

KINETICS OF PHASE TRANSFORMATIONS IN Cu-Al AND Cu-Zn-Al ALLOYS

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The non-isothermal kinetics of the solid-state reactions taking place in Cu-Al and Cu-Zn-Al alloys were studied by DTA and X-ray measurements. It was found that the degree of conversion, which represents the change in the reacting system, is a function of the area increase in the DTA peak. The kinetic analysis shows that DTA is a useful method for the study of formal kinetic laws. From the $f(\alpha)$ functions, conclusions on the mechanism of the phase transformations can be drawn.

Recent studies have shown that thermal methods can profitably be used to study the kinetics and mechanism of solid-state reactions under non-isothermal conditions [1]. Dynamic methods (DTA, DSC) as opposed to isothermal methods are popular for several reasons, of which the following are the most important [2, 3]:

- they are rapid,
- they can be used in a wide temperature range,
- several decomposition steps can be studied from one curve.

The success of kinetic data evaluation has been limited for solid-state reactions by certain difficulties and more or less justified hypotheses. First, in general the reaction rate is assumed to be a function of conversion and temperature:

$$\frac{d\alpha}{dT} = \frac{1}{\Phi} k(T) \cdot f(\alpha) \quad (1)$$

where α = degree of conversion, $k(T)$ = temperature-dependent rate constant, and Φ = heating rate. This kinetic equation, deduced for reactions taking place in a homogeneous system, is never valid for those in a heterogeneous system. Furthermore, for heterogeneous processes a difficulty arises due to the fact that the process may not be monotonous, i.e. no single process can be treated as the rate-controlling process. In this case the kinetic analysis is directed towards arranging experimental conditions such as to make possible the investigation of the kinetics of

a single partial process [3]. Under non-isothermal conditions this is often impossible. The complex process is then described by one $f(\alpha)$ function. This function was proposed for solid-state reactions by Sestak and Berggren [4] in the general form $f(\alpha) = \alpha^m \cdot (1 - \alpha)^n \cdot [-\ln(1 - \alpha)]^p$.

The problem lies in choosing the most suitable of the various possible reactions for each experimental case studied. Skvara and Sestak [5] proposed 3 criteria for this choice: the interval of linearity in the plot of the integral function $g(\alpha)$ vs. $1/T$, the minimum value of the standard deviation in the considered α interval, and a value of the preexponential factor between 10^4 and 10^{24} s^{-1} . Such a procedure, however, is not sensitive to selection of the correct form of $f(\alpha)$, and does not permit different nucleation mechanisms to be distinguished [5].

The next problem is the determination of the degree of conversion from the DTA peak. The procedure most often used is to obtain the α factor on the basis of the increase in area of the DTA effect. However, the shape of the thermal effect is a function not only of the reaction kinetics, but also of the geometry and thermal diffusivity within the furnace, sample and thermocouple assembly [1-3]. It is uncertain which part of the thermal effect is connected with the phase transformation and can be used for kinetics computing, and which part is connected with other phenomena such as heat transition. Thus, DTA is still of questionable validity, because a representative value which would unambiguously define the change in the system is not available from the DTA peak [3]. The following question may be posed: if the kinetic parameters obtained from DTA measurements can be explained analogously as for homogeneous reactions, then do these parameters have any physical sense at all? For this reason, DTA results must be verified by comparison with the results of other methods.

It should also be checked whether changes in the physical measurement parameters lead to the finding of a different activation energy. If this should happen, then according to Garn [3]:

- the assumption that the rate of transformation is a function only of temperature and the fraction remaining is incorrect,
- there is no uniquely described activated state and the Arrhenius equation has no application to the solid reaction, or
- the experiment has very probably tested the apparatus, rather than measured the kinetics of the process.

To conclude, there are a number of effects which complicate studies of the kinetics of solid-state reactions and can lead to serious errors, in this way disrupting the physical basis of kinetic calculations from DTA measurements.

