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Original scientific paper

Mechanism and kinetics of the oxidation of synthetic α-NiS

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Abstract: The results of an investigation of the mechanism and kinetics of the oxidation process of synthetic α-NiS are presented in this paper. The mechanism of α-NiS oxidation was investigated based on the comparative analysis of DTA–TG–DTG and XRD results, as well as the constructed phase stability diagrams (PSD) for the Ni–S–O system. The kinetic investigations of the oxidation process were performed under isothermal conditions (temperature range 823–1073 K). The obtained degrees of desulfurization were used in the calculation process according to the Sharp model and the kinetic parameters, including the activation energies and the rate constants of the characteristic reactions, for the oxidation of α-NiS were determined. These results enabled the formulation of a kinetic equation for the desulfurization process: $-\ln(1-\alpha) = k_1\tau = 27.89\exp(-9860/T)\tau$, with an activation energy of 82 ± 4 kJ mol^{-1}, for the first stage of the process and $-\ln(1-\alpha) = k_2\tau = 1.177\exp(-4810/T)\tau$, with an activation energy of 40 ± 2 kJ mol^{-1}, for the second stage.

Keywords: α-NiS; oxidation; mechanism; kinetics; DTA.

INTRODUCTION

Knowledge of the mechanism and kinetics for oxidation processes of metallic sulfides is of great significance in practical applications.[1–3] The problematic nickel sulfides (millerite – NiS, heazlewoodite – Ni_3S_2, pentlandite – $(Fe,Ni)_9S_8$, *etc*.) oxidation processes have been the subject of investigation,[4–13] due to their importance in nickel metallurgy. However, the documentation concerning on this subject is still incomplete and some discrepancy may be noticed when comparing different references.

Regarding to the mechanism of NiS oxidation, Dunn and Kelly[4] explored the oxidation of synthetic millerite ($Ni_{0.994}S$) using DTA, TG and MS analyses up to 1273 K and defined the following: a) complete oxidation of millerite followed by

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the formation of $NiSO_4$, Ni_3S_2 and NiO in the temperature range 823–973 K; b) continuation of $NiSO_4$ formation and oxidation of Ni_3S_2 between 973 and 1073 K and c) the existence of only NiO above 1073 K. The newest research dealing with the oxidation of α-NiS is presented in the work of Wang *et al.*,[6] in which a three-step mechanism, including 1) the oxidation of α-NiS to NiO, occurring in the temperature range 943–953 K; 2) oxidation of α-NiS to Ni_3S_2 at 973 K and 3) oxidation of Ni_3S_2 to NiO above 973 K. Ni_3S_2 is a transient/intermediate species during the oxidation of α-NiS and is not an end product of α-NiS oxidation once the reaction reaches equilibrium.

The kinetics of the processes occurring during the oxidation of NiS was also investigated by Wang *et al.*[6,12] and Bishop *et al.*,[11] in which the values of the characteristic kinetic parameters were given.

As a contribution to a better understanding of the process of α-NiS oxidation, the results of an investigation of the mechanism and kinetics of the oxidation of synthetic α-NiS are presented in this paper.

EXPERIMENTAL

The main characteristics of different nickel(II) sulfide types[1] are presented in Table I, one of which, *i.e.*, α-NiS, was synthesized and investigated in this study.

TABLE I. The main characteristics of different types of nickel(II) sulfide types[1]

Nickel sulfide	Color	Crystal structure	Melting temperature, K	Solubility
α-NiS	Black	Amorphous	–	HCl
β-NiS	Black	NiAs type	810	HCl
γ-NiS	Black	Hexagonal	–	Sparingly in dilute HCl

Synthesis of α*-NiS samples*

Samples of α-NiS synthesized at the University “Paisiy Hilendarsky”, Plovdiv, Bulgaria, were used in this investigation.

The α-NiS sample was synthesized according to the following procedure: an aqueous solution of Na_2S was added slowly in proportions to an aqueous solution of $NiSO_4$ under continuous stirring with a magnetic bar, whereby nickel sulfide precipitated. The black precipitate of α-NiS was washed a few times with water and filtered. The filtered precipitate was placed in a crucible and then dried in a furnace at 373 (1 h), 473 (1 h) and 673 K (5 h). In order to prevent the oxidation of the obtained α-NiS, all operations are performed in a nitrogen environment, for which special equipment was created.[15,16]

Applied experimental techniques

The analyses of the thermal behavior and mass changes of the starting sample during oxidation under non-isothermal conditions were performed using the results of simultaneous DTA–TG–DTG analysis. The thermal analysis was performed using a Derivatograph-Q (MOM, Hungary) with the conditions: sensitivity DTA – 1 mV and DTG – 1 mV, TG – 100 mg, heating rate of 10 °C min^{-1}, sample mass 100 mg and $T_{max} = 1273$ K. A ceramic crucible was used. All experiments were performed in an air atmosphere.

