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DETERMINATION OF KINETICS OF SUPERCOOLED β-PHASE DECOMPOSITION IN CAST ZnAl8Cu2 ALLOY

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Temperature changes T_1 (τ) of a sample during the decomposition of the β-phase of ZnAl8Cu2 alloy supercooled from 360°, and the cooling curve T_2 (τ) from about 100° were determined. The cooling curve shows temperature changes of the sample in which no transformation proceeds. From the heat balance and courses of the curves T_1 (τ) and T_2 (τ), the temperature changes T_3 (τ) of the sample were determined, under adiabatic conditions. On the assumption that the capacity is constant, the following relationship arises:

$$T_3(\tau) = T_1(\tau) - \int_0^{\tau} \left(\frac{dT_2}{d\tau}\right) d\tau \; T_2 = T_1(\tau)$$

The degree of transformation x (τ) was determined from the temperature changes T_3 (τ). The transformation rate constant K and transformation enthalpy were calculated. A value ΔH = 34.0 J/g was obtained. The method used seems to be of value for phase changes characterized by a relatively large heat effect and an intensive course.

The kinetics of supercooled β-phase decomposition in cast ZnAl8Cu2 alloys has not been the subject of many papers. During the ageing of ZnAl8Cu2 alloys, decomposition of supersaturated η-phase takes place with precipitation of the β and ε-phases. Eutectoidal decomposition of the β-phase also occurs, according to the scheme $\beta \rightarrow \beta' + \eta$. The processes influence not only the mechanical properties, but also the volume changes of the alloys, and the instability of the linear dimensions limits their practical application [1–4].

This paper presents results concerning the usability of methods of measuring spontaneous changes in temperature for investigations of phase transformations characterized by a relatively large thermal effect and an intensive course [5–8].

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Experimental procedure and results

Research was conducted to determine the kinetics and enthalpy of supercooled β-phase decomposition for a cast ZnAl8Cu2 alloy with the following composition: 7.85% Al; 2.05% Cu; 0.3% Mn; 0.5% Pb; 0.45% Fe; 0.005% Mg; balance—Zn. Spontaneous changes in temperature of ZnAl8Cu2 alloy samples as a result of β-phase decomposition were measured. The method was described in detail in [5].

This method consists of the calculation of the transformation degree dependence on time. Thus the transformation kinetics was analyzed from temperature changes when transformation occurs in it. The other methods, e.g. the electrical resistance are loaded with the error resulting in the temperature changes.

Investigations were carried out with a derivatograph. Samples with dimensions of ∅ 12 × 25 mm and with a hole measuring ∅ 4.5 × 18 mm were used. Temperature (T) and temperature difference (ΔT) were recorded. The following curves were obtained:

T_1 (τ) = changes in temperature of the sample in which transformation occurs,
T_2 (τ) = changes in temperature during cooling of the sample when no transformation takes place.

In order to obtain the T_1 (τ) curve, a sample of the examined alloy was quenched from 360°, after previous holding at this temperature for 3 hours, in cold water at 2–5° for 15 s.

For attainment of room temperature (20°), the sample was held in water at 20° for 30 s. To obtain the T_2 (τ) curve, a sample of ZnAl8Cu2 alloy was quickly heated up to about 100°. The sample had the same dimensions as that used to obtain the T_1 (τ) curve. On the basis of considerations presented in [5], it was assumed that the T_2 curve showed exactly the changes in temperature during cooling of the sample in which no transformation occurred.

The transformation degree was evaluated by determining the temperature changes T_3 (τ) of the sample in which transformation occurred under adiabatic conditions from the course of the T_1 (τ) and T_2 (τ) curves.

Thus

$$T_3(\tau) = T_1(\tau) - \int_0^{\tau} \left(\frac{dT_2}{d\tau}\right) d\tau \, T_2 = T_1(\tau) \qquad (1)$$

assuming that the heat capacity of the examined sample $c(T)$ = const.

At the same time

$$\left(\frac{dT_2(\tau)}{d\tau}\right)_{T_2 = T_1(\tau)}$$ = rate of change in temperature T_2 from the cooling curve of the sample without transformation at temperature $T_1(\tau)$.

