International Journal of Minerals, Metallurgy and Materials
Volume 29, Number 4, April 2022, Page 750
https://doi.org/10.1007/s12613-022-2424-5

Invited Review

Slags containing transition metal (chromium and vanadium) oxides—Conversion from ticking bombs to valuable resources: Collaborative studies between KTH and USTB

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(Received: 14 October 2021; revised: 29 December 2021; accepted: 25 January 2022)

Abstract: As the steel industry expands worldwide, slag dumps with transition metals (especially chromium and vanadium) are becoming more common, posing a serious environmental threat. Understanding the properties of slags containing transition metal oxides, as well as how to use the slags to recover and recycle metal values, is critical. Toward this end, the University of Science and Technology Beijing (USTB) and Royal Institute of Technology (KTH) have been collaborating on slags containing transition metals for decades. The research was carried out from a fundamental viewpoint to get a better understanding of the structure of these slags and their properties, as well as industrial practices. The research focused on the three "R"s, viz. retention, recovery, and recycling. The present paper attempts to highlight some of the important achievements in these joint studies.

Keywords: transition metals; vanadium; chromium; recovery; collaborative study

1. Introduction

Metal production and utilization are progressing at a galloping speed globally. Fig. 1 depicts the data from 2012 statistics on the production of industrially important materials (Fig. 1(a)) and the comparison of steel production between China and the rest countries during the period of 2015 to 2021 (Fig. 1(b)).

Among metallic materials, steel occupies an important position owing to its wide range of applications in construction and vehicles. This is illustrated in Fig. 2.

As global steel production rises, with China in the dominating position, the amount of slag produced is also expected to rise correspondingly. Steel alloying elements are required for the development of new steel grades. Slags containing oxides of these alloying elements will most likely be dumped as well. For example, the final slag to be dumped from stainless steel production contains Cr in the range of 5wt%–18wt% depending on the plant practice. When slag is dumped in the natural environment, chromium could be leached by acid rain and eventually end up in the groundwater as Cr^{6+}, a human carcinogen. It is worth noting that these metals being dumped as wastes are very valuable if they can be recovered by economically viable processes.

Table 1 shows the amount of some of the alloying elements by Swedish steel industries annually and the amounts wasted in the final slags (Data from 2012).

With process development as the objective, the Royal Institute of Technology (KTH) in Stockholm partnered with the University of Science and Technology Beijing (USTB) to establish a knowledge base on slag properties and new process routes. High-caliber Chinese students from the USTB visited KTH, conducted path-breaking experiments, and produced astonishing results that have become milestones in steelmaking technologies. While the interactions include salts and fluxes, the present paper focuses on the characteristics of slags containing transition metals and environmental solutions that have evolved.

2. ThermoSlag database

There are a few commercial databases on slag properties available today. All of these are predominantly empirical, with models and corresponding equations to describe slag properties. This exercise was initially restricted to the thermodynamic properties. A broader base was required to describe all of the properties of slags, including molar volumes and viscosities. Professor Chou and his group in USTB made a significant contribution in this direction by developing geometric models [1]. Simultaneously, at KTH, experimental studies were carried out to measure the thermodynamic activities, sulfide capacities, and viscosities of steel slags

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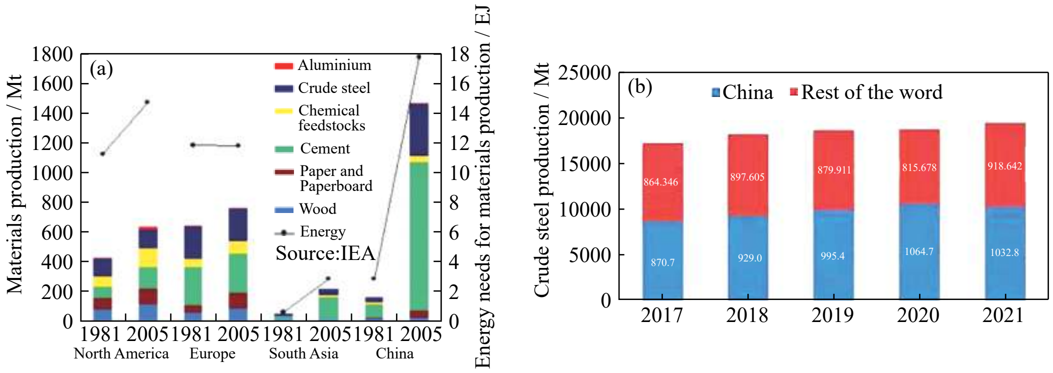

Fig. 1. (a) Production of industrial materials and energy use (Source: Swedish Steel Producers Association, 2012). (b) Comparison of crude steel production between China and the rest countries during the period of 2015 to 2021 (Source: World Steel Association, CRU, IMnI, [2022-1-25]).

