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PREFACE

Innovations in metallurgical and materials processes: advancing liquid theory and honoring Prof. Han-jie Guo's contributions to physical chemistry in metallurgy

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Spanning three decades, Prof. Han-jie Guo's research group has dedicated itself to exploring the fundamental theories and practical applications of physical chemistry within the realm of metallurgy. Operating under the assumption that molecular entities and complexes persist in liquid states, the team has unearthed pivotal insights. A remarkable congruence between the calculated mole fractions of compounds or complexes in multi-component equilibria and the experimentally obtained activities was explored, derived from mass action law. This leads to the profound inference that "solutions exhibit no distinct activity but are characterized only by concentration". The scope of the team's inquiry encompasses a broad spectrum of systems: diverse metal solutions, complex metallurgical slags, and various aqueous systems with chloride fluoride. In addition, over 200 binary and ternary electrolyte systems have been validated. These validations demonstrate a high degree of alignment between the component mole fractions calculated through multivariate equilibrium and the activities obtained through experimentation, assuming the persistence of solid-state molecules in liquids. Therefore, "atom–molecule coexistence theory" for metal solutions and "ion–molecule coexistence theory" for slags and aqueous solutions were established.

Based on the atom–molecule coexistence theoretical model and related metallurgical physicochemical theories, Prof. Han-jie Guo's research group has navigated and resolved numerous complex challenges within the domains of metallurgical processes and materials. A critical facet of their inquiry pertains to the deoxidation mechanisms integral to the steel refining process. By integrating the concentration and activity coefficients of deoxidation reaction elements into temperature-correlated equilibrium constants, the team has formulated complex mathematical expressions. These higher-order equations enable the determination of the constrained objective function, pinpointing the minimum value of oxygen content. The studies confirmed that the optimal deoxidizer concentration yields the lowest oxygen saturation when elements like Al and C are used as deoxidizers. Addressing the quality requirements for iron ingot in sectors like wind power, the team has also illuminated the thermodynamic processes necessary for the removal of impurities such as Si, Mn, P, S, and Ti, based on the coexistence theory. The conditions for the oxidation of Si, P, and Ti and the reduction in S are relatively attainable with current industrial process. However, the neutral condition required for Mn extraction, poised between oxidation and reduction, presents a significant technical obstacle.

Based on the ion–molecule coexistence theory, Prof. Han-jie Guo's research group devised a thermodynamic model delineating the activity of components in slag as well as the equilibrium Mn partition ratio between slag and molten metal. The model adeptly forecasts the equilibrium partition ratio of Mn during the demanganization process, quantifies the influence of free FeO in the slag and dissolved oxygen in hot metal on Mn removal, and allocates their respective removal efficiencies at 37% and 63%. Kinetic analyses indicated the mass transfer of ferro-Si, ferro-Ti, and ferro-S in the metal phase as the rate-controlling step for their removal. Conversely, the extraction of P is contingent upon the mass transfer of its oxide in slag phase. The removal rate-controlling kinetics for Mn in hot metal are complex: for a binary basicity $R \leq 0.6$, the Mn mass transfer in the metal phase is the rate-limiting step; for R = 0.6–1.0, the process is governed by the mass transfer of both Mn in the metal and MnO in the slag; and when $R \geq 1.0$, the rate-controlling shifts only to the mass transfer of MnO in slag phase. In an examination of experimental data reported in the literature, which pertains to Mn distribution ratio across complex slag systems like $CaO–SiO_2–FeO–MgO–MnO–Al_2O_3$, CaO–

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SiO_2–MgO–FeO–Fe_2O_3–MnO–P_2O_5, and CaO–SiO_2–MgO–FeO–Fe_2O_3–MnO–Al_2O_3–P_2O_5 slag systems, the research group conducted a comprehensive validation of more than 200 industrial datasets. These datasets represent a vast range of compositional diversity in slag–steel interactions sourced from pertinent iron and steel production entities. Through this extensive analysis, the efficacy of IMCT-L_{Mn} and IMCT-C_{Mn} models was validated. These innovative models enable a thermodynamic calculation of Mn distribution ratio, facilitating the quantification of the partition ratio $L_{Mn,i}$ and Mn capacity $C_{Mn,i}$ for products MnO, MnO–SiO_2, 2MnO–SiO_2, and MnO–Al_2O_3 in the context of slag–steel interactions. The deoxidation potentials for FeO, FeO + Al_2O_3, and FeO + SiO_2 within the slag matrix are markedly high, at 98.8%, 1.8%, and 0.2%, respectively.

