

Some interpretation problems of thermal studies of the reversible martensitic transformation

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The reversible martensitic transformation in the NiTi and CuZnAl shape memory alloys were examined by the use of DTA and DSC methods. The problem of adequately established temperature, heats and kinetics of transformation were considered. The influence of the various types of DTA/DSC devices and changes in the experimental conditions on the results were determined.

1. Introduction, DTA/DSC theory

Two different thermal techniques, differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are often used for the investigation of phase transformation in metals [1-3]. DTA is a method in which the temperature difference between a substance and a reference material is measured as a function of temperature (Fig. 1). DSC is a technique in which the difference in energy is measured. Two modes, power compensation DSC (Fig. 1b, Perkin Elmer Calorimeter) and heat-flux DSC (Fig. 1c DuPont Calorimeter) can be distinguished depending on the method measurement used [4]. Apart from several differences in the DTA and DSC techniques, both methods can yield some information about temperature of phase transformations, the kind and quantity of thermal effects and about the kinetics. From DTA one can obtain temperatures more precisely because of the smaller thermal inertia. DSC, however, strictly gives the energy of transformation. Every physical or chemical change creates a peak on the DTA/DSC curve. In the case of first-order phase changes (i.e. martensitic transformation) a corresponding enthalpy change occurs at constant temperature, giving rise to an ideal DTA or DSC curve. In practice, however, DTA/DSC of the majority of substances gives a shape far from ideal, mainly because of temperature gradients created in the sample [1, 2]. An idealized, hypothetical DTA/DSC curve is represented in Fig. 2. The DTA/DSC curve is usually characterized by several temperatures. The temperature at the beginning of the transformation could be marked by T_1 or T_2 . Temperature T_1 is marked by the point of departure from the base line. If it is difficult to find T_1 , then according to the International Committee of Thermal Analysis (ICTA) the extrapolation onset point, T_2 , is assumed as the temperature of the beginning of transformation [3]. This means of specifying the temperatures of transformations is also the most often used in the literature. The temperature at the end of the transformation could be marked by temperatures T_m , T_x or

T_4 . The temperature of the peak (T_m) could correspond to the end of the first-order transformation if the temperature is measured in the centre of the sample [1]. Because the temperature gradient is created in the sample, the point T_x often corresponds to the end of the transformation [1, 2]. Part of the DTA/DSC peaks between T_m or T_x and T_4 corresponds, therefore, to the temperature compensation. In the case of chemical reactions or transformations controlled by diffusion, point T_4 (or extrapolated T_3) often marks the temperature at the end of the transformation. The temperature of the peak (T_m) then corresponds to the maximum rate of transformation. The problem of establishing an adequate temperature of transformation is connected with heat of transformation, because heat is proportional to the DTA/DSC peak area between the onset and final temperatures of transformation. As the heat of transformation is proportional to the amount of reacting substance, the

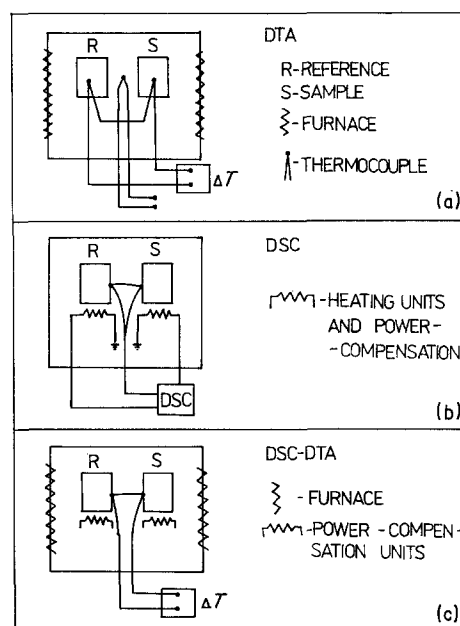


Figure 1 (a) DTA and (b, c) DSC techniques.

