Vol. 4 №. 2 TRANSACTIONS OF NFsoc Jun. 1994

DETERMINATION OF HEAT EFFECT OF ANODIC PROCESS OF $Ni_3S_2$①

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ABSTRACT

The electrowinning of Ni_3S_2 was designed to take place in a calorimeter in order to measure the heat effect of the electrolysis with electrochemical calorimetry. The effect was determined under different cell voltages ranging from 1.50 to 2.16 V, and based on the data the heat effect of the anodic dissolution of Ni_3S_2 was figured out to be $\Delta_a H_m = 22.4 \sim 99.0\,kJ \cdot mol^{-1}$ ($z = 2$) within the anode potentials 0.74~1.30 V (*vs* SCE).

Key words: electrochemical calorimetry heat effect anodic process potential distribution Ni_3S_2

1 INTRODUCTION

The anodic process of Ni_3S_2, the main ingredient of nickel matte, has been researched frequently with electrochemical methods for many years [1~9], and a lot of understanding was achieved. With the improvement of the electrochemical means utilized and the development of the technique in electrochemistry, the research becomes more and more complete and profound. Even so, there is no any report about the thermochemical research on the anodic process of Ni_3S_2 so far. In order to further research the mechanism of the anodic process of Ni_3S_2, and to obtain the basic data for the energy balance calculation of the process, the heat effect of the anodic dissolution of Ni_3S_2 will be determined with electrochemical calorimetry in the present work.

2 EXPERIMENTS AND RESULTS

2.1 *Samples and Apparatus*

The sample of Ni_3S_2 was synthesized from high-purity element sulfur and metal nickel in a vacuum atmosphere at high temperatures, and then was melted and cast to form the desired Ni_3S_2 electrode. The phase composition of the electrode was examined by XRD, and the single phase was confirmed.

The electrolytic system was

$$(-)Ni \left| \begin{array}{l} NiSO_4(1.0\ mol \cdot dm^{-3}) \\ Na_2SO_4(1.0\ mol \cdot dm^{-3}) \\ H_3BO_3(0.2\ mol \cdot dm^{-3}) \end{array} \right| Ni_3S_2(+)$$

of which the anode was the Ni_3S_2 electrode with an outer diameter of 10 mm, and the cathode was the nickel sheet 40 mm × 10 mm in dimension. The pH value of the electrolyte solution was about 5.

The main apparatus used in the present work include a HT1000 micro-calorimeter (SETARAM, FRANCE), a HDV-7 potentiostat, a XFD-8 signal generator, and a WYJ-S high-precision direct volt power, etc. All experiments were performed at the room temperature (23 °C).

2.2 *Measurement of Polarization Curves and Potential Distribution to Electrodes*

Out of the consideration that it is necessary to have a general understanding of the elctrochemical behavior of the system to be studied in order to carry out the electrochemical calorimetry of the anodic

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① Supported by the National Natural Science Foundation; Manuscript received Sept. 29 1993

process of Ni_3S_2 under proper experimental conditions, the polarization curves of each electrodes and the potential distribution to the anode and the cathode were measured in the process of the electrowinning of Ni_3S_2. Fig. 1 shows the polarization curves of both the anodic dissolution of Ni_3S_2 and the reduction of Ni^{2+} on the cathode. The results coincide with the literatures[6,10].

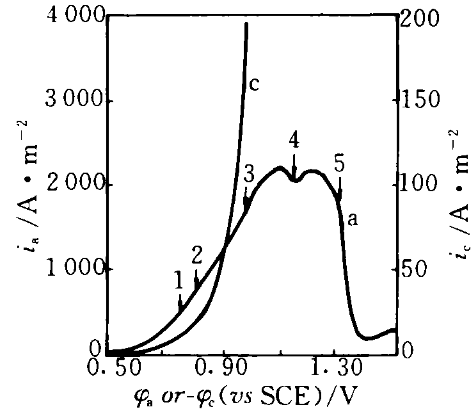

Fig. 1 Polarization curves of both anodic dissolution and cathodic reduction of Ni^{2+} (5 mV/s)

