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# TWO-STAGE KINETIC MODEL FOR THE α–β PHASE RECRYSTALLISATION IN NICKEL SULPHIDE

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## Abstract

Toughened glass panels used as a glazing material in multistorey buildings are known to fracture prematurely when they contain nickel sulfide inclusions as a result of the α–β phase recrystallisation in nickel sulfide. The kinetics of this recrystallisation were studied by differential scanning calorimetry (DSC) under isothermal and non-isothermal conditions. The recrystallisation was observed to be a two-step process with an induction period followed by the phase change. A two-stage kinetic model was used to estimate the recrystallisation time under ambient conditions. These values were found to correlate well with the observed time to failure for glass panels installed in multistorey buildings.

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

## Introduction

Stoichiometric nickel sulfide (NiS) is known to cause the failure of thermally toughened glass [1–4]. The failure mechanism has been related to the recrystallisation, at ambient temperatures, of the metastable high temperature α form to the thermodynamically stable low temperature β form. The α form is observed to exist at ambient temperatures due to the high cooling rates used during the toughening process. The recrystallisation to the β form occurs over time and is accompanied by a significant volume increase (4%) inducing stresses in the glass which can cause the catastrophic failure of the glass panels [2].

Panels have been observed to fail from approximately 6 months to 2 years after installation [1]. The incidence of failure was found to be dependent on the position of the glass panels. For instance, panels with a higher degree of exposure to the sun were observed to fail at a greater rate. The process of recrystallisation induced failure of glass panels is therefore likely to be a thermally activated phenomenon. A preliminary investigation into the kinetics of the recrystallisation was carried out applying

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first order kinetics to the recrystallisation step [5]. This methodology produced a value for the pre-exponential factor, $A$, of $6 \cdot 10^4$ $s^{-1}$ and a value of the activation energy of 62 kJ $mol^{-1}$. The current paper proposes to further investigate the kinetics of recrystallisation. The model is based on a two-step process for the recrystallisation where the first step of the process is an induction period and is followed by the second step of recrystallisation, the latter is assumed not to occur until the conclusion of the induction period. The two steps are therefore investigated separately. The nature of the induction period is investigated using both isothermal and non-isothermal techniques and the recrystallisation step is investigated using the Avrami model for recrystallisation [6]. Both steps are investigated using differential scanning calorimetry (DSC).

## Experimental

The material used was high purity nickel(II) sulfide powder (99.95%, 100 μm particle size) supplied by Johnson Mathey GmbH and was confirmed to be Millerite, β-NiS by X-ray analysis using a Siemens D5000 diffractometer with $CuK_\alpha$ radiation.

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 air quenching using compressed air to rapidly cool the DSC furnace. The cooling rates were measured to be approximately 100°C $min^{-1}$ between 450 and 200°C for samples of NiS which were measured to be 10.0±0.2 mg in mass enclosed in aluminium crucibles of mass 26.1±0.2 mg. Samples of α-NiS prepared in this manner were confirmed to be as such from their X-ray diffraction patterns. No measurable conversion to the β-form was observed. X-ray measurements were carried out on samples of both α and β-NiS prepared in the DSC in open aluminium pans by heating to 450°C in a nitrogen atmosphere followed by either air quenching or slow cooling at 5°C $min^{-1}$ to room temperature. These samples were confirmed to be stoichiometric α- and β-NiS, respectively. In a previous paper [5] the X-ray measurements were carried out under vacuum in a temperature stage fitted to the diffractometer. It is believed that the vacuum induced the decomposition of the NiS to $Ni_7S_6$ through the volatilisation of sulfur. In this study, the DSC experiments were carried out in a nitrogen atmosphere at atmospheric pressure. Under these conditions the decomposition is inhibited.

The DSC measurements were made using a TA Instruments 2930 calorimeter. Samples of NiS were enclosed in aluminium pans and placed in the sample compartment 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 non-isothermal measurements, the heating rates used were 20, 15, 10, 5, 2, 1 and 0.5°C $min^{-1}$. For each heating rate a separate calibration curve was determined using indium as the standard. The isothermal measurements were carried out at 120, 125, 130, 135, 140, 145 and 150°C. The isothermal recrystallisation temperature was reached by heating samples of α-NiS at a rate of 25°C $min^{-1}$ from room temperature.