Assuming, that the temperature increase in the sample is directly proportional to the transformation progress, and that the degree $x = 0$ meets the starting temperature of the test and $x = 1$ meets the temperature at the end of the test, the degree of transformation in time can be determined [5]:

$$x(\tau) = \frac{T_3 - T_0}{T_{3k} - T_0} \tag{2}$$

where:
T_0 = ambient temperature at which the test is carried out, T_{3k} = temperature value T_3 at the moment of the end of the test. The transformation enthalpy was evaluated for $T_3(\tau) = T_{3k}$ and $c(T) = c_{\text{middle}}(c_m)$ from the relationship:

$$\Delta H = c_m(T_{3k} - T_0) \tag{3}$$

Changes in temperature T_3 were calculated from relation (1) on a WANG–2200 minicomputer. Differentiation and integration were carried out by numerical methods. The procedure for determination of the transformation temperature curve was described in detail in [5].

The transformation kinetics was evaluated on the basis of the following equation:

$$\frac{dx}{d\tau} = K^n \cdot \tau^{n-1} \cdot (1 - x) \tag{4}$$

where:

K = transformation rate constant,
τ = transformation time,
x = degree of transformation,
n = coefficient of transformation type.

The time and degree of the transformation were evaluated from the plots of x against time for the period of transformation increase. For this range the value $n = 1$ was assumed, and the value of K was calculated from the formula:

$$K = \frac{\Delta x}{\Delta \tau} \cdot \frac{1}{1 - x} \tag{5}$$

The values of K calculated in this way refer to the time interval in which the corresponding changes in the transformation degree x take place [5].

Changes in temperature T_2 (τ) during cooling of the examined alloy sample in air at 20° are shown in Fig. 1. Changes in temperature T_1 (τ) in the sample during decomposition of the supercooled β-phase (recorded continuously) are shown in Fig. 1, too. In the same Figure, changes in T_3 (τ), i.e. the temperature transformation curve, are also shown. The changes were calculated on the basis of relation (1).

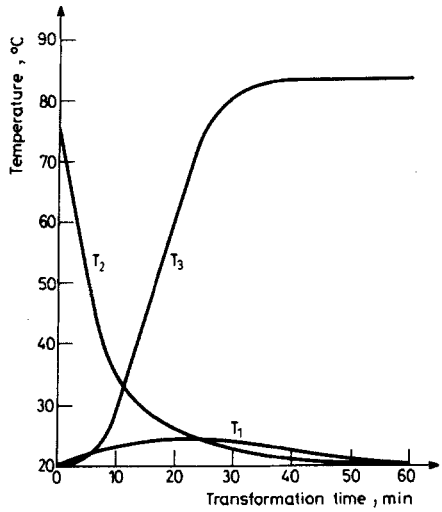

Fig. 1 Changes in temperature of ZnAl8Cu2 alloy sample during decomposition of supercooled β-phase. 1 – measured curve for $T_1(\tau)$; 2 – changes in temperature $T_2(\tau)$ during cooling of examined sample (cooling in air at room temperature); 3 – temperature *vs.* transformation curve

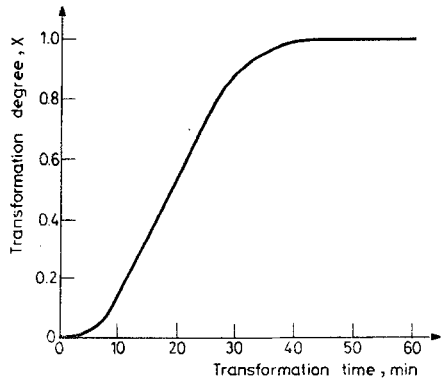

Fig. 2 Kinetic curve of decomposition of supercooled β-phase

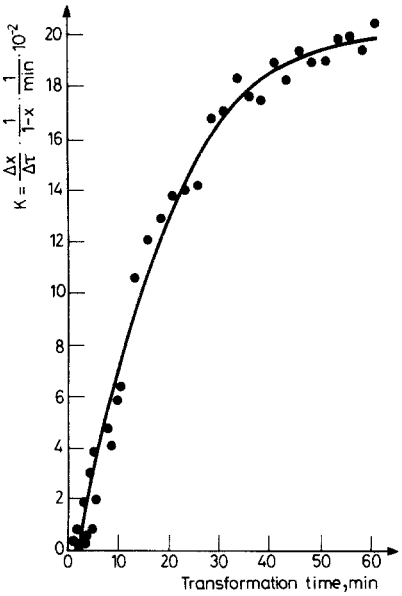

Fig. 3 Values of transformation velocity constant K, depending on transformation time

