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THE EFFECT OF THERMAL HISTORY ON THE MORPHOLOGY OF NICKEL SULPHIDE

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Abstract

The DSC characterisation of the morphology of the metastable α phase of stoichiometric nickel sulphide was carried out using two calorimeters; a TA Instruments 2920 MDSC and a Perkin Elmer DSC-7, and two quenching histories. Based on these quenching histories, significant differences were observed in the heat flow curves, including the observation of a second exothermic peak which is tentatively assigned to be a metastable phase to metastable phase transformation. The kinetic constants for the α to β recrystallisation were determined as a function of degree of conversion using a mechanism free isoconversional model. Variations in the values of the kinetic constants were also ascribed to the quenching histories. Although the differences in morphology observed were ascribed to the processing history, the shift in the position of the α to β recrystallisation peak was partially attributed to the thermal resistances of the instruments used.

Keywords: DSC, isoconversional kinetics, morphology, nickel sulphide, recrystallisation

Introduction

The morphology of nickel sulphide (NiS) is of interest due to its implication in the catastrophic failure of toughened glass panels [1–3]. NiS inclusions are known to cause the failure of thermally toughened glass through the recrystallisation at ambient temperatures of the metastable high temperature α-form to the thermodynamically stable low temperature β-form. The recrystallisation to the β-form occurs over time and is accompanied by a volume increase of 4%, significant enough to induce stresses in the glass which can cause catastrophic failure of the toughened panels [4]. Kinetic studies have been carried out using differential scanning calorimetry (DSC) to estimate the rate of the recrystallisation under normal exposure conditions [1], and at elevated temperatures in heat soak ovens [2]. The kinetics is further complicated by the presence of contaminant elements, such as iron, as well as slight variances in the nickel to sulphur ratio [2]. The phase morphology of the NiS inclusions has also been observed to be complex, as inclusions have been observed to contain more than one stoichiometric phase [3].

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A comprehensive study of the phase morphology of the nickel sulphide system was published by Kullerud and Yund [5]. A few modifications have since been made to this phase diagram, the most notable of which is in the identification of the stable low temperature phase, Ni_9S_8, which has replaced the β-Ni_7S_6 phase [6, 7]. A number of metastable phases have also been observed in this compositional range. The quenching of specimens in the $Ni_{7+x}S_6$ (44 to 48% Ni) compositional range has been observed to produce four separate metastable phases whose existences are strongly dependent on the annealing temperature, time or heating rate [7]. Although the high temperature phase, α-NiS, has also been observed as a room temperature metastable phase [1, 2], evidence of intermediate phase transformations between metastable phases of the sort observed in the $Ni_{7+x}S_6$ compositional range has only been observed below room temperature [8]. This study continues the characterisation of the phase morphology of α-NiS using DSC. Two heat treatment regimes were used in the preparation of α-NiS. Varying the heat treatment was, indeed, observed to alter the morphology of the α-NiS as observed from the DSC heating curves and, although tentative, as further structural characterisation is required, evidence of a second metastable phase at intermediate temperature is reported.

Experimental

The material used was high purity nickel(II) sulphide powder (99.95%, 100 μm particle size) supplied by Johnson Matthey GmbH. The 'as received' material was observed to be slightly in excess in sulphur. The 'as received' NiS was, therefore, conditioned at 450°C for 3 h to remove the excess sulphur. The slow cooled resultant material was confirmed to be β-NiS by X-ray analysis using a Siemens D5000 diffractometer with CuK_α radiation. This annealed material was used in the DSC experiments with no further mass loss and, therefore, no further loss of sulphur observed.

The DSC measurements were carried out using a TA Instruments 2920 (TA) and a Perkin Elmer DSC-7 (PE) calorimeter. For each set of experiments, a sample of NiS (approximately 15 mg) was enclosed in an aluminium pan and placed in the sample compartment of the calorimeter using an empty pan as the reference. The sample compartment was purged continuously with nitrogen using a flow rate of 150 $cm^3\ min^{-1}$ for the TA and 50 $cm^3\ min^{-1}$ for the PE experiments. Samples of α-NiS, at ambient temperatures, were prepared by heating the β-NiS to 450°C. The samples were held at 450°C for 10 min before quenching to 100°C. For the TA experiments, the quenching process was carried out using compressed air to rapidly cool the DSC furnace. The cooling rates were observed to be variable, but in excess of 80°C min^{-1} between 450 and 250°C (Fig. 1). Samples of NiS, prepared in this manner, have been shown to be in the α-form from their X-ray diffraction patterns [1]. For the PE experiments, α-NiS was prepared by cooling at approximately 100°C min^{-1} (Fig. 1). The cooling program was maintained down to 200°C before a noticeable drop off in the rate occurred.

