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Multiphase equilibrium modeling of oxygen bottom-blown copper smelting process

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Abstract: A computational thermodynamics model for the oxygen bottom-blown copper smelting process (Shuikoushan, SKS process) was established, based on the SKS smelting characteristics and theory of Gibbs free energy minimization. The calculated results of the model show that, under the given stable production condition, the contents of Cu, Fe and S in matte are 71.08%, 7.15% and 17.51%, and the contents of Fe, SiO_2 and Cu in slag are 42.17%, 25.05% and 3.16%. The calculated fractional distributions of minor elements among gas, slag and matte phases are As 82.69%,11.22%, 6.09%, Sb 16.57%, 70.63%, 12.80%, Bi 68.93%, 11.30%, 19.77%, Pb 19.70%, 24.75%, 55.55% and Zn 17.94%, 64.28%, 17.79%, respectively. The calculated results of the multiphase equilibrium model agree well with the actual industrial production data, indicating that the credibility of the model is validated. Therefore, the model could be used to monitor and optimize the industrial operations of SKS process.

Key words: multiphase equilibrium modeling; oxygen bottom-blown copper smelting; SKS process; element distribution

1 Introduction

The oxygen bottom-blown copper smelting process is a newly developed technology for copper smelting, which is originally from the Shuikoushan (SKS) copper smelting method, and the intellectual property belongs to China. Recently, this copper smelting technology is widely adopted by copper companies due to its significant advantages over other copper smelting technology [1,2], such as higher oxygen enrichment, lower slag copper content, stronger adaptability of raw materials, higher efficiency of pyretic smelting and easily controlled matte grade. The main equipment of the SKS process is a d4.4 m × 16.5 m horizontal cylindrical airtight reactor as shown in Fig. 1, similar to the Noranda and Teniente furnace [3].

Because the copper concentrates are becoming lower grade and more complex, which contain multifarious impurity elements such as arsenic, lead and zinc. Interest in the deportment of those elements between phases is growing. Investigation on the process multiphase equilibrium is essential to make it clear, and the concern now is mainly focused on two aspects. One is the existing form and behavior of both minor and major elements as well as intensification of the elements distribution for further poly-metallic extraction or disposal during the smelting process. The other is the efficient and reliable algorithm for solving the complex multiphase equilibrium model. In the copper metallurgical area, GOTO et al [4−6] developed a basic copper multiphase equilibrium model and then improved it. TAN et al [7] solved the model using a modified form of the Newton−Raphson technique and applied it to the various copper pyro-metallurgy processes to simulate the distribution behaviors of Ni, Zn, As, Sb, Bi, etc. The model [8] for the Isasmet process is based on the concept that there were two independent reaction sites in a slag bath: one for fast oxidation and the other for slow reduction. In this model the oxidizing and reducing reactions were assumed to proceed under a separate set of equilibrium conditions. TONG et al [9] simplified the model development to some extent and deduced element-potential-based copper flash smelting multiphase equilibrium to calculate equations using the element potential concept coupled with the Gibbs function principle, and solved it with RAND algorithm. But the correctness of the results was closely determined by

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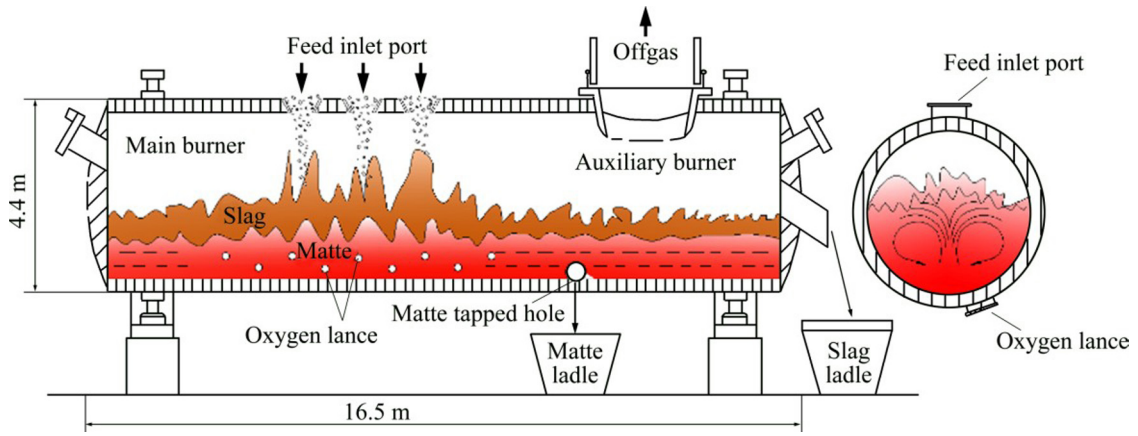

