JOURNAL OF MATERIALS SCIENCE 5 (1970) 955–959

Activation Energy of Isothermal Martensitic β—α' Transformation

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The kinetics of isothermal β—α' martensitic transformation in the U—0.45 wt % Mo alloy has been investigated. The specimens were quenched from the β region (690° C) and held isothermally at temperatures from 120 to − 196° C (liquid nitrogen). By quantitative metallographic methods the percentage of the newly formed α'-phase was determined and the half-thickness *c* and radius *r* of plates calculated. The activation energy for nucleation period was estimated. It was found that ΔG depends linearly on temperature. The nucleation rate N was determined to be a parabolic function of temperature. A part of the T-T diagram below the M_s temperature was determined.

1. Introduction

The estimation of the activation energy Q and the rate of nucleation N of isothermal martensitic transformation is connected with serious experimental difficulties, although in 1958 Kaufman and Cohen [1] worked out theoretically the relevant thermodynamics and transformation kinetics. Neglecting for the moment the long debated question as to which of the systems has "pure" isothermal martensitic transformation without athermal nucleation, the main difficulty in applying the theory used by Kaufman, Cohen and other authors [2] was in obtaining reliable data about the incubation period and dimensions of initially formed plates of martensite. Although in some papers [3] it is stated that the rate of nucleation in the Ni—Mn—Fe alloy can be successfully determined, nevertheless this statement must be taken with reserve since the period of nucleation for 0.2 % transformation is determined by extrapolation from the 5 % value. This uncertainty in determining the nucleation period is caused by the fact that the said alloy transforms quickly, so that initially formed plates cannot be measured at all by a direct method.

The efforts of many researches have been directed mainly towards a generalisation of the data obtained on one system, and thus to set down principles that would be valid for isothermal martensitic transformation kinetics in general. However, these efforts appeared incorrect [4] owing to the lack of knowledge about the phenomena themselves in many systems.

In our previous papers [5, 6] we found that transformation in the U − 0.45 wt % Mo alloy develops very slowly, also that this system is an ideal model for quantitative kinetic data.

2. Material and Methods

The U − 0.45 wt % Mo alloy was made of uranium with a total of 500 ppm metal impurities and of 99.9 % pure molybdenum. The specimens, 2 mm thick and 8 mm in diameter, were annealed in vacuum during 2 h at 850° C and furnace-cooled. The homogenised specimens were oil-quenched from 690° C. The specimens retaining the metastable beta phase after quenching were held at the following temperatures: − 196° C, + 25° C, + 40° C, + 80° C and + 120° C. The

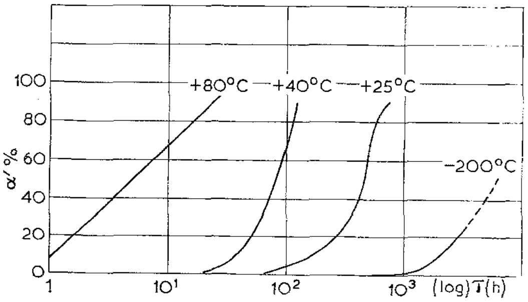


Figure 1 Isothermal curves for β–α' transformation.

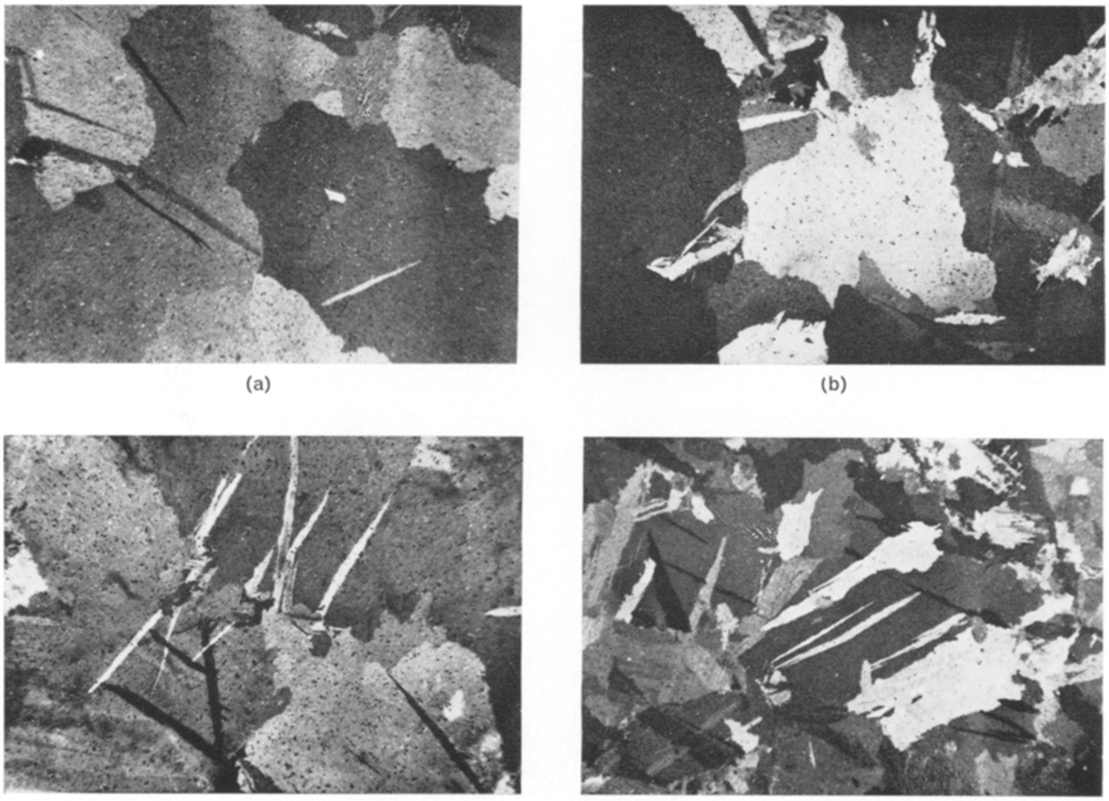
samples were polished electrolytically at regular time intervals and examined microscopically to estimate the amount of α' phase formed during martensitic transformation. The microstructure was taken in parallel on at least two similar samples. A minimum of three micrographs with different spots on the samples were taken. The mean value of the amount of α' phase and of the half thickness and radius of the plates formed was determined. While preparing the specimens, we did not use mechancial polishing in order to avoid induction of transformation.

