Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 605–614

KINETIC ANALYSIS OF THE α-β HgI_2 PHASE TRANSITION

Using isothermal and non-isothermal DSC

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(Recevied May 6, 2002; in revised form June 15, 2002)

Abstract

The kinetics of the α-β phase transition of HgI_2 were investigated by isothermal and non-isothermal differential scanning calorimetry. The effective activation energy of the transition, 415±40 kJ mol^{-1}, was determined applying the methods of Kissinger and Ozawa. The transition kinetics were described by the Johnson–Mehl–Avrami model and the value of the Avrami exponent n was found to range from high values ($n>3$) at the early stages to lower values at later stages of the transformation, with an average value of 2.

Keywords: activation energy, DSC, HgI_2, kinetics, phase transition

Introduction

HgI_2 exists in two modifications, the red α-HgI_2 which belongs to the tetragonal crystallographic system, with space group $P4_2$/nmc, and the yellow β-HgI_2, belonging to the orthorhombic one with space group $Cmc2_1$. Red α-HgI_2 is stable at room temperature, and transforms to the yellow, orthorhombic phase around 130°C with a first order transition [1]. According to Buerger, this is a reconstructive transformation involving change in the first coordination, where the coordination number of Hg changes from 6:3 to 4:2. Such transformations may generally involve high energies of activation and may therefore be sluggish [2].

Although the factors affecting the transition temperature have been studied extensively by means of differential scanning calorimetry (DSC) [3–6], the kinetics of the transition have not been studied yet. In the present work, with a combination of non-isothermal and isothermal calorimetry, the activation energy of the phase transi-

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1418–2874/2002/ $ 5.00
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Kluwer Academic Publishers, Dordrecht

tion is estimated as well as a kinetic model and mechanism of the transformation are proposed.

Experimental

DSC data were obtained by a Setaram DSC 141 device using N_2 atmosphere. The samples were in the form of thin plates with a mass around 20 mg, and were obtained by cleaving from vapor-grown HgI_2 crystals. In non-isothermal scans the phase transition curves were recorded *vs.* temperature, as the temperature of the samples was increased from room temperature to 200°C, with constant heating rate ranging from 1 to 11°C min^{-1}. In isothermal scans, the phase transition curves were recorded *vs.* time, while the temperature was kept constant, a few degrees below the transition temperature (130–132°C), after heating from room temperature at a rate of 2.5°C min^{-1}. The same experiments were repeated several times with different samples making certain the reproducibility of the results.

Results and discussion

Non-isothermal measurements

Figure 1a shows DSC curves of a HgI_2 sample at different heating rates. The α-β phase transition is clearly shown with the endothermic peak above 130°C. The onset temperature of the transition and the temperature at the peak maximum, for the different heating rates are given in Table 1. There is a shift of the transition temperatures with the increase of the heating rate towards higher temperatures. The enthalpy of the transition, calculated from the area below the peak using as baseline a straight line, is also given in Table 1 for each heating rate. The average value is found equal to 2.2±0.10 kJ mol^{-1}.

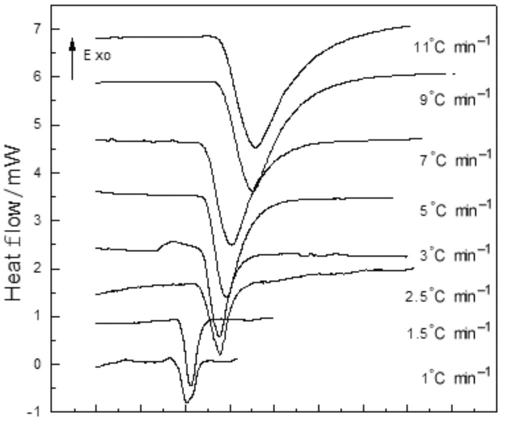

Fig.1a DSC curves of the α-β phase transition of HgI_2 at different heating rates

Table 1 Onset temperature T_{on}, temperature at peak maximum T_p and enthalpy change ΔH of the α-β phase transition of HgI_2 at different heating rates Φ

Φ/°C min^{-1}	T_{on} /°C	T_p /°C	ΔH/kJ mol^{-1}
1.0	134.16	135.23	2.42
1.5	134.53	135.67	2.10
2.5	136.82	138.91	2.36
3.0	137.04	138.87	2.24
5.0	137.47	139.63	2.14
7.0	137.44	140.23	2.17
9.0	139.21	142.61	2.17
11.0	139.19	142.93	2.16

The dependence of the degree of transformation α on temperature is given, for different heating rates, in Fig. 1b. The fraction transformed, α is obtained from the DSC curves as follows: $\alpha_i=\Delta H_i/\Delta H$, where ΔH is the total enthalpy change of the transformation, and ΔH_i is the partial enthalpy change at temperature *i*. The rate of the phase transformation dα/d*t* is expressed as: $d\alpha/dt=(dH/dt)(1/\Delta H)1/m$, where d*H*/d*t* is the DSC signal deviation from the baseline at a given temperature *i*, and *m* is the mass of the sample.