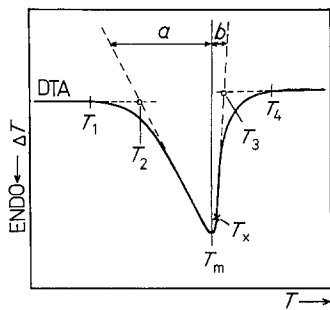


Figure 2 Method of determination of the DTA/DSC peak temperatures.

DTA/DSC curve may also give valuable information about reaction kinetics. However, characteristic temperatures as well as the shape of the DTA/DSC curves depend not only on the type of process but also on the kind of apparatus and a number of experimental conditions.

Although the DTA and DSC methods have often been used for the investigation of reversible martensitic transformation in shape memory alloys [5–12], little attention has been paid to the correct interpretation of thermal results. DTA/DSC thermograms in the literature typically show exothermic and endothermic peaks associated with martensitic (P–M) and reverse (M–P) transformation (Fig. 3). However, the characteristic transformation temperatures, as well as other kinetic parameters (peak height and width, shape, area), were defined in different ways. Typical

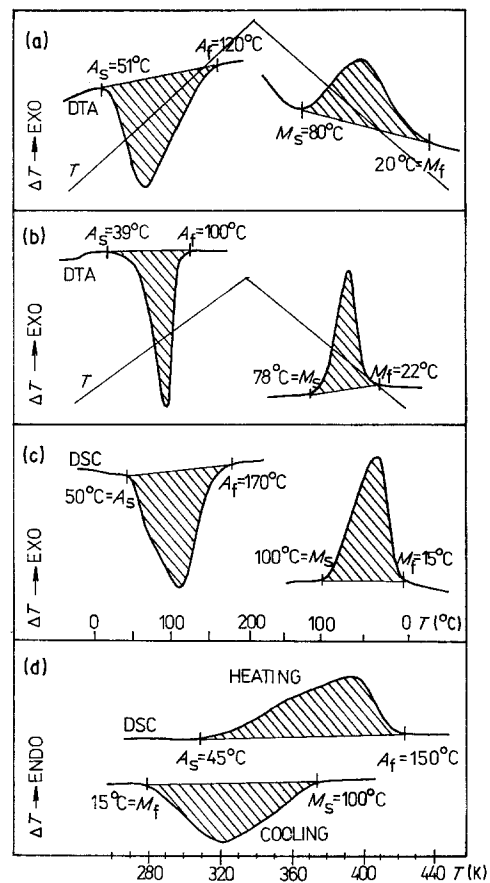


Figure 4 DTA and DSC curves of Cu–14.4 wt % Zn–8.4 wt % Al alloy obtained using a (a) derivatograph, (b) Mettler Thermanalyser, (c) DSC/DTA DuPont Calorimeter and (d) Perkin-Elmer DSC 1B Calorimeter.

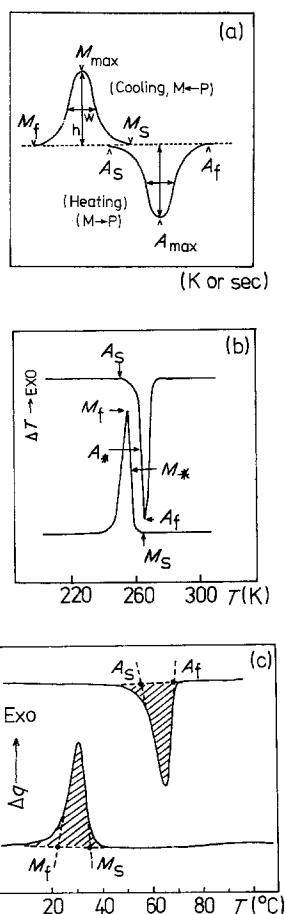


Figure 3 (a, b) DSC [5, 7] and (c) DTA [8] curves of CuZnAl shape memory alloys.