X-Ray diffraction analysis was performed in order to characterize the investigated samples after oxidative roasting at different temperatures. The phase composition was determined on a Siemens X-ray equipment with a Cu anticathode and Ni filter at a voltage of 40 kV and a current of 18 mA.

The investigations under isothermal conditions were performed using standard equipment. The experiments were performed using an electric resistance furnace with thermostatic control. A measured volume of air was introduced into the reaction volume, while the gaseous reaction products (mainly SO_2) were passed from the furnace tube to absorption tubes filled with an aqueous solution of hydrogen peroxide, whereby sulfuric acid was produced. The formed sulfuric acid produced was titrated against a standard solution of sodium hydroxide in the presence of indicator to determine of the sulfur content. Thus, the degree of desulfurization during oxidation roasting was calculated with an error expected to be ±0.1 %.

RESULTS AND DISCUSSION

Mechanism of synthetic α-NiS oxidation process

The Ni–S–O system is of interest for the investigation of the oxidation of NiS in air. Therefore, characteristic phase stability diagrams were constructed based on the starting thermodynamic data for the reactions occurring in the system of interest at temperatures of 923 and 1073 K, as shown in Fig. 1.

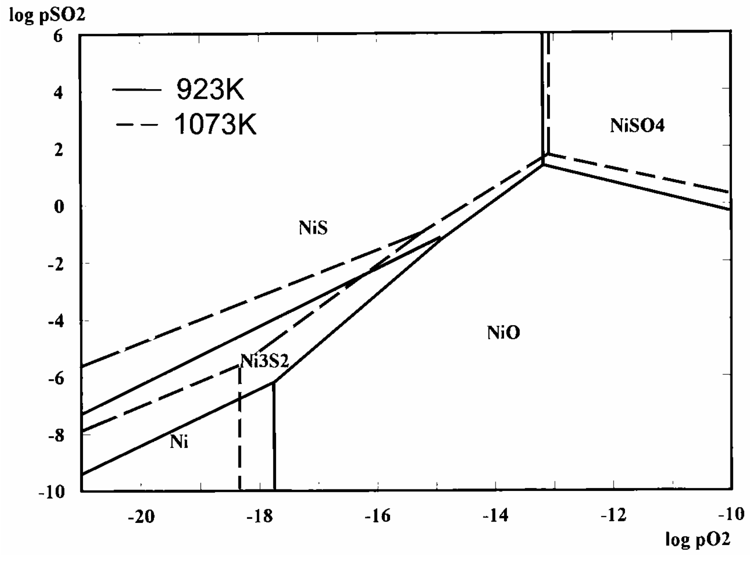

Fig. 1. Constructed phase stability diagrams (PSD) for the Ni–S–O system at 923 and 1073 K.

The obtained results show equilibrium between the phases: Ni–NiS–Ni_3S_2––$NiSO_4$–NiO, with NiO as the final product of the oxidation process for defined concentrations of SO_2 and O_2.

The results of the thermal analysis of the synthesized sample of α-NiS, obtained using the simultaneous DTA–TG–DTG method, are presented in Fig. 2, while the results of the X-ray diffraction measurements, including diffractograms of samples heated at 923 and 1073 K and then recorded at room temperature, are presented in Fig. 3.

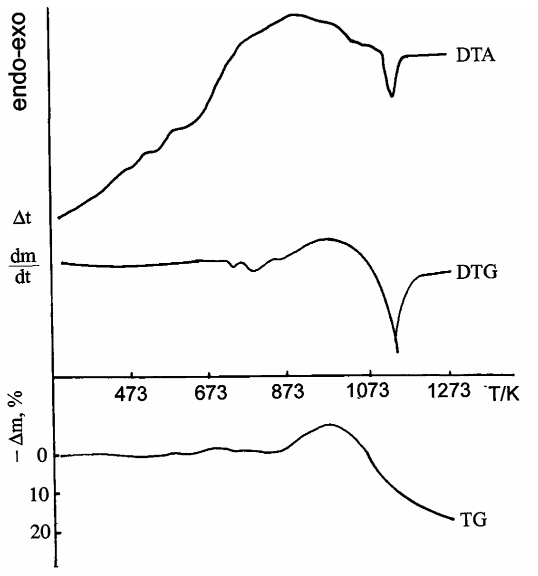

Fig. 2. DTA–TG–DTG Curves of NiS oxidation (atmosphere: air, heating rate: 10 °C min^{-1}).

