

α - β PHASE RE-TRANSFORMATION KINETICS IN NICKEL SULPHIDE

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Abstract

Nickel sulphide (NiS) was characterised using X-ray diffraction, thermal gravimetric analysis (TG) and differential scanning calorimetry (DSC). The 'as received' Millerite, stoichiometric NiS, observed to be slightly nickel deficient, was found to readily decompose in a nitrogen atmosphere at elevated temperatures (450°C max.) to the sulphur deficient Godlevskite, Ni₇S₆. DSC and X-ray measurements demonstrated that the high temperature form of the Godlevskite was readily stabilised at room temperature. The kinetics of the α - β re-transformation in Godlevskite were then investigated using DSC and were observed to be first order.

Keywords: DSC, nickel sulphide, TG, toughened glass, X-ray diffraction

Introduction

Nickel sulphide (NiS) occurs in a number of stoichiometric compositions as well as a variety of non-stoichiometric intermediaries [1]. NiS with compositions ranging from 32 to 42% by mass sulphur are observed to have β - α transitions in the range 280 to 400°C. The actual value of transition temperature is strongly dependent on nickel to sulphur ratio. These transitions are of importance as, due to the strong covalent character of NiS, the high temperature phase is easily stabilised at room temperature. This is particularly true of toughened window glass where NiS is known to occur as inclusions and, in some cases, has been identified as a cause of the premature failure of toughened glass panels [2]. The mechanism of failure is believed to be associated with the phase re-transformation of NiS from the metastable α to the thermodynamically stable β form [1-2]. The α form of NiS is stabilised at room temperature by the toughening process through the heating of glass panels at elevated temperature (\approx 600°C) followed by air jet quenching. The re-transformation is accompanied by a substantial increase in the volume (\approx 4%) [3]. This increase in volume on re-transformation, coupled with the tensile and compression zones in the glass panels induced by the toughening process, is believed to be a cause of failure. It is therefore of interest to investigate the kinetics of the re-transformation and thereby gain an understanding of the processes and rates of re-transformation. The current study investigates the kinetics of the re-transformation of the α phase, stabilised at room temperature by quenching, to the β phase using differential scanning

calorimetry (DSC). The materials used were also characterised using X-ray diffraction and thermogravimetric analysis (TG).

Experimental

The material used in this study was a high purity nickel(II) sulphide powder (99.95%, 100 μm particle size) supplied by Johnson Mathey GmbH. The sample was confirmed to be Millerite, β -NiS, by X-ray analysis using a Siemens D5000 diffractometer with $\text{CuK}\beta$ radiation. The diffractometer was also fitted with a temperature stage for measurement of the diffraction pattern at elevated temperature. Heating and cooling rates of greater than 1°C s^{-1} were feasible allowing the measurement of the diffraction pattern of the α -form stabilised at room temperature. The sample compartment in each case was evacuated in order to avoid oxidation of the NiS. It should be noted that in addition to the NiS diffraction pattern, the diffraction pattern for platinum substrate was also present with three characteristic peaks at $2\theta=40^\circ$, 46° and 67° .

The DSC measurements were made using a TA Instruments 2920 calorimeter. Samples of NiS between 10 and 25 mg were enclosed in aluminium pans and analysed using seven heating rates; 20, 15, 10, 5, 2, 1, $0.5^\circ\text{C min}^{-1}$. For each heating rate a separate calibration curve was determined. The temperature calibration was performed on indium. At all times the sample compartment was purged with nitrogen at a flow rate of $150\text{ cm}^3\text{ min}^{-1}$. The DSC curves were measured by ramping the temperature at the specified heating rate over the range 35 to 450°C . The samples were then held at 450°C for 10 min before air quenching, with the aid of compressed air. The air quenching process was used to stabilise the α -form at room temperature for the subsequent heating program. During air quenching, the nitrogen purge was maintained in the sample compartment. Each sample was cycled in this manner through each of the heating rates. The cooling rates in the air quenching process were measured to be approximately $100^\circ\text{C min}^{-1}$ between 450 and 200°C . The ratio of the areas of the exothermic α - β re-transformation peak to the endothermic β - α transformation peak indicated that an estimated 90% of the α -form was stabilised at room temperature.

