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Failure of Kissinger(-like) methods for determination of the activation energy of phase transformations in the vicinity of the equilibrium phase-transformation temperature

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Abstract The activation energies of heterogeneous equilibrium phase transformations have been frequently determined by Kissinger(-like) analysis. This work demonstrates that the applicability of Kissinger(-like) method(s) to determine activation energies of heterogeneous phase transformations is justified if the phase transformation occurs far away from the equilibrium phase-transformation temperature but not if the phase transformation is investigated in the vicinity of the equilibrium phase-transformation temperature. Experimental results on the kinetics of the order–disorder transformation in Ni_3Sn_2, obtained both near the equilibrium phase-transformation temperature and considerably below it (using quenched samples), expose the non-validity and confirm the validity, respectively, of activation-energy values obtained by Kissinger(-like) analyses applied in the corresponding temperature ranges. Application of the Kissinger(-like) analysis in a temperature range close to the equilibrium phase-transformation temperature leads to erroneous, abnormally high values for the activation energy.

Introduction

Nowadays, the so-called Kissinger method [1, 2] (and its derivatives; see a listing of these in Ref. [3]) is used extremely often to obtain values of (effective) activation energies of thermally activated reactions/transformations. For example the number of references to just the original works by Kissinger [1, 2], in the years 2006, 2007, 2008 and 2009 amounts to 290, 352, 409 and 418, respectively.

The method, as originally proposed, is based on the analysis of the maximum reaction/transformation rate as a function of (constant) heating rate (isochronal anneals). It was originally developed, using *n*th-order reaction kinetics ($n = 0, 1, 2\ldots$), for homogeneous reactions (as occurring in liquids or gases) [1, 2]. Later it was shown [4] that a Kissinger-like method is also possible for heterogeneous (solid state) reactions/transformations. Usually one is not aware of this distinction and applies the Kissinger method to heterogeneous solid state transformations without recognising that the original Kissinger method cannot be applied without more ado to these cases. In the following we will therefore speak of Kissinger-like methods.

Kissinger-like methods are, in particular, popular for evaluation of heating-rate-dependent differential thermal analysis (DTA) or differential scanning calorimetry (DSC) data, recorded for tracing, e.g. precipitation reactions [5–7] and crystallization of metallic glasses [8–11].

Occasionally, the Kissinger-like method has been used to determine activation energies of equilibrium phase transformations $\alpha \rightleftarrows \beta$ occurring at the equilibrium phase-transformation temperature T_e, with α being stable below and β above T_e, (i.e. at T_e both phases constitute a two-phase equilibrium). Strikingly, such kinetic analyses led to abnormally high values for the activation energy that appear to have no physical meaning [12–14]: For example, thus determined "activation-energy" values of 8500, 1765, 1860 and 963 kJ/mol were reported for an equilibrium phase transformation (i.e. occurring in the vicinity of T_e) between two polymorphs of $Ba_2In_2O_5$ [12], of potassium nitrate (α-$KNO_3 = \alpha \rightarrow \beta$-$KNO_3 = \beta$) [13], for hexamethylbenzene

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(triclinic = $\alpha \rightarrow$ orthorhombic = β) [13], and for the melting of ice (H_2O (solid) = $\alpha \rightarrow H_2O$ (liquid) = β) [14], respectively.

It has been demonstrated previously that analysis of the kinetics of precipitation reactions just below the solvus line, while adopting Arrhenius-type temperature dependence of the reaction rate, may give negative values for the activation energy [15]. Further, if the equilibrium state of a precipitation reaction depends pronouncedly on temperature, activation energies evaluated using Kissinger-like methods, are systematically affected [16]. The origin of such problems was ascribed to a more or less strong variation of the thermodynamic driving force within the temperature range investigated [16].

