

# Research on a Quasi-Equilibrium Method for Reduction of Indium-Containing Slag in Immersion Bath Smelting

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**Abstract:** The grade of Indium in various concentrates is relatively low and usually can not meet the requirements of direct extraction. Primary indium can only be recovered from intermediate products and by-products in the smelting process of lead, zinc, copper and tin. In order to recover indium from indium containing slag more effectively, through the thermodynamic analysis and research of reduction smelting reaction of indium containing slag melted in submerged bath, combined with budol thermodynamic theory, the quasi equilibrium experiment of reducing indium containing slag is designed, and the quasi equilibrium condition of reducing indium containing slag is determined. Thus, it lays a good experimental analysis foundation for the subsequent experimental research on the reduction of indium containing slag in submerged bath smelting, which is conducive to tamping the relevant basic theory of indium containing slag recovery and provides theoretical basis and new methods and technical support for the recovery of indium and other valuable metals from indium containing slag.

**Keywords:** submerged bath melting; indium containing slag; quasi-equilibrium experiment; thermodynamic analysis; Indium

## 1. Introduction

Indium is a dispersed element with a crustal abundance of only  $0.04 \times 10^{-6}$ . It does have independent minerals, such as Indium copper ( $\text{CuInS}_2$ ), Indium sulphide iron ore ( $\text{FeInS}_4$ ), aqueous Indium ore [ $\text{In}(\text{OH})_3$ ], Indium mainly exists in marmatite (Indium content is 0.0001% ~ 0.1%), hematite, galena and other polymetallic sulfide ores [1,2]. Indium has a relatively low grade in various concentrates [3], usually not up to direct extraction requirements, only from lead, zinc, copper and tin smelting process intermediate products [4] And by-product recovery of native Indium [5,6]. The recovery of Indium from Indium-containing slag basically uses acid leaching technology to enrich Indium in Indium-containing slag, but the application of acid leaching technology will lead to the volatilization of acid,

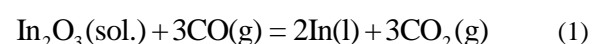
and the tail slag is not harmless treatment, so it is easy to lead to environmental pollution [7-15].

Therefore, it is necessary to carry out basic research on the thermodynamic mechanism of Indium recovery by reduction of Indium-containing slag. This project by immersion bath smelting slag containing Indium smelting reaction thermodynamics analysis and research, combined with the cloth doll thermodynamics theory, design the reductive slag containing Indium nearly balance experiment, and the reduction of slag containing Indium were determined nearly equilibrium condition, thus for subsequent immersion bath smelting slag containing Indium reduction of experimental study laid a good basis of experimental analysis. It is beneficial to consolidate the relevant basic theories of recovery of Indium-containing slag and provide theoretical basis and new methods and technical support for recovery of valuable metals such as Indium from Indium-containing slag.

## 2. The Thermodynamic Theory of Indium-containing Slag Melting Reaction in Submerged Molten Pool

### 2.1. Theoretical Activity of $\text{In}_2\text{O}_3$ in Slag Melt Containing Indium

The reduction of Indium-containing slag in immersion bath smelting was studied by using high-temperature tubular atmosphere push-rod furnace. The thermodynamic principle is to judge the direction of reaction according to the dominant zone diagram of In-S-O system. This process is the  $\text{In}_2\text{O}_3$  in Indium-containing slag melt reduction reaction with CO to reduce Indium from Indium-containing slag melt, as shown in Equation (1). Therefore, this part mainly conducts thermodynamic calculation on the reduction of Indium-containing slag melt, in order to obtain the theoretical standard equilibrium constant of Indium-containing slag melting reaction and Indium-containing high temperature melt activity of  $\text{In}_2\text{O}_3$  and other related thermodynamic data.



$$\Delta_r G_{m(1)}^\ominus / (\text{kJ} \cdot \text{mol}^{-1}) = 72.319 - 0.0587 \times T \quad (1a)$$

$$K_{\alpha(1)}^\ominus = (p_{\text{CO}_2})^3 / \alpha_{\text{In}_2\text{O}_3(\text{sol.})} \times (p_{\text{CO}})^3 \quad (1b)$$

$$\Delta_r G_{m(1)} = \Delta_r G_{m(1)}^\ominus + RT \ln [\alpha_{m(1)}^2 \times (p_{CO_2}/p^\ominus)^3 / \alpha_{In_2O_3} \times (p_{CO}/p^\ominus)^3] \quad (1c)$$

