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The mechanism and kinetics of α-NiS oxidation in the temperature range 670–700 °C

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ABSTRACT

The oxidation behavior of synthetic α-NiS in air has been investigated over the temperature range 670–700 °C. The α-NiS was ground and sieved to give a particle size ranging from 53 to 90 μm. Three oxidation paths were observed:

$$\text{(i) } \alpha\text{-NiS} + 3/2\ O_2 \rightarrow NiO + SO_2$$
$$\text{(ii) } 3\alpha\text{-NiS} + O_2 \rightarrow Ni_3S_2 + SO_2$$
$$\text{(iii) } Ni_3S_2 + 7/2\ O_2 \rightarrow 3NiO + 2SO_2$$

No Ni_3S_2 (heazlewoodite) was observed over the course of α-NiS oxidation at 670 and 680 °C. The dominant oxidation path at this temperature is path i. At 700 °C, however, all three oxidation paths were observed. As an intermediate oxidation product, Ni_3S_2 steadily exsolved from α-NiS, reaching a maximum quantity after about 80 min of oxidation, declining afterward, and approaching annihilation at 160 min of oxidation. Experimental results show that the exsolution of Ni_3S_2 is likely triggered by the loss of one third of S in the α-NiS structure with the release of SO_2 rather than by an intrinsic thermal decomposition of α-NiS to α-$Ni_{1-x}S$ + Ni_3S_2. The eventual annihilation of Ni_3S_2 was caused by a further oxidation of Ni_3S_2 to NiO. Oxidation paths 2 and 3 form a typical single chain reaction:

$$\alpha\text{-NiS} \xrightarrow{k_1} Ni_3S_2 \xrightarrow{k_2} NiO$$

The approximate values of k_1 are k_2 are $3 \times 10^{-4}s^{-1}$ and $5 \times 10^{-4}s^{-1}$ respectively.

Oxidation temperature was found to play important roles both in the oxidation kinetics and the oxidation mechanism. By decreasing 10 °C from 680 to 670 °C, the average reaction rate (dy/dt, where y is the reaction extent) over the experiment time scale almost decreased to one third of its original rate (from $3.3 \times 10^{-5}s^{-1}$ to $1.2 \times 10^{-5}s^{-1}$). The reaction mechanism in the temperature range 670 to 680 °C is constant with E_a = 868.2 kJ/mol.

Keywords: NiS, oxidation, chain reaction, kinetics