The non-isothermal recrystallisation measurements were carried out on the samples of α-NiS at the following heating rates: 20, 15, 10, 7.5, 5, 2.5, 1 and 0.5°C min^{-1}. For the PE experiments a three-point temperature calibration was performed using in-

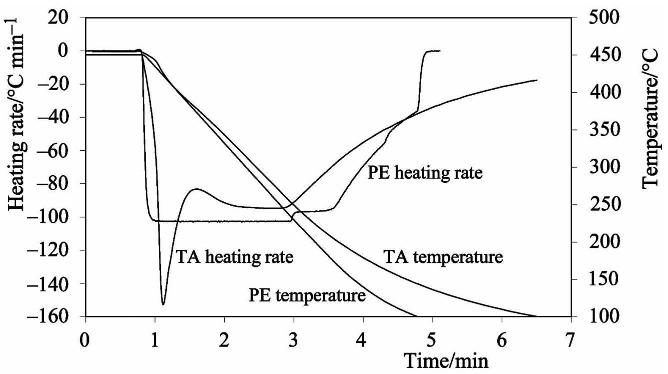

Fig. 1 The measured cooling rates and temperature profiles for the cooling programs used to prepare α-NiS in TA Instruments and Perkin Elmer DSC calorimeters

dium, tin and zinc as the standards at a heating rate of 10°C min^{-1}. Melting endotherms at the other heating rates were measured using tin as the standard. The temperature axis was then corrected once the DSC curves had been collected. For TA experiments, the three-point temperature calibration was carried out at a heating rate of 10°C min^{-1} using indium, tin and lead as the standards. A separate calibration curve for each heating rate was collected to determine the baseline slope. Additionally, the cell constant was also corrected for each heating rate using indium as the standard.

Results and discussion

The DSC heating curves for the recrystallisation of α-NiS are shown in Fig. 2 for the Perkin Elmer (PE) instrument. As the α-phase is a metastable phase at temperatures below the β- to α-transition temperature, an exothermic peak is observed as the recrystallisation of α- to β-NiS occurs. As the temperature is raised further, and through the phase transformation temperature (≈400°C), an endothermic peak is observed as the β-phase transforms to the α-phase. The peak and onset temperatures are listed in Tables 1 and 2 for the recrystallisation and phase transformation peaks, respectively. Expansion of the scale of Fig. 2, to show the shape of the lower heating rate curves, reveals a second exotherm (Fig. 3). The second exotherm is only observed distinctly in the lower heating rate curves with peak positions at 318, 323 and 347°C for the 0.5, 1 and 2.5°C min^{-1} heating rates, respectively. For the higher heating rates, this peak apparently merges into the phase transformation endotherm around 400°C. The areas for these exotherms were measured as 188, 70 and 29 J g^{-1} for the 0.5, 1 and 2.5°C min^{-1} heating rates, respectively. The origins of this second peak are uncertain, but may be due to the formation of a second metastable phase from the α-NiS as it is heated at these low rates. The possibility of this second exotherm being an experimental artefact was discounted due to its reproducibility for α-NiS specimens heat treated by constant cooling at 100°C min^{-1} and from its absence in baseline curves measured at each heating rate. Additionally, this type of heating rate dependence has been observed for the interconversion between metastable