Fig. 1 Schematic diagram of SKS furnace

the algorithm's initial values. WEI et al [10] used modified τ-method, LIN et al [11] used genetic algorithm and XU et al [12] used one-step algorithm for the chemical multiphase equilibrium calculation, but all the algorithms used were only allowed to handle the variable numbers below ten as it was quite time consuming.

Up to date, no work on the computational thermodynamics model considering the characteristics of SKS process has been reported. In this work, we developed a multiphase equilibrium model based on the thermodynamic principle of Gibbs energy minimization and the characteristics of SKS process, which could be used to optimize the industrial operations of SKS process.

2 Establishment of SKS thermodynamic model

2.1 Thermodynamic theory for model establishment

The SKS process is a typical multiphase and multicomponent system coupling with various chemical reactions. According to the second law of thermodynamics, spontaneous reaction always conducts towards the direction that the total Gibbs free energy decreases. An isothermal and isobaric chemical system is at equilibrium when the total Gibbs free energy is minimized [13]. It is assumed that the SKS process is under the isothermal and isobaric condition and reaches its thermodynamic equilibrium, so the total Gibbs free energy of the SKS system attains its minimization.

The total Gibbs free energy function [14] for a multiphase and multicomponent system can be expressed as

$$G(n,T,P)=\sum_{j=1}^{N_p}\sum_{i=1}^{N_c}n_{ij}\mu_{ij}=\sum_{j=1}^{N_p}\sum_{i=1}^{N_c}n_{ij}\left[\Delta G_{ij}^{\Theta}+RT\ln\left(\frac{f_{ij}}{f_{ij}^{o}}\right)\right] \quad (1)$$

where N_p and N_c are the number of phases and component in phases, respectively; n_{ij} is the mole number of component i in phase j; μ_{ij} is the partial molar Gibbs free energy, i.e., chemical potential of component i in phase j in the system conditions, which is composed of two parts to modify its non-ideality, one part is ΔG_{ij}^{Θ}, the standard Gibbs free energy of formation of component i in phase j under the system temperature and standard pressure. This modifies the impact of temperature on the standard Gibbs free energy [13] and can be calculated by

$$\Delta G_{ij}^{\Theta}=\Delta H_{ij}^{\Theta}+T\Delta S_{ij}^{\Theta} \quad (2)$$

The other part is $RT\ln(f_{ij}/f_{ij}^{o})$, which modifies the influence of pressure or concentration under non-ideal condition on the standard Gibbs free energy; R is mole gas constant; T is the thermodynamic temperature in Kelvin; f_{ij} is the partial fugacity of component i in the phase j; f_{ij}^{o} is the fugacity of component i in the phase j at reference state. The value of fugacity is depended on the system temperature and pressure. In the SKS process, the gas phase is treated to be ideal. The high temperature melts are non-ideal liquid solutions, therefore, activity coefficient is introduced to substitute fugacity to modify the chemical potential of constituents in real solution against the in-adaptation of the ideal solution. So, the fugacity of components in molten phase and gas phase can be expressed by [14,15]

$$RT\ln\left(\frac{f_{ij}}{f_{ij}^{o}}\right)=\begin{cases}RT\ln(\lambda_{ij}x_{ij})\\RT\ln(y_{ij}p)\end{cases} \quad (3)$$

where λ_{ij} and x_{ij} are respectively the activity coefficient and mole fraction of component i in the phase j. y_{ij} is the partial pressure of component i in the gas phase and p is the total pressure of the gas phase.

At the same time, according to the element conservation law principle, the inputs of elements to the system should be equal to the outputs and the mole