differences in the literature are shown in Fig. 3 [5–8]. As seen from Fig. 3, the thermal effects obtained for similar chemical compositions of CuZnAl alloys have different shapes (symmetrical in Fig. 3a, asymmetrical in Fig. 3b) [5, 7]. Moreover, the temperatures corresponding to the beginning and end of the transformations and to the maximum rate of transformations (M_{max} , A_{max} in Fig. 3a, M_* , A_* in Fig. 3b) are marked by different points on the DSC curves. In Fig. 3c the tangential extrapolation method was used to define the temperatures for “martensite or austenite start and finish” [8]. This method was also used for NiTi alloy [9]. The differences between the characteristic temperatures obtained from the beginning of the peaks (Figs 3a and b) and from the extrapolation method (Fig. 3c) could be considerable. These differences can be important from the practical point of view. The shape memory alloys have been used in industry and medicine, so it is necessary to know the real temperatures at which the shape memory phenomenon occurs.

Different ways of interpreting thermal effects stimulated the present investigation. The main object of this work was to establish characteristic temperatures, thermal effects and kinetics of martensitic transformation in NiTi- and copper-base shape memory alloys on the base DTA and DSC measurements. The influence of different types of apparatus on thermal results was also examined.

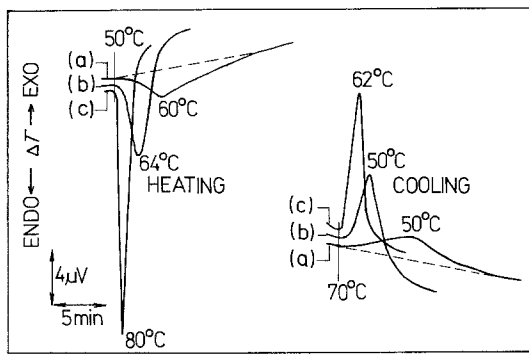


Figure 5 DTA curves of Cu-14.4 wt % Zn-8.4 wt % Al alloy obtained at different heating and cooling rates: (a) 1 K min⁻¹, (b) 4 K min⁻¹; (c) 25 K min⁻¹.

2. Experimental techniques

Several CuZnAl and NiTi shape memory alloys were investigated. Two alloys, as representative, were chosen for this paper, Cu-14.4 wt % Zn-8.4 wt % Al and Ni-45 wt % Ti alloys. These alloys were prepared by vacuum induction melting. The ingots were hot-rolled, homogenized and quenched from the β -phase into ice-water. Thermal measurements were performed with Mettler TA1 Thermoanalyser and Derivatograph Paulik-Paulik-Erdey system (DTA method) and DuPont DTA/DSC Calorimeter as well as Perkin-Elmer DSC 1B Calorimeter (DSC methods). The DSC measurements were typically performed in aluminium crucibles. For DTA measurements NiCr-Ni and PtRh-Pt thermoelements were used. To determine the temperatures of phase transformation, the cylindrical samples were placed directly at the end of the thermoelement. To determine the heat of transformation, samples were placed in a crucible, thus simulating the conditions in which the calibration curve and measurements were obtained. Phase analysis of specimens was performing using a Dron X-ray diffractometer with a high-temperature Philips programmer. The X-ray diffractometer tracing was

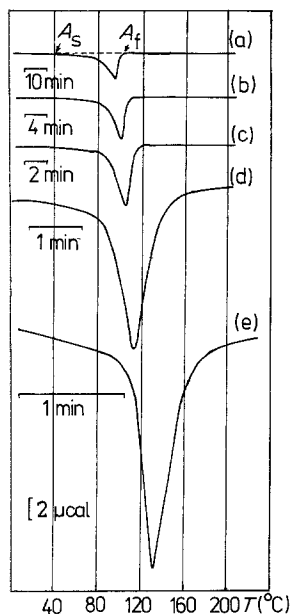


Figure 6 DSC curves of Ni-45 wt % Ti alloy obtained at different heating rates: (a) 2°C min⁻¹, (b) 5°C min⁻¹, (c) 10°C min⁻¹, (d) 50°C min⁻¹, (e) 100°C min⁻¹ (DuPont Calorimeter).