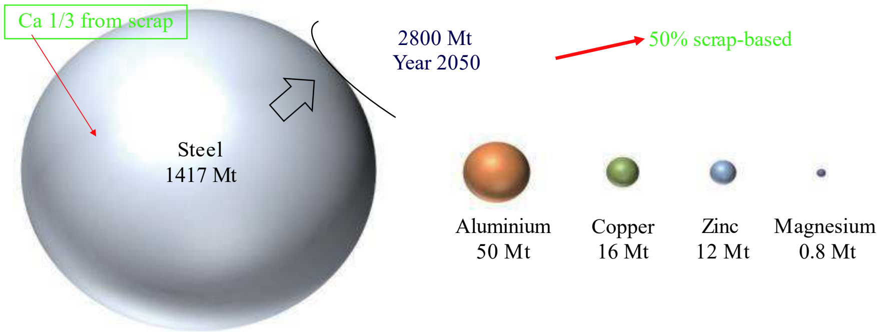

Fig. 2. Production of steel compared to the production of other metals (Source: Swedish Steel Producers Association, 2012).

Table 1. Metals lost in the emissions and amounts needed per annum in Sweden, 2012 (Source: Swedish Steel Producers Association)

Metal	Amount lost as waste emissions per annum / t	Annual demand / t
Chromium	180000	100000
Manganese	70000	50000
Zinc	33000	15000
Nickel	17500	25000
Molybdenum	8000	10000

containing CaO, MgO, MnO, FeO, Al_2O_3, and SiO_2. These properties were tested under identical conditions for binary, ternary, quaternary, quinary, and six-component slags to be incorporated into a model developed by the research group at the Division of Theoretical Metallurgy, KTH, in collaboration with the USTB. ThermoSlag, the software developed at USTB [2], allowed for reliable extrapolation of these properties and the establishment of inter-property correlations. The database was later extended to include the molar volumes of the slags [3]. The molar volumes were estimated using the Gibbs–Helmholtz equation and the enthalpies of mixing, which were derived from the thermodynamic activities. The structure of the modern version of ThermoSlag is presented in Fig. 3.

One of the major limitations of the ThermoSlag software is the lack of data for slags containing transition metal oxides, such as Cr or V oxides. Herein, the work done collaboratively by both the universities to provide a better understanding of these slags, which are important in alloy steel production, is described.

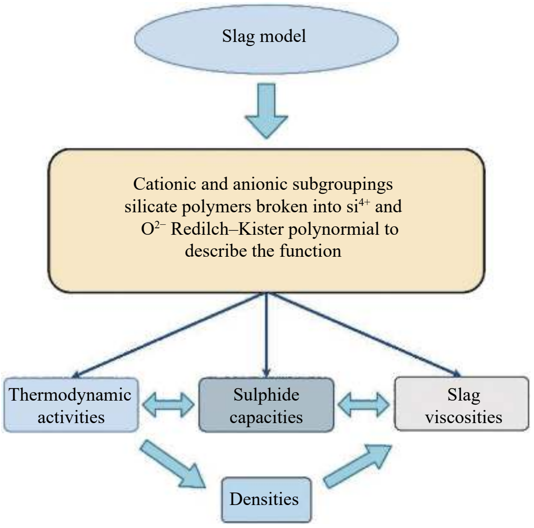

Fig. 3. Concept of the ThermoSlag software.

3. Fundamental studies

3.1. Thermodynamic activities of Cr and V oxides in slags at low oxygen potentials

One of the first attempts to measure the thermodynamic activities of Cr oxide in CaO–MgO–Al_2O_3–SiO_2–CrO_x slags was made by Dong *et al.* [4]. A CO–CO_2–Ar gas mixture was equilibrated with the slag in the temperature range 1803–

1923 K. The partial pressures of oxygen (P_{O_2}) in the gas mixture were kept around 10^{-4} Pa to maintain the valence state of Cr in the slag almost entirely at Cr^{2+}, and the system was found to attain equilibrium in 12 h. The Pt crucibles used to contain the slags during equilibration were found to have a uniform composition of Cr dissolved in Pt, confirming the attainment of equilibrium between the gas phase, slag, and Pt crucible. The slags and Pt crucibles were subjected to total chemical analysis. The activity of CrO (a_{CrO}) in the slag could be evaluated using Eq. (1) to account for Cr activity in the Pt crucible. The results obtained are summarized in Fig. 4(a). In this system, pure solid Cr and pure liquid CrO are the standard states of Cr and CrO, respectively. In Eq. (1) and Fig. 4(a), X_{Cr} and X_{CrO} represent the mole fraction of Cr in Pt–Cr alloys and more fraction of CrO in slag respectively, with 1 as the unit, and r_{Cr} represents the activity coefficient of Cr in Pt–Cr alloys. Similar activity measurements of $VO_{1.5}$ were carried out by the gas equilibration method at low oxygen pressures in the case of the slag system CaO–MgO–Al_2O_3–SiO_2–$VO_{1.5}$ [5]. The vanadium content was also kept to a minimum (<1.0wt%). The $VO_{1.5}$ activities ($a_{VO_{1.5}}$) obtained in this study are also presented in Fig. 4(b). Similarly, the pure solid substances of vanadium and vanadium oxide were used as standard states. Here, $X_{VO_{1.5}}$ represents the mole fraction of $VO_{1.5}$.

