Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 77–80

A PSEUDO-ISOTHERMAL KINETIC ANALYSIS OF THE RECRYSTALLISATION OF NICKEL SULPHIDE MEASURED BY NON-ISOTHERMAL DSC

P. Thomas[1]* *and P. Šimon*[2]

[1]Department of Chemistry, Materials and Forensic Sciences, University of Technology, Sydney, PO Box 123, Broadway, NSW 2007, Australia
[2]Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

A pseudo-isothermal method for the kinetic analysis was applied to the recrystallisation of α to β nickel sulphide based on the Ozawa model for non-isothermal crystallisation in the presence of pre-existing nuclei. The aim of the analysis was to determine the number of steps involved in the recrystallisation and, hence, determine the applicability of the kinetic equation based on a single step mechanism, as is commonly applied in the kinetic analysis of solid-state processes using thermal methods. The kinetic analysis yielded evidence of at least two processes indicating that physical and mechanistic significance should not be drawn from the use of a single step approximation of the rate equation.

Keywords: *DSC, kinetics, nickel sulphide, recrystallisation*

Introduction

The kinetic analysis of the α to β phase recrystallisation of nickel sulphide (NiS) has recently been the topic of a number of papers [1–3]. The application of the kinetic models has yielded a number of values for the activation parameters using the Arrhenius temperature dependence. Even though recrystallisation may appear to be a fairly simple transformation process (for example, in recrystallisation, nucleation is likely to have already occurred and is, therefore, not likely to be a significant influence), the application of mechanistic kinetic models has yielded a variety of mechanisms which fit the data with equal alacrity [1–3]. The inference of a particular mechanistic process is, therefore, fraught with error even for such an apparently simple transformation.

The inference of mechanistic significance of rate equations using the Arrhenius temperature dependence has also been a topic of concern in the literature in recent years especially when applied to non-isothermal data [4–6]. Typical concerns are; the validity of applying the Arrhenius temperature dependence for the activated state; that the transformation process is commonly assumed to be a single step process which can be fit by a single step rate equation and; that, as multi-parameter models are force fitted to data (with extremely low residual error) a number of solutions, and hence a range of values for the kinetic parameters, are possible. In order to understand why the kinetic modelling of solid state processes, in particular, the recrystallisation of NiS, can produce a range of values for the kinetic parameters, a further analysis of the recrystallisation has been carried out in this paper.

The model adopted in this paper is that proposed by Ozawa for the analysis of the solid-state transformation under non-isothermal conditions [7]:

$$-\ln(1-\alpha)=\frac{Z}{\beta^{n}}\int_{T_0=0}^{T} f(T)\mathrm{d}T \tag{1}$$

where α is the degree of conversion, *Z* is an amalgamation of constants, β is the heating rate, *n* is the number of growth dimensions and *f*(*T*) is the temperature dependence of the rate constant. The conversion is considered to be dependent solely on the growth process and is not a function of coincident random nucleation. The model is similar to the Johnson–Mehl–Avrami model with the condition that pre-existing nuclei are already present for crystal growth.

If it is assumed that the function of α and *f*(*T*) are independent of each other, then the parameters of Eq. (1) may be separated through a logarithmic transformation:

$$\ln[-\ln(1-\alpha)]=\ln Z-n\ln\beta+\ln\left[\int_{T_0=0}^{T} f(T)\mathrm{d}T\right] \tag{2}$$

Given that the mechanism for transformation at a particular temperature is independent of heating rate,

---

* Author for correspondence: paul.thomas@uts.edu.au

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

and, therefore, the temperature integral can be considered to be constant for a set of heating rate curves at a specific temperature, a plot of ln[–ln(1–α)] as a function of lnβ will yield the value of *n* as the slope. The form of the temperature integral, therefore, does not need to be specified for the assessment of the value of *n*. Measurement of the magnitude of *n* at several temperatures throughout the recrystallisation step will aid the determination of the number of processes that are occurring during recrystallisation and, therefore, identify the validity of the application of a single step kinetic equation to the recrystallisation process. This application of a kinetic equation is similar to isoconversional methods in the sense that it uses the degree of conversion as the variable for a series of heating rate curves for fixed temperatures. It is, in effect, a pseudo-isothermal method of fitting the kinetic equation.

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. Annealing this material at 450°C for three hours removed the excess sulphur. Once annealed, slow cooling produced β-NiS as determined by X-ray analysis using a Siemens D5000 diffractometer with CuK$_\alpha$ radiation. Additionally, although sample mass decreased on the initial removal of the excess sulphur, no further mass loss, and, therefore, further removal of sulphur, was observed as the DSC experiments were carried out. Due to the presence of excess sulphur in the ‘as received’ material, all the specimens of the NiS characterised were annealed at 450°C for 3 h prior to DSC characterisation.