When the reaction reaches equilibrium,  $\Delta_r G_{m(1)} = 0$

According to the thermodynamic relationship, we have the (2)

$$\Delta_r G_{m(1)}^\ominus = -RT \ln K_{\alpha(1)}^\ominus \quad (2)$$

The standard Gibbs free energy change of the smelting reaction can be obtained according to Equation (1a), which is based on references standard thermodynamic data, the equation of the standard Gibbs free energy change and temperature obtained from equation (1). At each temperature, equation (1) should have a standard Gibbs free energy variation for each pair.  $\Delta_r G_m^\ominus$  Therefore, the

value of the standard equilibrium constant of the smelting reaction can be obtained according to Equation (2).  $K_{\alpha(1)}^\ominus$  According to Equation (1b), the standard

equilibrium constant  $K_{\alpha(1)}^\ominus$  is mainly related to  $\alpha_{In_2O_3}$  and  $p_{CO}/p_{CO_2}$ , simultaneous equations (1a), (1b) and (2) can be used to calculate the value of  $\alpha_{In_2O_3}$  when reaction

(1) reaches equilibrium at different temperatures and under different reducing atmosphere conditions, as shown in Table 1.

**Table 1.** Activity of  $In_2O_3$  in equilibrium state of reaction (1) at different temperatures and different reducing atmospheres

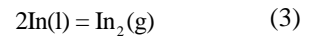
T (K)	$\Delta_r G_m^\ominus$ (kJ mol <sup>-1</sup> )	$K_\alpha^\ominus$	$p_{CO}/p_{CO_2}$	$\alpha_{In_2O_3} \times 10^5$
1273.150	3.450	1.385	20	9.023
1273.150	3.450	1.385	25	4.620
1273.150	3.450	1.385	30	2.674
1323.150	6.226	1.761	20	7.098
1323.150	6.226	1.761	25	3.634
1323.150	6.226	1.761	30	2.103

**Table 2.** Activity of  $In_2O_3$  in the equilibrium state of reaction (4) at different temperatures and different reducing atmospheres

T (K)	$\Delta_r G_m^\ominus$ (kJ mol <sup>-1</sup> )	$K_\alpha^\ominus$	$p_{In_2(g)}$	$p_{CO}/p_{CO_2}$	$\alpha_{In_2O_3} \times 10^5$
1273.150	223.432	$6.797 \times 10^{-10}$	$4.906 \times 10^{-10}$	20	9.023
1273.150	223.432	$6.797 \times 10^{-10}$	$4.906 \times 10^{-10}$	25	4.620
1273.150	223.432	$6.797 \times 10^{-10}$	$4.906 \times 10^{-10}$	30	2.674
1323.150	213.736	$3.644 \times 10^{-9}$	$2.069 \times 10^{-9}$	20	7.098
1323.150	213.736	$3.644 \times 10^{-9}$	$2.069 \times 10^{-9}$	25	3.634
1323.150	213.736	$3.644 \times 10^{-9}$	$2.069 \times 10^{-9}$	30	2.103
1373.15	204.065	$1.725 \times 10^{-8}$	$7.854 \times 10^{-9}$	20	5.692
1373.15	204.065	$1.725 \times 10^{-8}$	$7.854 \times 10^{-9}$	25	2.914 <sup>5</sup>
1373.15	204.065	$1.725 \times 10^{-8}$	$7.854 \times 10^{-9}$	30	1.687
1423.15	194.415	$7.306 \times 10^{-8}$	$2.715 \times 10^{-8}$	15	11.01
1423.15	194.415	$7.306 \times 10^{-8}$	$2.715 \times 10^{-8}$	20	4.644
1423.15	194.415	$7.306 \times 10^{-8}$	$2.715 \times 10^{-8}$	25	2.378
1473.15	184.786	$2.801 \times 10^{-7}$	$8.625 \times 10^{-8}$	15	9.122
1473.15	184.786	$2.801 \times 10^{-7}$	$8.625 \times 10^{-8}$	20	3.848
1523.15	175.175	$9.819 \times 10^{-7}$	$2.504 \times 10^{-7}$	15	7.665