3. Results

The change in the amount of phase formed (%) as a function of time is given in fig. 1 for each isothermal curve separately [6]. For 120° C no curve is given since we could not determine the points with accuracy, except at the beginning and the end of transformation. The appearance of microstructure at the beginning of transformation is shown in figs. 2a, b, c, d. On the basis of the data in fig. 1, a part of the T—T diagram for the beginning of transformation (M_s), 50% transformation and the end of transformation (M_f) was deduced (fig. 3).

4. Discussion and Conclusions

The kinetics of isothermal martensitic transformation has been investigated very often in Ni—Mn steels since they show pure isothermal transformation without athermally formed centres. It is characteristic of the above-mentioned type of steels that the transformation develops very fast even at temperatures below 0° C. Thus, for example, Entwistle [3] states that Ni—Mn steels transform by about 40% after 100 min at −60° C, with an incubation period of some tenths of a second. On the other hand, as already stated [6], the isothermal transformation of the U −0.45% Mo alloy develops very slowly. It becomes evident, if the data given by Entwistle on Ni—Mn steel are compared with a curve for 50% transformation of the U −0.45% Mo alloy (fig. 3),



(a) (b) (c) (d)

Figure 2 Beginning of β–α′ transformation at different temperatures. (a) 1300 h — 200° C × 60. (b) 170 h + 25° C × 60. (c) 40 h + 40° C × 60. (d) 4 h + 80° C × 60.

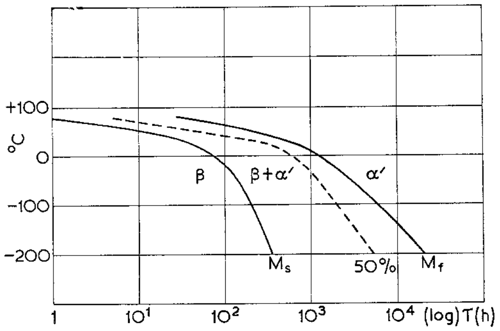


Figure 3 Part of T–T diagram.

TABLE I Change of ΔG and N in temperature range + 80 to + 200° C

Temperature °C	$\tau_{\text{nucl.}}$ (h)	$\Delta G_{\text{nucl.}}$ (cal/mol)	N (cm^{-3}/h)
+ 120	0.025	—	24 000
+ 80	0.80	26 000	750
+ 40	20	18 000	30
± 0	80	6000	7.5
– 40	150	2000	4
– 80	160	660	3.7
– 120	220	480	2.7
– 160	270	220	2.2
– 200	350	100	1.7

that 50% transformation at –60° C in the U –0.45% Mo alloy is reached after 60000 min.

Such a slow transformation proves that U—Mo alloys are ideal as a model to study isothermal martensitic transformation. It is characteristic of the U—Mo alloy that reaction is greatly slowed down with the decrease of temperature. As shown on part of the T—T diagram (fig. 3) at +80° C the incubation period is about 1 h and 50% transformation is achieved after 5 h. At a temperature of about –196° C, the incubation period is 350 h and 50% transformation is reached at about 5000 h, which shows that thermal activation has a marked effect on the complete development of transformation, including nucleation. (It should be mentioned that the symbol (M_S) on the nucleation curve (fig. 3) relates to the curve representing the beginning of the martensitic transformation and not to the conventional M_S temperature).