Comparative analysis of the presented results was performed in order to obtain the mechanism of the process of NiS oxidation.

The first small endothermic peak in the DTA curve, shown in Fig. 2, occurred at a temperature near 550 K. It was not accompanied with a mass change on the TG curve and could correspond to the $\alpha \rightarrow \beta$ phase transition of NiS, as given in the literature.[12]

The oxidation of NiS commences in the temperature range 873–973 K, accompanied by a large exothermic effect with a maximum at 903 K and a significant mass, evidenced on the TG curve, which corresponds to the oxidation of nickel sulfide according to the reaction:

$$2NiS + 7/2\ O_2 \rightarrow NiSO_4 + NiO + SO_2 \qquad (1)$$

The process of $NiSO_4$ dissociation commences at 973 K, showing intensive a minimum on the DTA curve at the temperature of 1123 K and a significant decrease of the sample mass on the TG curve, due to the occurrence of the following reaction:

$$NiSO_4 \rightarrow NiO + SO_2 + 1/2\ O_2 \qquad (2)$$

The reactions proposed using the results of thermal analysis are in accordance with the obtained XRD data. Namely, the results of X-ray diffractometry showed the existence of $NiSO_4$ and NiO, as well as the presence of NiS still non-oxidized at 923 K, and the existence of NiO at the higher temperature of 1073 K, which is also in accordance with the constructed PSD diagram.

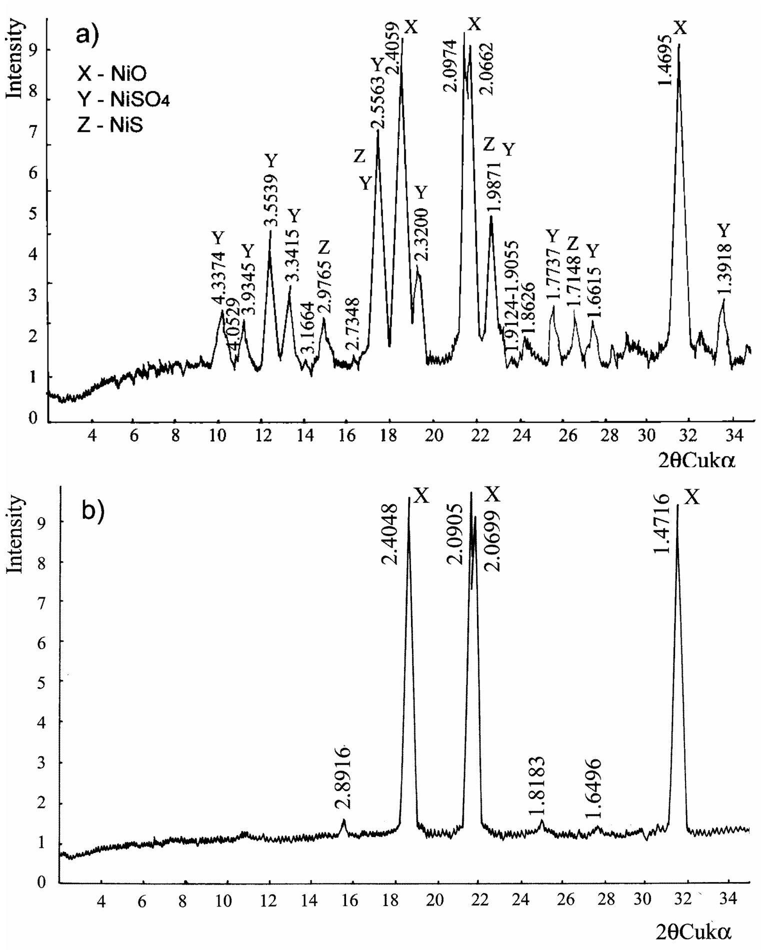

Fig. 3. X-Ray diffractograms of the investigated sample at 923 (a) and 1073 K (b).

