

# In-situ high temperature X-ray diffraction study on the phase transition process of polymetallic sulfide ore

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**Abstract.** The phase transformation of the polymetallic sulfide ore is quite complicated, especially the variety and diversity of the roasted intermediate. The mineralogy properties of the ore particles were characterized by XRF, ICP and SEM-EDS. The thermal stability of the complex ore was investigated using TG-DSC under different atmosphere (pure N<sub>2</sub> and 1% O<sub>2</sub>-N<sub>2</sub>). The phase changes and intermediates were revealed by the in-situ XRD in pure N<sub>2</sub> and 1% O<sub>2</sub>-N<sub>2</sub> atmospheres with the temperature range from 25 to 800 °C. These results indicated that the crystal transformation of the pyrrhotite from monoclinic to hexagonal at 320 °C, and the pentlandite and chalcopyrite were decomposed into monosulfide solid solution in pure N<sub>2</sub>. While the pentlandite and chalcopyrite were completely oxidized into M<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub> (M\*=Fe, Ni, Cu) and Fe<sub>2</sub>O<sub>3</sub>, which is also the final product of the ore sample oxidized under 1% O<sub>2</sub>-N<sub>2</sub> atmosphere.

## 1. Introduction

The pyrometallurgical process of polymetallic sulfide minerals is relatively energy efficient compared with hydrometallurgical extraction, which mainly due to the comprehensive utilization of the exothermic oxidation of sulfide ores. The oxidation process of metal sulfides is particularly important, besides, it is of much complexity and variability. Terkel Rosenqvist [1] has investigated and mapped the phase equilibria in roasting and smelting complex sulfide, but these systems were relatively simple compared with the nature sulfide minerals. Later, J. G. Dunn [2] has studied the oxidation behavior of natural pentlandite using thermogravimetry (TG) and differential thermal analysis (DTA). The oxidation process of the synthetic pentlandite under the 973K isothermal condition could be divided into three steps: firstly pentlandite oxidized into Fe<sub>2</sub>O<sub>3</sub>, Ni<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub>, SO<sub>2</sub>, NiSO<sub>4</sub>, and NiO; secondly, a nickel-rich phase and a sulfur-rich phase were generated; Also, Ni<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub> and NiO were observed as the final oxidation products [3, 4]. Lately, the oxidation mechanism of nickel concentrate was investigated using TG-DTA and X-ray diffraction (XRD) by Dawei Yu [5, 6]. The thermodynamic properties of chalcopyrite were performed by B. R. Conard [7] and the phase transition of chalcopyrite under the oxidative roasting process was investigated by Bayer.G [8]. S.Prasad [9] summarized the alternative processes to treat chalcopyrite and pointed out that the roasting of chalcopyrite was an important step for the extraction of copper. By adsorbing and integrating the previous research results, this paper mainly studied the application of the in-situ XRD and simultaneous thermal analysis (STC), probing into the temperature programmed reactions of the complex nickel sulfides and the mechanism



of sulfides transition during the pure N<sub>2</sub> and 1% O<sub>2</sub>-N<sub>2</sub> atmosphere respectively. In-situ XRD pattern provides unique information about important properties of phases under controllable non-ambient conditions [10-14]. The application of in-situ techniques may lead to considerable advances in understanding of phase decomposition and oxidation reactions in pyrometallurgical and hydrometallurgical processes [15-17].

## 2. Experiments and characterization

### 2.1. Sample preparation and elements analysis

The collected sulfide nickel ore sample (Sinkiang, China) was dried at 100 °C for 24h and ground into fine powder (-200 mesh) using an agate mortar. The fine powder was carried out for the identification and quantification of chemical elements by the X-ray fluorescence (XRF) analysis (XRF-1800, SHIMADZU LIMITED). Furthermore, the inductively coupled plasma atomic emission spectrometry (ICP-AES) was measured to accurate analysis of several main elements on a PERKINE 7300DV.

### 2.2. SEM-EDS characterization

The cross section view of raw ore sample was prepared in an epoxy mount and polished. Subsequently the mineralogical characterization was performed by a tungsten filament scanning electron microscope (SU-1510, Hitachi, Japan), and the elements distribution was characterized by the energy-dispersive X-ray spectroscopy (EDS) mapping features within the TEAM™ EDS Analysis System in a SU-1510.