The aim of the present work was to check different theoretical formulae for the non-isothermal kinetics of solid-state reactions taking place in Cu-Al and Cu-Zn-Al alloys. Cu-Al and Cu-Zn-Al alloys were used for the investigations as they

exhibit a number of solid-state transformations [6] and also several experimental difficulties are eliminated, e.g. the effects of gaseous decomposition, the effect of particle size, etc. It is well known that the β -type Cu-Al alloys undergo the eutectoid transformation $\beta \rightarrow \alpha + \gamma_2$ at 565° and 11.8% Al [6, 7]. Below 360° the α -phase ordering process occurs and the α_2 superstructure appears. The eutectoid transformation is a phase change of the first order, whose rate is dominated by volume or boundary diffusion [8]. The order-disorder transformation occurs as a homogeneous reaction, which may be a nucleation and growth process or a continuous process of atomic interchange. The energy activation of this process in Cu-Al alloys varies from 160 to 190 kJ/mol [9] and depends on the chemical composition of the alloys.

In the present study, an attempt was made to determine from the DTA peaks the activation energy and the $f(\alpha)$ function which best describe the order-disorder and eutectoid transformation in copper alloys. We also endeavoured to draw certain conclusions as to whether the results obtained have a real physical meaning and can give reliable information about the mechanism of the investigated process.

Experimental

The Cu—12.4 wt. % Al and Cu—14.4 wt. % Zn—8.4 wt. % Al alloys were prepared from 99.97% Cu, 99.95% Al and 99.95% Zn by induction melting. Investigations were performed with a Mettler TAl thermalyzer in a protective helium atmosphere. The cylindrical samples, 5 mm high and 5 mm in diameter, with a bored aperture, were placed directly at the end of the thermoelement. Pure copper was used as a standard. Additionally, phase analysis of specimens was carried out with a Philips X-ray diffractometer. X-ray diffractometer tracing was done during heating of the specimens. Filtered CuK_α radiation was used. The lines used for identification of the phases were situated at $2\theta = 58.5^\circ$ for the α -phase, $2\theta = 51.8^\circ$ for the γ_2 -phase and $2\theta = 50.8^\circ$ for the β -phase.

Results

After slow cooling, from the β -phase of the Cu-Al and Cu-Zn-Al alloys one can obtain a eutectoid mixture of $\alpha + \gamma_2$ -phases with ordered α_2 superstructure [6, 10]. During reheating, disordering of the α_2 -phase and formation of the β -phase from the eutectoid take place. The DTA curves obtained during heating from 25° to 600° of Cu-Al and Cu-Zn-Al alloys previously cooled from 700° at a rate of 0.5 deg/min show two typical peaks (Fig. 1). The DTA effects in the temperature interval

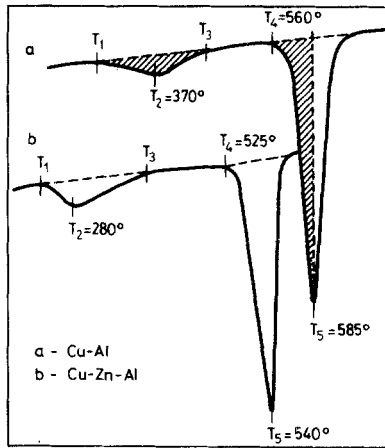


Fig. 1 DTA curves obtained during heating of Cu-Al (a) and Cu-Zn-Al (b) alloys at a rate of 6 deg/min

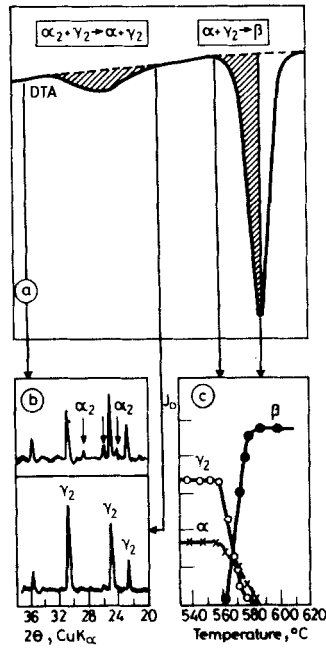


Fig. 2 DTA curve for Cu-Al alloy (a) and the parts of the X-ray diffraction patterns corresponding to the beginning and end of the first DTA effect (b) and the change of the X-ray line intensities vs. temperature for the second DTA effect (c)