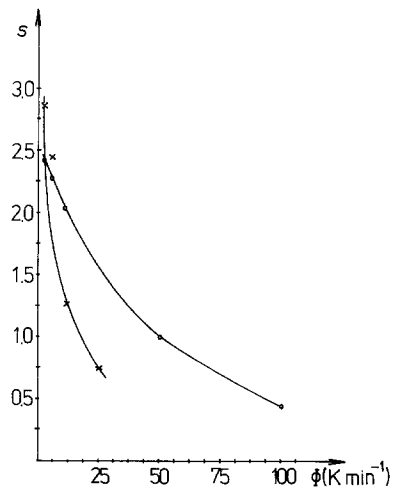


Figure 7 Effect of the heating rates on the Kissinger shape index of the DTA/DSC peaks of Ni-45 wt % Ti alloy, (●) DuPont Calorimeter, DSC; (×) Mettler Thermoanalyses, DTA.

obtained during heating and cooling of the quenched specimens. Filtered CuK α radiation was used.

3. Results and discussion

3.1. Shape of the thermal peaks

The DTA/DSC curves of martensitic and reverse transformations obtained on various devices are shown in Fig. 4. It was ascertained that the shape of the DTA/DSC peaks depends on the rate of heating and cooling (Figs 5 and 6) and the kind of apparatus used. For a quantitative characterization of the degree of asymmetry of the thermal effects, the Kissinger shape index, s , of the DTA peak was used [1]. This index was defined as relation $s = a/b$, where a and b are shown in Fig. 2. It can be seen from Fig. 7 that when the rate of heating or cooling decreases the Kissinger shape index increases. The shape of DTA/DSC peaks can also depend, however, on a number of experimental conditions such as the mass of samples and the manner of measurement (e.g. with or without a crucible, atmosphere, etc). The mass of the samples in our measurements varied from 0.1 to 5 g. The temperatures were measured from the surface of the sample or from the centre of the drilled cylindrical sample and from samples put inside a crucible. Generally, for measurements on larger samples put inside a crucible the DTA peaks were more symmetrical than

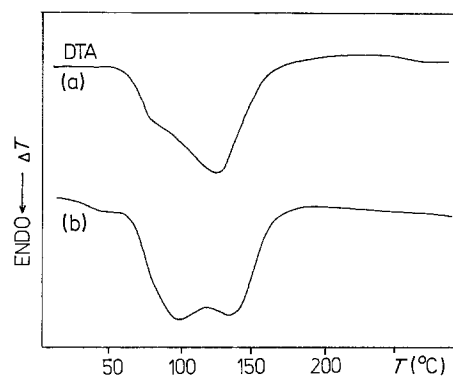


Figure 8 DSC curves of Cu-14.4 wt % Zn-8.4 wt % Al alloy obtained at a heating rate of (a) 10°C min⁻¹ and (b) 50°C min⁻¹. (DuPont Calorimeter).

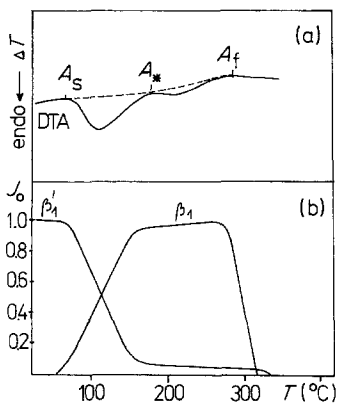


Figure 9 (a) DTA curves and (b) relative intensities of X-ray lines for Cu-12.9 wt% Zn-7.9 wt% Al alloy.

for smaller samples put directly at the end of the thermocouple. However, because the shape of the DTA/DSC peaks also depends on several additional factors (such as the type of crucible, thermocouple and furnace) it is unfortunately difficult to give any quantitative results. Only qualitative and general information about the shapes of DTA/DSC peaks can be presented.