TG was used to determine the stability of the NiS. The TG measurements were performed on a TA Instruments SDT 2960 instrument using a heating rate of $10^\circ\text{C min}^{-1}$ in both nitrogen and air atmospheres.

Results and discussion

The sample of NiS used in this study was verified as being Millerite, β -NiS, by X-ray diffraction (Fig. 1). Figure 1 also shows the diffraction patterns for NiS at 450°C , NiS quenched to room temperature and NiS slow cooled to room temperature. Each of the three heat treated samples show diffraction patterns which are characteristic of Godlevskite, Ni_7S_6 . Godlevskite is also known to undergo a β - α phase transition in this temperature region at 397°C [1]. This was verified by the X-ray

measurements which show a number of peaks for the high temperature form that are absent for the low temperature form. The X-ray data also show evidence of the α -form in the slow cooled β -form at room temperature and that of the β -form in the quenched α -state.

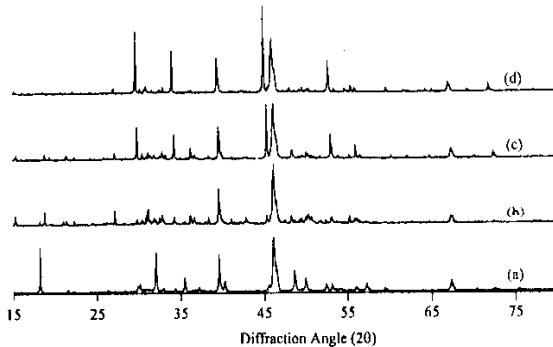


Fig. 1 X-ray diffraction patterns for nickel sulphide in the: (a) 'as received' Millerite, NiS , in the β -form, (b) Millerite heated to 450°C and slow cooled to room temperature to form the β - Ni_7S_6 , (c) Millerite heated to 450°C and quenched to form the α - Ni_7S_6 at room temperature and (d) Millerite at 450°C in the α - Ni_7S_6 form

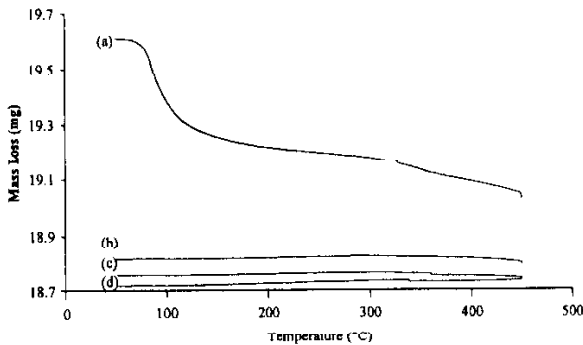


Fig. 2 TG curves for nickel sulphide cycled between 40° and 450°C : (a) 'as received' Millerite in a nitrogen atmosphere, (b) and (c) 2nd and 3rd cycles in a nitrogen atmosphere and (d) 4th cycle in an air atmosphere

The conversion from Millerite to Godlevskite is also observed in the TG data shown in Fig. 2. After an initial mass loss associated with the evaporation of water, the mass was observed to steadily decline with increasing temperature. This is most likely to be associated with the loss of sulphur resulting in a sulphur deficient NiS_{1-x} . As the sample was further cycled between 40 and 450°C , further loss of mass was observed. The mass loss observed after three cycles between 40 and 450°C , dis-

counting the water loss, was measured to be approximately 3.1%. This accounts for the variation in the measured value of the transition in the heat treated NiS. In the current study, the transition was measured between 391 and 401°C (onset between 380 and 398°C). The actual value was found to be dependent on both the heating rate and the age of the sample under study. Once the sample had been 'equilibrated' to the cycling program, the transition was observed between 397 and 401°C peak (Table 1). Curve (d) in Fig. 2 was measured in an air atmosphere to test the oxidative stability of the NiS. Up to 450°C no abnormal increase/decrease in the mass loss was observed. It was therefore surmised that under these conditions no oxidation had taken place.