The purpose of the present paper is to demonstrate how a strongly temperature-dependent driving force near an equilibrium phase-transformation temperature T_e affects the kinetics of different sub-steps (e.g. nucleation and growth) of a solid-state phase transformation. This influence of the driving force leads to non-validity of an Arrhenius-type temperature dependence of the sub-steps and thus also of the overall transformation rate, which is one of the cardinal assumption(s) made in the derivation of the Kissinger-like method and its variants, and leads to the above-mentioned unphysical activation-energy values. The discussion is presented by a consideration of the application of the Kissinger-like analysis to DSC data of the well-known order–disorder transformation LT → HT and HT → LT (LT = low-temperature phase, α; HT = high-temperature phase, β) of Ni_3Sn_2 ($Ni_{1.50}Sn$) [17, 18], in the vicinity of the equilibrium phase-transformation temperature $T_e \approx$ 750–780 K [19, 20] ($T_e \approx 780$ K will be used in the following [20]) and considerably below it. It will be demonstrated that application of the Kissinger-like method(s) is only permitted in the second case.

Theoretical background

Kissinger-like method

The progress of a phase transformation[1] can be determined by measuring a macroscopic physical property of the transforming material (as length, hardness, resistivity, etc.). From such measurements the degree of transformation f can be calculated ($0 \leq f \leq 1$) as function of the temperature–time program ($T = T(t)$), to which the sample is subjected. The transformed fraction f of the sample is determined by the thermal history of the sample, i.e. for non-isothermal analysis t and T are not state variables for the degree of transformation f. Then, for isokinetic transformations (i.e. transformations following the same mechanism in the time–temperature window investigated) the transformation rate $\mathrm{d}f/\mathrm{d}t$ can be written as a product [4, 21–23]:

$$\frac{\mathrm{d}f}{\mathrm{d}t} = g(f)k(T), \tag{1}$$

where $g(f)$ is a purely fraction-transformed f-dependent function and $k(T)$ is a purely temperature T-dependent function, which is commonly referred to as the rate constant.[2] For the rate constant an Arrhenius-type temperature dependence is adopted:

$$k(T) = k_0 \exp\left(-\frac{Q}{RT}\right), \tag{2}$$

with Q as the activation energy, R as the gas constant and k_0 as the pre-exponential factor.

On this basis it has been shown in Ref. [4] that, independent of the nature of the transformation being homogeneous or heterogeneous, the temperature $T_{f'}$ corresponding to a fixed stage of transformation f' depends systematically on the heating rate $\Phi = \mathrm{d}T/\mathrm{d}t$ and it follows:

$$-\ln\frac{\phi}{T_{f'}^2} = -c + \frac{Q}{RT_{f'}} \tag{3}$$

with c as a constant. This implies that from the values of the temperatures $T_{f'}$, determined for a number of constant heating rates Φ, a value for the activation energy can be obtained from the slope of the straight line fitted to the experimental data in a plot of $-\ln\frac{\phi}{T_{f'}^2}$ vs. $\frac{1}{RT_{f'}}$ (cf. Eq. 3).

It has also been shown in Ref. [4] that the temperature of maximal transformation rate, T_M always occurs at *about* the same value of f. Thus, the temperature T_f in Eq. 3 can be replaced by the temperature of maximum transformation/reaction rate T_M (e.g. for DSC measurements the temperature of maximum transformation/reaction rate is given by the peak temperature). This last much more restricted form of Eq. 3 (i.e. with T_M instead of $T_{f'}$) is the original equation as derived by Kissinger [1, 2] for simple "nth-order reaction kinetics" occurring for homogeneous transformations. Hence, as long as the assumption of an Arrhenius-type temperature dependence for $k(T)$ is justified, a replacement of $T_{f'}$ by T_M is justified, for both homogeneous and heterogeneous transformations.

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[1] Here the phase transformation $\alpha \rightarrow \beta$ is focus of the attention. However, the considerations of "Kissinger-like method" section also pertain to other transformations, e.g. of the type $\alpha \rightarrow \beta + \gamma$, as long as start state and end state are identical for the range of temperatures for which the Arrhenius-type temperature dependence of the reaction rate (cf. Eq. 2) is adopted.

[2] Note that without recourse to a specific rate law in practice explicit values for k are not determinable because g/A together with kA, with A being a f- and T-independent constant, gives the same transformation rate.

The derivation of the Kissinger(-like) equation (Eq. 3) relies on the assumed Arrhenius-type temperature dependence for the rate constant (cf. Eq. 2). Then, for (solid state) heterogeneous transformations, governed by separate nucleation and growth (and impingement) modes, the assumption of an Arrhenius-type temperature dependence for $k(T)$ (see Eq. 2) requires that the temperature-dependent sub-steps of the transformations, as nucleation and growth modes, are thermally activated according to an Arrhenius-type relationship. This needs not generally be the case, which is discussed next.