Different rates of heating and cooling not only influence the shape of the DTA/DSC peaks, but may also reveal the multi-stage mechanisms of martensitic transformation. Fig. 8 shows DSC curves for the martensite of investigated CuZnAl alloy which was heated at a rate of 10 and 50°C min⁻¹. For a smaller rate of heating the “nose” on the DSC peak was registered. This peak is divided into two overlapping peaks on heating at higher rates. A contrary phenomenon can be observed in Cu-7.9 wt% Al-13.5 wt% Zn. Two separate peaks were registered on the DTA curve during a relatively slow rate of heating of the martensite (Fig. 9a). In the temperature range A_s to A_* about 90% of the martensite transforms to the parent phase. The balance of the martensite transforms during further heating between A_* and A_f . These results are confirmed by the changes of the X-ray line intensities of the martensite (β') and parent phase (β_1) (Fig. 9b). For the higher rates of heating (about 20°C min⁻¹) the thermal peak of the second stage of transformation merged with the DTA base-line, thus it could not be seen on the DTA curve. The rates of heating of

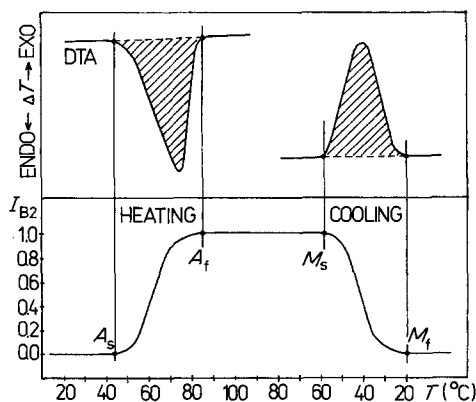


Figure 10 DTA curves and relative intensities of X-ray lines for Ni-45 wt% Ti alloy.

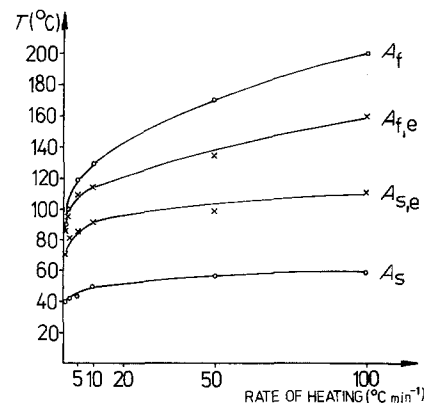


Figure 11 Effect of the heating rates on the A_s , A_f and extrapolated values $A_{s,e}$, $A_{f,e}$ temperatures for Ni-45 wt% Ti alloy.

the martensite can also change the kind of phase transformation that may occur. For instance, martensite of the Cu-12.4 wt% Al alloy transforms to the parent phase during high rates of heating or changes into the eutectoid mixture for slow rates of heating [12].

3.2. Characteristic transformation temperatures

Temperatures of reversible martensitic transformations were determined from the DTA/DSC curves by comparing them with the results of X-ray high-temperature measurements (Fig. 10). Temperatures of the beginning and end of martensitic and reverse transformations are marked by the points of departure from the base line and the points of return of the peak to the base line. For the investigated martensitic transformations the difference in the temperatures obtained from the points of departure from the base line and from the extrapolation method proposed by ICTA can differ by several or several dozen degrees (Fig. 11). This depends on the rate of cooling and heating. Thus, the extrapolation method proposed by ICTA is not the best one for martensitic transformations. The DTA/DSC curves presented in the literature were obtained more often during heating and cooling at a rate of about 10°C min⁻¹. Temperatures registered on the DTA/DSC curves depend, however, on the rates of heating and cooling (Fig. 12). Temperatures A_s , A_f

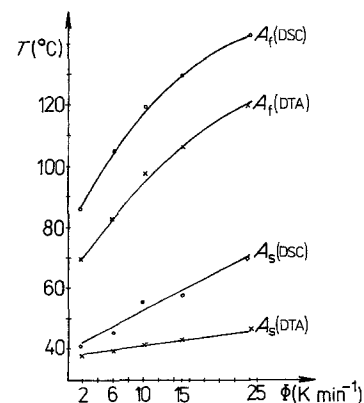


Figure 12 Effect of the heating rates on the A_s and A_f temperatures for Ni-45 wt% Ti alloy obtained using Mettler (DTA) and DuPont Calorimeter (DSC).