In the pursuit of improved refining efficiency within metallurgical processes, Prof. Han-jie Guo's research group conducted studies into the metallurgical kinetics of the desulfurization reaction in H13 electroslag metallurgical process by employing solute permeation theory. This approach yielded highly promising results. Furthermore, for the desulfurization reaction between slag and steel, the studies posited that interfacial chemical reactions do not serve as the rate-controlling step. Utilizing the dual-membrane theory, the team simplified the four interfacial rate equations, representing the mass transfer steps in the slag and steel under steady state, into a single one-dimensional quadratic equation. This simplification exclusively ties the rate of reaction to the concentration of interfacial oxygen $C^{*}_{[O]}$. The resultant equation offers the first general expression for the kinetics of the desulfurization reaction. Such a breakthrough provides a theoretical basis for future endeavors in smelting ultra-low S steel from molten steel within complex systems.

The team applied physicochemical principles to the development of novel metallurgical processes and procedures. Based on the ion–molecule coexistence theory, the research group obtained the optimal composition for micro-oxidizing slag within smelting reduction vessel of the core melting unit in HIsmelt process. This discovery clarified the mechanism preventing the reduction of Si and P in liquid steel obtained from the processing of high-P ores, thereby reducing the load on subsequent steelmaking processes. By utilizing the principle of minimum free energy, the team explored the direct reduction of iron ore using low-volatile coal through both "C-cycle" and "H-cycle". The findings confirmed that incorporating a minor H_2 presence can lower the reduction temperature by approximately 200 °C. This theoretical proposition is in remarkable agreement with the empirical data from industry on coal-based hydrometallurgy. In collaboration with Mr. Wang from Shanxi Xinli Technology Co., Ltd., the theoretical research on gas-based direct reduction for over two decades culminated in the design of revolutionary "exothermic direct reduction shaft furnace". The computations and experimental validations have demonstrated the energy and reduction efficiencies of the externally heated direct reduction shaft furnace, resulting in an integrated one-step steelmaking process that includes "pure hydrogen direct reduction–fusion refining–re-refining". In laboratory conditions, Prof. Han-jie Guo's research group obtained 99.9868% high-purity iron with an oxygen content of 10×10^{-6} and high-purity GCr15-bearing steel with a total oxygen content of 4.8×10^{-6} and Ti content of 6×10^{-6}. These results indicated the potential to eliminate the reliance on coke in ironmaking, potentially replacing the blast furnace and converter processes. Such advancements could integrate coal chemical processes with metallurgy, forming a "one-step" process from iron ore to steel in a low-order coal–hydrogen metallurgical framework.

Employing the basic principles of metallurgical thermodynamics, Prof. Han-jie Guo endeavors to bridge the knowledge gap between specialized metal materials and the broader field of metallurgical disciplines. It undertook a systematic investigation into the solidification dynamics of various compounds that precipitate during the solidification of metal materials such as hot die steel H13, M42 high-speed steel, Fe–Cr–Al heat-resistant alloys, Ni-based superalloys, maraging steels for critical turbine spool forgings in ultra-high-parameter steam turbines (630 °C), large-scale tunnel boring machine cutterhead steel, and AZ61 Mg alloy. The studies emphasized the genesis and transformation of carbon compounds, delving into the precipitative and decompositional mechanisms of carbides and oxides at different solid-phase ratios. By extending the scope of metal material formation research to include the solidification processes succeeding super-purification smelting, the team provided a robust foundation for the preparation of advanced materials and a novel way for the exploration of new material compositions.

This special column presents a curated collection of scholarly works from Prof. Han-jie Guo's research group, featuring 11 manuscripts, alongside a notable contribution from Prof. Changling Zhuang. The compendium includes two reviewing papers and 10 research articles. Among these, three manuscripts were regarding to hydrogen metallurgy, while another three expounded upon the production of high-purity steel. Four additional papers contributed to the discourse on controlling secondary phase particles within high-alloy steels. These manuscripts collectively underscored Prof. Han-jie Guo's substantial research interests and are imbued with his profound insights into physical and chemical phenomena. Additionally, two further papers ventured into contemporary column, with one exploring the synthesis of Cu–graphene composites and the other examining the applications of machine learning and deep learning techniques within the steelmaking process. These two studies showed the efforts of Prof. Han-jie Guo's research group to advancing research on cutting-edge topics within the metallurgy field.