Nucleation

The classical theory of nucleation provides the following general expression for the nucleation rate per unit volume $\dot{N}(T(t))$ [24, 25]:

$$\dot{N}(T(t)) = C\omega \exp\left(-\frac{\Delta G^{*}(T(t)) + Q'_{\mathrm{G}}}{RT(t)}\right), \tag{4}$$

with C as the density of potential sites for nucleation, ω is a function that depends on the vibration frequency of the atoms [24, 25], Q'_{G} as the activation energy for atoms jumping through the interface and $\Delta G^{*}(T(t))$ as the critical Gibbs energy for nucleus formation (= formation of a particle of critical size).

Evidently, $\dot{N}(T(t))$ as given by Eq. 4 does not obey an Arrhenius-type temperature dependence. However, with increasing overheating or undercooling $\Delta G^{*}(T(t))$ decreases (e.g. for spherical nuclei $\Delta G^{*}(T(t))$ is approximately proportional to $\frac{1}{\Delta T^2}$ [26]) and becomes small as compared to RT. Then Equation 4 reduces to:

$$\dot{N}(T(t)) = N_0 \exp\left(-\frac{Q_{\mathrm{N}}}{RT(t)}\right), \tag{5}$$

where N_0 denotes the temperature-independent nucleation rate which contains $C\omega$. In this case the nucleation rate exhibits an Arrhenius-type temperature dependence with Q_{N} as the activation energy for nucleation with $Q_{\mathrm{N}} = Q'_{\mathrm{G}}$.

Kinetics of growth

Two extreme cases of growth kinetics can be considered: Diffusion-controlled and interface-controlled growth [24, 25]. If long-range compositional changes are necessary for the phase transformation, diffusion plays a role, but needs not be dominating. Atomic-jump processes in the direct vicinity of (across) the interface may generally effect the growth rate and they dominate the growth rate (interface control) if the compositions of the parent phase and (the single) product phase are equal.

Interface-controlled growth

The growth velocity v in the case of interface-controlled growth is in general given by [24, 25]:

$$v(T(t)) = v_0 \exp\left(-\frac{Q_{\mathrm{G}}}{RT(t)}\right)\left(1 - \exp\left(\frac{\Delta G}{RT(t)}\right)\right), \tag{6}$$

with v_0 as a pre-exponential factor, Q_{G} as the activation energy of growth and ΔG (= $G_{\mathrm{end}} - G_{\mathrm{begin}}$) as the Gibbs energy difference between the new phase and the parent phase. Thus, ΔG is negative for a spontaneously occurring transformation. Evidently, $v(T(t))$ as given by Eq. 6 does not obey an Arrhenius-type temperature dependence. However, for large undercooling or overheating the absolute value of ΔG is large as compared to RT. Then Eq. 6 reduces to:

$$v(T(t)) = v_0 \exp\left(-\frac{Q_{\mathrm{G}}}{RT(t)}\right). \tag{7}$$

In this case the growth velocity exhibits an Arrhenius-type temperature dependence.

In the vicinity of the equilibrium phase-transformation temperature T_{e} (i.e. for small undercooling or overheating) the driving force $|\Delta G|$ is small as compared to RT and Eq. 6 becomes

$$v(T(t)) = M_0 \exp\left(-\frac{Q_{\mathrm{G}}}{RT(t)}\right)(-\Delta G(T(t))), \tag{8}$$

with the mobility $M_0 = v_0/RT$.

Diffusion-controlled growth

Also for the case of "diffusion-controlled" growth a simple Arrhenius-type temperature dependence of the growth velocity does not generally hold, as can be demonstrated for precipitate-phase growth near the equilibrium phase-transformation temperature T_{e}, as follows.