At a given cell voltage in the electrowinning of Ni_3S_2, there exist a certain anode potential and a certain cathode potential, i. e. the potential distributes to the two electrodes. The potential distribution with respect to the saturated calomel electrode (SCE) was measured with the high independence voltmeter of the HT1000. The results are shown in Fig. 2. It is demonstrated that the anode potential of the dissolution of Ni_3S_2 increased linearly with the increase of the cell voltage, yet the potential of the cathodic reduction almost stayed at -0.8 V. A comprehensive combination of Fig. 1 and Fig. 2 revealed that the Ni_3S_2 anode dissolved in different reactions at different anode potentials, and that there was only one reduction reaction of Ni^{2+} taking place in the cathode, for the ions SO_4^{2-} and H^+ did not participate the cathodic reaction[10] and the cathode potential remained almost constant. Consequently the heat effect of the anodic process of Ni_3S_2 can be obtained by subtracting that of the cathode process of the reduction of Ni^{2+} from the total heat effect of the electrowinning process.

2. 3 *Determination of Heat Effect of Anodic Process of* Ni_3S_2

The electrochemical calorimetry were conducted in an experimental set-up that coupled the HT1000 micro-calorimeter with the usual electrochemical equipment. The experimental data was collected and processed by a micro-computer with the software for electrochemical calorimetry, THEL[11]. The accuracy and the reliability of the set-up were verified and confirmed by the standard system, the electrolysis of water[11].

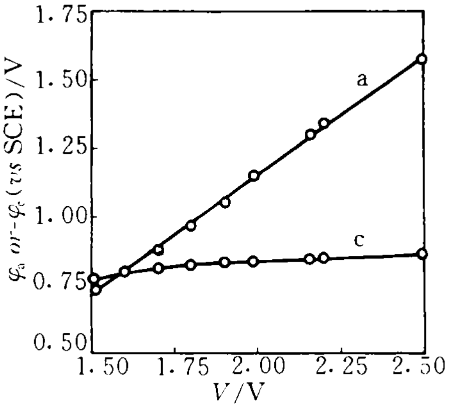

Fig. 2 Potential distribution to both anode and cathode in process of electrowinning of Ni_3S_2

The principle of electrochemical calorimetry is as follows:

At a certain temperature and pressure, the first law of thermodynamics employed to electrochemical reactions becomes[13]:

$$\triangle H = Q_P - W_e$$

where $\triangle H$ represents the enthalpy change of the electrochemical process, Q_P the process heat, and W_e the electrical work done. For electrolysis, the above equation becomes(I, $V > 0$):

$$\triangle H = Q_P + \int IV \mathrm{d}t$$

or $$\triangle H_m \cdot \frac{\int I \mathrm{d}t}{zF} = Q_P + \int IV \mathrm{d}t$$

i. e. $$\triangle H_m = (Q_P + \int IV \mathrm{d}t) zF / \int I \mathrm{d}t \qquad (1)$$

$\triangle H_m$ in equ. (1) is the molar enthalpy change of the electrochemical reaction (the electron transfer number is z), Q_P the heat absorbed, and I and V the current and the cell voltage of the electrolysis respectively. The signals, the heat flow of the electrochemical process h, the current I, the voltage V, the temperature and the time t were all collected automatically by the computer, and then such quantities as the process heat $Q_P = \int h\mathrm{d}t$, the electrical work $W_e = -\int IV\mathrm{d}t$, the mole number of the electrochemical reaction $N = \int I\mathrm{d}t/zF$, the process heat per molar reaction Q_P/N, and the molar enthalpy change of the reaction $\triangle H_m$, etc. were all computed.

The electrochemical calorimetry of the anodic process of Ni_3S_2 were performed at five anode potentials of polarization (Fig. 1) and their corresponding cell voltages as well. Fig. 3 is an example of the record of one experiment. Experimental results are tabulated in Table 1 in which $\triangle H_m$ is the total heat effect of the whole electrolytic reaction ($z = 2$). From the table, it is known that the total heat effect increased with the increasing cell voltage.