The DSC curve of the 'as received' Millerite was measured up to 450°C and was observed to undergo a number of transitions the most prominent of which peaked at 358°C (Fig. 3). This value is somewhat below the literature value for the β - α transi-

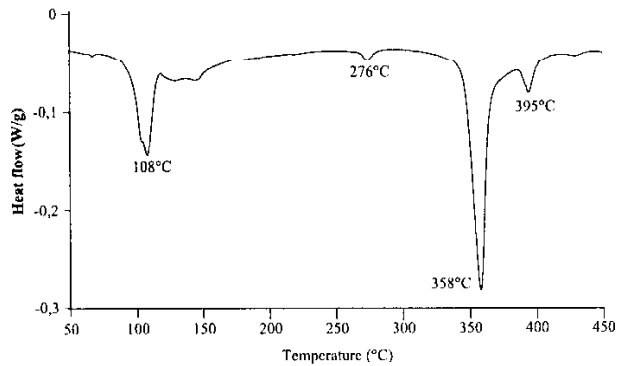


Fig. 3 DSC curve of the 'as received' Millerite

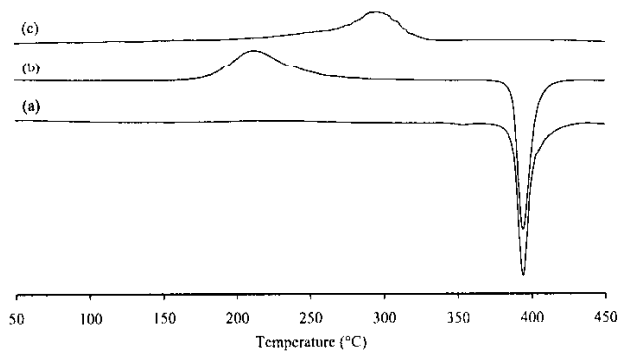


Fig. 4 Typical heating and cooling DSC curves for nickel sulphide using different thermal histories: (a) heating curve ($5^{\circ}\text{C min}^{-1}$) for nickel sulphide slow cooled at $5^{\circ}\text{C min}^{-1}$ from 450°C, (b) heating curve ($5^{\circ}\text{C min}^{-1}$) for nickel sulphide 'air quenched' at $100^{\circ}\text{C min}^{-1}$ from 450°C and (c) cooling curve at $5^{\circ}\text{C min}^{-1}$ from 450°C

Table 1 The averaged DSC data for α - β re-transformation and β - α transformation in NiS

Heating rate/ °C min ⁻¹	α - β re-transformation				β - α transformation			
	onset/°C	peak/°C	area/J g ⁻¹	peak height/W g ⁻¹	onset/°C	peak/°C	area/J g ⁻¹	peak height/W g ⁻¹
0.5	131	151	29.9	0.009	398	401	37.5	0.021
1	150	167	31.8	0.020	398	401	38.8	0.060
2	156	182	31.7	0.030	395	400	37.8	0.133
5	177	206	32.3	0.067	393	398	36.5	0.392
10	191	222	31.3	0.113	392	397	36.7	0.708
15	202	237	34.1	0.155	391	397	36.0	0.902
20	207	243	28.9	0.16	388	397	35.7	1.067

tion for NiS (379°C) [1]. The position of the transition has been observed to be dependent on the stoichiometry according to the value of x in $Ni_{1-x}S$, dropping to 280°C [1]. The 'as received' NiS is therefore slightly Ni deficient. The curve in Fig. 3 also shows the presence of peaks at 276 and 395°C indicating the presence of small quantities of sulphur excess and sulphur deficient forms of NiS respectively. A peak at 108°C is consistent with the water loss observed in the TG measurements. After the initial cycling of the 'as received' material to 450°C, the sample transition was observed to be consistently in the region of 397 to 400°C, at peak, indicating the formation of Godlevskite. It was on this equilibrated material that the kinetic studies of the α - β re-transformation were carried out. Typical DSC heating/cooling curves for quenched and slow cooled samples are shown in Fig. 4.

