

ACTIVATION MECHANISM OF AlCl_3 DURING THE LEACHING OF Cu-Ni ORE WITH FeCl_3 ^①

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ABSTRACT

After Cu-Ni ore powder pre-soaked in AlCl_3 solution, the leaching ratios of copper and nickel can increase obviously. By X-ray diffraction analyses, electron energy spectrum analyses and electrochemical experiments, it is affirmed that, the activation of aluminum ion includes two aspects: one is the surface change of the ore by the absorption of hydrolysates, and the other is the change of semiconductor characteristics of the metal sulfides by impurity aluminum ion entering the lattice, so that leaching reactions are accelerated.

Key words: oxidative leaching copper-nickel sulfide ore aluminium chloride activation

1 INTRODUCTION

The traditional technology for nickel metallurgy is based on the combining method of the hydro- and pyro-metallurgy, namely, ore → concentrate → low grade matte → high grade matte → product nickel. However, this technology has been finding some disadvantages, such as long technical procedure, high energy consumption, valuable metals lost and large capital investments. It is worthy to try a direct leaching of original ores under atmosphere pressure.

Comparing with high grade nickel matte, original ore's composition is more complicated, its contents of valuable metals are much lower, interference factors are much more, its crystal structure is not beneficial to leaching without being treated at high temperature let alone under atmosphere pressure. So, the activation and catalysis to leaching processes are very important and alu-

minum chloride was found by our experiments. After the original ore pre-soaked in aluminum chloride solution, the leaching ratios can increase obviously, as shown in Table 1.

Table 1 Effects of AlCl_3 activation on leaching ratios of copper and nickel

	content in original ore	leaching ratio		increased by percent
		original	after activated	
Ni(%)	1.62	30.21	42.19	39.52
Cu(%)	5.45	27.11	58.60	116.2

Notes: (1) Soaking ore powder into $1 \text{ mol/dm}^3 \text{ AlCl}_3$ solution for 20 h before leaching, the leaching ratios of copper and nickel are individually calculated with the total contents in soaking and leaching solutions.

(2) Leaching conditions: $0.5 \text{ mol/dm}^3 \text{ FeCl}_3$, $0.3 \text{ mol/dm}^3 \text{ HCl}$, 85 °C, 3 h, L/S=8:1, 10g-200 mesh powder, mechanical stirred.

(3) The original ores came from some province, in which copper and nickel are existed in forms of CuS_2 and Ni_3S_2 respectively, and the total content of these two metals is about 10 %.

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After ore powder soaked in AlCl_3 solution, the leaching ratio of copper doubled, and that of nickel also increased obviously, if the soaking period prolongs for 36 h, leaching ratio of nickel increased by 88%. However, the leaching ratios can not meet the need of industrial requirements, so we are working for further research. And now, we just discuss the activation mechanism of AlCl_3 to Ni_3S_2 . Pure Ni_3S_2 used in this research was synthesized with pure sulphur and nickel, and tested by X-ray analysis to be pure Ni_3S_2 phase.

2 EXPERIMENTALS

2.1 Chemical Analyses

After soaking ore powder (— 200 mesh) into 1.0 mol/dm^3 AlCl_3 solution for 20 h, about 5~10% of copper and nickel in the soaking solution were detected by a WYX — 402 atomabsorption spectrophotometer.

2.2 X-ray Diffraction Analyses

After being soaked in AlCl_3 solution, then filtered, washed and dried, the ore powder was analyzed by X-ray. The XRD spectrum shows a few Al_2S_3 and/or Al_2O_3 in the sample (these two materials is very difficult to be distinguished).

The synthesized Ni_3S_2 was also used for the above analysis, and the lattice constants were calculated respectively before and after soaking, results are listed in Table 2.

The tested values are very close to those in literature^[1]. In Table 2, the constant c is of somewhat difference after soaked, i. e., the length of c axis of Ni_3S_2 lattice becomes a little short. In periodical table of chemical elements^[2], Al^{3+} has its ionic radius of 51 pm, which is smaller than Ni^{2+}

(69 pm) and also smaller than the lattice constant of Ni_3S_2 (57 pm). So it is possible for Al^{3+} to enter the lattice and replace Ni.