### 2.3. Thermal analysis

The effect of different atmospheres on the decomposition and oxidation processes of the fine powder sample has been studied over the temperature range of 25-1000 °C using the STC (the simultaneous application of TG and DSC to one and the same sample in a single instrument.) in a NETZSCH STA 449 F3 Jupiter.

### 2.4. In-situ XRD

In-situ high temperature XRD data were collected using a Bruker D8 Advance diffractometer with a Bruker TC-DOME temperature stage and a platinum-rhodium heating strip with TCPU1 temperature controller, in dynamic pure N<sub>2</sub> and 1% O<sub>2</sub>-N<sub>2</sub> atmosphere respectively. Cu-K $\alpha$  radiation was used for scans of 20 to 70° 2 $\theta$  with a step size of 0.02° 2 $\theta$ , a dwell time of 2 seconds/step and a heating and cooling rate of 5°C/min. Diffraction patterns were collected at room temperature, then every 50 °C between 300 °C and 600 °C and every 100 °C between 600 °C and 800 °C on heating with a holding time of 30 minute prior to data collection on reaching the measurement temperature. The fine mineral powder sample (-200 mesh) was deposited on a platinum foil substrate for heating, which was placed on the Pt-Rh heating strip.

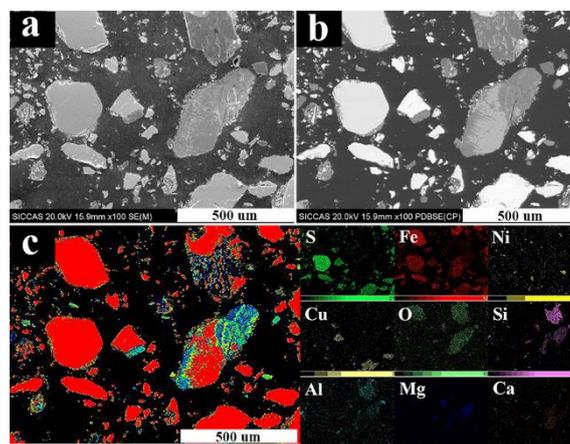
## 3. Results and discussion

### 3.1. The mineralogy properties of polymetallic sulfide ore

**Table 1.** Elemental analysis (wt%) of the mineral sample using XRF and ICP.

	Fe	S	O	Si	Cu	Ni	Mg	Al	Ca	Na	Co
XRF	40.12	26.64	15.32	5.96	3.58	2.35	2.29	1.94	0.94	0.57	0.16
ICP	43.31	--	--	3.15	3.13	2.33	0.81	0.93	0.57	0.27	0.14

The chemical composition of the complex mineral fine powder sample are showed in table 1 using XRF and ICP-AES methods. The comparison of the data shows a good agreement between the XRF analysis results and those obtained by ICP, although there is some deviation in some certain elements (Mg, Al, Si). The major elements of this mineral are iron, nickel and copper. As a result, this is a complex nickel sulfide ore with rich iron.



**Figure 1.** a) SE and b) BSE image of the sulfide ore particles, and c) the element distribution of the mineral particles' cross section.