The course of temperature T_3 (τ) showed the increase to be even and monotonous. This strengthens the hypothesis that the principal transformation occurs by direct decomposition of the β-phase into stable β' and η-phases [1, 2, 5]. The temperature T_3 at the moment of the end of the test is $T_{3k} = 82.45°$. The transformation enthalpy calculated according to relation (3) for $c_m = 0.544$ J/g deg is $\Delta H = 34.07$ J/g. The transformation degree *vs.* time, i.e. the curve of the decomposition kinetics of the supercooled β-phase, is shown in Fig. 2. The curve is sigmoidal in shape.

The values of transformation rate constant K *vs.* time are shown in Fig. 3. The values were calculated from relationship (5) for the whole range of the transformation degree. As the transformation time rises, an increase in constant K is observed. It is maximum after 10 minutes of transformation.

Conclusions

1. The presented method of temperature determination during transformation from the changes in degree and transformation enthalpy is useful in investigations concerning phase transformations in ZnAl8Cu2 alloys.

2. The heat of decomposition of the β-phase supercooled from 360° is $\Delta H = 34.0$ J/g.

3. During transformation, increase in the transformation rate constant K is observed. For example, values of K depending on the interval are: for 5–10 minutes: $K = 0.03\text{–}0.072 \frac{1}{\text{min}}$; for 30–35 minutes: $K = 0.167\text{–}0.178 \frac{1}{\text{min}}$; for 55–60 minutes: $K = 0.194\text{–}0.198 \frac{1}{\text{min}}$.

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Zusammenfassung — Die Temperaturveränderungen $T_1(\tau)$ während der Zersetzung der unterkühlten β-Phase der ZnAl4Cu1-Legierung (360°) und die Abkühlungskurve $T_2(\tau)$ der Probe ab etwa 100° wurden bestimmt. Aus der Wärmebilanz und dem Verlauf der Kurven $T_1(\tau)$ und $T_2(\tau)$ wurden die Temperaturänderungen $T_3(\tau)$ der Probe unter adiabatischen Bedingungen bestimmt. Mit der Annahme, daß die Wärmekapazität konstant ist, ergibt sich folgender Zusammenhang:

$$T_3(\tau) = T_1(\tau) - \int_0^{\tau} \left(\frac{dT_2}{d\tau}\right) d\tau \quad T_2 = T_1(\tau)$$

Der Grad der Umwandlung $x(\tau)$ wurde aus den Temperaturänderungen $T_3(\tau)$ bestimmt. Die Geschwindigkeitskonstante K der Umwandlung und die Umwandlungsenthalpie (ΔH = 34,0 J/g) wurden berechnet. Die angewandte Methode scheint bei mit relativ großen Wärmeeffekten einhergehenden Phasenumwandlungen vorteilhaft anwendbar zu sein.

Резюме — Определены температурны изменения $T_1(\tau)$, происходящие при разложении сверхохлажденной β-фазы сплава ZnAl4Cu1, начиная от температуры 360° и кривые охлаждения $T_2(\tau)$ образца, начиная от температуры около 100°. Кривые охлаждения показали температурные изменения образца без какого-либо его превращения. На основе теплового баланса и кривых $T_1(\tau)$ и $T_2(\tau)$ были определены в адиабатических условиях изменения температуры $T_3(\tau)$. Предполагая постоянство теплоемкости, выведено следующее соотношение

$$T_3(\tau) = T_1(\tau) - \int_0^{\tau} \left(\frac{dT_2}{d\tau}\right) d\tau \quad T_2 = T_1(\tau)$$

Ихсодя из температурного изменения $T_3(\tau)$, была определена степень превращения $x(\tau)$. Вычислены константа скорости превращения и энтальпия превращения, равная 34.0 дж/г. Используемый метод является полезным для изучения быстрых фазовых изменений, сопровобдающихся относительно большим тепловым эффектом.