$T_1 - T_3$ are connected with disordering of the α_2 -phase (Fig. 2). Above temperature T_4 , the β -phase is formed from the eutectoid mixture. This $\alpha + \gamma_2 \rightarrow \beta$ -transformation finished at temperature T_5 , as confirmed by the results of X-ray high-temperature phase analysis (Fig. 2). Hence, the beginning and the end of the eutectoid transformation corresponded to the beginning and minimum of the DTA effect and only part of the effect was connected with this transformation. The order-disorder transformation, however, was related to the whole area of the thermal effect.

From a comparison of the DTA and X-ray analysis results it may be concluded that the increase in area of the DTA effect can be taken as the degree of conversion. The degree of conversion is then defined as $\alpha = a_i/A$, where a_i is the area of the thermal effect from its beginning to temperature T_i , and A is the whole area of the thermal effect. The α vs. T curves obtained in this way have a sigmoidal shape (Fig. 3). However, in the non-isothermal cases all the expressions give sigmoidal α vs. T

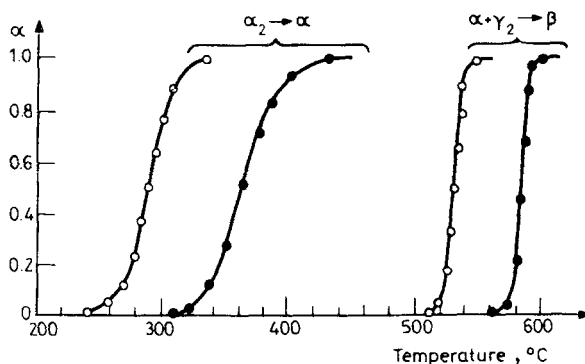


Fig. 3 Degree of conversion for the $\alpha_2 \rightarrow \alpha$ and $\alpha + \gamma_2 \rightarrow \beta$ transformations in Cu-Al and Cu-Zn-Al alloys

curves. The degree of conversion as shown above was used to investigate the kinetics of the disordering and eutectoid transformations using the modified Borchardt-Daniel (B-D) and Rogers-Smith (R-S) methods. The Kissinger and Pilojan methods, in which the α vs. T dependence is not used, have also been applied to these transformations. The application of different methods, with and without the α factor, allowed the kinetic results to be verified. In the modified B-D method we use the general type equation [11]:

$$k(T) = \frac{\Delta T/A}{\alpha^m \cdot (1-\alpha)^n \cdot [-\ln(1-\alpha)]^p} \quad (2)$$

where A is the area of the DTA peak. The following equation was applied in the modified R-S method [11]:

$$\left(\frac{1-\alpha}{b^2}\right) \frac{db}{dt} - \left[\frac{m(1-\alpha)}{A \cdot \alpha} + \frac{p}{A[-\ln(1-\alpha)]} \right] = \frac{\Phi E}{bRT} (1-\alpha) - \frac{n}{A} \quad (3)$$

where b is the deflection of the DTA peak from the base line, and Φ is the heating rate.

The problem lies in choosing a suitable $f(\alpha)$ function which gives the best linear relation versus reciprocal temperature. For the order-disorder transformation, the best linear correlation was found for the function $f(\alpha) = (1-\alpha)^{1/3} \cdot [-\ln(1-\alpha)]^{-1}$ (Figs 4 and 5). The diffusion-controlled reaction and strictly speaking the three-

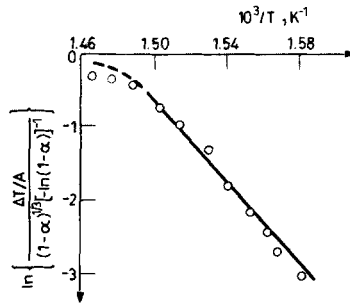


Fig. 4 Plot according to the B-D method for the $\alpha_2 \rightarrow \alpha$ transformation in Cu-Al alloy