The growth velocity v of a precipitate $\beta(X_\beta)$ (with X_β as the molar fraction of solute in the precipitate precipitating from the supersaturated solid solution $\alpha(X_0)$ (X_0 = (initial) molar fraction of solute in the bulk) according to

$$\alpha(X_0) \rightarrow \alpha'(X_{\mathrm{e}}) + \beta(X_\beta), \tag{9}$$

where X_{e} is the molar fraction of solute in the matrix adjacent to the $\beta(X_\beta)$-precipitate which can be taken equal to the equilibrium value [26], can be given according to a simplified approach [27], for isothermal growth as:

$$v(T,t) = \frac{\Delta X_0}{2(X_\beta - X_e)}\sqrt{\frac{D}{t}}. \tag{10}$$

where $\Delta X_0 = X_0 - X_{\mathrm{e}}$ denotes the "supersaturation" before the precipitation starts and D represents the diffusion coefficient obeying an Arrhenius-type temperature dependence. X_e and X_β depend on temperature and X_0 depends on time. Evidently, $v(T,t)$ as given by Eq. 10 does not obey an Arrhenius-type temperature dependence. At large undercooling the growth velocity is low since the diffusion is slow; i.e. then the growth velocity is dominated by the diffusion process (i.e. truly diffusion controlled) and obeys an Arrhenius-type temperature dependence. At small undercooling, i.e. in the vicinity of the equilibrium phase-transformation temperature T_e (near the solvus line), the growth velocity is low since the supersaturation ΔX_0 is small, i.e. then the temperature dependence of the growth velocity can be governed by the temperature dependence of the solvus lines (for α and β) in the phase diagram. Similar considerations can be applied to the case of ("diffusion controlled") dissolution [28].

Effective nature of the activation energy

Kissinger-like methods yield values for *effective* activation energies for (solid state) heterogeneous transformations. These effective activation energies can be conceived as some (see below) combination of the separate activation energies for nucleation, Q_N, and growth, Q_G, provided that the nucleation and growth modes comply with Arrhenius-type temperature dependencies. Then, for a range of nucleation and growth modes, the effective activation energy Q is given by [24]:

$$Q = \frac{(d/m)Q_G + (n - d/m)Q_N}{n} \tag{11}$$

where d is the dimensionality of growth and m is the growth mode parameter [24] ($m = 1$ for interface-controlled growth; $m = 2$ for diffusion-controlled growth), where the growth exponent n depends on temperature and time (and thus on the transformed fraction f; especially, if n is constant it has also been called the Avrami coefficient [25]), and where the activation energies Q_N and Q_G are genuine constants. Hence, the effective activation energy depends on time (and thus on f) even if iso-kinetics holds. Even recognising that Q is not constant during a phase transformation, Kissinger-like methods can be proposed which allow straightforward determination of kinetic parameters like the growth exponent n, the activation energy for nucleation Q_N and the activation energy for growth Q_G [24, 29].

Experimental

Specimen preparation

A Ni_3Sn_2 rod (40 at.% Sn, "$Ni_{1.50}Sn$") was prepared by induction heating of high purity Ni sheets (99.98 wt%, Goodfellow) and Sn bars (99.999 wt%, Heraeus) and subsequent casting into a water-cooled copper mould. The alloy was homogenised at 1023 K. Upon water quenching from this temperature the hexagonal high-temperature phase HT-$Ni_{1.50}Sn$ can be preserved. Upon subsequent annealing at 673 K for 120 h the orthorhombic low-temperature phase LT-$Ni_{1.50}Sn$ is produced (for details concerning alloy preparation and heat treatment see [30, 31]). Both modifications differ by the ordering of one type of Ni atoms in the crystal structure [31]: Whereas these Ni atoms are disordered (i.e. do not show long-range ordering) in the HT phase, they are long-range ordered in the LT phase. The equilibrium phase-transformation temperature of the LT ⇆ HT first-order transformation is $T_e \approx 780$ K.

Differential scanning calorimetry measurements

DSC measurements were performed using a Pyris 1 apparatus (Perkin Elmer). The measurements were performed under a protective argon atmosphere (99.99%; flow rate 30 ml/min). The DSC apparatus was calibrated with respect to temperature and heat flow by measuring the heats of fusion and the melting temperatures of pure In, Pb and Zn. For the DSC measurements the Ni_3Sn_2 rod was crushed into small pieces. For both the sample pan and the reference pan aluminium pans were used. The sample pan was filled with pieces of the crushed rod (sample weight: approx. 40–60 mg). Both the sample pan and the reference pan were sealed with an aluminium lid.