$$\lg r_{Cr} = -4.42 + 11.39X_{Cr} - 7.35X_{Cr}^2 \tag{1}$$

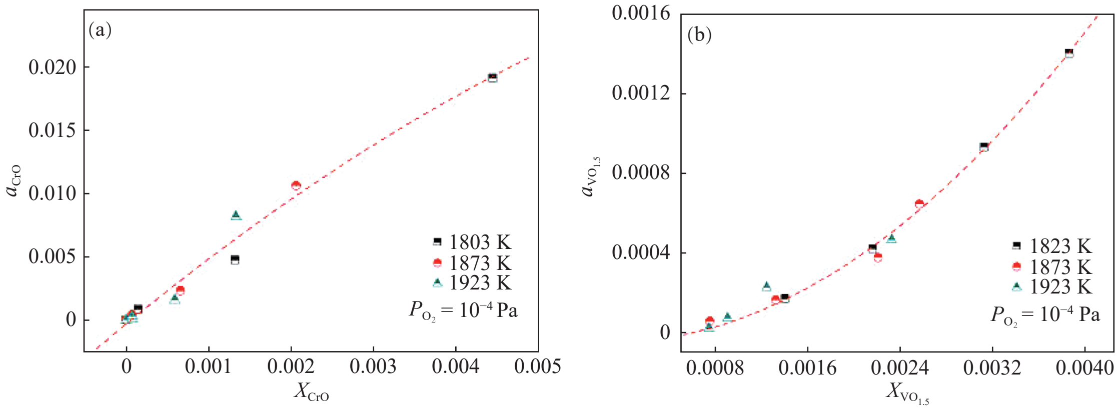

Fig. 4. Thermodynamic activities of CrO (a) and $VO_{1.5}$ (b) as measured by Dong *et al.* (a) P.L. Dong, X.D. Wang, and S. Seetharaman, *Steel Res. Int.*, vol. 80, 202-208 (2009) [4]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. (b) P.L. Dong, X.D. Wang, and S. Seetharaman, *Steel Res. Int.*, vol. 80, 251-255 (2009) [5]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

3.2. Valence states of Cr and V in slags

Since the measurements of Dong *et al.* [4–5] were performed at low oxygen potentials, it was justified to assume that Cr would exist as Cr^{2+} and V would exist as V^{3+}, which are their respective lower and stable valence states. During alloy steel refining, the oxidation states of these elements would vary based on the oxygen potentials prevailing, the basicities of the slags, and the temperature. The literature contained contradicting data. Hence, attempts were made to measure the valence states of Cr and V oxides in slags at various P_{CO} and basicities at steelmaking temperatures.

The P_{CO} was controlled by the CO–CO_2–Ar gas mixture. The gas ratios for a given P_{O_2} were determined by calculations using the Thermo-Calc database. All the gases were purified so that the impurity oxygen levels in the commercial, high purity gases were less than 10^{-4}–10^{-5} Pa. To obtain the equilibrium state, the samples were placed in Pt crucibles for 20 h (as indicated by preliminary studies) at the experimental temperature. The experiments were conducted at temperatures ranging from 1873 to 1973 K. After the equilibration, the samples were quenched under the same atmosphere [4–5].

The wet chemistry method was commonly used to determine the valence states of chromium and vanadium in the slag system [6]. Owing to the strong affinity of these metal cations for oxygen, there was a risk of oxidation during the dissolution of the slag in various acids, resulting in errors in determining the valence ratios of the cations. In the KTH–USTB collaborative work, sophistication was introduced in the analytical methods, such as X-ray photoelectron spectroscopy (XPS) [7] and X-ray absorption near edge structure (XANES) method [8–10]. The results of the XANES method for Cr- and V-slags are presented in Fig. 5.