The DSC measurements were made using a TA Instruments 2930 (TAI) and a PerkinElmer DSC-7 (PE) calorimeter. For each series of variable heating rate 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 TAI 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 TAI 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 K min^{-1} between 450 and 250°C. Samples of α-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 between 95 and 100 K min^{-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: 5, 7.5, 10, 15 and 20 K min^{-1}.

Results and discussion

The recrystallisation of β-NiS from α-NiS occurs as an exotherm and is shown in Fig. 1 for the TAI DSC data. A similar set of curves for the PE instrument is also observed [8]. From these data the degree of conversion can be measured and can be plotted in accordance with Eq. (2) as a function of the heating rate. These data are shown in Figs 2 and 3 for the TAI and PE instruments, respectively. From the slope of each curve, the value of *n*, which, in the Ozawa model, corresponds to the number of crystal growth dimensions, can be determined. Figure 4 is a plot of *n* as a function of the temperature. The temperature range in which *n* can be measured, by the proposed pseudo-isothermal method, is limited by the degree of conversion for

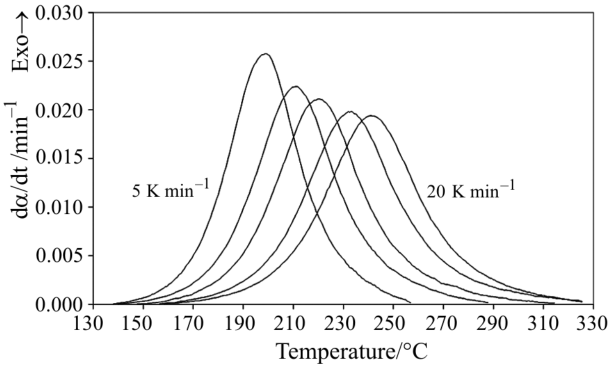

Fig. 1 Heat flow curves for the conversion of α-NiS to β-NiS for 5, 7.5, 10, 15 and 20 K min^{-1} measured on a TA Instruments 2930 MDSC

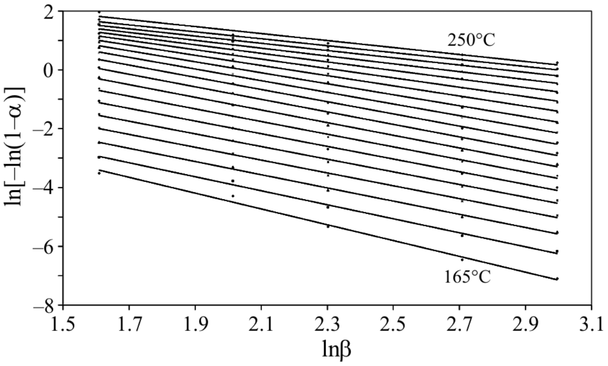

Fig. 2 Plot of ln[–ln(1–α)] as a function of lnβ for the conversion of α-NiS to β-NiS measured on a TA Instruments 2930 MDSC

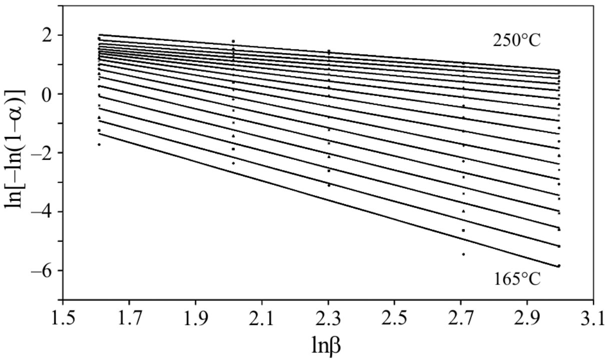

Fig. 3 Plot of ln[−ln(1−α)] as a function of lnβ for the conversion of α- to β-NiS measured on a PerkinElmer DSC-7

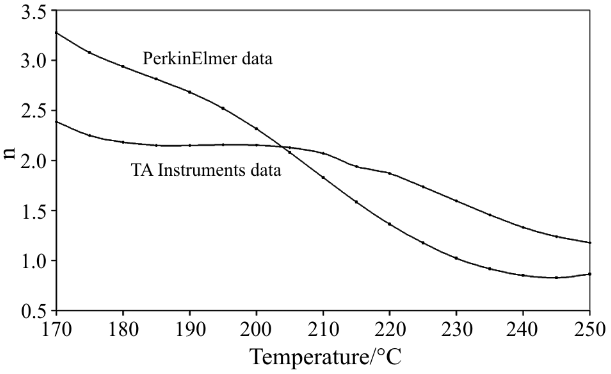

Fig. 4 Values of n determined from the slopes of the curves of Figs 2 and 3 plotted as a function of temperature

the 5 heating rates used. A minimum conversion of 0.2, and a maximum of 99.8%, was used. These extremes test the limit of experimental certainty as the onset and end point of the transformation are determined qualitatively. The heating rates used in this study were based on the fact that at low heating rate (less than 5 K min^{-1} in the PE instrument) a broad endotherm is observed and has been attributed to a second metastable (α′) state [8].