Isochronal DSC anneals up to 873 K were preformed with both the LT and the (quenched) HT specimen, allowing investigation of, respectively, the LT → HT transformation close to T_e and the HT → LT transformation in the temperature range of 600 K to 645 K, i.e. considerably below T_e. Four different heating rates (5, 10, 20 and 40 K/min) were applied. The temperatures at the transformation-peak maxima, T_M, were determined for the various heating rates.

Results

The LT → HT phase transformation, near the LT ⇆ HT equilibrium phase-transformation temperature T_e

The isochronal DSC runs of the LT-phase specimens exhibit occurrence of the LT → HT phase transformation in the vicinity of the equilibrium phase-transformation temperature $T_e \approx 780$ K, in association with an endothermic heat effect (see Fig. 1). The values of the heating-rate-dependent peak maxima T_M have been gathered in Table 1.

The corresponding “Kissinger plot” exhibits linear behaviour as prescribed by Eq. 3 (see Fig. 2). From the straight line fitted to the data shown in Fig. 2 an activation-energy value was determined (cf. Eq. 3): $Q_{\mathrm{LT}\rightarrow\mathrm{HT}} = (12600 \pm 800)$ kJ/mol.

From the area of the peaks the enthalpy difference $\Delta H_{\mathrm{LT}\rightarrow\mathrm{HT}}$ between the LT- and the HT-phase was determined. It was found to be heating-rate independent and its value (referring to one formula unit $\mathrm{Ni}_{1.5}\mathrm{Sn}$) is $\Delta H_{\mathrm{LT}\rightarrow\mathrm{HT}} = H_{\mathrm{end}} - H_{\mathrm{begin}} = H_{\mathrm{HT}} - H_{\mathrm{LT}} = (2.2 \pm 0.2)$ kJ/mol.

The HT → LT phase transformation, considerably below the LT ⇆ HT equilibrium phase-transformation temperature T_e

The isochronal DSC runs of the quenched HT-phase specimens show occurrence of the HT → LT phase transformation in the temperature range of 600 to 645 K ($T_e \approx 780$ K), in association with an exothermic heat effect (see Fig. 3).

The peak-maximum temperature T_M shows distinct heating-rate dependence (see Table 2). The corresponding “Kissinger plot” exhibits linear behaviour as prescribed by Eq. 3 (see Fig. 4). From the straight line fitted to the data shown in Fig. 4 an activation-energy value was determined (cf. Eq. 3): $Q_{\mathrm{HT}\rightarrow\mathrm{LT}} = (161 \pm 5)$ kJ/mol.

Table 1 The endothermic peak maxima T_M of the LT → HT equilibrium phase transformation for various heating rates Φ

Heating rate Φ (K/min)	5	10	20	40
Peak maximum[a] T_M (K)	781.40	781.65	781.90	782.25

[a] Note that the evaluation by the Kissinger(-like) method relies (much more) on the variation of T_M with heating rate than on the absolute values of T_M

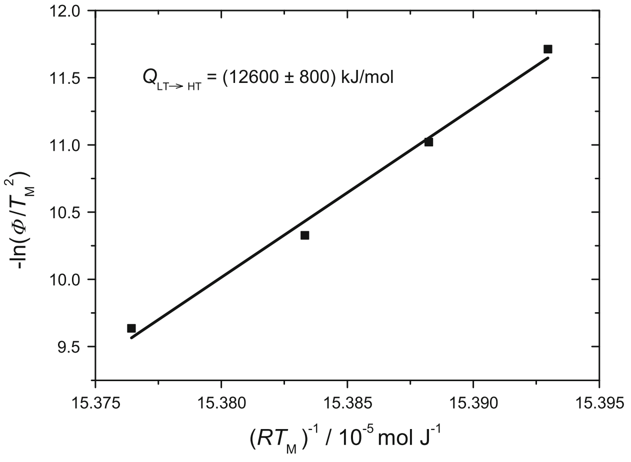

Fig. 2 “Kissinger plot” for the LT → HT transformation (see data in Table 1)