Furthermore, a new method for measuring the ratios of valence states in the case of Cr and V in slags was developed as part of the collaboration between KTH and USTB. The Knudsen cell-mass spectrometry was used for the first time to determine the valence states in slags. In this regard, the traditional Knudsen cell-mass spectrometric method was applied to detect the vapor pressures. The vapor emanating through the orifice of a tungsten cell at the experimental temperature will follow the Knudsen diffusion equation if the orifice diameter is less than the mean free path of the vapor species. The species can be identified by channeling the emanating collimated ion stream through a mass spectrometer. In a Knudsen cell-mass spectrometric arrangement heated to 2000 K, slags containing Cr or V were subjected to the evaporation process [9–11]. Using mass spectrometric peaks, the valence ratios of the transition metals in the slags, viz. Cr and V were identified. A link was developed between the valence ratios of the transition metal ions in the vapor and condensed states using standard calibration results, and the valence states were

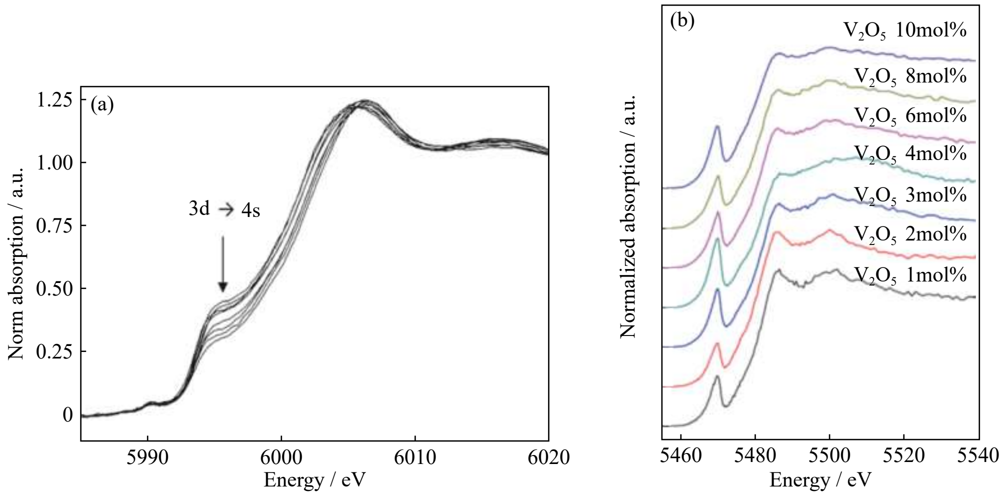

Fig. 5. K-edge XANES spectra of (a) Cr slags and (b) V slags. (a) Reprinted by permission from Springer Nature: *Metall. Mater. Trans. B*, Experimental studies on the oxidation states of chromium oxides in slag systems, L.J. Wang and S. Seetharaman, Copyright 2010 [10]. (b) H.J. Wang, L.J. Wang, and S. Seetharaman, *Steel Res. Int.*, vol. 87, 199-209 (2016) [8]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

evaluated. The results were consistent with those obtained using the XANES method.

According to the results of the valence state measurements in the case of Cr-containing slags, the Cr^{2+}/Cr^{3+} ratio increased with increasing temperature, lowering both the slag basicity and the P_{CO} prevailing in the system. The variation of the Cr valence ratio as a function of slag basicity (B) defined as (CaO + MgO)/(SiO_2 + Al_2O_3) is shown in Fig. 6 [10,12–18]. Thus, a correlation of $X_{CrO}/X_{CrO_{1.5}}$ as a function of temperature, P_{CO}, and basicity was developed in the present work based on the present results as well as those assessed from relevant earlier data [18].

$$\lg\left(\frac{X_{CrO}}{X_{CrO_{1.5}}}\right) = -\frac{11534}{T} - 0.25\lg P_{O_2} - 0.203\lg B + 5.74 \tag{2}$$

Fig. 7 summarizes the results obtained in the case of the oxidation states of VO_x in metallurgical slags [8,11,19–20].

3.3. Sulfide capacities and structural aspects of slags containing Cr

Sulfide capacity (C_S) is the most effective index to reflect the desulfurization capacity of a slag system. It is a function of temperature and slag compositions, and it is often used by researchers to investigate the structure and composition of slag. To understand the influence of varying Cr valence states on the physicochemical properties of slags containing trans-

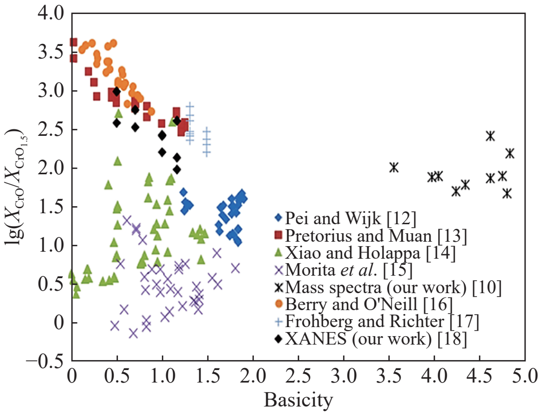

Fig. 6. Literature values of $X_{CrO}/X_{CrO_{1.5}}$ replotted as a function of basicity by separating the temperature and P_{CO} effects. The scatter in the values corresponding to earlier results is attributed to the errors in wet chemical analysis.