# Results and discussion

## *Induction period*

The isothermal DSC curves for the recrystallisation of α- to β-NiS are shown in Fig. 1. The induction periods for isothermal recrystallisation were measured from these curves at the inflection and are listed in Table 1. The induction period shows a strong temperature dependence which can be expressed in an exponential form [7]:

$$t_{\mathrm{i}}=A\exp\left(\frac{B}{T}\right) \qquad (1)$$

where $t_{\mathrm{i}}$ is the induction time, $A$ and $B$ are constants and $T$ is the absolute temperature. The exponential dependence of the induction period on the inverse of temperature is shown in Fig. 2 and is observed to conform to the relationship given in Eq. (1). The parameters $A$ and $B$, obtained from the treatment of the data using Eq. (1), are listed in Table 2.

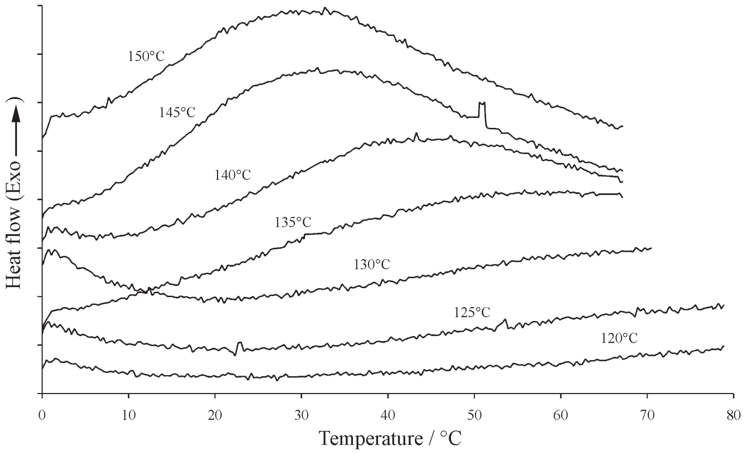

**Fig. 1** Isothermal DSC curves of the α–β recrystallisation in NiS

**Table 1** Induction periods obtained from DSC measurements at various temperatures for isothermal α–β recrystallisation

| Temperature/°C | Induction period/min |
|---|---|
| 120 | 71 |
| 125 | 52 |
| 130 | 40 |
| 135 | 29 |
| 140 | 24 |
| 145 | 17 |
| 150 | 14 |

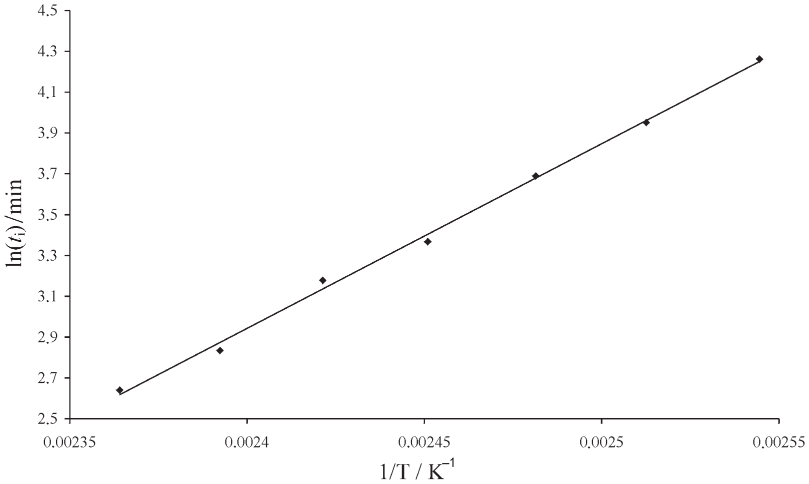

**Fig. 2** Plot of ln($t_i$) on $1/T$ for the induction periods measured from the isothermal DSC data shown in Fig. 1

**Table 2** Values of the kinetic parameters $A$ and $B$ obtained by isothermal and non-isothermal DSC measurements for the induction period

| Method | $10^8 \cdot A$/min$^{-1}$ | $10^{-3} \cdot B$/K |
|---|---|---|
| Isothermal | 0.70 | 9.05 |
| Non-isothermal | 2.28 | 8.56 |