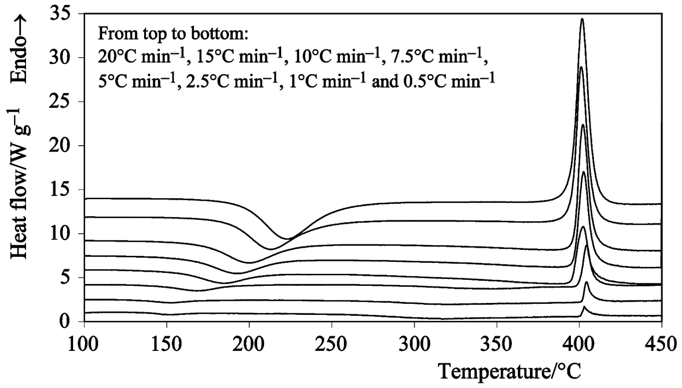

Fig. 2 DSC recrystallisation curves measured in the PE DSC-7

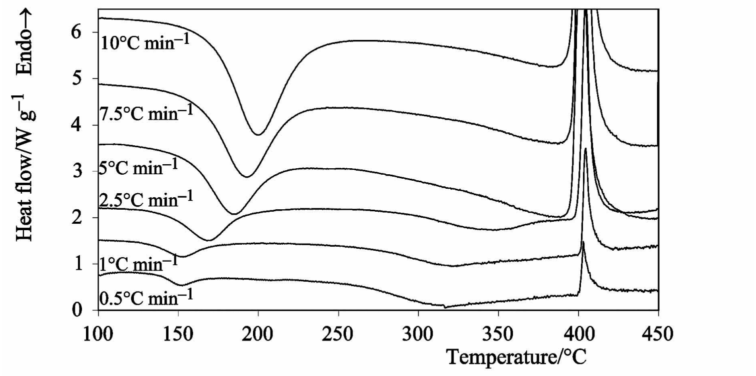

Fig. 3 Expanded region of the data shown in Fig. 2

phases in quenched specimens of $\alpha\text{-Ni}_{7+x}\text{S}_6$ [7]. It is, therefore, possible that a similar metastable to metastable phase transformation is occurring here.

Table 1 Data for the α and β recrystallisation exotherm

β/°C min^{-1}	Onset/°C		Peak/°C		Area/J g^{-1}	
	PE	TA	PE	TA	PE	TA
0.5	139	128	150	149	65	39
1.0	131	143	145	165	37	40
2.5	141	157	169	183	40	40
5.0	155	169	185	198	40	41
7.5	163	178	192	210	37	41
10.0	170	186	200	220	38	40
15.0	186	197	213	232	39	38
20.0	195	204	223	241	39	36

Table 2 Data for the β to α phase transformation endotherm

β/°C min^{-1}	Onset/°C		Peak/°C		Area/J g^{-1}	
	PE	TA	PE	TA	PE	TA
0.5	400	397	403	400	38	56
1.0	402	398	404	399	44	52
2.5	401	395	404	398	47	53
5.0	396	393	402	398	47	52
7.5	397	392	403	397	46	50
10.0	397	389	402	396	44	46
15.0	396	390	401	396	42	43
20.0	395	391	402	397	41	43

For the TA measurements, only the expanded region of the DSC curves is included (Fig. 4). The full range of measured data for both the recrystallisation peak and the phase transformation peak are, however, included in Tables 1 and 2, respectively. No sign of a second exotherm is observed in any of the curves. Indeed, the curves follow the expected pattern of a single exotherm for the α to β recrystallisation followed by the β- to α-phase transformation endotherm. The position of the onset and peak temperatures is consistent with the previously published data [1]. The magnitudes of the areas of these peaks are also consistent and compare well with the higher heating rate values measured for the PE data. It is notable, however, that the measured values of the onset and peak temperatures for the recrystallisation are significantly higher in the TA measurements (on average 13°C higher for each heating rate with no apparent dependence on the heating rate). Differences in the measured onset temperatures for the phase transformation are also observed, but in this case the transformation temperature in TA measurements is on average 5°C lower than the corresponding PE measurements. It is also interesting to note that these onset temper-

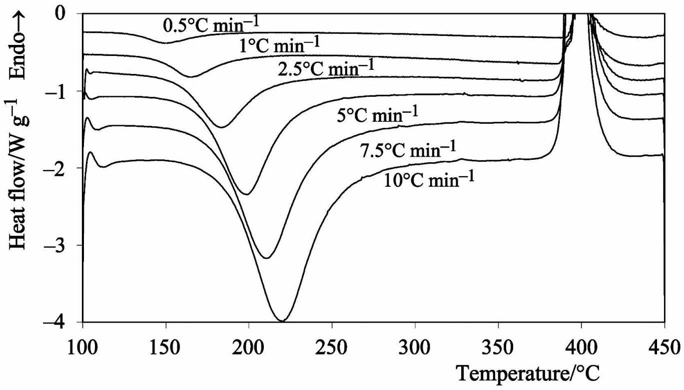

Fig. 4 Expanded region of the DSC data for the recrystallisation of α-NiS measured in the TA Instruments MDSC 2920

atures are observed to decrease with increasing heating rate for both instrument types with the greater drop in values for the TA instrument.