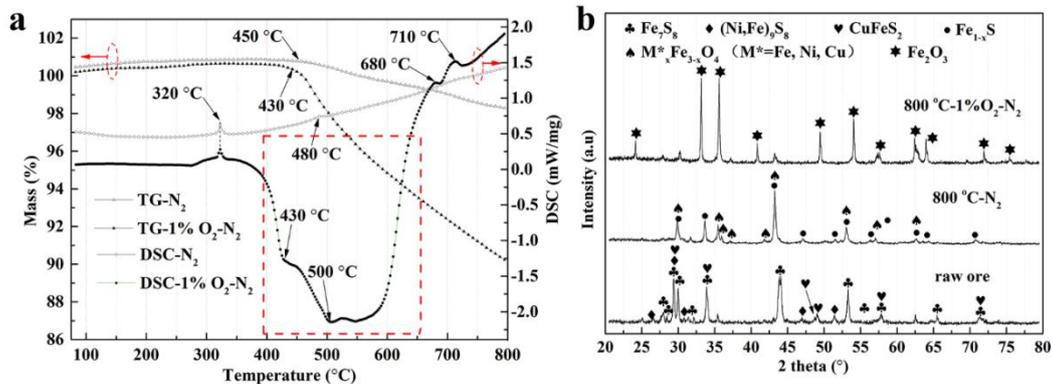
Figure 1 a and b show the secondary electron (SE) and backscattered electron (BSE) micrograph of the cross sections of the ore grains. The elements distribution of the complex ore particles is shown in Figure 1c. It is clearly revealed that the large particles mainly consist of iron sulfide, iron oxide or silicon-magnesium oxide. And the nickel-iron sulfide and copper-iron sulfide were distributed sporadically in smaller granule. The complex sulfide nickel ore is composed of pyrrhotite, pentlandite, chalcopyrite, magnetite and gangue phases, which is detected by the XRD pattern in figure 2b.

### 3.2. The thermal stability of the complex ore sample in different atmosphere

In order to evaluate the effects of the atmosphere on the thermal stability of mineral, the TG-DSC measurements were performed in pure  $N_2$  atmosphere and 1%  $O_2-N_2$  atmosphere respectively for comparison. As shown in figure 2a, an obvious weight loss peak appeared in both atmospheres, which indicated that there is at least one weight-loss reaction in the temperature range of 450-800 °C. For further study on the thermal events, the analysis of the DSC curves revealed that there are only two endothermic peaks under pure  $N_2$  atmosphere. The endothermic reaction at 320 °C without any weight changes, indicated that there may be a structure transition. The weak endothermic peak at 480 °C may be a certain decomposition reaction of one or more phases, as the TG curve appeared a slight weight loss at the temperature range from 450 °C to 800 °C under the pure  $N_2$  atmosphere. In 1%  $O_2-N_2$  atmosphere, the DSC curve is much more complicated. The large exothermic peak broadened in a temperature range from 400 °C to 650 °C, this might be the effect of a series of oxidative reactions by micro-aerobic environment. And the two endothermic peaks appeared later at 680 °C and 710 °C, as a result, it may be the decomposition of two or more kinds of intermediate products.

The final products, which were measured by TG-DSC test under different atmospheres, were investigated by XRD shown in figure 2b. The tested sample consist of hexagonal pyrrhotite ( $Fe_{1-x}S$ ) and magnetic ferrite ( $M^*_xFe_{3-x}O_4$ ,  $M^*=Fe/Ni/Cu$ ) under the pure  $N_2$  atmosphere. However, the nickel and copper sulfides were not detected, one of the reason is that such small amounts of the nickel and copper phases that it could not be detected by XRD. But there is also the possibility, but unsubstantiated and discussed using in situ XRD later, that the major elements (Ni/Cu) might solubilize in hexagonal pyrrhotite and magnetic ferrite. Hematite ( $Fe_2O_3$ ) and magnetic ferrite ( $M^*_xFe_{3-x}O_4$ ) were the main phases of the TG-DSC measured residuals in 1%  $O_2-N_2$  atmosphere. It

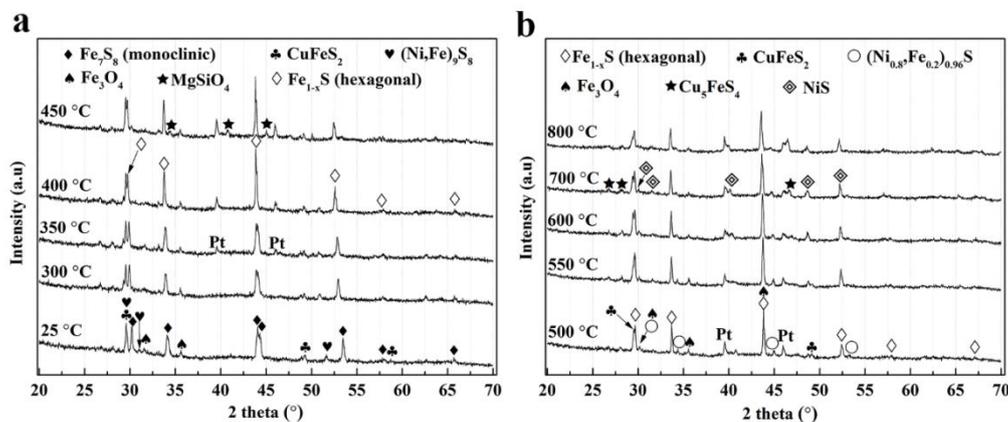
indicated that the nickel and copper have been oxidized into nickel ferrite and copper ferrite respectively, and it was confirmed by previous work [5, 6, 9, 11].