For the analysis of the kinetics of the phase transformation studied, the following differential equation was used [7]:

$$d\alpha/dt=f(\alpha)k(T) \tag{1}$$

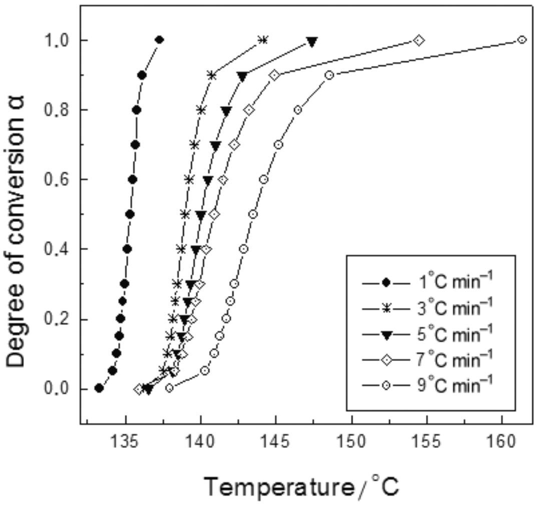

Fig. 1b Degree of transformation α *vs*. temperature for different heating rates

The term $f(\alpha)$ is a mathematical expression of α, corresponding to the kinetic model. The term $k(T)$ is the rate constant, whose temperature dependence is given by the Arrhenius equation:

$$k(T)=A\mathrm{e}^{-E/RT} \tag{2}$$

where A is the pre-exponential factor, E is the activation energy in J mol^{-1} and R is the perfect gases constant (8.31 J mol^{-1} K^{-1}).

Activation energy E was calculated by two methods. The first one is based on the Kissinger equation [8]:

$$\ln(\Phi/T_\mathrm{p}^2)=-E/RT_\mathrm{p}+const. \tag{3}$$

where Φ is the heating rate and T_p is the temperature at the DSC peak maximum.

The second method is proposed by Ozawa [9] and Flynn and Wall [10], who have shown that if different heating rates, Φ, are used, the temperature T_α for a given degree of conversion α obeys the following equation:

$$\ln(\Phi)=-1.05E/RT_\alpha+\ln AE/R-5.33-\ln g(\alpha) \tag{4}$$

For α=const. the plot lnΦ *vs.* $1/T_\alpha$ obtained from measurements at different heating rates Φ, should be a straight line, with a slope equal to $-1.05E/R$.

The Kissinger plot is given in Fig. 2a. In accordance with Kissinger's model, the DSC data are rather well approximated with the linear relationship $\ln(\Phi/T_\mathrm{p}^2)$ *vs.* $1/T_\mathrm{p}$. The activation energy obtained from the slope of the Kissinger plot is equal to 415±40 kJ mol^{-1}.

The Flynn–Wall–Ozawa (FWO) plots, which were made for several degrees of conversion α are shown in Fig. 2b. All plots are linear, and the activation energy calculated is ranging from 430±40 kJ mol^{-1} (for α=0.2) to 300±30 kJ mol^{-1} (for α=0.7). The activation energy estimated by the FWO method for α≈0.3 is about 400±40 kJ mol^{-1}, a value which is very close to that determined by the Kissinger method (415±40 kJ mol^{-1}).