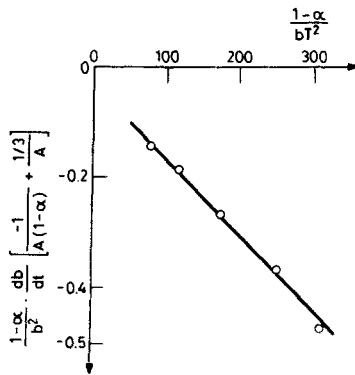


Fig. 5 Plot according to the R-S method for the $\alpha_2 \rightarrow \alpha$ transformation in Cu-Zn-Al alloy

dimensional transport in a sphere (Jander's equation) are described by this kind of $f(\alpha)$ function. The activation energy of the order-disorder transformation in Cu-Al and Cu-Zn-Al alloys, obtained by means of the B-D and R-S methods and from the Kissinger and Pilojan methods (Figs 6 and 7), was approximately 200 kJ/mol (Table 1). This is in agreement with the literature data [9].

The kinetics of eutectoid transformation were investigated using the endothermic

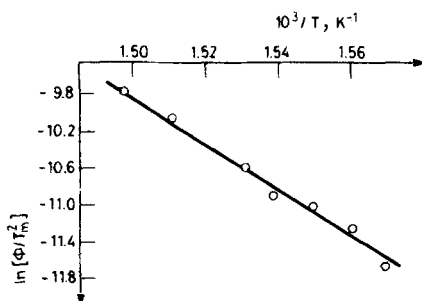


Fig. 6 Plot according to the Kissinger method for the $\alpha_2 \rightarrow \alpha$ transformation in Cu-Al alloy

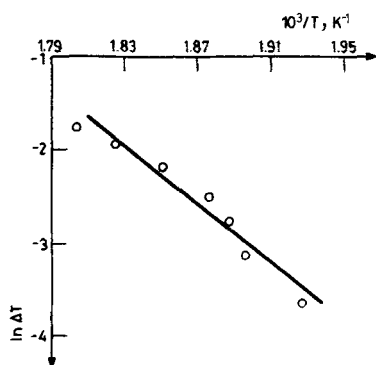


Fig. 7 Plot according to the Pilojan method for the $\alpha_2 \rightarrow \alpha$ transformation in Cu-Zn-Al alloy

Table 1 Values of the activation energy of order-disorder transformation in Cu-Al and Cu-Zn-Al alloys

Method	Function $f(\alpha)$	Cu-Al $E_a, kJ/mol$	Cu-Zn-Al $E_a, kJ/mol$
Kissinger	—	195 ± 25	160 ± 25
Pilojan	—	168 ± 25	145 ± 25
B-D	$(1-\alpha)^{1/3} \cdot [-\ln(1-\alpha)]^{-1}$	195 ± 25	175 ± 24
R-S	$(1-\alpha)^{1/3} \cdot [-\ln(1-\alpha)]^{-1}$	184 ± 25	152 ± 25

DTA effects of the $\alpha + \gamma_2 \rightarrow \beta$ transformation. Two different forms of $f(\alpha)$ function, i.e. $f(\alpha) = (1-\alpha)^n$ and $f(\alpha) = (1-\alpha)^n \cdot [-\ln(1-\alpha)]^p$, describe the $\alpha + \gamma_2 \rightarrow \beta$ process equally well. This confirms the fact that non-isothermal measurements provide a non-sensitive procedure of selecting the correct form of the $f(\alpha)$ function. However, by comparing these results with those found with the Kissinger method, it is possible to conclude that $f(\alpha) = (1-\alpha)^n$ is the correct function describing the

eutectoid transformation. The activation energy obtained with the function $f(\alpha) = (1-\alpha)^n[-\ln(1-\alpha)]^p$ was much higher than that found with methods where the degree of conversion was not used (Table 2). The function $f(\alpha) = (1-\alpha)^{1/2}$ describes a phase boundary-controlled process [1, 4]; hence, under non-isothermal conditions the eutectoid transformation is a process of this type. The energy activation values obtained for the eutectoid transformation using the function $f(\alpha) = (1-\alpha)^{1/2}$ and with the Kissinger method are unfortunately higher than those reported in the literature [12, 13].