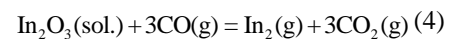
1373.15	8.980	2.196	20	5.692
1373.15	8.980	2.196	25	2.914 <sup>5</sup>
1373.15	8.980	2.196	30	1.687
1423.15	11.714	2.691	15	11.01
1423.15	11.714	2.691	20	4.644
1423.15	11.714	2.691	25	2.378
1473.15	14.428	3.248	15	9.122
1473.15	14.428	3.248	20	3.848
1523.15	17.122	3.866	15	7.665
1523.15	17.122	3.866	20	3.234
1573.15	19.796	4.543	15	6.522
1573.15	19.796	4.543	20	2.752
1623.15	22.450	5.279	15	5.613
1623.15	22.450	5.279	20	2.386
1623.15	22.450	5.279	25	1.212

When the product is  $In_2(g)$  gas, there are reactions (3) and (4) as follows:



$$\Delta_r G_{m(3)}^\ominus / (kJ \cdot mol^{-1}) = 403.59 - 0.1387 \times T \quad (3a)$$

$$K_{\alpha(3)}^\ominus = p_{In_2(g)} \quad (3b)$$



$$\Delta_r G_{m(4)}^\ominus / (kJ \cdot mol^{-1}) = 471.25 - 0.1924 \times T \quad (4a)$$

$$K_{\alpha(4)}^\ominus = (p_{CO_2})^3 \times p_{In_2(g)} / \alpha_{In_2O_3(sol.)} \times (p_{CO})^3 \quad (4b)$$

Similarly, equations (2), (3a), (3b), (3-4A) and (4b) can be established simultaneously. The value of  $\alpha_{In_2O_3}$  of reaction (4) when it reaches equilibrium under different temperature and reducing atmosphere conditions is shown in Table 2.

Based on Table 1 and Table 2, it can be known that under the same temperature and atmosphere, even The reduction products of  $In_2O_3$  is  $In(l)$  Or  $In_2(g)$ , but in both types of reactions, when the reaction reaches equilibrium, The theoretical activity of  $In_2O_3$  is the same. The details were shown in Table 3.

1523.15	175.175	$9.819 \times 10^{-7}$	$2.504 \times 10^{-7}$	20	3.234
1573.15	165.583	$3.174 \times 10^{-6}$	$6.986 \times 10^{-7}$	15	6.522
1573.15	165.583	$3.174 \times 10^{-6}$	$6.986 \times 10^{-7}$	20	2.752
1623.15	156.006	$9.531 \times 10^{-6}$	$1.806 \times 10^{-6}$	15	5.613
1623.15	156.006	$9.531 \times 10^{-6}$	$1.806 \times 10^{-6}$	20	2.386
1623.15	156.006	$9.531 \times 10^{-6}$	$1.806 \times 10^{-6}$	25	1.212

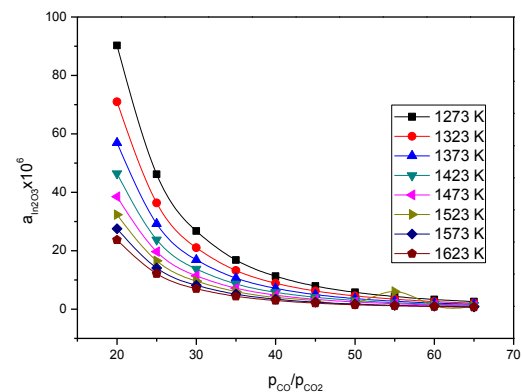
**Table 3.** Activity of In<sub>2</sub>O<sub>3</sub> in equilibrium state of reaction (1) or (4) at different temperatures and different atmosphere ratios