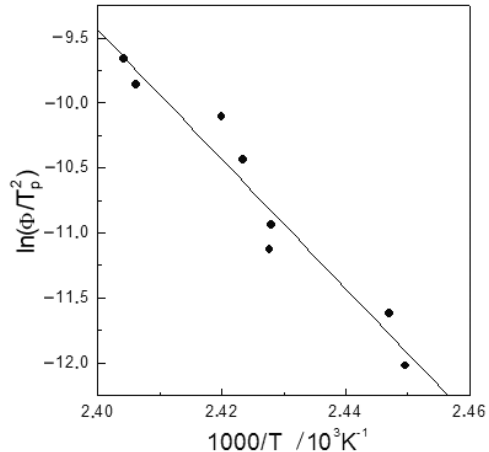

Fig. 2a Kissinger plot $\ln(\Phi/T_\mathrm{p}^2)$ *vs.* $1000/T_\mathrm{p}$

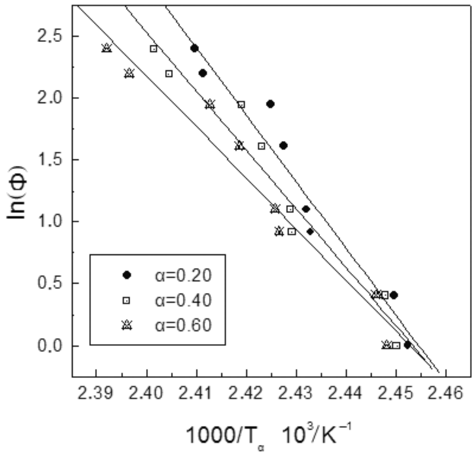

Fig. 2b Ozawa plots ln(Φ) *vs.* $1000/T_\alpha$ for α=0.2, 0.4 and 0.6 for the α-β phase transition of HgI_2

For the description of the kinetics and the mechanism of the phase transition studied, the Johnson–Mehl–Avrami (JMA) model was applied [11], which in differential form is given by the following expression [12]:

$$d\alpha/dt = kn(1-\alpha)[-\ln(1-\alpha)]^{n-1/n} \quad (5)$$

where n is the Avrami exponent, a dimensionless constant related to the nucleation and growth mechanism, with typical values in the range 1–4 [11–13].

Application of the above model (Eq. (5)) to the non-isothermal kinetic data, assuming an activation energy value of 415 kJ mol^{-1} (the effective value found previously from the Kissinger analysis), is shown in Fig. 3 for heating rate 7 K min^{-1},

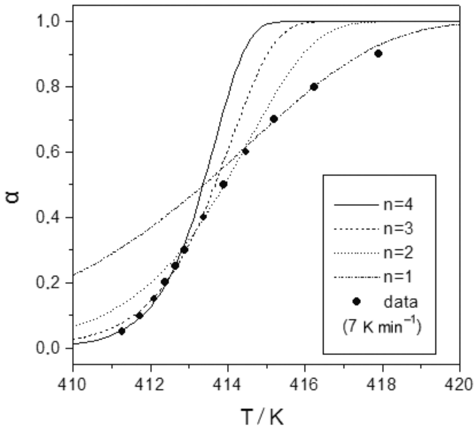

Fig. 3 Calculated α values *vs.* temperature according to JMA model together with experimental α values for heating rate 7 deg min^{-1}

where the α values, calculated according to the Johnson–Mehl–Avrami model are plotted *vs*. temperature. A strong dependence of the Avrami exponent, *n*, on the degree of transformation α was observed. The different α(*t*) curves, predicted according to the JMA model, correspond to different Avrami exponents *n* (mentioned on the plots). For the initial stages of the process (α≅0–0.4), *n* has high value ($n\geq3$), while at later stages of the transition *n* decreases continuously, approaching values around 1 for $\alpha>0.8$. There is also a weak dependence of the *n* value on the heating rate, as well. For lower heating rates (<3 K min^{-1}) *n* ranges from $n>4$ for lower to $n=2$ for higher α, while for higher heating rates (>7 K min^{-1}) *n* ranges from $n=3$ for lower α to $n\approx1$ for higher α.

For more accurate determination of the Avrami exponent, the kinetic analysis was limited to the initial stages of the transition (α≅0–0.4); *n* was calculated by means of the ln[–ln(1–α)] *vs.* 1/*T* plots [14]. All plots are linear, with a slope ($-En/R$), where *E* is the activation energy and *n* is the Avrami exponent. For activation energy value of 415 kJ mol^{-1}, the Avrami exponent *n* is calculated and it is found that at lower heating rates it has a high value ($n\geq4$), while at higher heating rates it reaches the value $n\cong3$.