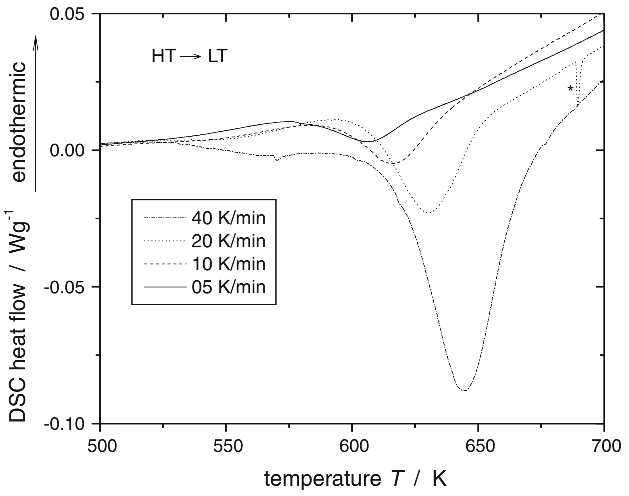

Fig. 3 Isochronal DSC runs showing the HT → LT phase transformation for the heating rates indicated (The *asterisk* indicates a measurement artefact)

Discussion

The value obtained in this work for the activation energy of the HT → LT transformation, 161 kJ/mol (see “The HT → LT phase transformation, considerably below the LT ⇆ HT equilibrium phase-transformation temperature T_e” section), by application of the Kissinger-like method agrees very well with values of 165–170 kJ/mol found for the first stage of the HT → LT transformation as obtained from transformation induced lattice-parameter changes as

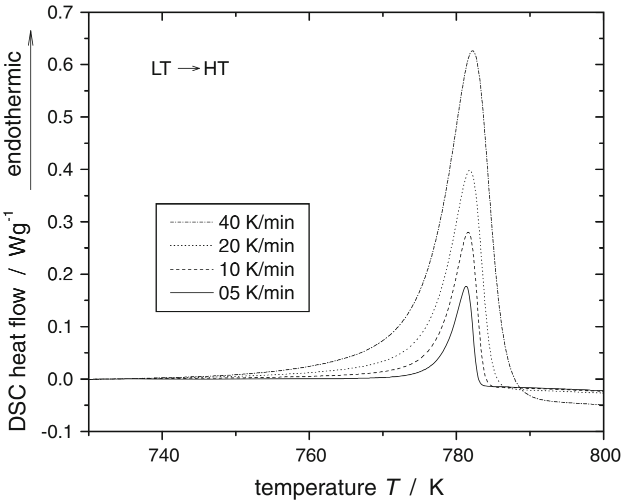

Fig. 1 Isochronal DSC runs showing the LT → HT phase transformation for the heating rates indicated

Table 2 The exothermic peak maxima T_M of the HT → LT phase transformation for various heating rates Φ

Heating rate Φ (K/min)	5	10	20	40
Peak maximum[a] T_M (K)	606.65	617.85	630.75	645.25

[a] Note that the evaluation by the Kissinger(-like) method relies (much more) on the variation of T_M with heating rate than on the absolute values of T_M

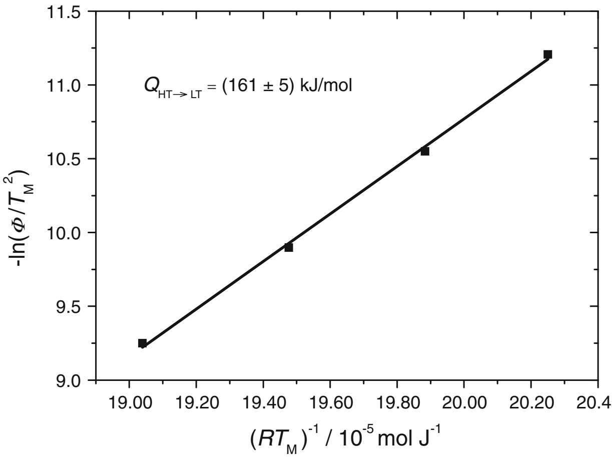

Fig. 4 Kissinger plot for the HT → LT transformation (see data in Table 2)

measured in X-ray powder-diffraction patterns [17, 18].[3] As discussed in Refs. [18] and [32], this first stage of the HT → LT transformation corresponds to spinodal ordering of the Ni atoms whereas in a second stage coarsening of ordered twin domains occurs; the second stage obviously is associated with a relatively minor heat effect. Thus, the DSC signal is predominantly due to the first stage of the HT → LT transformation.