Table 2 Values of the energy activation of $\alpha + \gamma_2 \rightarrow \beta$ transformation in Cu-Al and Cu-Zn-Al alloys

Method	Function $f(\alpha)$	Cu-Al E_a , kJ/mol	Cu-Zn-Al E_a , kJ/mol
Kissinger	—	650 ± 50	800 ± 50
Pilojan	—	630 ± 50	810 ± 50
B-D	$(1-\alpha)^{1/2}$	670 ± 50	830 ± 50
	$(1-\alpha)^{1/3} \cdot [-\ln(1-\alpha)]^{-1}$	2200 ± 100	2420 ± 100

Discussion and Conclusions

From non-isothermal experiments it was possible to determine the kinetic parameters and mechanism of phase transformations in Cu-Al and Cu-Zn-Al alloys. It was found that the degree of conversion, which represents the change in the reacting system, is a function of the area increase in the DTA peak, so this may be used for kinetic computing. However, it is first necessary to know which part of the DTA effect is connected with the phase transformation.

For the order-disorder transformation, symmetrical effects extending over a broad temperature interval were observed. The whole area of these effects was connected with phase transformation. The extremum of this effect (T_2 in Fig. 1) indicates the temperature at which the maximum rate of transformation occurs. On the other hand, the DTA effect connected with the eutectoid transformation has an asymmetric shape, and the start and finish of the transformation are indicated by the beginning and extremum of the thermal effect. The temperature half way between the beginning and the extremum of the DTA effect would correspond to the maximum rate of transformation.

The kinetic analysis shows that the order-disorder transformation for both investigated alloys is a diffusion-dominated reaction. The function $f(\alpha) = (1-\alpha)^{1/3} \cdot [-\ln(1-\alpha)]^{-1}$, which describes the three-dimensional transport process in a sphere [1, 4], was used to describe these transformations.

The kinetics of eutectoid transformation was found to be best described by the function $f(\alpha) = (1 - \alpha)^{1/2}$. This means that the $\alpha + \gamma_2 \rightarrow \beta$ transformation under non-isothermal conditions is a phase boundary-dominated process.

In conclusion, it may be said that DTA is a useful method for the study of formal kinetic laws. From the $f(\alpha)$ function, conclusions may be drawn about the mechanism of the phase transformation. For each individual case of phase transformation, it is essential to check the relation between the DTA peak and the change in the reacting system. Further, it is not advisable to draw any general conclusions on the basis of one individual case, as this may lead to serious errors.

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Zusammenfassung — Die nicht-isotherme Kinetik von in Cu-Al und Cu-Zn-Al-Legierungen verlaufenden Festkörperreaktionen wurden mittels DTA und Röntgenmessungen untersucht. Es wurde festgestellt, daß die Zunahme der Fläche des DTA-Peaks abhängig von dem die Veränderungen im Reaktionssystem repräsentierenden Konversionsgrad ist. Die kinetische Analyse zeigt, daß die DTA eine nützliche Methode zur Untersuchung der formalen kinetischen Gesetzmäßigkeiten ist. Aus den Functionen $f(\alpha)$ können Schlußfolgerungen hinsichtlich des Mechanismus der Phasenübergänge gezogen werden.

Резюме — Методом ДТА и рентгенофазовым анализом изучена неизотермическая кинетика твердотельных реакций, протекающих в сплавах Cu-Al и Cu-Zn-Al. Найдено, что степень превращения, показывающая изменения в реакционной системе, является функцией увеличения площади пика ДТА. Кинетический анализ показал полезность метода ДТА при изучении формальных кинетических законов. Из функциональных зависимостей $f(\alpha)$ могут быть сделаны заключения о механизме фазовых превращений.