**Figure 2.** a) TG-DSC curves of the nickel mineral at 10 °C/min in the different atmosphere condition (1% O<sub>2</sub>-N<sub>2</sub> and pure N<sub>2</sub> atmosphere); b) the XRD patterns of the residuals of TG-DSC measured samples compared with the raw ore powder sample.

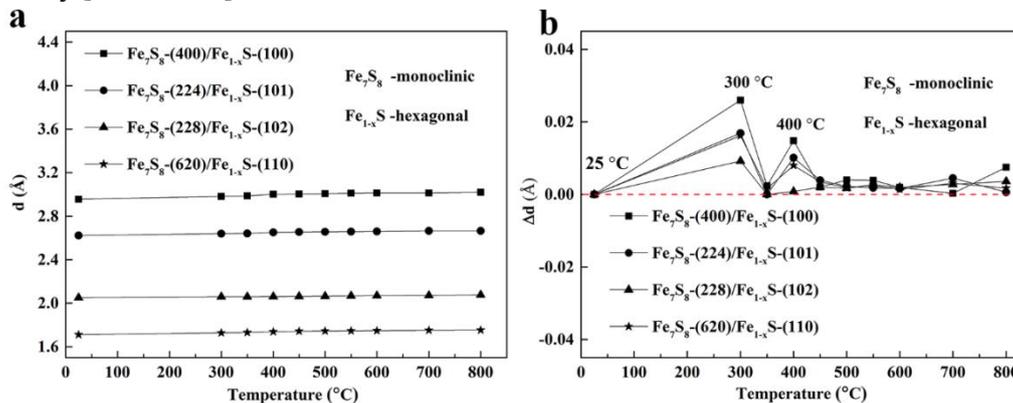
### 3.3. The phase transition process of main phases

In order to investigate the phase transition process of the complex ore in detail, the in-situ XRD was used to study the reactions during the high temperature under different atmospheres. Figure 3a shows that pentlandite was stable below 450 °C, then turned into a monosulfide solid solution ((Ni<sub>0.8</sub>, Fe<sub>0.2</sub>)<sub>0.96</sub>S) at 500 °C, and finally decomposed into monosulfide (NiS), which was confirmed by Zhu et al [3]. However, chalcopyrite was more stable than pentlandite, and partially decomposed into bornite (Cu<sub>5</sub>FeS<sub>4</sub>) beyond 600 °C under pure N<sub>2</sub> atmosphere, as shown in figure 3b. The monoclinic pyrrhotite (Fe<sub>7</sub>S<sub>8</sub>) transformed into hexagonal structure from 350 to 400 °C, and then grew into Fe<sub>1-x</sub>S (hexagon) beyond 400 °C in pure N<sub>2</sub> atmosphere. The changes of the pyrrhotite diffraction peak and interplanar spacing with the changes of temperature were further investigated in figure 4. It is obvious that the variations of different interplanar spacing ( $\Delta d_i$ ) were non-negative values, besides there were two maximum values at 300 °C and 400 °C, which results from the crystal lattice volume expansion and structure transition of iron-sulfide phase with the rise in temperature during pure N<sub>2</sub> atmosphere. And the maximum value at 300 °C was reported due to the magnetic transition which accompanied by a structural transformation from the monoclinic structure to hexagonal structure by Anthony V. Powell [18]. From the transition of pentlandite and chalcopyrite, it is possible to suggest that the crystal lattice volume expansion of pyrrhotite at 400 °C may be due to the monosulfide solid solution (Ni-Cu-Fe-S) formed by the migration of nickel and copper atoms.