$\frac{p_{CO}}{p_{CO_2}}$ \ T	1273 K	1323 K	1373 K	1423 K	1473 K	1523 K	1573 K	1623 K
20	90.232	70.981	56.922	46.441	38.481	32.341	27.511	23.681
25	46.211	36.342	29.241	23.781	19.724	16.562	14.091	12.121
30	26.742	21.031	16.872	13.761	11.401	9.581	8.152	7.016
35	16.841	13.241	10.621	8.666	7.181	6.034	5.134	4.418
40	11.281	8.872	7.115	5.805	4.811	4.042	3.439	2.96
45	7.922	6.231	4.997	4.077	3.379	2.839	2.416	2.079
50	5.775	4.543	3.643	2.972	2.463	2.07	1.761	1.515
55	4.339	3.413	2.737	2.233	1.851	1.601	1.323	1.139
60	3.342	2.629	2.108	1.72	1.425	1.198	1.019	0.877
65	2.629	2.068	1.658	1.353	1.121	0.942	0.802	0.690

It can be seen from the table 3 that when the smelting reaction reaches equilibrium, the activity of In<sub>2</sub>O<sub>3</sub> is related to the atmosphere ratio. The higher the CO content, the smaller the activity value; It is also related to temperature, the higher the temperature, the smaller the activity value. It can also be seen from this table that the In<sub>2</sub>O<sub>3</sub> activity value of smelting reaction is relatively small, or it can be very small, which means that the smelting reaction can be carried out completely. Therefore, the recovery of Indium by smelting reaction can be carried out completely.

**2.2. Activity Trend of In<sub>2</sub>O<sub>3</sub> in Reduction Equilibrium of Indium Containing Slag under Different Conditions**

Through thermodynamic calculation and derivation, after the two reactions (1) and (4) reach equilibrium under the same external conditions, their theoretical activities in the equilibrium state are the same. Therefore, based on table 3, the activity change trend of In<sub>2</sub>O<sub>3</sub> in the equilibrium state of indium containing slag smelting and reduction in immersion bath under different temperatures and different reduction atmospheres can be drawn, as shown in Figure 1.



**Figure 1.** Activity trend of In<sub>2</sub>O<sub>3</sub> from reduced Indium-containing slag melted by immersion bath at different temperatures and different reducing atmosphere ratios

As can be seen from Figure 1, with the increase of temperature, the activity of In<sub>2</sub>O<sub>3</sub> in indium containing slag decreases rapidly and then tends to the same value. This means that the recovery of Indium by smelting reaction and appropriate smelting temperature can achieve ideal results; It also shows that the melting reaction is easy to reach equilibrium at high temperature. The thermodynamic theory of Bodol reaction

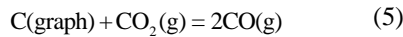
**3. Thermodynamic Theory of Budol Reaction**

Budol reaction is an important reaction in the process of carbothermal reduction. It is also used to prepare and control CO and CO<sub>2</sub> atmosphere when studying carbothermal reduction reaction (solid / gas reaction and molten pool smelting reaction).

**3.1. The Relationship between Gas Phase Composition**

and Temperature in the Budol Reaction System

For any reaction, different reaction conditions, such as temperature, pressure and concentration, may lead to different reaction results. For The Budol reaction, when the external conditions are constant, but only the temperature is different, the composition content of the reaction system changes with the change of temperature has a significant law. According to the thermodynamic theory, the contents of different gases in the budol reaction system at different temperatures can be calculated.



$$\Delta_r G_{m(5)}^\ominus / (\text{kJ} \cdot \text{mol}^{-1}) = 167.81 - 0.1725 \times T \quad (5a)$$

$$K_{\alpha(5)}^\ominus = P_{CO}^2 / P_{CO_2} \quad (5b)$$

When Equation (5) reaches equilibrium,, and

therefore,  $\Delta_r G_{m(5)}^\ominus = -RT \ln K_{\alpha(5)}^\ominus$

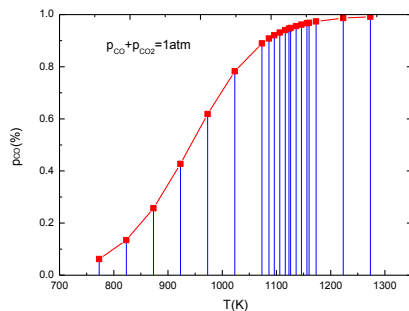
$$167.81 - 0.1725 \times T = -RT \ln P_{CO}^2 / P_{CO_2} \quad (5c)$$

In this reaction system, when the total pressure is not high,

$$P_{CO} + P_{CO_2} = 1 \text{atm} \quad (5d)$$

So,  $P_{CO} = -K_{\alpha(5)}^\ominus / 2 + \sqrt{K_{\alpha(5)}^{\ominus 2} / 4 + K_{\alpha(5)}^\ominus}$  (5e)

Therefore, by simultaneous (5b), (5c), (5d) and (5e),  $p_{CO}$  at different temperatures can be obtained,  $p_{CO_2}$  and  $p_{CO}/p_{CO_2}$ , as shown in Figure 2.

