Fe production technology, it is necessary to investigate thermodynamic properties of the niobium containing slag. At starting stage, for simplicity, CaO and FeO due to their small contents in the slag, were not taken into consideration. Phase diagrams of some component binaries, MnO-Nb_2O_5, $4MnO \cdot Nb_2O_5$-SiO_2, $4MnO \cdot Nb_2O_5$-$2MnO \cdot SiO_2$ and $MnO \cdot Nb_2O_5$-SiO_2 in MnO-Nb_2O_5-SiO_2 ternary were investigated [31]. The equilibrium between liquid-iron containing Nb with MnO-Nb_2O_5-SiO_2 molten slag was investigated at 1828 K [33]. The activity of oxygen in liquid iron was determined using solid electrolyte oxygen concentration cell. Activities of Nb_2O_5 and MnO in the slag were attained from the oxygen activity in liquid iron. The results show that with a constant ratio SiO_2/MnO or SiO_2 concentration, the activity of Nb_2O_5 increases with the increasing Nb_2O_5 content. While the activity of Nb_2O_5 exhibits a maximum at a molar fraction range of Nb_2O_5 between 0.10 and 0.15 if MnO content is fixed. The activity of Nb_2O_5 is found increasing with the increasing SiO_2 content. The distribution of Nb between MgO_{sat}-Fe_tO- MnO-SiO_2 -NbO_x slag and liquid iron at 1873K was investigated [34]. The results show the increase partition ratio between slag and metal with the increase of Fe_tO content.

SUMMARY

The thermodynamics of Cr, Ti, Nb and V in molten slags indicates that higher slags basicity, strong oxidized atmosphere are generally preferable to the existence of more oxidized valency states. Temperature is found less influential in this regard. The content ratio of different valency states of a transition metal depends on activity coefficient ratio of the oxides. The information regarding activity coefficient of relevant metal oxides in previous studies are analyzed in this paper. For Cr and Ti, the information mainly corresponds to CaO-SiO_2 based slags. For titanium, the analysis of MnO-SiO_2 slags is also included. For Nb and V, the information in Na_2O-SiO_2, CaO-CaF_2-SiO_2 is provided. Experimental studies on Nb_2O_5-MnO-SiO_2 system are also introduced. It appears that data available regarding to Cr and Ti in molten slags are more than those for Nb and V. Due to the differences existing in slag basicity, composition and in oxygen partial pressure for various process, such as ESR, ladle treatment and ferroalloy smelting and for variety of steel, extensive efforts in this direction are still desired to meet the need of process optimization and controlling.

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