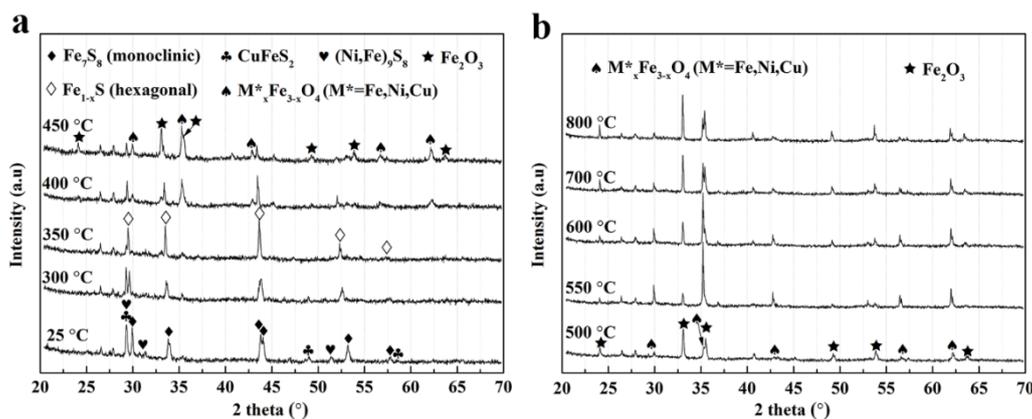


**Figure 3.** In situ XRD spectra of the nickel mineral sample from 25 °C to 800 °C (a. 25 to 450 °C, b. 500 to 800 °C) in pure N<sub>2</sub> atmosphere.

Figure 5a revealed that the structural transformation of pyrrhotite also appeared at around 350 °C, however the magnetic ferrite increased with the disappearance of the pentlandite and chalcopyrite at temperatures above 450 °C under the 1% O<sub>2</sub>-N<sub>2</sub> atmosphere. As shown in figure 5b the hematite was formed during the oxidation of pentlandite and chalcopyrite. As was reported by previous work, nickel and copper atoms migrated to the crystal lattice of magnetic ferrite and transformed into solid solution lastly [5, 6, 19, 20].



**Figure 4.** The calculating crystalline interplanar spacing (a) and lattice space variation gradient (b) of the Fe-S phase as a function of temperature in the pure N<sub>2</sub> atmosphere.



**Figure 5.** In situ XRD spectra of the nickel mineral sample from 25 to 800 °C (a. 25 to 450 °C, b. 500 to 800 °C) in pure 1% O<sub>2</sub>-N<sub>2</sub> atmosphere.

#### 4. Conclusion

The mineralogy properties of the complex sulfide ore were further investigated by means of XRF, ICP, SEM-EDS and XRD. The thermal stability tested by TG-DSC suggests that the ore sample is more active by micro-aerobic environment than that under pure N<sub>2</sub> atmosphere as the temperature rises. A further study of the phase transition was performed using the in-situ XRD in different environment. It is demonstrated that the structural transformation from the monoclinic to a hexagonal structure appeared in pyrrhotite phase with temperatures over 300 °C, while the pentlandite and chalcopyrite turned into monosulfide solid solution with temperature increasing under pure N<sub>2</sub> atmosphere. In 1% O<sub>2</sub>-N<sub>2</sub> environment, the pentlandite and chalcopyrite transformed into magnetic ferrite solid solution (M<sup>\*</sup>Fe<sub>3-x</sub>O<sub>4</sub>, M<sup>\*</sup>=Fe/Ni/Cu) and Fe<sub>2</sub>O<sub>3</sub>, as a result of the migration of nickel and copper. Meanwhile, the pyrrhotite was gradually oxidized into Fe<sub>2</sub>O<sub>3</sub> by temperatures above 400 °C. From these results, it is possible to illustrate the phase transition process of the complex sulfide nickel ore and it may be a fundamental one for the new process of nonferrous metallurgy in controllable products with gentle conditions.

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