The induction period may also be determined from the measurement of the onset temperature in the non-isothermal DSC data shown in Fig. 3. The onset temperatures were measured by extrapolation of the tangent of the first inflection of the recrystallisation peak to the baseline and are listed in Table 3. The dependence of the onset temperature on the heating rate is shown in Fig. 4. Although the onset temperature is indicative of the induction period, the induction period is a function of temperature (Eq. (1)). Therefore, the measurement of the induction period from the non-isothermal data must take this temperature dependence into account. If the induction period is assumed to conform to [8]:

$$I=\int_0^{t_i}\frac{\partial t}{t_i(T)} \tag{2}$$

where the dependence of $t_i$ on temperature is given by Eq. (1) and the linear increase of furnace temperature can be expressed as:

$$T_f=T_0+\beta t \tag{3}$$

where $T_f$ is the furnace temperature, $T_0$ the starting temperature of the measurement and β is the heating rate and, given that the temperature of the sample equals that of the furnace, the combination of Eqs (1)–(3) gives the result:

$$\beta = \int_{T_0}^{T_i} \frac{\mathrm{d}T}{A\exp\left(\frac{B}{T}\right)} \tag{4}$$

where $T_i$ is the temperature at the end of induction period and is assumed to be equal to the onset temperature of the recrystallisation peak. From this expression the values of the parameters $A$ and $B$ can be obtained. The solution to Eq. (4) was determined by using the trapezium method to solve the integration. The values of $A$ and $B$ were then determined by minimising the sum of the squares between experimental and theoretical values of $T_i$ for each heating rate using the simplex method [9]. The values of $A$ and $B$ obtained by this treatment are given in Table 2.

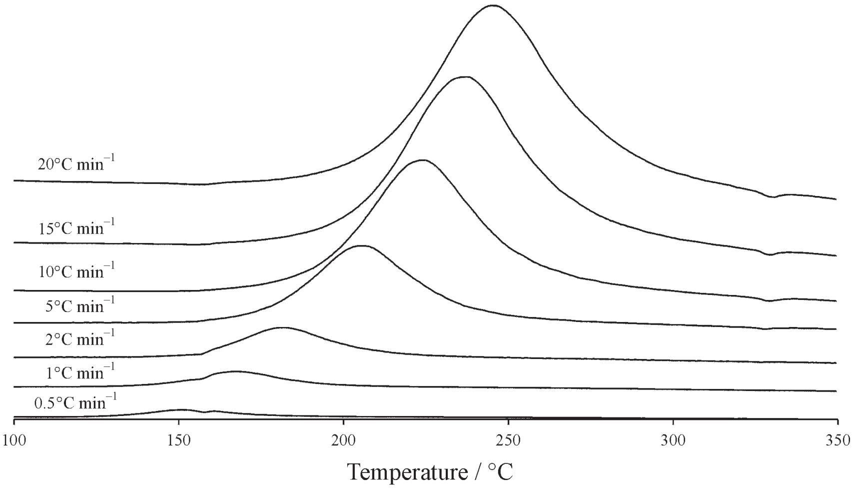

**Fig. 3** Non-isothermal DSC curves for the α–β recrystallisation in NiS

**Table 3** Onset temperatures for the α–β recrystallisation measured from non-isothermal heat flow curves

| Heating rate/°C min$^{-1}$ | Temperature/°C |
|---|---|
| 0.5 | 131 |
| 1 | 145 |
| 2 | 156 |
| 5 | 177 |
| 10 | 191 |
| 15 | 202 |
| 20 | 207 |