The formation of the stable LT phase from the quenched HT phase (i.e. the ordering of (one type of) the Ni atoms) becomes significant for the applied heating rates at about 600 K (see Fig. 3). This implies that the HT → LT transformation occurs at large undercooling $\Delta T = T_e - T$. This assures Arrhenius-type temperature dependencies for the phase-transformation kinetics as the thermodynamical driving force generally disappears from (becomes negligible in) the rate expressions (e.g. for nucleation and growth processes, see "Theoretical background" section). Hence application of a Kissinger-like analysis is validated.

The value obtained in this work by application of the Kissinger-like method for the activation energy of the LT → HT phase transformation, $Q_{LT\to HT} = 12600$ kJ/mol (see "The LT → HT phase transformation, near the LT ⇆ HT equilibrium phase-transformation temperature T_e" section), is physically unrealistic (i.e. unreasonably high). The activation energy of the LT → HT transformation should be similar to that of the HT → LT transformation, i.e. of the same order of magnitude.

Obviously, at $T < T_e$ the thermodynamic driving force for the LT → HT transformation, $-\Delta G_{LT\to HT} = -(G_{end} - G_{begin}) = -(G_{HT} - G_{LT})$, is negative. The activation energy for a (hypothetical) LT → HT transformation equals the activation energy $Q_{LT\to HT}$ as determined for the HT → LT transformation at $T < T_e$ (cf. "The HT → LT phase transformation, considerably below the LT ⇆ HT equilibrium phase-transformation temperature T_e" section) *plus* $\Delta H_{LT\to HT}$ (cf. "The LT → HT phase transformation, near the LT ⇆ HT equilibrium phase-transformation temperature T_e" section). Thus, the activation energy for the LT → HT transformation should amount $Q_{LT\to HT} = Q_{HT\to LT} + \Delta H_{LT\to HT} \approx 161.0\,\text{kJ/mol} \approx 163.2\,\text{kJ/mol}$, i.e. the activation energies for the LT → HT and the HT → LT transformations are similar indeed.

Upon increasing temperature the driving force for the LT → HT transformation becomes less negative and equals zero at $T = T_e$. At this temperature the LT and HT phases coexist and the transformation LT → HT can occur at $T \geq T_e$ with an activation energy similar to that of the HT → LT transformation at $T < T_e$. Evidently, $-\Delta G_{LT\to HT}$ at T well below T_e is large, whereas $-\Delta G_{LT\to HT}$ above but close to T_e is small.

The above discussion implies that occurrence of Arrhenius-type temperature dependencies for the transformation kinetics are violated for the LT → HT transformation. Hence, in this case application of the Kissinger-like analysis is not allowed.

For the LT → HT transformation growth of the HT domains in the LT matrix will be interface controlled. For small values of $\Delta G_{LT\to HT}$ it holds $\Delta G_{LT\to HT} = \frac{\Delta H_{LT\to HT}}{T_e}(T_e - T)$ (assuming that $\Delta H_{LT\to HT}$ and $\Delta S_{LT\to HT}$ are practically temperature-independent in a (restricted) temperature range around T_e) and it follows from Eq. 8:

$$v = M_0 \exp\left(-\frac{Q_G}{RT(t)}\right)\left(-\frac{\Delta H}{T_e}(T_e - T)\right). \qquad (12)$$

This result indicates a linear increase of v with T for small $T_e - T$ and hence no Arrhenius-type temperature dependence (see Fig. 5). This less distinct, i.e. non-exponential, dependence on temperature for the transformation velocity v also explains the only slight dependence of T_M on Φ (cf. Table 1), which facilitates a (seemingly) successful fitting of a straight line in a Kissinger plot (Fig. 2). This may have misled previous authors and provides an explanation of very unrealistic activation-energy values published in the corresponding papers [12–14].

The experimental data points in Fig. 2 suggest a slight curvature even within the restricted $1/(RT_M)$ range of the

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[3] The XRPD analyses pertain to *isothermal* treatments of the alloys at various temperatures.