Isothermal measurements

Isothermal DSC analysis of the α-β phase transition was carried out in order to obtain more information about the mechanism of the transformation as well as to compare the kinetic results from both isochronal and isothermal studies. Varying the temperature of isothermal annealing it was possible to detect the entire transformation reaction only in a very narrow temperature range of few degrees. At lower temperatures ($T<130°C$) the reaction rate was too slow in order the phase transformation progress

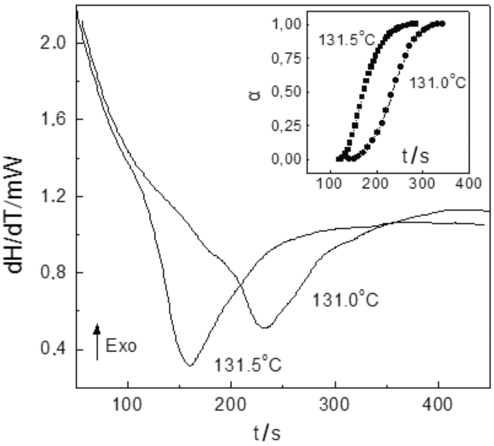

Fig. 4 DSC curves of heat flow d*H*/d*t* (mW) *vs.* time *t* (s) of the α-β phase transition of HgI_2 at two temperatures (131.5 and 131.0°C) and the corresponding degree of conversion α *vs.* time *t* curves in the inset

to be detected quantitatively by isothermal DSC and at higher temperatures (T>133°C) the onset of the reaction was difficult to be determined.

Figure 4 shows typical isothermal DSC curves of a HgI_2 sample at two different temperatures, where the α-β phase transition is revealed with the endothermic peak. Although the shape of the peaks does not allow an accurate determination of the beginning of the transition, approximate incubation times for the overall α-β transformation were determined directly from the experimental kinetic curves at several temperatures. The time for reaching degree of transformation α=0.5 was obtained for different temperatures, as well. The time where the temperature was set constant was taken as zero time. The enthalpy of the transition, calculated from the area below the peak using as baseline a straight line connecting in best possible approximation the beginning and the end of the transition, has an average value of 2.40±0.10 kJ mol^{-1}, a value slightly higher than the one obtained from the non-isothermal scans. The corresponding transformation curves 'degree of transformation α *vs*. time *t*' are also given in as an inset in Fig. 4.

For the description of the experimental isothermal α(*t*) curves the Johnson–Mehl–Avrami model in the following integral form was applied [11]:

$$\alpha = 1 - \exp[-k(T)(t-t_o)^n] \tag{6}$$

where α is the fraction transformed at time t, t_o is the incubation time and n is the Avrami exponent. $k(T)$ is the kinetic constant which is related to the activation energy of the process, E, through the Arrhenius Eq. (2).

The $\ln[\ln(1/1-\alpha)]$ *vs*. $\ln(t-t_o)$ plots for several temperatures of isothermal annealing are presented in Fig. 5a. These plots are generally linear, with slopes ranging from 2.0 to 2.5, which correspond to the value of the Avrami exponent n. These values are obtained for α ≅0.03–0.85, which means that they represent the average value of the whole reaction.

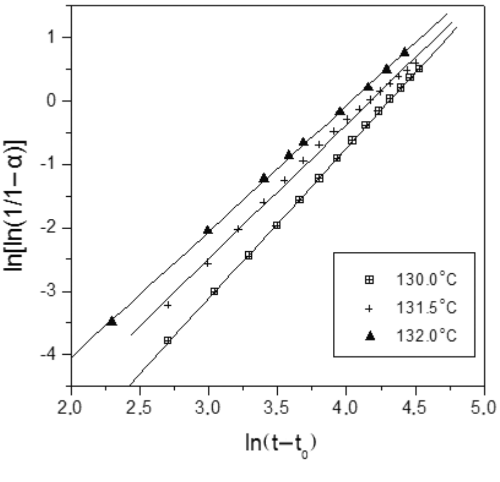

Fig. 5a Double logarithmic plots $\ln[\ln(1/1-\alpha)]$ *vs*. $\ln(t-t_o)$ for α≅0.03–0.85 derived from isothermal scans of the phase transition at three temperatures

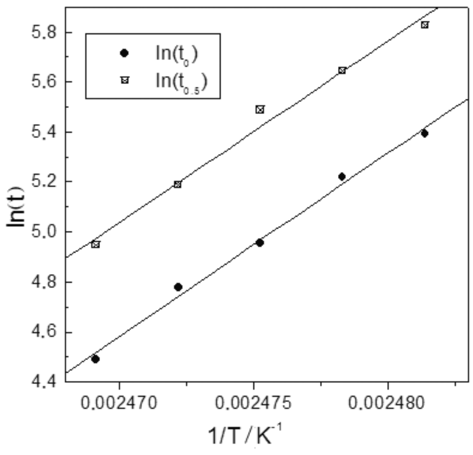

Fig. 5b Temperature dependence in Arrhenius coordinates of the incubation time t_0 and the time $t_{0.5}$ (time at α=0.5) of the phase transition

The temperature dependences of the incubation time and the time for half-reaction are given in Fig. 5b in Arrhenius coordinates [14]. The activation energies determined from both plots were found to be about 600±40 kJ mol^{-1}. This value is higher than the one obtained from the non-isothermal analysis. The higher value of E must be related to the initial stages of the transformation, where n has the higher value too, and the effective activation energy most probably includes the activation energy for nucleation, except that for growth.