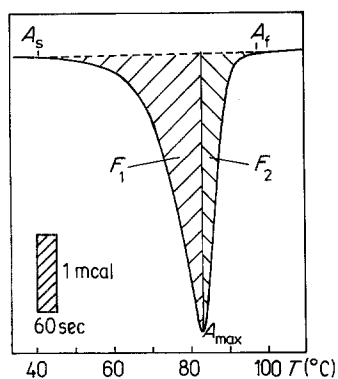


Figure 13 DSC peak of Ni-45 wt % Ti alloy obtained at a heating rate of 5°C min^{-1} (DuPont Calorimeter).

and M_s , M_f are well defined values and are stable for individual materials. M_s is the temperature at which the first martensite plate arises, and M_f that at which the last part of the parent phase transforms into martensite. If the observed changes of temperature are not caused by the apparatus but only by the thermal inertia of the material, then the problem of adequate determination of the transformation temperatures arises. The method of extrapolating the temperatures to the "zero" rate of heating or cooling can be proposed as a method of determining adequately M_s , M_f and A_s , A_f temperatures. However, this method demands several measurements. Thus, in practice, it is sufficient if temperatures are obtained at suitably slow cooling and heating rates.

3.3. Heats of transformation

The heats of transformation were calculated from the areas under the DTA/DSC curves in the temperature range M_s to M_f and A_s to A_f by multiplying them by equivalent calories per unit area (calibration constant of a thermoelement). The areas under the DTA/DSC curves were delimited by the straight line from the beginning of the peaks to the point where the DTA/DSC curves return to the base line (Fig. 10). The heats of martensitic and reverse transformations were in the typical range for investigated shape memory alloys, i.e. they were about 3 to 7.5 J g^{-1} for CuZnAl alloys and about 25 to 35 J g^{-1} for NiTi alloys. It was ascertained that the difference in the values of the heats obtained from the DTA and DSC methods differ by about 10 to 15%. For the copper-based alloys the heats of martensitic and reverse transformations were nearly equal. For the Ni-45 wt % Ti alloy the heat of the reverse transformation was less than the heat of the martensitic transformation by about 20%. This difference could be explained by the fact that the mechanism of the two transformations in the NiTi alloy studied proceeds via the R-phase, while the reverse transformation does not [11].

On the basis of measurements of the transformation heats one can, moreover, verify the characteristic temperatures of transformation, especially the temperatures of the transformation end (M_f , A_f). These temperatures, as mentioned before, can be marked by the extreme or final points of the DTA/DSC peaks. For the NiTi alloy, the heats were calculated from the thermal peaks obtained at different heating rates

TABLE I The heats of reverse transformation for Ni-45 wt % Ti alloy obtained from whole and part of DTA peaks.

heating rate ($^\circ\text{C/min}$)	ΔH (J/g) ($F_1 + F_2$)	ΔH (J/g) (F_1)
2	35.5	27.7
5	34.4	24.4
10	35.3	25.0
50	33.8	18.9
100	33.6	15.5

(Fig. 6). The heats were calculated from the whole areas of the peaks ($F_1 + F_2$ in Fig. 13) and from a part of the DTA peaks (F_1) assuming that the end of transformation was at the A_f or A_{max} temperature, respectively. The results (Table I) show that stable values of the heats were obtained from the whole areas of the DTA peaks. This confirms the fact that the temperature at the end of the martensitic transformation was marked by the point at which the DTA peak returns to the base line. In this case one can say that the DTA results are self-verifying.

3.4. Kinetics of transformation

Thermal methods can be used for the study of the mechanism and kinetics of solid state transformations. On the basis of DTA/DSC results, two different groups methods of investigation of non-isothermal kinetics can be distinguished: in the first the shape of the DTA/DSC peaks, and in the second the characteristic temperatures of the thermal effects were used for calculating the kinetics parameters. In the first group of methods it has been assumed that the quotient of the growth of the area of the DTA/DSC peak to the total area of the peak is proportional to the degree of conversion (α). The calculation of kinetic parameters is often simplified to the Arrhenius equation and based on the assumption that all processes in the solid state can be described by the $f(\alpha)$ function whose general type is $f(\alpha) = \alpha^m(1 - \alpha)^n[-\ln(1 - \alpha)]^p$ [13]. However, the DTA/DSC methods are still of questionable validity for the investigations of kinetics because of several problems. First, the Arrhenius equation deduced for homogeneous reactions is never valid for those in a heterogeneous system (i.e. for martensitic transformations). The second problem is