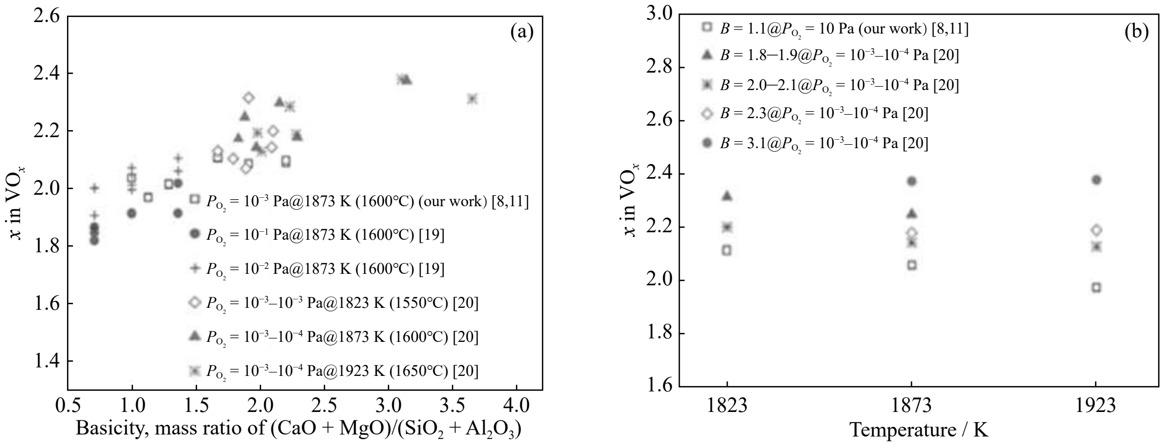

Fig. 7. Vanadium valance states as a function of (a) basicity of slag and (b) temperature. H.J. Wang, L.J. Wang, and S. Seetharaman, *Steel Res. Int.*, vol. 87, 199-209 (2016) [8]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

ition metals, the sulfide capacities of the CaO–SiO$_2$–CrO$_x$ system were examined under Ar–CO–CO$_2$–SO$_2$ atmosphere in the temperature range 1823–1923 K. By applying Eq. (2) to describe the Cr^{2+}/Cr^{3+} ratio developed earlier [12], it was possible to isolate the effect of CrO on C_S. As shown in Fig. 8, the logarithm C'_S (molar sulphide capacity in the system of silicate mixtures with two cations at the fixed mole fraction of silica) between two terminal binary silicates varies linearly along a constant SiO$_2$ mole fraction (even if a small deviation exists in the CaO·SiO$_2$–MnO·SiO$_2$ system) in the metasilicate region. It can be reasonable to believe that $\lg C'_\mathrm{S}$ for the CaO·SiO$_2$–CrO·SiO$_2$ system is linear to the mole fraction of CrO. When Cr^{2+} replaced Ca^{2+} in the system, the sulphide capacity decreased. With a further increase in Cr^{2+} content, the sulfide capacities showed a slightly increasing trend [21].

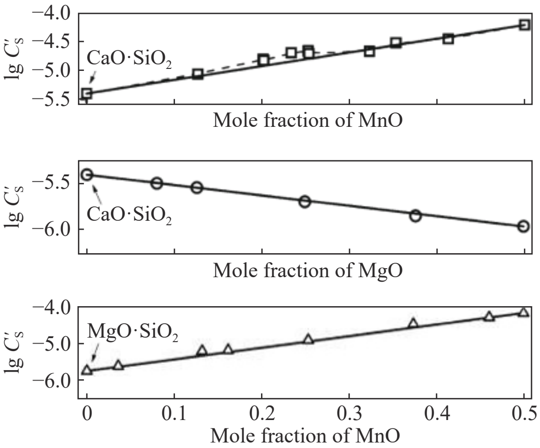

Fig. 8. Relationship between $\lg C'_\mathrm{S}$ and mole fraction of MO (where M = Mn or Mg) for metasilicates at 1923 K. Reprinted by permission from Springer Nature: *Metall. Mater. Trans. B*, Experimental studies on the sulfide capacities of CaO–SiO$_2$–CrO$_x$ slags, L.J. Wang and S. Seetharaman, Copyright 2010 [21].

The structural examination of the Cr-containing slags was carried out by Raman spectroscopy in the USTB [22]. The results showed that increasing the Cr content from 0 to 5 wt% increased the depolymerization degree of the silicate matrix, as presented in Fig. 9. However, increasing the Cr content to 7wt% reduced the depolymerization degree. This result is due to the average bridge oxygen content in Si–O structures of silicate. With the addition of CrO, the average bridge oxygen content in the slag decreased and subsequently increased, as evidenced by the opposite changes in depolymerization degree. The spectral results were consistent with prior results of sulphide capacity (C_S) measurements. Considering the slag structure with its properties, the enthalpy changes of the reaction 2O$^-$ = O + O^{2-}, viz. the value ΔH for the depolymerization of silicates could be considered to be an index of the basicity of silicate melts. The enthalpies corresponding to silicate polymerization reactions have been calculated from the slopes of the $\lg C'_S$ vs $1/T$ curves for four binary silicates MgO–SiO$_2$, CaO–SiO$_2$, MnO–SiO$_2$, and FeO–SiO$_2$; Here, T represent the temperature. Over the temperature range of 1723–1923 K, the magnitude of the ΔH values was in the order MgO > CaO > MnO > FeO, implying that the basicities increase in the order MgO < CaO < MnO < FeO. This basicity order is based on (i) the ionicity of chemical bonds between metallic and oxygen ions and (ii) metallic oxide clustering in silicates. Clustering of metallic oxides, in reality, corresponds to clustering of non-bridging oxygen ions, O$^-$, which may easily produce O^{2-} by electrons exchange [23].