The evident variation in the value of the Avrami exponent during the transformation indicates that different dominating mechanisms at different transformation stages exist. The value of $n\geq3$ at the beginning of the phase transformation has to be associated with nucleation and three-dimensional growth of the high temperature β phase. The mechanism thus proposed is confirmed by the high activation energy determined, corresponding to the initial stage of the transformation. Obviously in the advanced stage of the reaction only growth of the already formed crystals takes place, which explains the lower activation energy and n-values found for the later phases of the transition.

Conclusions

The α-β phase transition of HgI_2 was studied by means of DSC, as the transition was detected with both non-isothermal and isothermal scans. The enthalpy of the transition 2.2±0.10 kJ mol^{-1}, determined from non-isothermal scans, was found to be close to the value 2.40±0.10 kJ mol^{-1}, determined from the isothermal analysis.

The activation energy of the transition, calculated from non-isothermal scans applying Kissinger and FWO methods, was found to be about 415±40 kJ mol^{-1}, while from the isothermal analysis higher activation energy of 600±40 kJ mol^{-1} was determined. The value calculated from non-isothermal scans, however, is a mean value, corresponding to the whole transformation, while the higher value, calculated from isothermal scans, must be related to the earlier stages of the transition. Such high value for the activation energy however is not unusual for a transition, which involves changes in the first coordination of Hg [2].

The transition kinetics were described by the Johnson–Mehl–Avrami model. Application of this model to the non-isothermal scans showed a clear dependence of the Avrami exponent n on the degree of conversion α and a weak dependence on the heating rate. At early stages of the transformation ($\alpha\cong0$–0.4) the Avrami exponent n takes high values ($n>3$) while at later stages of the transition it decreases continuously, reaching values about 1 for $\alpha>0.9$. Application of the same model to the isothermal kinetic data shows Avrami exponent n ranging from 2.0 to 2.5. These values are calculated for $\alpha\cong0.03$–0.85, therefore they represent the average value of the whole reaction, which lies between the extreme values found from non-isothermal scans. The variation in the value of the Avrami exponent observed during the transformation indicates different dominating mechanisms at different transformation stages. The value of $n\geq3$ at the beginning of the phase transformation is most probably associated with nucleation and three-dimensional growth of the high temperature β-HgI_2 phase, which mechanism is confirmed by the high activation energy determined. Obviously in the advanced stage of the reaction only growth of the already formed crystals takes place, associated with lower activation energy and lower n-values.

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The authors would like to acknowledge the financial support of the Greek General Secretariat of Research and Technology in the frame of EPET97 EKBAN2#30#.

References

1 J. B. Newkirk, Acta Metal., 4 (1956) 316.
2 C. N. R. Rao and K. J . Rao, Phase Transitions in Solids–an approach to the study of the Chemistry and Physics of solids, McGraw-Hill Inc., 1978, Ch. 3.
3 S. N. Toubektsis, Growth and study of HgI_2 crystals by means of DSC, PhD Thesis, Univ. of Thessaloniki 1988.
4 S. N. Toubektsis and E. K. Polychroniadis, J. Thermal Anal., 34 (1988) 1247.
5 S. N. Toubektsis, E. K . Polychroniadis and J. Laskowski, J. Mat. Science Lett., 8 (1989) 768.
6 S. N. Toubektsis, E. K. Polychroniadis and C. A. Alexiadis, J. Thermal Anal. 36 (1990) 1057.
7 P. J. Haines, Thermal methods of analysis. Principles, applications and problems, Blackie Academic & Professional, 1995.
8 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
9 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
10 J. H. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 323.
11 M. Avrami, J. Chem. Phys., 7 (1939) 1103.
12 M. E. Brown, D. Dollimore and A. K. Galway in (Ed.) Reactions in the Solid State, Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam 1980, Ch.3.

13 J. W. Christian, The theory of transformation in metals and alloys, 2nd Ed., Pergamon Press, NY 1975, Ch. 12.
14 I. Šesták, Thermophysical properties of solids. Their measurements and theoretical analysis, Elsevier, Amsterdam 1984.