Kinetics of the process of synthetic NiS oxidation

The degree of desulfurization was used to determine the kinetic parameters of the process, using the Sharp isothermal model.[17] The degree of desulfurization presents the ratio of the sulfur reacted during the oxidation process compared to the starting concentration of sulfur in the sample.

In the course of the experiments, samples of NiS were oxidized and the amounts of emitted SO_2 were successively registered. These results are presented in Fig. 4.

The most important information concerning the desulfurization process of nickel sulfide, which may be concluded from the SO_2 emission curves, is that the process proceeds intensely only during several minutes at the beginning (*i.e.*, the first five to six minutes), thereafter, the SO_2 emission almost completely ceases.

The process is very rapid, particularly at higher temperatures, which means that several first minutes are essential for the degree of sulfide transformation.

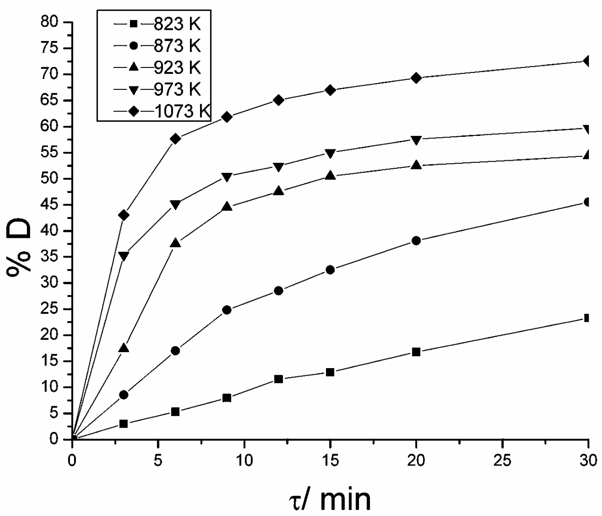

Fig. 4. Amount of sulfur which reacted with oxygen during the oxidative roasting of the NiS sample (D – degree of desulfurization, τ – time).

Linearization of the experimental results presented in Fig. 4 was tested using nine different kinetic equations proposed by Sharp.[17] The criteria for accepting an equation as the best for linearization of the experimental data was the least standard deviation of the linear data in comparison with linear fitting of the experimental data obtained by the iteration program provided by MLAB software (MLAB, Civilized Software).[18] This method for selection of the kinetic equation for the optimal fit of the experimental data points was described earlier.[19,20]

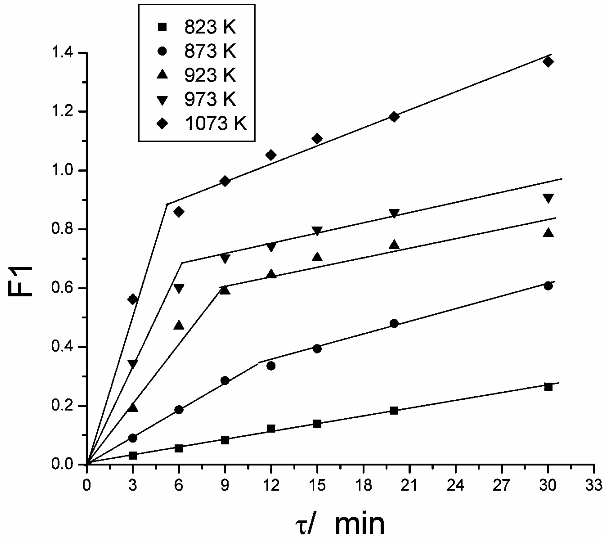

Fig. 5. Linearization of the experimental data points using the kinetic equation F_1: $-\ln(1-\alpha) = k\tau$ for the process.

The best linearization of the experimental data (*i.e.*, the minimum standard deviation for all the isotherms) was obtained using equation F_1: $-\ln(1-\alpha) = k\tau$ for desulfurization, where: α – degree of reaction, τ – time and k is the rate constant (Fig. 5). According to the Sharp theory, Equation F_1 describes a random nucleation of the new phase, with singular nuclei for each particle.[17] This stage could be considered as being dominant in controlling the reaction rate during the first period of time. An infraction of the linear isotherms (Fig. 5) was noticed for temperatures above 873 K, after the first 5–6 min. From the slopes of these linear isotherms, the rate constants were determined at the investigated temperatures (k_1 before the infraction and k_2 after the infraction) and a characteristic Arrhenius diagram was constructed, Fig. 6.