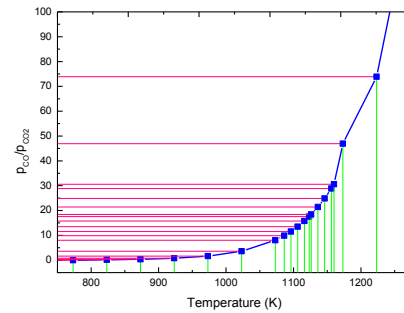


**Figure 2.** Relationship between gas phase composition and temperature in the reaction of C+CO2=2CO

Under constant pressure, the relationship between % $P_{CO}$  and temperature is shown in Figure 2, and the curve is in "s" shape, because the Budol reaction is endothermic. As can be seen from figure 2, with the increase of temperature, the equilibrium % $P_{CO}$  increases and the corresponding % $P_{CO_2}$  decreases. When the temperature is 700-900 K, the temperature increases and % $P_{CO}$  increases little; When the temperature is 900-1100 K, the temperature increases and % $P_{CO}$  increases sharply; At temperatures above 1273 K, % $P_{CO}$  is almost equal to 100% and % $P_{CO_2}$  = 0.

3.2. Relationship between PCO/PCO2 and Temperature in Budol Reaction System

Different atmosphere ratios ( $P_{CO}/p_{CO_2}$ ),  $P_{CO}/p_{CO_2}$  in the Budol reaction can be obtained according to the relations of (5b), (5c), (5d) and (5e). The relationship between the ratio of and temperature is shown in Figure 3.



**Figure 3.** Relationship between  $P_{CO}/P_{CO_2}$  and temperature in C+CO2=2CO reaction

According to Figure 3, different reducing atmosphere conditions can be obtained by setting different temperatures, and different reducing atmosphere conditions are required for Indium-containing slag at different temperatures to achieve the purpose of reducing volatilization.

**4. Experimental Design of Quasi Equilibrium Study on Reduction Smelting Reaction of Indium-containing Slag**

4.1. Raw Materials for Quasi Equilibrium Experiment of Reduction Smelting Reaction of Indium-containing Slag

The Indium-containing slag used in the quasi equilibrium experimental study is in FeO-CaO-SiO<sub>2</sub> prepared in flux. Iron trioxide, ferrous sulfide, silica and calcium oxide used in the experiment were analytically pure, produced by Xilong Chemical Co., LTD. Indium trioxide analytically pure was provided by Sinopril Chemical Reagent Co., LTD. First, according to  $w_{CaO}/w_{SiO_2} = 0.6$ ,  $w_{Fe}/w_{SiO_2} = 1.2$  Prepare flux, then go to FeO-CAO-SiO<sub>2</sub> Different  $w_{In_2O_3}$  are prepared in flux containing Indium slag. An S4 Pioneer XRF spectrometer was used to analyze the contents of each element in the self-made slag and a slag containing Indium, as shown in Table 4 and Table 5.

**Table 4.** Chemical composition of self-made FeO-CaO-sio2 flux

Element	Fe	Si	Ca	Al	O
Content (%)	34.45	15.83	14.19	1.66	24.7

**Table 5.** Chemical composition of Indium-containing slag

Element	Fe	Si	Ca	In	Al	O
Content (%)	31.44	15.21	13.16	2.419	3.24	25.7

4.2. Main equipment system used in the quasi equilibrium experimental study of Indium-containing slag reduction

The laboratory equipment for quasi equilibrium reduction of Indium-containing slag is composed of push-boat furnace and CO generator furnace. It mainly consists of Bodol reaction system, melt gas-liquid reaction balance system, conveying gas power and its circulation

system, propulsion power system, gas flow measurement system, gas drying system, air pressure balance system and temperature control system, as shown in Figure 2.

