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Thermodynamic and experimental study of C-S system and C-S-Mo system

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ABSTRACT

In order to better utilize the low-grade molybdenite concentrates and obtain high quality products, thermodynamic analysis and experimental study of vacuum smelting process of molybdenite concentrates were carried out in detail. The possible reactions of the C-S system were analyzed, and the indirect reduction reactions and direct reduction reactions of MoS_2 were discussed. To clarify the reaction mechanism under vacuum condition, the Mo-S-C system was also studied by thermodynamic and experimental methods. The results indicated that vacuum decomposition reactions and equilibrium reactions of Mo-S-C system were carried out simultaneously in the vacuum smelting process. Temperature and pressure are the main factors affecting the vacuum smelting process. There is reaction equilibrium of C, CS, CS_2 and S_2 in the vacuum smelting process and molybdenum sulfides can be easily reduced to Mo, Mo_2C, Mo_3C_2 and MoC. The contents of carbon and sulfur in the product have relationship with the reaction equilibrium of Mo-S-C system. The CS generated in carbon sulfidation reaction($C + CS_2 \rightarrow 2CS$) may accelerate the reaction rates in the vacuum smelting process. When the grade of molybdenite concentrates is 48%, the optimum content of carbon added in the molybdenite concentrates is about 4%, and the content of Mo in the metal molybdenum products can reach 92%, and the content of sulfur and residual carbon are all low.

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1. Introduction

Molybdenite is the most widely source of molybdenum. In the extractive metallurgy process of molybdenum, the sulfur dioxide released from the oxidation roasting of molybdenite concentrates is very harmful to the environment and the cost of recovery utilization is very high due to its low concentration. The traditional metallurgical process of molybdenum is long, complicated, and low yield of Mo [1,2]. In order to avoid pollution in the traditional process, some new metallurgical technologies of molybdenite concentrates were put forward, such as lime roasting [3,4], chlorination roasting [5], steam oxidation [6], direct hydrogen reduction [7], hydro-decomposition [8–10] and bio-metallurgy [11]. None of these processes are used for industrial application of mass production. The vacuum decomposition process of molybdenite concentrates was put forward very early, and the Climax Company in the United States had also focused on this process for many years, but there were no further application study [12,13]. In order to reduce the production cost and develop environmental friendly technology, a new vacuum decomposition process was put forward again [14,15]. The main step is the decomposition of molybdenite concentrates in a vacuum furnace, and metal molybdenum and sulfur can be obtained directly after one step decomposition [16,17]. This process offers possibility of no emission of SO_2, and it also makes molybdenum extraction easier. Semi-industrial experiments also show that high quality product can be obtained and there is great industrial significance [18].

In the experiment, it was found that if the carbon is added into the concentrates in the vacuum decomposition process, the reaction courses can be accelerated effectively and the impurities of Si, Ca, Mg and Al etc. in the metal product were reduced to less except that the recovery rate of sulfur was reduced. In order to understand this phenomenon, it is necessary to clarify the reaction mechanism of the vacuum smelting process of molybdenite concentrates. But there is almost no research in this area. Therefore, the thermodynamic analysis of the vacuum carbothermic reduction process of molybdenite concentrates is carried out to study the possible reactions in the process, and the thermodynamic and experimental study of Mo-S-C system is also carried out to obtain the reaction

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mechanism under vacuum condition. These results will provide theoretical guidance for the industrial application of vacuum smelting of molybdenite concentrates.

2. Thermal decomposition reactions of molybdenite concentrates under low pressure

In general, the grade range of molybdenite concentrates is from 45% to 57%, and the major phase is MoS_2 which accounts for about 75%–95% [1]. The main impurities are SiO_2 and CaO, and the other impurities are relatively less. So, the objects of thermodynamic calculation are the possible reactions of MoS_2 in molybdenite concentrates. In the vacuum smelting process, when the pressure of the system was reduced to the required pressure and the temperature was raised to the target temperature, the thermal decomposition reactions of molybdenite concentrates occur spontaneously.

In Mo-S system, there are two kinds of stable compounds, MoS_2 and Mo_2S_3. According to the principle of stepwise decomposition, MoS_2 decomposes to Mo_2S_3 firstly and then continue to decompose into Mo. The possible reactions in the vacuum decomposition process are listed as follows [19,20]:

$$4MoS_2(s) \rightarrow 2Mo_2S_3(s) + S_2(g) \tag{1}$$

$$\frac{2}{3}Mo_2S_3(s) \rightarrow \frac{4}{3}Mo(s) + S_2(g) \tag{2}$$

According to

$$\Delta G^{\Theta} = -RT \ln K^{\Theta} = -RT \ln P_{S_2} \tag{3}$$

The equilibrium pressure Ps_2 can be expressed as [21]:

$$P_{S_2} = P^{\Theta} \exp\left(\frac{-\Delta G^{\Theta}}{RT}\right) \tag{4}$$

Where ΔG^{Θ} is the standard Gibbs free energy, J/mol; K^{Θ} is the equilibrium constant; P_{S_2} is the equilibrium partial pressure of S_2, Pa; R is the gas constant, 8.314 J/(mol·K); T is the temperature, K; P^{Θ} is the standard atmospheric pressure, 101325Pa.