The experimentally measured isothermal induction times are plotted in Fig. 5 and are fitted to Eq. (1) using values of $A$ and $B$ derived from both the isothermal and

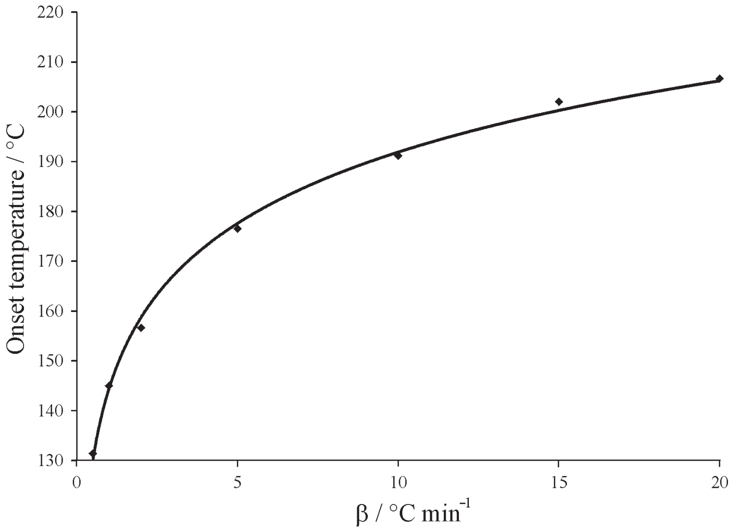

**Fig. 4** The dependence of the onset temperature for the α–β recrystallisation on the heating rate

non-isothermal measurements. The values of *A* and *B* determined from the non-isothermal treatment produces values which correlate with the isotherm measurements. This is a useful result as the onset temperature can be measured with greater precision than onset time.

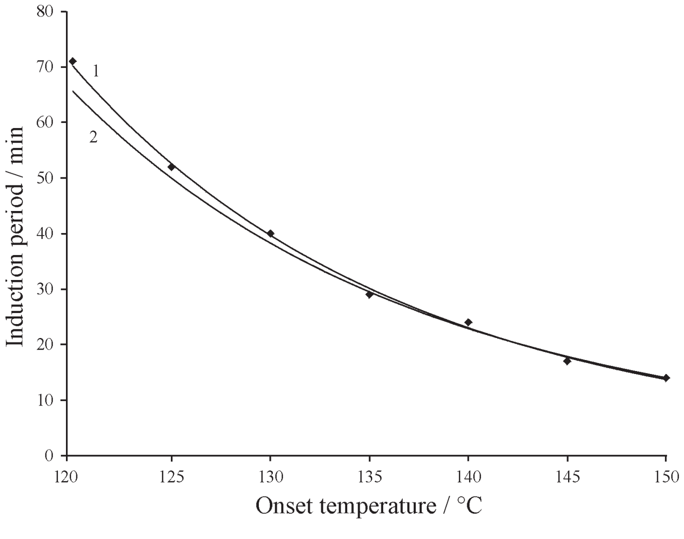

**Fig. 5** Plot of the induction period as a function of the temperature for the isothermal recrystallisation. Also drawn are the curves of Eq. (1) using the values of the constants for *A* and *B* listed in Table 2 derived from isothermal (1) and non-isothermal measurements (2)

From the model relating the induction period to the ambient temperature, it is possible to determine the length of the induction period for the climatic conditions in metropolitan areas where panels have been observed to fail. Archival data for the ambient temperature measured over the span of a year has been obtained for Sydney and Melbourne metropolitan areas. The induction periods for selected years are listed in Table 4. The magnitudes of the calculated induction periods correspond with the data reported by Ballantyne for the failure of panels in Melbourne where panels were observed to fail from 150 to 900 days after installation [1].