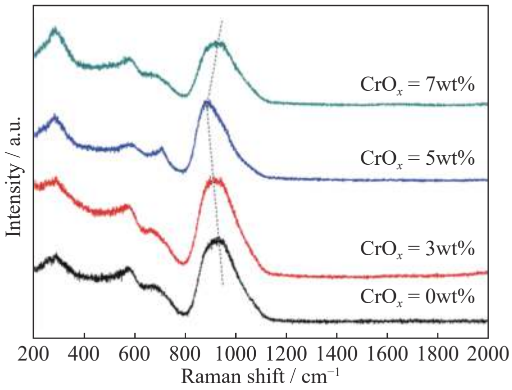

Fig. 9. Raman spectra results for CrO$_x$-containing slags. Reprinted by permission from Springer Nature: *Metall. Mater. Trans. B*, Raman structure investigations of CaO–MgO–Al$_2$O$_3$–SiO$_2$–CrO$_x$ and its correlation with sulfide capacity, L.J. Wang, Y.X. Wang, Q. Wang, and K.C. Chou, Copyright 2016 [22].

4. Process developments

4.1. Decarburization of alloy steels with CO$_2$-containing oxidant gas

Chromium is an essential and valuable element for alloy steelmaking. The retention of Cr in the metal phase during alloy steel production is critical for both process economics and environmental conditions. Wang and Seetharaman introduced CO$_2$ into the O$_2$ system for decarburization of alloy steels to lower the P_CO and reduce Cr oxidation. In the laboratory, 1 kg scale experiments were conducted, and a mathematical model was developed to describe the process [24–25]. Both experimental and modeling results revealed that CO$_2$ had a positive effect on decreasing Cr oxidation at the same decarburization level by O$_2$, as shown in Fig. 10(a) [26]. In the Fe–Cr–C melt, the reaction formula for decarburization and chromium retention was as follows: $(\mathrm{Cr_2O_3})_\mathrm{slag} + 3[\mathrm{C}] = 2[\mathrm{Cr}] + 3\mathrm{CO(g)}$. According to this equation, reducing the CO partial pressure can effectively reduce the oxidation transformation temperature of the reaction to achieve better decarburization and chromium retention under the condition that the melt remains unchanged. Compared with the decarburization process with pure O$_2$, CO$_2$ introduced into the O$_2$ system for the decarbonization of alloy steel can reduce the P_CO as a dilution gas in the system, lowering Cr oxidation. Wang *et al.* [27–28] expanded this concept to the ferroalloy field for decarburization of high carbon FeCr to produce medium and low carbon products (part of the results are shown in Fig.10(b) [27]). As shown in the figure, blowing CO$_2$ or CO$_2$–O$_2$ mixtures instead of pure O$_2$ resulted in increased Cr yield when removing carbon from 6.0wt% (high carbon FeCr) to about 3.0wt% (medium carbon FeCr). In addition,