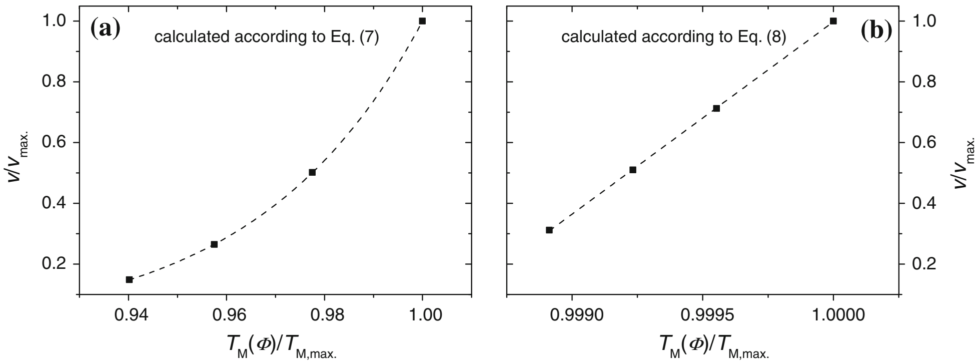

Fig. 5 Comparison of **a** the (normalised) growth velocity according to Eq. 7 and the data of Table 2 (HT → LT phase transformation well below T_e; Arrhenius-type temperature dependence) and **b** the (normalised) growth velocity according to Eqs. 8 or 12 and the data of Table 1 (LT → HT phase transformation close to T_e; linear temperature dependence). For calculation of the growth velocity the value of the activation energy for the phase transformation of Ni_3Sn_2 was adopted according to "The HT → LT phase transformation, considerably below the LT ⇆ HT equilibrium phase-transformation temperature T_e" section and the value of the enthalpy difference ΔH was taken as given in "The LT → HT phase transformation, near the LT ⇆ HT equilibrium phase-transformation temperature T_e" section

experiments. Indeed, exactly linear behaviour of $\ln\left(\phi/T_M^2\right)$ vs. $1/(RT_M)$ for all Φ cannot be expected, since T_e constitutes the minimum transformation temperature for the LT → HT transformation for $\Phi \rightarrow 0$. This implies that in Fig. 2 the curve through the experimental data has to diverge to infinity upon approaching $1/(RT_e)$.

Yet, a quantitative description of the LT → HT phase-transformation kinetics close to T_e is still possible, recognising the role of the (temperature dependent) thermodynamic driving force and using a modular model [24] which includes specific prescriptions for the nucleation, growth and impingement modes. One first such modelling was performed by Kempen et al. [33] and by Liu et al. [34] for the γ (austenite) → α (ferrite) transformation. Such an approach was also possible for the C36 ⇆ C14 phase transformation in the $TiCr_2$ Laves phase [35].

Conclusions

(i) Application of Kissinger(-like) methods to determine the activation energy of phase transformations relies on Arrhenius-type temperature dependences for the transformation kinetics (which, for example, incorporates nucleation and growth rates). This implies that the thermodynamic driving force plays a negligible role in the rate expressions. This is generally only the case for phase transformations taking place in temperature ranges remote from the equilibrium phase-transformation temperature T_e.

(ii) Application of Kissinger(-like) methods to phase transformations occurring close to the equilibrium phase-transformation temperature T_e can lead to (seemingly) linear behaviour in so-called "Kissinger plots" for limited ranges of Φ, in association with slight to moderate dependence of the peak-maximum temperature T_M on heating rate Φ. The values of the "activation energies" thus determined are physically nonsense. On this basis unusual values of "activation energies" thus determined and reported in the literature can be understood.

(iii) The application of the Kissinger(-like) method on DSC data of the polymorphic LT → HT-Ni_3Sn_2 transformation close to the equilibrium transformation temperature yields unreasonably high value for the activation energy. This artefact is a consequence of a strongly temperature-dependent driving force of the transformation in the vicinity of the equilibrium phase-transformation temperature. In contrast to that, using the same material (after quenching from high temperature), the application of the Kissinger(-like) analysis on DSC data of the reverse HT → LT transformation, considerably below the equilibrium transformation temperature, yields a physically reasonable value for the activation energy.

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