A number of significant differences in the apparent morphology of the α-NiS are observed by DSC characterisation. Two exothermic processes are observed in the PE data, a significant difference in the position of the recrystallisation temperature is observed, with higher temperatures observed in the TA measurements, and the phase transformation peak for the TA measurements is observed to be at lower temperature. Rationalisation of some of these observations may lie in the differences between the instruments used. The higher values of the measured temperatures of the recrystallisation peaks in the TA instrument may be explained in terms of the lower heat transfer coefficient (or time constant) for the instrument. The heat transfer coefficient may be determined from the slope of the melting endotherm of pure indium. For the two instruments used the onset slope for the melting of indium at a heating rate of 10°C min^{-1} was measured to be 39.9 and 7.4 mW $°\text{C}^{-1}$ for the PE and TA instruments, respectively. The higher thermal resistance of the TA instrument is likely to be at least partially responsible for the higher temperatures observed for the recrystallisation peak. The nature of the transformation is also likely to be a contributing factor in the shift in peak position. The metastable α to thermodynamically stable β recrystallisation involves a 4% increase in volume [4] resulting in the strong time dependence of the recrystallisation process. The lower heat transfer coefficient coupled with the time dependent nature of the recrystallisation results in the delay of the recrystallisation and hence the position of the recrystallisation peak is observed at higher temperatures in the TA instrument. The β to α first order transition, on the other hand, is observed at a lower temperature in the TA instrument than the PE instrument. This phase transformation corresponds with a contraction of the volume of the system and is therefore thermodynamically driven. The onset temperature also decreases with increasing heating rate for both instrument types; a phenomenon likely to be associated with the inclusion of an increasing number of imperfections in the β-NiS lattice during recrystallisation with increasing heating rate. The difference in temperature between the PE measurement and the TA measurements is therefore likely to be associated with the morphology of the β-NiS and therefore based on the thermal history.

The origin of the second exothermic peak observed in the PE measurements, not observed in the TA measurements, is also most likely to be associated with the heat treatment history used in the preparation of the α-NiS. In the PE instrument α-NiS was prepared by controlled cooling at a rate of approximately 100°C min^{-1} from 450 to 200°C. Below 200°C, the cooling rate was observed to drop off. The cooling rate, however, was observed to remain significantly higher throughout the cooling process than in the method used for the preparation of α-NiS in the TA instrument (Fig. 1). The control of these high rates is facilitated by the use of a heat exchange fluid circulating around the cell aiding the removal of heat from the cell. The coolant fluid was maintained at approximately –10°C throughout. In contrast, the TA instrument was cooled simply by dissipating heat to the surrounding atmosphere aided by the flow of compressed air. The cooling rate is, consequently, less controlled and varies from an initial value much higher than that measured in the PE instrument to a value consistently lower than that measured in the PE instrument. As the α-NiS is a kinetically stabilised phase it is likely that these differences in the preparation history are the cause of the observed differences in morphologies. It should be reiterated here that the second metastable phase is inferred from the DSC data. Confirmation of such a metastable phase will require further characterisation of the morphology of the species produced using complementary techniques such as X-ray diffraction. Such characterisations will be the subject of further investigation into the morphology of nickel sulphide.

As the DSC measurements were carried out as a function of heating rate, the kinetic parameters were determined for the recrystallisation process. The method adopted was that detailed in [9] used for the measurement of induction periods and is based on a mechanism free, isoconversional model:

$$\beta = \int_{\mathrm{T}_0}^{\mathrm{T}_\alpha} \frac{\partial T}{A\exp(-B/T)} \qquad (1)$$

where β is the heating rate, *A* and *B* are constants, *T* is the temperature in Kelvin and T_0 and T_α are the starting temperature and the temperature for a degree of conversion, α, respectively. The constant *A* contains the function of α, while the constant $B=E/R$, where *E* is the activation energy and *R* is the gas constant. This equation was solved iteratively using the trapezium method for the integration. The values of *A* and *B* were determined by fitting, simultaneously, the heating curves at 5, 7.5, 10, 15 and 20°C min^{-1} and minimising the sum of the squares between theoretical and experimental values of T_α for each heating rate using the simplex method. The lower heating rates were omitted in the determination of the kinetic parameters due to the presence of the second exotherm complicating the mechanism of recrystallisation.