Equation (2) holds well for the TAI data where linearity is observed even at the extremes of the temperature range (Fig. 2). Some scatter is observed in the PE data, particularly for the low temperature regime, but correspondence with Eq. (2) improves at higher temperatures (Fig. 3). In both cases a transition is observed in the value of n as the 'average' degree of conversion, or the temperature at which n is determined, increases. The value of n is approximately 2.4 for the TAI data and 3.3 for the PE data for the lowest temperature of measurement and decreases to 1.2 and 0.9, respectively, as the temperature is increased indicating a change in the mechanism of crystallisation as the average degree of conversion, or the temperature at which n is measured, increases. It should be noted that, although a similar trend in the values of n is observed for both instruments, differences in the magnitudes are observed. This may be due to an 'averaging affect' associated with the significantly higher thermal resistance of the TAI instrument. The thermal resistance may be measured from the onset slope of a melting transition. The onset slopes have been previously measured at 39.9 and 7.4 mW °C^{-1} for the TAI and PE instruments, respectively, for the melting of indium at a heating rate of 10 K min^{-1} [8].

The shift in the value of n from approximately 3 to 1 indicates a change in the mechanism of crystallisation as conversion proceeds. For the crystallisation process, two (or more) mechanisms may be expected due to the availability of material for conversion to the new phase. Initially, crystallisation can be expected to be multidimensional as crystal growth is unimpeded by other crystallites. At some point crystallites impinge on each other. Multi-dimensional growth, therefore, becomes more limited. An alternative mode of crystallisation, therefore, results. The data in Fig. 4 suggest that initially the recrystallisation process occurs through a three dimensional growth process. As the average degree of conversion, or the temperature at which n is measured, increases, further growth is apparently restricted to one dimension.

The data in Fig. 4 suggest that at least 2 growth processes are occurring. The assignment of a three to one dimensional growth transition is, however, tentative as this assignment is based on the assumption that the mechanism for recrystallisation is the same for each degree of conversion measured from each heating rate curve at each, fixed, temperature. The fact that there is a significant shift in the value of n as the temperature increases does, however, suggest that a change in the mechanism of the recrystallisation is occurring. For the application of a kinetic model to the determination of the mechanism, a multi-mechanism model for the rate equation is required. Increasing the number of mechanistic terms in the rate equation, however, increases the number of fitting parameters and is, therefore, likely to reduce the physical significance of the mechanistic model applied. The fitting of a single step kinetic model, however good the fit, can have no physical or mechanistic significance for this apparently simple transformation of recrystallisation from α- to β-NiS. The use of a single step kinetic model is, therefore, an approximation of the true (and more complex) mechanism of transformation. The fact that the mechanism changes during the conversion process explains the number of different mechanisms and values of the kinetic parameters reported in [1–3]. It should be stressed that, even though no physical significance can be derived from the approximations used to model the kinetics of recrystallisation, the application of these approximations to the prediction of the rate of recrystallisation extrapolated to low temperature, or at elevated temperature, is not invalidated as has been demonstrated by the good correlation between prediction and experience reported in [1–3].

Conclusions

The use of the single step approximation in the modelling of the kinetics of recrystallisation of β- from α-NiS using nonisothermal methods has been demonstrated to be an approximation of the rate of multiple, but unspecified, mechanistic processes that are occurring during the transformation. Mechanistic inference should, therefore, be avoided. The use of this approximation is, however, important in the prediction of the rate of transformation extrapolated to temperatures outside the region of study, especially as accelerated testing allows the rapid characterisation of the kinetics of the transformation.

References

1 D. W. Bishop, P. S. Thomas, A. S. Ray and P. Šimon, J. Therm. Anal. Cal., 64 (2001) 201.
2 A. Kasper, F. Bordeaux and L. Duffrene, Glasstech. Ber. Glass Sci. Technol., 73 (2000) 130.
3 P. Šimon, P. S. Thomas, J. Okuliar and A. S. Ray, J. Therm. Anal. Cal.,72 (2003) 867.
4 P. Šimon, J. Therm. Anal. Cal., 76 (2004) 123.
5 J. H. Flynn, Thermochim. Acta, 300 (1997) 83.
6 A. K. Galwey, Thermochim. Acta, 397 (2003) 249.
7 T. Ozawa, Bull. Chem. Soc. Japan, 57 (1984) 639.
8 P. S. Thomas, P. Šimon and A. S. Ray, J. Therm. Anal. Cal., 72 (2003) 801.