The equilibrium pressures of S_2 when MoS_2 and Mo_2S_3 decompose are shown in Fig. 1. It can be seen in Fig. 1 that the decomposition equilibrium pressure of S_2 increases as the temperature rises, and in the same temperature range the equilibrium pressure (Ps_2) of decomposition reaction of MoS_2 is higher than that of Mo_2S_3. Combining with the above calculation formulas (Equations (3) and (4)), when the pressure is 30Pa, the phase changes with the temperature rising: MoS_2 decomposes to Mo_2S_3 firstly at about 1547K and then Mo_2S_3 decomposes to metal Mo at about 1632K.

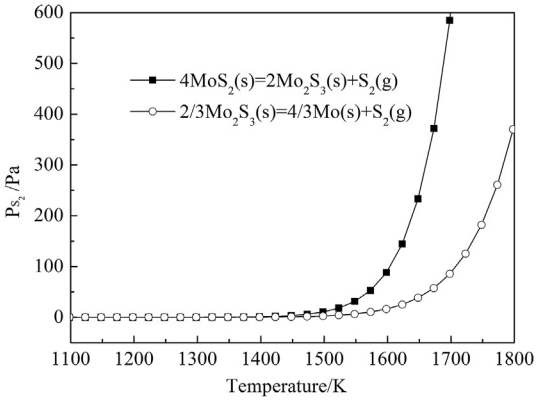

Fig. 1. Decomposition pressure of MoS2 and Mo2S3 at different temperature.

3. Thermodynamic calculation of Mo-C-S system

3.1. Reaction analysis of C-S system

In the vacuum smelting process, when the carbon is added, S_2 produced by vacuum decomposition reactions of molybdenite concentrates may react with carbon, and the possible reactions of C-S system are as follows [19,20]:

$$C + S_2(g) = CS_2(g),\ \Delta_r G^{\Theta} = -11002 - 6T \tag{5}$$

$$2C + S_2(g) = 2CS(g),\ \Delta_r G^{\Theta} = 428385 - 178T \tag{6}$$

$$C + CS_2(g) = 2CS(g),\ \Delta_r G^{\Theta} = 439388 - 172T \tag{7}$$

Reaction (7) is CS_2 reacting with carbon as an oxidant and can be referred as "carbon sulfidation reaction", which is the coupling of reaction (5) and reaction (6). When the same substance S_2 in the two reactions is eliminated, the Gibbs free energy of reaction(7) $\Delta_r G^{\Theta}{}_{(7)} = \Delta_r G^{\Theta}{}_{(6)} - \Delta_r G^{\Theta}{}_{(5)}$.

When the system pressure is 30Pa, the Gibbs free energy of carbon sulfidation reaction (reaction (7)) is 0 at 1850K. Above this temperature, the equilibrium content of CS in the gas phase is higher than the equilibrium content of CS_2, and below this temperature, the equilibrium content of CS is lower than CS_2's. The equilibrium diagram of carbon sulfidation reaction can be obtained by Gibbs free energy and equilibrium constants.

$$\begin{aligned} &\Delta_r G^{\Theta} = -RT \ln K^{\Theta} = -RT \ln \frac{p_{CS}^2}{p_{CS_2}} \times \frac{1}{a_C} \\ &p_{CS} = \frac{\varphi(CS)p}{100},\ p_{CS_2} = \frac{\varphi(CS_2)p}{100},\ a_C = 1 \end{aligned} \tag{8}$$

Where $\varphi(CS)$ is the volume fraction of CS in the gas component; $\varphi(CS_2)$ is the volume fraction of CS_2 in the gas component; P is the total pressure of the system, Pa; P_{CS} is the partial pressure of CS, Pa; P_{CS_2} is the partial pressure of CS_2, Pa; a_C is the activity of carbon;

When there are only CS and CS_2 in the gas component,

$$\varphi(CS) + \varphi(CS_2) = 100\% \tag{9}$$

$$\lg K^{\Theta} = \lg \frac{[\varphi(CS)]^2 p}{100[100 - \varphi(CS)]} \tag{10}$$

$$\varphi(CS) = 50 \times \frac{K^{\Theta}}{p} \times \left[\sqrt{1 + \frac{4p}{K^{\Theta}}} - 1\right]\% \tag{11}$$

Fig. 2 is the equilibrium diagram of carbon sulfidation reaction($C + CS_2 \rightarrow 2CS$). In Fig. 2, the equilibrium curve of CS in the gas phase divides the figure into two parts: above the curve is decomposition zone of CS (the stable area for solid carbon) and below the curve is stable zone of CS (carbon sulfidation zone).

Because the stoichiometry of the gas species in the reactants and products of carbon sulfidation reaction are different, the pressure has an effect on the equilibrium composition. According to the Le Chatelier's principle, the pressure decreasing can promote the reaction equilibrium shifting toward $C + CS_2 \rightarrow 2CS$ which is the direction of volume increasing. As a result, the volume fraction of CS (φ(CS)) increases. Therefore, with the pressure decreasing the

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