**Table 4** Table of the induction periods and recrystallisation times calculated using temperature data for the Sydney and Melbourne metropolitan areas. The induction periods were calculated from Eq. (1) using the values of $A$ and $B$ listed in Table 2. The recrystallisation times were determined from Eq. (6) using the temperature dependence defined by Eq. (7)

| Place | Date | Induction period in days | | Transformation in days for 90% conversion |
|---|---|---|---|---|
| | | isothermal | non-isothermal | |
| Sydney | 1996 | 193 | 114 | 13 |
| | 1958 | 185 | 110 | 13 |
| Melbourne | 1996 | 265 | 154 | 15 |
| | 1958 | 290 | 168 | 15 |

## *The phase change*

On the completion of the induction period the recrystallisation of α- to β-NiS occurs. The recrystallisation step is a crystallisation process and may therefore be modelled using the Avrami equation [6] such that the degree of conversion, α, varies according to:

$$\alpha=1-\exp[-kt^{n}] \qquad (5)$$

where $k$ is the rate constant, $t$ is the time after termination of the induction period and $n$ is an exponent. The value of the exponent, $n$, is a function of the geometry of the growth process and is indicative of the mechanism of growth. If the rate constant is assumed to have an Arrhenius temperature dependence, differentiation of Eq. (5) with respect to temperature gives:

$$\frac{\partial\alpha}{\partial T}=\frac{A_{\mathrm{k}}}{\beta}\exp\left[-\frac{E}{RT}\right]n(1-\alpha)\,t^{\,(n-1)} \qquad (6)$$

where $A_{\mathrm{k}}$ is the pre-exponential factor, $E$ is the activation energy, $R$ is the gas constant and β is the heating rate as defined by Eq. (3). The non-isothermal DSC data for the recrystallisation step was modelled using the Eq. (5). The value of $\partial\alpha/\partial t$ was determined directly from the DSC curve as the ratio of the magnitude of the heat flow to the area of the recrystallisation peak. The value of α, normalised between zero and one, was determined by integrating the recrystallisation peak.

In order to determine the values of $A_k$, $n$ and $E$, Eq. (5) was fitted to the non-isothermal DSC data for the heating rates between 0.5 and 5°C $\text{min}^{-1}$ (Fig. 3). A non-linear least squares method was used to fit the data where the sum of the squares were minimised using the simplex method [9]. As the kinetics of the transformation are dependent on the knowledge of the onset temperature, $T_i$, the parameter $T_i$ was also allowed to vary. The values of these parameters are listed in Table 5 (data set A). The values of $n$ for the data set A are observed to be very close to a value of $n=2$. Data set B in Table 5 was determined using a fixed value of $n=2$. Fixing the value at $n=2$ produced little change in the magnitudes of the standard deviations and therefore negligible change in the quality of the fit. The value of the activation energy was also observed to be consistent for all the heating rates fitted. As this value is approximately zero, the value of $E/R=0$ was used to determine data set C. The values determined under the conditions of set C were observed to be identical with those of set B confirming, within experimental error, the values; $n=2$ and $E/R=0$.

**Table 5** Parameters of Eq. (5) obtained using a non-linear least-squares fit. Set A are the results for the best fit when all the parameters were allowed to vary. For set B, $A_k$, $E/R$ and $T_i$ were determined for $n=2$. For set C $A_k$ and $T_i$ were determined for $n=2$ and $E/R=0$. σ is the standard deviation of the residual difference between the experimental and the calculated values