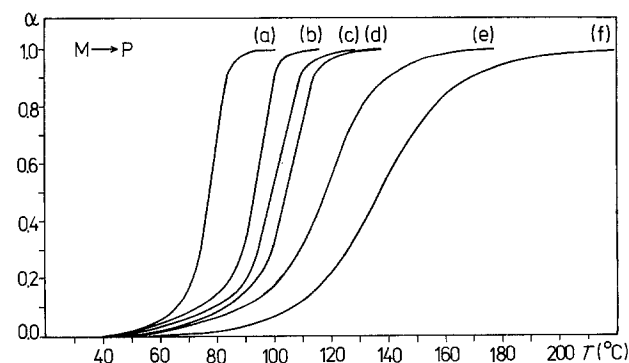


Figure 14 The degree of conversion (α) as a function of temperature obtained for Ni-45 wt % Ti alloy during heating at different rates: (a) $0.5^\circ\text{C min}^{-1}$, (b) 2°C min^{-1} , (c) 5°C min^{-1} , (d) $10^\circ\text{C min}^{-1}$, (e) $50^\circ\text{C min}^{-1}$, (f) $100^\circ\text{C min}^{-1}$.

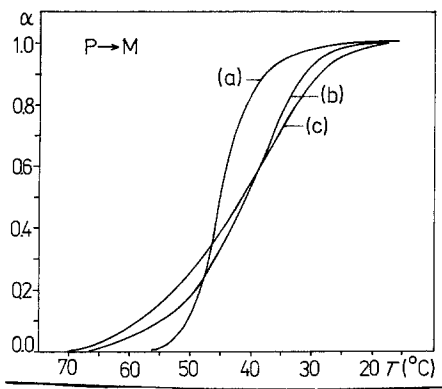


Figure 15 The degree of conversion (α) as a function of temperature obtained for Ni-45 wt % Ti alloy during cooling at different rates: (a) 0.5 K min⁻¹, (b) 5 K min⁻¹, (c) 10 K min⁻¹.

connected with the nature of martensitic transformation. This kind of transformation does not involve diffusion. Transformation on cooling begins spontaneously at the M_s temperature and finishes at M_f . The amount of phase transformation is characteristic of temperature. The velocity of transformations, however, is probably independent of temperature [14]. We cannot regard the growth of martensite as a combination of transport process (atomic diffusion) with a chemical reaction (formation of a new phase). Thermally supplied activation energy could not account for such a process and probably, the concept of activation energy is not generally as useful in martensitic transformations, except in the nucleation stage [14]. The next problem is to define the degree of conversion from the areas of the DTA/DSC peaks, because, as mentioned before, the shape of the thermal peaks is a function not only of the reaction kinetics but also of the geometry and thermal diffusivity of the furnace, etc. Moreover, the degree of conversion in the non-isothermal conditions always gives the sigmoidal shape of the α - T curves (Figs 14, 15). Because of these facts, the α - T relationship was also obtained from high-temperature X-ray measurements. The increase and decrease of the $(110)_\beta$ line during linear heating and cooling of the Ni-45 wt % Ti alloy were used for calculating the quantity of martensite and parent phase. The α - T relationships obtained from the DTA/DSC curve and from the X-ray measurements

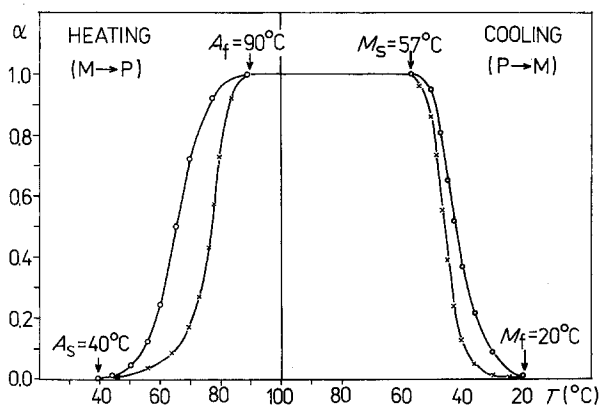


Figure 16 The degree of conversion (α) as a function of temperature obtained from (x) the DTA measurements and (o) X-ray $(110)_\beta$ line intensities for Ni-45 wt % Ti alloy.