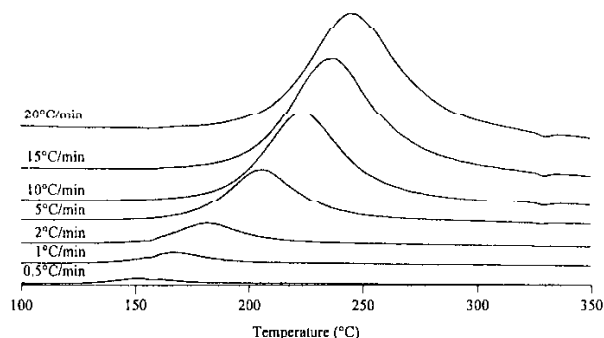


Fig. 5 DSC heating curves between 100 and 350°C showing the α - β re-transformation for the heating rates specified

The curves for the α - β re-transformation are shown in Fig. 5. Data averaged over all the heating cycles is listed in Table 1. The kinetics of the re-transformation were determined using a first order solid state reaction model for the re-transformation [4]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - \alpha) \quad (1)$$

where α is the degree of conversion, T is the temperature, E is the activation energy for the process and R is the gas constant. The degree of conversion was determined from the ratio of the area under the peak up to time of measurement (normally peak maximum where α approximates to 0.5 for a symmetric transformation) to the total area under the exothermic peak. The rate of reaction was measured as the magnitude of the heat flow curve (normally at the exothermic peak maximum). The data fitted to this model is plotted in Fig. 6 and shows good agreement. The activation energy, E , for the re-transformation was calculated to be 62 kJ mol⁻¹ and the pre-exponential factor, $\ln(A)$, was determined to be 11.

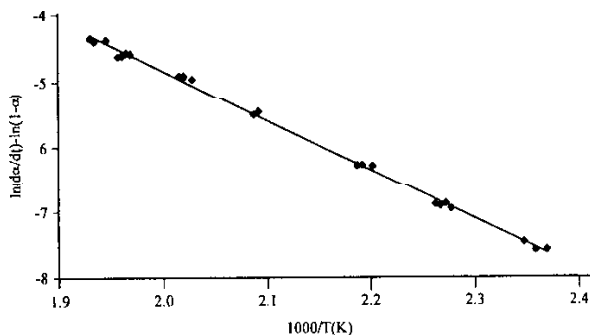


Fig. 6 The data for the re-transformation plotted in accordance with Eq. (1)

First order kinetics is to be expected for a re-transformation such as that observed in the nickel sulphide. Nucleation sites for the re-transformation are already present due to the presence of approximately 10% of the β form. In addition, diffusional factors can also be neglected as the phase change is a localised rearrangement of the components.

The value of the activation energy for re-transformation is relatively low thus supporting the mechanism of failure in toughened glass as being initiated by the re-transformation process. The rate equation predicts re-transformation in the order of a few years at ordinary temperatures which is consistent with the time frame for failure in toughened window panels [2]. In addition, as nickel sulphides of higher sulphur composition have been observed in the glass environment [2], a lower magnitude of the rate constant would be expected as the higher sulphur content sulphides have lower β - α transformation temperatures. The re-transformation times would therefore be further reduced, accelerating the failure mechanisms and thus inducing the failure of toughened glass in shorter times.

Conclusions

In summary, this study investigated the thermal stability of NiS and the re-transformation kinetics of Ni_7S_6 . The 'as received' Millerite, NiS, was found to readily decompose on heating to the sulphur deficient Ni_7S_6 . The kinetic measurements were therefore performed on Ni_7S_6 and were observed to be first order in nature. A relatively low value of the activation energy was measured for the re-transformation supporting the re-transformation mechanism for failure in toughened glass.

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