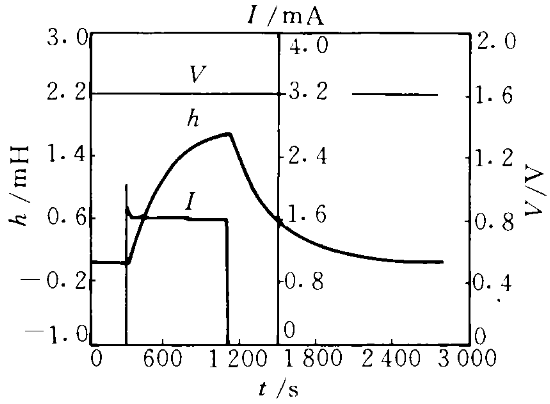

Fig. 3 Record of electrochemical calorimetry

With the thermodynamic data from the literature[10], the enthalpy change of the cathodic reduction of Ni^{2+} is:

$$Ni^{2+} + 2e = Ni$$

$$\triangle_c H^\circ_m(298\,K) = 54.0\,\mathrm{kJ \cdot mol^{-1}}$$

Considered that the concentration of the solution less influences the enthalpy change of the process, the actual enthalpy change of the cathode reaction, $\triangle_c H_m$, equals to $\triangle_c H^\circ_m$ (298 K) in approximation, hence:

$$\begin{aligned}\triangle_a H_m &= \triangle H_m - \triangle_c H_m \\ &= \triangle H_m - \triangle_c H^\circ_m(298\,K) \\ &= \triangle H_m - 54.0\,\mathrm{kJ \cdot mol^{-1}} \qquad (2)\end{aligned}$$

$\triangle_a H_m$ in Table 1 was thus calculated with equ. (2). The heat effect of the process of the anodic dissolution of Ni_3S_2 increases with the anode potential (Fig. 4). The curve shows a "～" shape.

Table 1 Results of electrochemical calorimetry of electrowinning of Ni_3S_2 ($z = 2$, φ being *vs* SCE)

No.	1	2	3	4	5
Cell Voltage/V	1.50	1.60	1.80	1.99	2.16
φ_a (Ni_3S_2)/V	0.71	0.81	0.97	1.15	1.30
φ_c (Ni)/V	0.77	0.80	0.83	0.84	0.85
$\triangle H_m$ /kJ·mol^{-1}	76.4	83.8	89.3	98.5	153.0
Q_P/N /kJ·mol^{-1}	-212.9	225.8	257.6	285.2	-262.4
$\triangle_a H_m$ /kJ·mol^{-1}	22.4	29.8	35.3	44.5	99.0

2.4 *Discussion*

Based on the results shown in Fig. 4, we conclude that:

(1) The varying $\triangle_a H_m$ with φ_a proved that the process of the anodic dissolution of Ni_3S_2 is not a simple reaction, otherwise the $\triangle_a H_m$ should be a datum invariant with the potential.

(2) The $\triangle_a H_m - \varphi_a$ diagram can be divided into three potential regions in general: Region Ⅰ (0.70～0.85 V), Region Ⅱ (0.85～1.10 V) and Region Ⅲ (1.10～1.30 V). In Region Ⅰ and Ⅲ where $\triangle_a H_m$ increases with the increasing φ_a, it is probable that there are two or more parallel reactions taking place, the fraction of each reaction changes with the potential, and thus $\triangle_a H_m$ also changes with φ_a. Region Ⅱ is the transient part from Region Ⅰ to Ⅲ, where the reactions taking place in Region Ⅰ and Ⅲ may all occur and then reach a relative stable state, thus $\triangle_a H_m$ appears constant approximately.

Fang *et al.*[6] concluded that: within 0.7～0.9 V (it is comparable to Region Ⅰ in Fig. 4), the end product of the anodic dissolution of Ni_3S_2 is β-NiS:

$$Ni_3S_2 = 2NiS + Ni^{2+} + 2e$$

within 1.2～1.5 V (it is comparable to Region Ⅲ in Fig. 4), Ni_3S_2 forms element sulfur directly:

$$Ni_3S_2 = 3Ni^{2+} + 2S + 6e$$

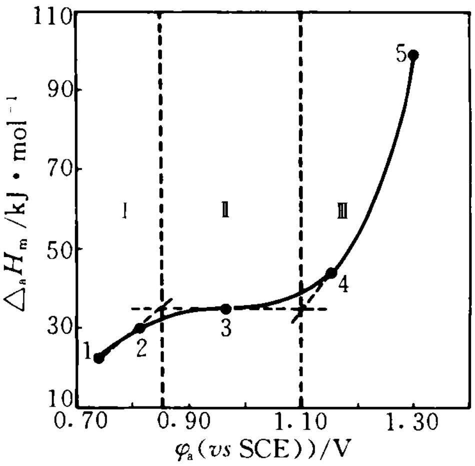

Fig. 4 Heat effect of process of anodic dissolution of Ni_3S_2($z = 2$)

and within 0.9～1.2V(it is comparable to Region Ⅱ in Fig. 4), Ni_3S_2 may form a series of intermediate products except β-NiS:

$$Ni^{2+} + S$$

$$NiS \rightarrow Ni_3S_4$$

$$NiS_2 \rightarrow Ni^{2+} + HSO_4^-$$

Evidently, the reactions in Region Ⅱ covered those of Region Ⅰ and Ⅲ, which is in accordance with the point(2). As a matter of fact that $\Delta_a H_m$ changes with φ_a (as shown in Fig. 4), the reactions in Region Ⅰ and Ⅲ should not be a simple one, for in such a case $\Delta_a H_m$ is constant. Hence the reactions tacking place in each region should contain another one or other reactions except those stated in ref. [6] Further research to the chemistry of the anodic dissolution of Ni_3S_2 with the thermo-electrochemical information will be published later.

3 CONCLUSIONS

(1) In the process of the electrowinning of Ni_3S_2 the potential distribution to the anode and the cathode were measured. It is found that during the electrolysis the potential of the cathodic reduction of nickel ions maintains almost constant, while the anode potential of the dissolution of Ni_3S_2 increases linearly with the increase of the cell voltage.

(2) The heat effect of the process of the electrowinning of Ni_3S_2 at the cell voltages ranging from 1.50～2.16 V was measured with electrochemical calorimetry, and based on the measured data the heat effect of the anodic dissolution of Ni_3S_2 was derived. It is found that the heat effect of the anodic process changes from 22.4 to 99.0 kJ·mol^{-1}($z = 2$) with the anodic potential changing from 0.74 to 1.30V(*vs* SCE).

REFERENCES

1 梅津良之，栗原工部. 电气化学，1962，23：333.
2 加藤登季男，冲猛雄. 日本金属学会志，1974，38(7)：663.
3 Price，D C；Davenport W G. J Appl Electrochem. 1981，12：281.
4 Power，G P. Aust J Chem. 1981，34(11)：2287.
5 Jiang，Hanying；Shu，Yude；Zhang，Zhenglin. JCSIMM，1986，(4)：100.
6 Fang，Zhaoheng；Chem，Jiayong. In：Symposium of the 1st National Conference on Nickel and Cobalt. Jinchang，1988. 296.
7 Zhou，Yongmao：Wang，Lichuang. JCSIMM，1987，18(3)：275.
8 Fang，Zhaoheng；Fu，Chongyue；He，Huanhua；Zhang，Chuangfu. In：Proc of Intern Conf on Mining and Metallurgy of Nickel Complex Ores. Beijing：Inter Academic Publishers，1993，314.
9 Qin，Yihong；Yang，Songqing *et al*. In：Proc of Intern Conf on Mining and Metallurgy of Nickel Complex Ores. Beijing：Intern Academic Publishers，1993，358.
10 Zeng，Zhenou；Zhao，Ruirong. In：Symposium on the 1st National Conference on Nickel and Cobalt. Jinchang，1988. 305.
11 Zhang，Hengzhong：Fang，Zheng；Zhang，Pingmin. In：Symposium on the 6th STTT Academic Conference，Zhengzhou，1992. 253.
12 Zhang，Pingmin；Zhang，Hengzhong；Fang，Zheng. In：Symposium on the 6th STTT Academic Conference，Zhengzhou，1992. 294.
13 Sherfey，J M；Brenner A J. J Electrochem Soc 1958. 105：665.
14 Dean，J A. Lange's Handbook of Chemistry. Beijing：Science Publisher，1991；9－1 to 9－67.