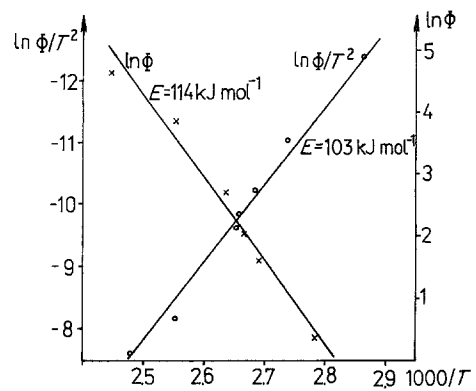


Figure 17 Plots of $\ln\phi/T^2$ against $1/T$ (Kissinger method) and $\ln\phi$ against $1/T$ (Ozawa method) for martensitic transformation in Ni-45 wt % Ti alloy.

unfortunately have different shapes (Fig. 16). To sum up, the group of methods of kinetics investigations in which the characteristic temperatures of DTA/DSC peaks have been used seems to be more trustworthy. From those methods the Kissinger ($\ln\phi/T^2$ against $1/T$), Ozawa ($\ln\phi$ against $1/T$), where ϕ is the heating or cooling rate, and Piloyan ($\ln\Delta T$ against $1/T$) methods have often been used. These methods give linear relationships for investigated martensitic transformations and can be used for calculating activation energy (Figs 17, 18). Unfortunately, the values of activation energy obtained from these methods differ and depend on the measurement conditions (heating and cooling rates). To conclude, it can be said that DTA/DSC is of questionable validity in the study of phase transformations. For the martensitic transformation the question may be passed if the kinetics parameters obtained from thermal methods have any physical sense at all.

4. Conclusions

1. The shape of DTA/DSC peaks of martensitic and reverse transformations depends on conditions of measurement (the cooling and heating rates) and the kind of apparatus. Different heating and cooling rates could sometimes reveal the complex mechanisms of transformation.

2. Temperatures of reversible martensitic transformations were marked by the points of first depar-

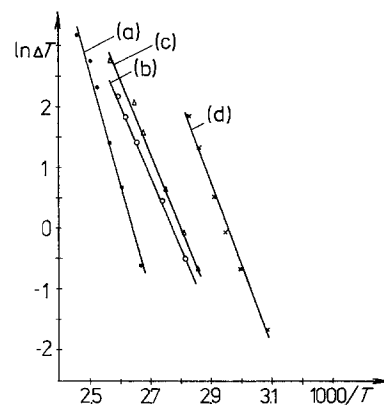


Figure 18 Plot of $\ln\Delta T$ against $1/T$ (Piloyan method) for reverse transformation in Ni-45 wt % Ti alloy. (a) 100 K min⁻¹, $E = 132$ kJ mol⁻¹; (b) 50 K min⁻¹, $E = 102$ kJ mol⁻¹; (c) 10 K min⁻¹, $E = 92$ kJ mol⁻¹; (d) 5 K min⁻¹, $E = 109$ kJ mol⁻¹.

ture from the base line (M_s, A_s) and by the points of return of the peaks to the base line (M_f, A_f). Temperatures of the extremum of the DTA/DSC peaks could correspond to the maximum rate of transformation.

3. Heats of transformation should be estimated from the whole areas under the DTA/DSC peaks. The difference between heats of martensitic and reverse transformations can sometimes reveal a difference in the mechanisms of both transformations.

4. The DTA/DSC methods are of questionable validity in the study of martensitic transformation kinetics. For each individual case of transformation it is essential to check the relation between the DTA/DSC peak and the change in the reacting system and to compare the thermal results with other methods of investigation of kinetics.

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