Values of the constants ln(*A*) and *B* were determined for conversions between 5 and 95% and are shown in Fig. 5. The kinetic parameters for the PE data appear to be fairly independent of the degree of conversion. This is particularly true for the values of ln(*A*), although there is some scatter in the measured values of *B*. The TA data, in contrast, show a trend in both sets of data with increasing degree of conversion; the value of *B* decreases with increasing conversion while the value of ln(*A*) increases. Again, these differences are likely to be associated with the differences in the quenching histories. The relative independence of the kinetic parameters for the PE measurements reflects the more controlled nature of the quenching process while the variation in the cooling rate during the air quench of the TA data results in a range of kinetic parameters that reflect the changing morphology of the metastable phase as cooling is completed. The range of calculated values of *B* for both instruments, however, is similar with a maximum-minimum difference of approximately 600 K^{-1} in both sets of data between a 20 and 80% conversion. The values of ln(*A*) also fall into a narrow distribution in this range of conversions. Both sets of data provide consistent values of the kinetic constants to the point that the magnitudes of the kinetic parameters derived from these data sets for a 50% conversion, calculated to be $3.1\cdot10^{-6}$ min^{-1} and 56.6 kJ mol^{-1} for the PE instrument and $3.7\cdot10^{-6}$ min^{-1} and 56.1 kJ mol^{-1} for the

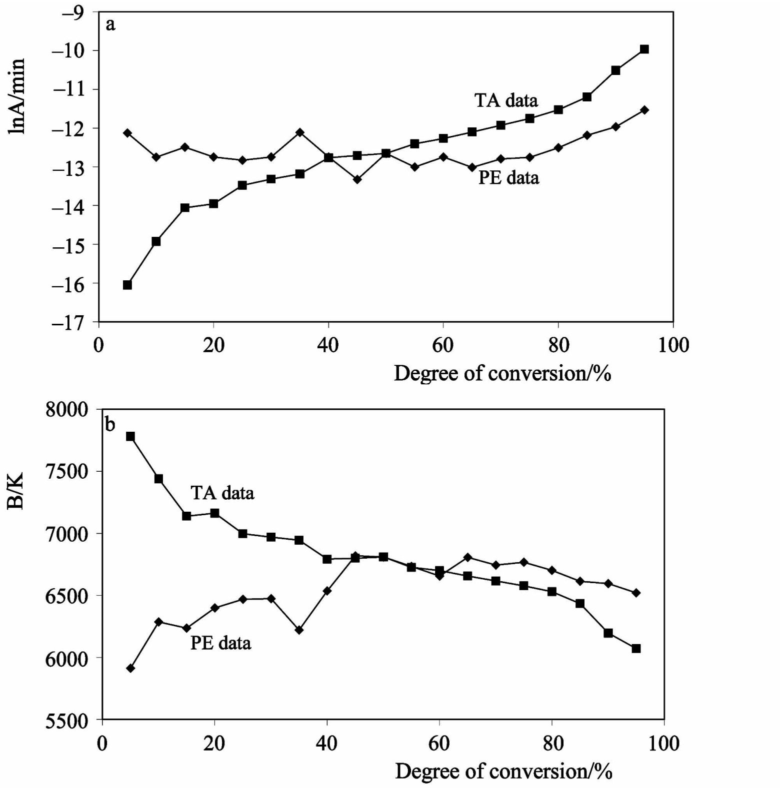

Fig. 5 Kinetic parameters determined for the mechanism free model of Eq. (1); a – ln$A$ and b – B as a function of the percent degree of conversion, α

TA instrument, are, within experimental error, identical. This is a surprising result given influence of thermal history on the morphology alluded to above.

Conclusions

The characterisation of the morphology of quenched specimens of NiS was carried out using two instruments and two quenching histories. The two quenching histories produced two different morphologies as observed from the DSC measurements. The effect of thermal history on the morphology is further underlined by the dependence of the kinetic parameters on the degree of conversion and, although independent confirmation is still required, under certain thermal histories a metastable phase to metastable phase transition has been identified. Some instrumental factors were also believed to be responsible for the differences in the measured data, in particular, the position of the recrystallisation peak. However, the sensitivity of the morphology of nickel sulphide to thermal history suggests that, for instrumental differences to be deconvolved, exact conditions need to be reproduced. As the quenching histories for each set of experiments differed, this latter criterion was not fulfilled. The sensitivity of nickel sulphide to environmental conditions may, however, make this material a suitable candidate for the characterisation of the reproducibility of measurement systems in future studies.

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