Table 2 Lattice constants of Ni_3S_2

	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$
before activating	5.7438	5.7438	7.1352
after activating	5.7438	5.7438	7.1346
in literature[1]	5.74	5.74	7.139
	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$
before activating	90.000 0	90.000 0	90.000 0
after activating	90.000 0	90.000 0	90.000 0
in literature[2]	89.175	89.475	

2.3 Electrochemical Experiments

Experiments were performed with EG&G PARC Model 351 system, K0047 cell, synthesized Ni_3S_2 as working electrode, graphite as counter reference electrodes. Potentials in this paper are all vs. SCE. Fig. 1 shows the cyclic polarization curves with 5 mV/s for scan rate.

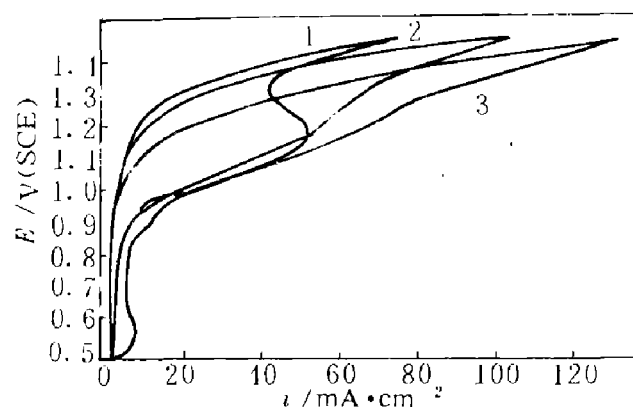


Fig. 1 Cyclic polarization curves of Ni_3S_2

Curve 1—synthesized Ni_3S_2 pre-soaked in 1.0 mol/dm^3 AlCl_3 solution for 10 h;

Curve 2—After experiment for curve 1, the Ni_3S_2 electrode was carefully polished with fine sand paper for 30 s;

Curve 3— Ni_3S_2 electrode was polished for another 90 s.

In curve 1, a peak appears at 1.15 V for the activated Ni_3S_2 electrode, it is also obvious in second curve obtained after the electrode has been scrapped off a thin layer. If a further layer of the electrode was scrapped, then the peak disappeared from the polarization curve. So, there were some things exactly existed on the activated electrode's surface and they changed the surface's characteristics, and the content of the new materials changes with the depth of the electrode.

2.4 Electron Energy Spectrum Analyses

The X-ray photoelectron energy spectrum (XPS) of the original surface of the activated synthesized Ni_3S_2 is shown in Fig. 2.

From Fig. 2, we can ascertain the existing state of aluminum. Theoretically, the binding energy of electron of C atom is 284.6 eV, but its corresponding peak appears at 290.3 eV in Fig. 2, so the system has an error of 5.7 eV ($290.3 - 284.6 = 5.7$). In other words, the aluminum peak for its 2p electron appears at 80 eV, so its

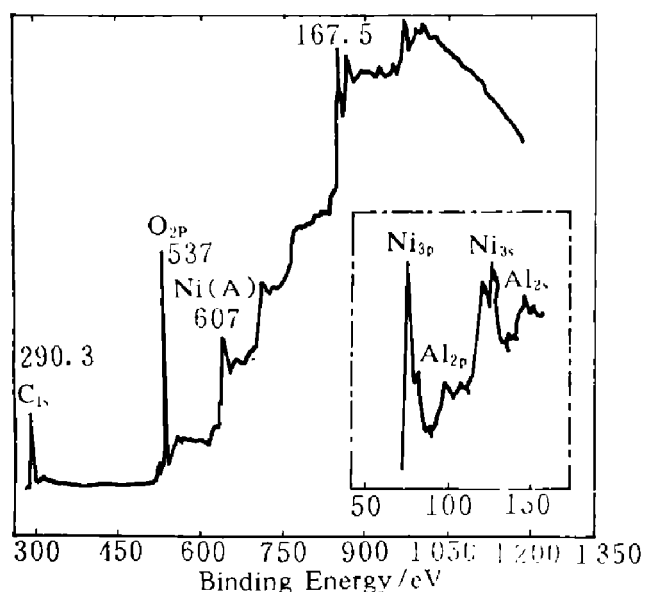


Fig. 2 X-ray photoelectron energy spectrum

exact binding energy is 74.3 eV, which is very close to the standard values of Al_2S_3

(74.2 eV) and Al_2O_3 (74.5 eV). Fig. 3 is the results of XPS depth analysis, which shows the relation of aluminum content with the depth. From outside to inside, there is a content gradient. First, we can see a constant high aluminum content because of the absorption materials on the surface, aluminum content decreases rapidly, and then remains constant again, so aluminum must enter the lattice besides its absorption on the surface.