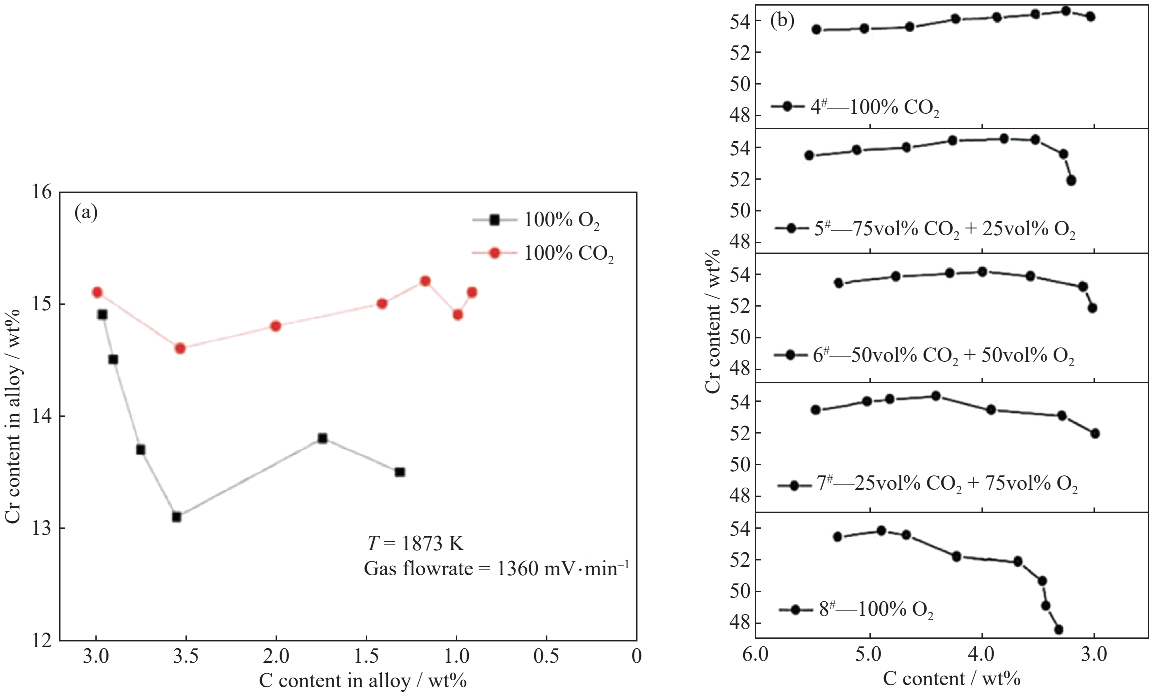

Fig. 10. Content of Cr variation with decarburization when blowing different ratios of CO_2–O_2 into different melts: (a) alloy steel [26]; (b) high carbon FeCr [27].

USTB researchers adopted CO_2 in the electric arc furnace (EAF), ladle furnace (LF), and converter processes for alloy steel production [29–31].

4.2. Vanadium recovery from slags

The high vapor pressure of V_2O_5 at steelmaking temperatures has been long known. Wang and Seetharaman [32] first discovered the vaporization of V from melts while studying the oxidation of Fe–V melts with CO_2-containing gas mixtures. This idea was later used to extract vanadium from thin oxide films [33]. The success of these experiments could be attributed to the large surface/volume ratio of the slag film, which exposed a large surface for V_2O_5 evaporation from the surface of the slag film. The accurate SEM mapping of the thin slag film played a crucial role in verifying the theory.

Experiments for vanadium recovery with 1 kg slags by injecting air or oxygen into the V-containing slags were not very successful. It was surmised that this could be due to the formation of micro V_2O_5 bubbles in the slag melt that became entrapped in the viscous slag. Vacuum treatment combined with continuous oxygen purging could dislodge these microbubbles and transport them to the surface of the slag. This was attempted and proven to be successful in the TU Bergakademie Freiberg, Germany [34].

A schematic of the experimental set-up used in this work [34] is given in Fig. 11.

The formation of V_2O_5 bubbles in slag melt is currently being modeled along the lines of Wang *et al*. [24] in the case of CO_2–Fe melt reactions.

In the vapor phase, the process was extended to recover chromium from stainless steel slag films as CrO_3 vapor [35]. The loss of Cr from the slag in the form of Cr^{6+} under oxidizing conditions could be confirmed.

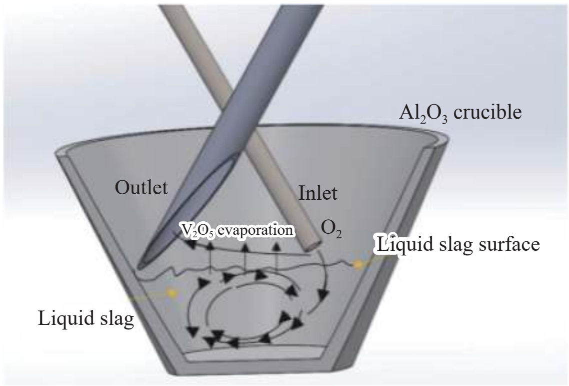

Fig. 11. Schematic illustration of the cross-sectional view of a method for recovering V_2O_5 from a slag. Reprinted by permission from Springer Nature: *Metall. Mater. Trans. B*, Vaporization of vanadium pentoxide from CaO–SiO_2–VO_x slags during alumina dissolution, T. Shyrokykh, X.W. Wei, S. Seetharaman, and O. Volkova, Copyright 2021 [34].

4.3. Salt extraction process

One of the most important process developments in recovering metal values from dumped slags was the invention of the salt extraction process via joint studies between KTH and USTB. Dr. Xinlei Ge (now Professor), a bright researcher from USTB, was tasked with developing this process at KTH. The basic principle of this process is to extract metal values from slags into a molten salt phase at the same time as electrolyzing the melt to deposit the metals at the cathode. The chlorinating agent in the salt melt was $AlCl_3$. The temperature range was 1023–1223 K. The deposition sequence of various metals or alloys is $CrCl_3 > FeCl_2 > MnCl_2 > AlCl_3 > MgCl_2 > NaCl > CaCl_2 > KCl$, depending on cell potential and theoretical decomposition voltage. Under certain conditions, Fe and Cr will deposit first, resulting in the formation of ferrochrome alloy products [36]. A schematic of the electrolytic cell and the cathode deposit, viz. Fe–Cr alloy is presented in Fig. 12.