4.3. Analysis Method Used in the Quasi Equilibrium Experimental study of Indium-containing Slag Reduction

The contents of indium and calcium in indium containing slag were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-OES). The analytical instrument is a full spectrum direct reading emission spectrometer, model: spectroblue SOP (produced in Germany), wavelength range: 165 ~ 770 nm, CCD detector.

4.4. Steps of Quasi-equilibrium Experiment for Reduction of Indium-containing Slag

From immersion bath smelting slag containing Indium reduction nearly equilibrium experiment equipment, the device containing the cloth doll system, gas liquid equilibrium system of melt and functions of the system, each function system has a corresponding operating procedures and methods, thus containing Indium slag reduction nearly equilibrium experiment process is relatively complex, involving more experimental steps, experiment process key steps are as follows:

Weigh the predetermined Indium-containing slag and place it in the quartz porcelain boat. Push the boat furnace 34 cm away from the port from the air outlet; The charcoal slices obtained from 8-mesh and 4-mesh metal mesh screens were placed in a vertical crucible furnace, and the height of the carbon layer was about 8 cm high. According to the needs of reaction, the temperature of push-boat furnace and vertical crucible furnace are set respectively. Adjust the speed of the micro pump and the flow of the flowmeter; Seal the whole reaction system. The three-way switch ventilation switch of the inlet end of the push-boat furnace points to the push-boat furnace, and the three-way valve ventilation switch of the outlet port of the push-boat furnace points to the vertical tubular atmosphere furnace, and the ventilation enters the furnace chamber of the push-boat furnace to start the gas circulation. The reaction time was about 16 h. After the reaction is completed, the product is cooled quickly, and the sample is removed by opening the sealing cover of the air outlet.

When the reaction is finished, close the pushing the boat furnace inlet side three-way switch, makes the 3-way switch opened mouth pointing in the direction of gas separation pipe, at the same time open the gas separation pipe ends of the 3-way switch with vertical tubular furnace atmosphere connected to another gas loop formation, prevent system CO gas into the atmosphere cause harm to the operator and environment.

5. Determination of Quasi Equilibrium State of Indium-containing Slag Reduction in Melting Reaction

The empirical equilibrium constant of the melting reaction can be determined by quasi-equilibrium experiment, but it must be guaranteed that the melting reaction really reaches quasi-equilibrium or

quasi-equilibrium state.

5.1. Method and Principle of Quasi Equilibrium Test to Determine Quasi Equilibrium State of Indium-containing Slag Reduction

There are usually three ways to determine whether a reaction reaches chemical equilibrium. One is to verify the content of each substance in the reaction system through different reaction time under the same external conditions, and whether the reaction reaches a certain stage is basically consistent; Second, under the premise of the same external conditions, when the material layer thickness of the reactants is different, the content of each substance in the reaction system at a certain stage after the reaction is consistent, if basically consistent, it can be determined that the chemical reaction has reached equilibrium under this condition; The third is to test whether the content of each substance in the reaction can reach a certain same value at a certain stage by carrying out the smelting reaction forward and backward, so as to prove whether a chemical reaction of the system has reached the equilibrium state.

In view of the limitation of experimental conditions, this study mainly verifies whether the reduction of Indium-containing slag under the same experimental conditions has reached the quasi equilibrium state with different reaction time and thickness of reactants.

5.2. Quasi-equilibrium Experimental Determination of Indium-containing Slag in Reduction Smelting at Different Times

At 1 atmospheric pressure, 1573 K, the atmosphere ratio of the reaction system ( $P_{CO}/P_{CO2}$ ) is 25.  $In_2O_3$  is found in the Indium-containing slag at different times. The mass fraction of is shown in Table 6.

Table 6.  $W_{In_2O_3}$  determined by quasi equilibrium reduction experiment of Indium-containing slag at different reduction time

$T (h)$	$W'_{In_2O_3} \times 10^2$	$w_{In_2O_3} \times 10^2$
	16	3.595
	24	3.504
	32	3.293

Note: All symbols in the following tables have the same meaning

$w_{In_2O_3}$ -- Mass fraction of initial Indium-containing slag  $In_2O_3$

$W'_{In_2O_3}$ -- Mass fraction of tailings after experiment  $In_2O_3$

It can be seen from Table 6 that at 1 atmospheric pressure, the temperature is 1573 K, and the atmosphere ratio ( $P_{CO}/P_{CO2}$ ) is 25. Through the reduction of the same Indium-containing slag with the same mass (initial Indium content is 2.925%) at different times (16 h, 24 h, 32 h) quasi equilibrium study, the concentration of  $In_2O_3$  in the tailing slag after the reaction. The mass fraction is basically close. Therefore, it can be preliminarily inferred

that when the reaction lasts for 16 h, the Indium-containing slag with the same content reduced by immersion bath smelting basically reaches "quasi equilibrium state".