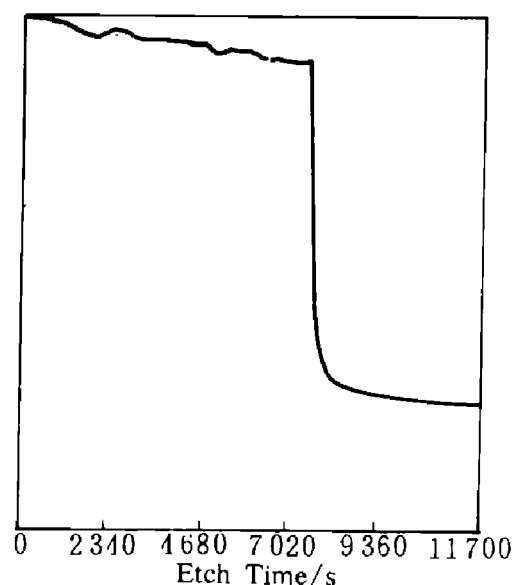


Fig. 3 XPS depth analysis
start: 77.2 eV; end: 84.2 eV

3 DISCUSSIONS

From above the followings can be affirmed. (1) After Ni_3S_2 pre-soaked in AlCl_3 solution, there is a layer of new materials absorbed on its surface, which are tested to be Al_2S_3 and/or Al_2O_3 by X-ray and XPS analyses. (2) The soaking solution contains some copper and nickel ions, and XPS also shows a constant aluminum content inside the Ni_3S_2 surface after activated, so aluminum must enter the sulfide lattice and replaced some nickel and copper ions. On the other hand, the change in lattice constants also affirms this hypothesis.

Ni_3S_2 belongs to hexagonal crystal sys-

tem, Sulphur atom arranges in the body-centered cubic form, four nickel atoms combine a sulphur atom to be the tetrahedral configuration^[3], as shown in Fig. 4. Differentiated with general standard ionic crystals, Ni_3S_2 can not be analyzed with typical electrostatic and ionic crystalline field theories. According to molecular orbital theory and coordination field theory, the $3d$, $4s$ and $4p$ orbits of nickel atom can form molecular orbits by overlapping with $2s$ and $2p$ orbits of sulphur atom, which enhances metallic coordination bond and raises the energy difference between orbits, and so Ni_3S_2 is of some characteristics similar to alloy or semi-metal.

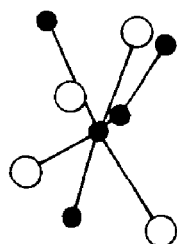


Fig. 4 Lattice of Ni_3S_2
(○)—Ni; (●)—S

Many papers have said that highvalence ions can strongly affect the surface of solid particles, and their absorption capacities and effections on double-layer obey the following sequence: $\text{Fe}^3 > \text{H} > \text{Al}^3 > \text{Ba}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ \dots\dots$ ^[1] and, ionic absorption and ion-exchange can alter electric characteristics and electric potential.

During the copper-nickel ore soaked in

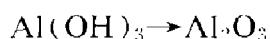
AlCl_3 solution, aluminum ion enters the double-layer on the particles surface, and then hydrolyzes



Also aluminum replaces nickel in Ni_3S_2 lattice to form a complex (Al-S) sulphide, and then hydrolyzes in the surface layer as



This is the reason why there is a little smell of H_2S during pre-soaking. And the hydrolytic product $\text{Al}(\text{OH})_3$ decomposes continuously:



Al_2O_3 or Al_2S_3 absorbed on the particles change the surface's characteristics. And at the same time, the semiconductor of Ni_3S_2 would have some differences because of doping of impurity aluminum in lattice (similar to p-type), its electric conductivity is enhanced and more beneficial to the leaching reactions.

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