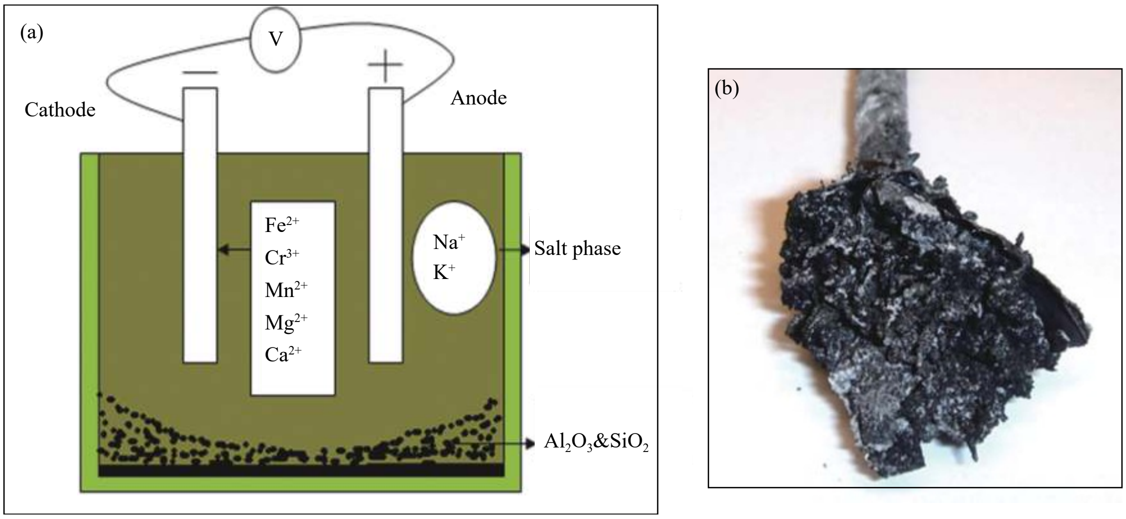

Fig. 12. Electrolytic cell (a) and cathode deposit (b) in the salt extraction process [36].

The process was applicable in Cu production, allowing electrolytic copper to be deposited directly from sulfide concentrates [37]. This method could also be used to extract environmentally hazardous elements such as Pb from cathode ray tubes and discarded crystal glass wastes [38]. It was found that some parts of $AlCl_3$ got evaporated during the process because of its high vapor pressure. A novel solution to this problem was found by the introduction of a sacrificial anode. Liquid Al was used as the anode, allowing for the absorption of Cl_2 gas generated by chloride electrolysis at the anode, as well as production of $AlCl_3$ *in situ* needed for chlorination. The method was later extended to extract rare earth from magnet scrap [39–40]. The concept of the sacrificial anode was also introduced in fluoride electrolysis for the extraction of Nd [41].

5. Summary

Over the last few decades, KTH and USTB have collaborated to better understand the properties of steelmaking slags containing transition metals to improve alloy steelmaking processes. The research provided a fundamental understanding of the slag structure and helped in the development of processes for retaining transition metals in steel while minimizing losses, as well as the recovery of metal values lost in the slag via suitable and economically viable processes. The following are significant achievements.

(1) Measurements of the thermodynamic activities of Cr and V in molten slags at low oxygen potentials.

(2) Determination of Cr and V valence states in metallurgical slags by XANES as well as Knudsen cell-mass spectrometric methods.

(3) Understanding of slag structure from the temperature dependence of sulfide capacities as well as Raman spectroscopy.

(4) Minimization of Cr loss to the slag using CO_2–O_2 mixtures for decarburization of alloy steel melts.

(5) Development of vaporization processes to capture higher Cr and V oxides emanating from molten slags at high oxygen potentials.

(6) A new salt extraction process for recovering transition metal oxides from slags.

These efforts are unique as they are the pioneering work in the entire world to come up with such important results.

Acknowledgements

The authors sincerely acknowledge the contributions of Dr. Pengli Dong, Prof. Xinlei Ge, Dr. Lidong Teng, Dr. Galina Albersson, Ms. Tatiana Shyrokikh, Professor Piotr R. Scheller, and other researchers who contributed to the present achievements. Parts of the work were carried out as part of the Eco Steelmaking project funded by the Swedish Foundation for Strategic Environmental Research (MISTRA) through the Swedish Steel Producers Association. Chinese Academy of Science is acknowledged for its partial finical support through the “Transfer and commercialization of scientific and technological achievements” project (No. 2020 109).

Conflict of Interest

The authors declare no potential conflict of interest.

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