### 5.3. Quasi-equilibrium Experimental Determination of Indium-bearing Slag in Reduction Smelting with Different Thickness of Feed Layer

At 1 atmosphere pressure, 1573 K, reaction time 16 h, the atmosphere ratio of the reaction system ( $P_{CO}/p_{CO_2}$ ) is 25, the same Indium-containing slag with Indium content of 2.925% and different thickness is studied to conduct quasi equilibrium experiment in the same time, and  $In_2O_3$  is in the tailing slag. The mass fraction of is shown in Table 7.

**Table 7.**  $W'_{In_2O_3}$  determined by quasi equilibrium experiment of reduction of slag containing Indium with different thickness

Thickness of $In_2O_3$ (mm)	$W'_{In_2O_3} \times 10^5$	$W_{In_2O_3} \times 10^2$	2.925
10.400			3.595
9.200			3.544
8.000			3.301

It can be seen from Table 7 that at one standard atmosphere, the temperature is 1573 K, the reaction time is 16 h, and the atmosphere ratio ( $P_{CO}/p_{CO_2}$ ). Through the reduction quasi equilibrium study of Indium-containing slags of different thickness (8.000 mm, 9.200 mm, 10.400 mm, the mass of Indium-containing slags is 15.000 g, 20.000 g, 25.000 g respectively), the concentration of In In the tailing slag after the reaction  $In_2O_3$  The mass fraction of theta is very close.

Therefore, it can be inferred that for Indium-containing slags with the same Indium composition, even if the thickness of Indium-containing slags in the porcelain boat is different, when the reaction goes on for 16 h, the Indium-containing slags reduced by immersion bath smelting will all reach the same state, and their final state is basically close to "quasi equilibrium state".

### 5.4. Determination of Quasi Equilibrium State of Indium-containing Slag Reduction Smelting Reaction

Under the same external conditions, the reduction experiments were carried out on Indium-containing slag at different times (16 h, 24 h, 32 h) and different thicknesses (8.000 mm, 9.200 mm, 10.400 mm), and the Indium-containing mass fraction of the final reduction products was almost the same. Therefore, it can be inferred that, the melting chemical reaction of reduced Indium-containing slag can reach the "quasi equilibrium" state at about 16 h.

## 6. Conclusion

Based on the thermodynamic theory analysis of the molten pool melting reaction of reduced Indium-containing slag, the quasi-equilibrium experiment

of reduced Indium-containing slag was designed and the quasi-equilibrium condition of reduced Indium-containing slag was determined. Specific studies are as follows:

(1) Through analysis, it is found that under the condition of different temperature and different reduction atmosphere ratio, with the increase of temperature, the  $In_2O_3$  of the reduction slag containing Indium is melted by immersion bath. The activity decreased rapidly and then approached the same value. This means that the recovery of Indium through smelting reaction can achieve ideal results with appropriate smelting temperature; It also shows that the melting reaction is easy to reach equilibrium at high temperature. In the analysis of Budol reaction, it is found that to obtain  $In_2O_3$  different reducing atmosphere conditions can be obtained by setting different temperatures to achieve the purpose of reducing volatilization of Indium-containing slag at different temperatures under different reducing atmosphere conditions.

(2) Under the same external conditions, different time (16 h, 24 h, 32 h) and different thickness (8.000mm, 9.200 mm, 10.400 mm, The corresponding Indium-containing slag with the mass of 15.000 g, 20.000 g, 25.000 g) was reduced experimentally, and  $In_2O_3$  was found in the tail residue of the final reduction product. The mass fraction is almost the same, so it can be inferred that the melting chemical reaction of reduced Indium-containing slag can reach the "quasi equilibrium" state in about 16 h under appropriate temperature conditions.

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