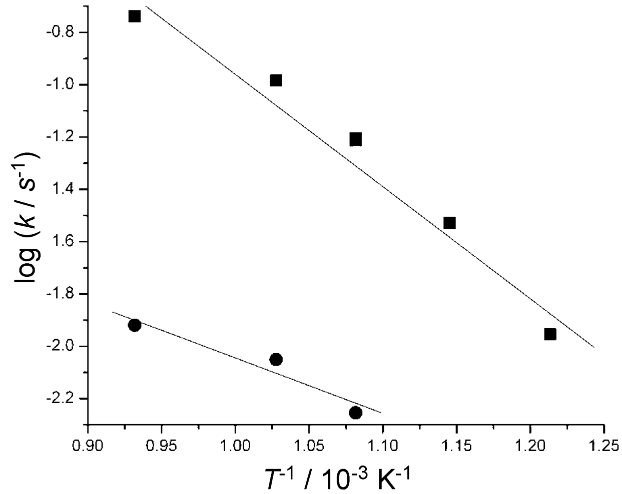

Fig. 6. Arrhenius diagram for the process of NiS oxidative roasting constructed from the rate of sulfur removal during the process (■ – before the infraction; ● – after the infraction).

According to the Arrhenius diagrams, the activation energy of the process under isothermal conditions was calculated. The kinetic equation for the oxidation stage of the desulfurization process was found to be: $-\ln(1-\alpha) = k_1\tau = 27.89\exp(-9860/T)\tau$, with an activation energy of 82±4 kJ mol^{-1}, and $-\ln(1-\alpha) = k_2\tau = 1.177\exp(-4810/T)\tau$, with an activation energy 40±2 kJ mol^{-1} for the dissociation stage of the desulfurization process, as given above. The expected errors were calculated using the error in the slope of the relevant regression line for each Arrhenius plot.

CONCLUSIONS

The results of this investigation of the process of synthetic α-NiS are presented in this paper. Based on the experimental results of thermal and X-ray diffraction analysis, as well as thermodynamic analysis of the stability of the phases in the Ni–S–O system in the investigated temperature range, the mechanism of NiS oxidation was deduced. It was shown that α-NiS firstly transforms to β-NiS at temperatures around 550 K, after which the oxidation process commenced between 873 and 973 K, when NiS was oxidized to $NiSO_4$ and NiO, while with further increasing of the temperature, at 973 K, dissociation of the formed $NiSO_4$ started. Hence, the final product of oxidation was NiO. The kinetics of the process was investigated using the Sharp method and it was determined that the oxidation process commences quite fast at the beginning of the process (during the first 5–6 min, depending on the temperature), with an activation energy which places the process in the kinetic region. After this first period of the reaction, the activation energy fell to the value on the limit of the kinetic-to-transition region, meaning that diffusion of the reactants and the reaction products began to have an influence on the overall rate of reaction.

ИЗВОД

МЕХАНИЗАМ И КИНЕТИКА ПРОЦЕСА ОКСИДАЦИЈЕ СИНТЕТИЧКОГ α-NiS

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У овом раду су представљени резултати истраживања механизма и кинетике оксидационог процеса пржења синтетичког α-NiS. Механизам оксидације α-NiS је испитиван применом компаративне анализе DTA–TG–DTG и XRD резултата, као и конструисања дијаграма стабилности фаза (PSD) за Ni–S–O систем. Кинетичка испитивања оксидационог процеса су урађена под изотермским условима у опсегу 823–1073 K. Резултати степена десулфуризације су употребљени у процесу прорачуна кинетичких параметара процеса оксидације α-NiS према Шарповој методи. Прорачунате су вредности енергије активације и константе брзине карактеристичних реакција. Ови резултати омогућили су формулацију кинетичке једначине процеса десулфуризације: $-\ln(1-\alpha) = k_1\tau = 27{,}89\exp(-9860/T)\tau$, са енергијом активације од 82±4 $\mathrm{kJ\,mol^{-1}}$, за први стадијум процеса и $-\ln(1-\alpha) = k_2\tau = 1{,}177\exp(-4810/T)\tau$, са енергијом активације од 40±2 $\mathrm{kJ\,mol^{-1}}$, за други стадијум.

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