| Set | $\beta$/K $\text{min}^{-1}$ | $A_k/\text{min}^{-1}$ | $E/R$/K | $n$ | $T_i$/°C | $10^2\cdot\sigma$ |
|---|---|---|---|---|---|---|
| A | 0.5 | $1.92\cdot10^{-3}$ | $3.77\cdot10^{-4}$ | 1.53 | 131.5 | 1.58 |
|  | 1 | $7.62\cdot10^{-4}$ | $6.34\cdot10^{-2}$ | 2.05 | 141.4 | 1.48 |
|  | 2 | $3.36\cdot10^{-3}$ | $4.48\cdot10^{-5}$ | 1.98 | 154.1 | 1.27 |
|  | 5 | $1.83\cdot10^{-2}$ | $4.32\cdot10^{-5}$ | 1.95 | 172.6 | 1.37 |
| B | 0.5 | $1.87\cdot10^{-4}$ | $6.18\cdot10^{-4}$ | 2 | 125.0 | 1.83 |
|  | 1 | $9.53\cdot10^{-4}$ | $9.31\cdot10^{-4}$ | 2 | 141.7 | 1.48 |
|  | 2 | $3.17\cdot10^{-3}$ | $1.42\cdot10^{-3}$ | 2 | 153.9 | 1.27 |
|  | 5 | $1.58\cdot10^{-2}$ | $2.92\cdot10^{-4}$ | 2 | 171.9 | 1.38 |
| C | 0.5 | $1.87\cdot10^{-4}$ | 0 | 2 | 125.0 | 1.83 |
|  | 1 | $9.53\cdot10^{-4}$ | 0 | 2 | 141.7 | 1.48 |
|  | 2 | $3.17\cdot10^{-3}$ | 0 | 2 | 153.9 | 1.27 |
|  | 5 | $1.58\cdot10^{-2}$ | 0 | 2 | 171.9 | 1.38 |

A value of two for $n$ indicates a two-dimensional growth mechanism. As the recrystallisation is from a hexagonal crystal structure of the α-NiS to the rhombohedral crystal structure of the β-NiS, the transformation is likely to be based on a process of recrystallisation around the basal plane of the hexagonal structure. The value of the activation energy is observed to be approximately zero for all the data sets listed in Table 5. The zero activation energy indicates that the recrystallisation process is dependent solely on $A_k$. $A_k$, and hence $k$, is observed to increase in value with increasing heating rate and is observed to be an exponential function of $T_i$ (Fig. 6):

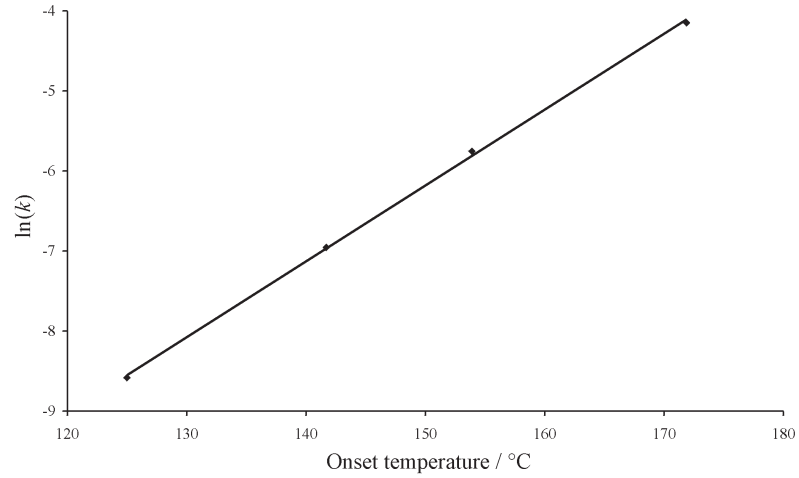

**Fig. 6** The dependence ln($k$) on the onset temperature

$$k \approx A_k = a\exp[bT_i] \qquad (7)$$

where the values of the constants $a$ and $b$ are $1.4\cdot10^{-9}$ $\mathrm{min}^{-1}$ and 0.09 $(°\mathrm{C})^{-1}$, respectively. If this relationship is extrapolated to a value of $T_i$ at ambient temperatures, the time for transformation may be estimated for panels installed in metropolitan environments. Values of the recrystallisation time were estimated using temperature data for Sydney and Melbourne for a 90% conversion and are included in Table 4. Given that such a degree of conversion is required for failure, the conversion time of the order of 15 days corresponds to 5–10% of the total time for recrystallisation.

## Conclusions

The two stage recrystallisation model of an induction period followed by a recrystallisation step has been successfully used to fit the DSC data for the recrystallisation of α- to β-NiS. The times for recrystallisation using this model have been calculated to be of the order of 120 to 300 days. These values correlate well with the times observed (150 to 900 days) for the failure of installed panels, further implicating the α–β recrystallisation as a mechanism for the premature failure of toughened glass panels.

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