The usual empirical equation (Becker, Fisher) for a homogenous nucleation is

$$N = k \exp - [(\Delta G + Q)/RT]$$

where N is nucleation rate, ΔG is activation energy for the formation of a nucleus of critical size, and Q is the activation energy for atom migration (diffusion). This equation could be expressed in terms of time required for nucleation

$$\ln \tau = \frac{\Delta G}{RT} + \frac{Q}{RT} + c$$

The term with Q, which describes the processes in the cases where diffusion controls the growth, can be neglected [1] because β/α' interface mobility exists in the U – low Mo alloys even at temperatures as low as ~ –200° C [6].

The activation energy ΔG was calculated from the slope of the plot lnτ *vs* $1/T°$ K in the temperature range + 80 to – 196° C for the period of nucleation (0.1% transformation). The ΔG (± 10%) values (fig. 4) show on the one hand, that the difference in activation energies for maximum and minimum reaction temperatures is ~ 10^3 cal/mol; on the other hand, the linear temperature-dependence indicates that the temperature rise does not change the control mechanism of the reaction. Pati and Cohen [7] came to the same conclusion for 24Ni – 3Mn steel – namely, that log $G_{\text{nucl.}}$ increases linearly with a rise of reaction temperature. However, the values for ΔG found by them for the maximum and minimum temperatures of reaction: –70° C, 15000 cal/mol and –196° C 5800 cal/mol are significantly higher in comparison with our values for the same temperatures, i.e.~1000 cal/mol and 100 cal/mol.

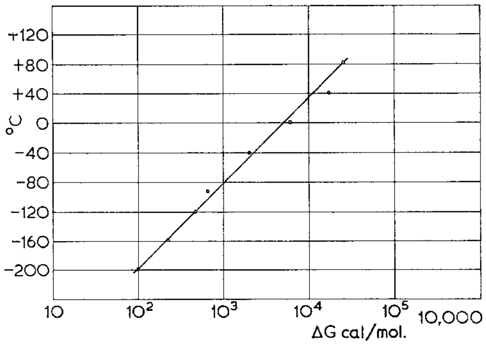


Figure 4 Plot : ΔG vs. reaction temperature.

To determine the nucleation rate, Shih *et al* [8] proposed the following empirical expression:

$$N.\nu.\tau = A$$

where N = nucleation rate, ν = volume of initially formed plates; τ = incubation period, and A = percentage of newly formed phase. From this it follows that $N = A/\nu$. One of the main problems in applying this equation is the determination of v; this is usually solved by the methods of quantitative metallography. The volume of a disc-shaped spheroid is given by:

$$v = \frac{4}{3}\tau . r^2 . c$$

where r = radius and c = half-thickness.

To calculate the value of radius r correctly by the linear intercept method, the diameter of grain and radius of the flattened spheroid are related. In our case, we had no need to determine these values in this way. Owing to slow growth, we were in a position to measure c and r precisely. It was found that the mean value regardless of isothermal temperature (for about 50 needles), is: $c = 0.0004$ cm and $r = 0.01$ cm at a time τ which is equal to the period of incubation. Putting $A = 0.001$ (0.1 %) for τ =incubation period from (table I), and $r = 0.01$ cm and $c = 0.0004$ cm, we calculated the change in nucleation rate N as a function of the reaction temperature (table I), using the relationship $N = A/v$.

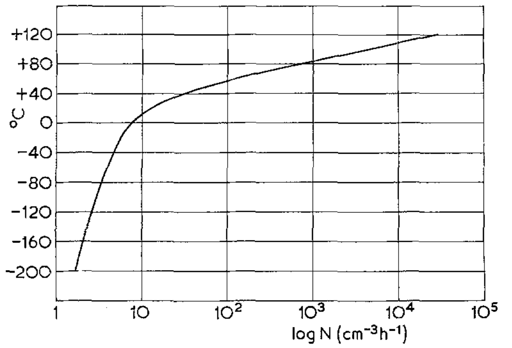


Figure 5 Plot: Nucleation rate vs. reaction temperature.

The curve showing the change in nucleation rate N with temperature up to +120° C (fig. 5) has the approximate shape of a parabola with a sudden rise of N value over 0° C. To carry out a complete analysis showing the dependence of the rate of transformation on reaction temperture, it is necessary to possess data regarding the effect of temperature on the growth rate of the martensitic plates. Qualitative indications, according to an estimation of microstructure, suggest that temperature rise increases the growth rate of the plates, but owing to lack of quantitative data at present, we must in further discussion neglect the effect of the growth rate of the plates on the β—α' transformation. A sudden increase in nucleation rate above room temperature, from about 7.5 at 0° C to 24000 ($cm^{-3}h^{-1}$) at +120° C is in agreement with the effect of temperature as found on transformation. Bearing in mind the fact that the mechanism of reaction does not change at temperatures ranging from −196° to + 120° C, as well as the fact that the rate of nucleation increases with rise in temperature, it can be assumed that nucleus formation is dependent on thermal activation. A rate of nucleation N close to unity was obtained by extrapolation of the curve from −196° C to absolute zero −273° C, i.e. the transformation process would practically be stopped.

In the previous work [9], a part of T—T diagram of the U −0.45 % Mo alloy for temperature below M_S, similar to the diagram given by

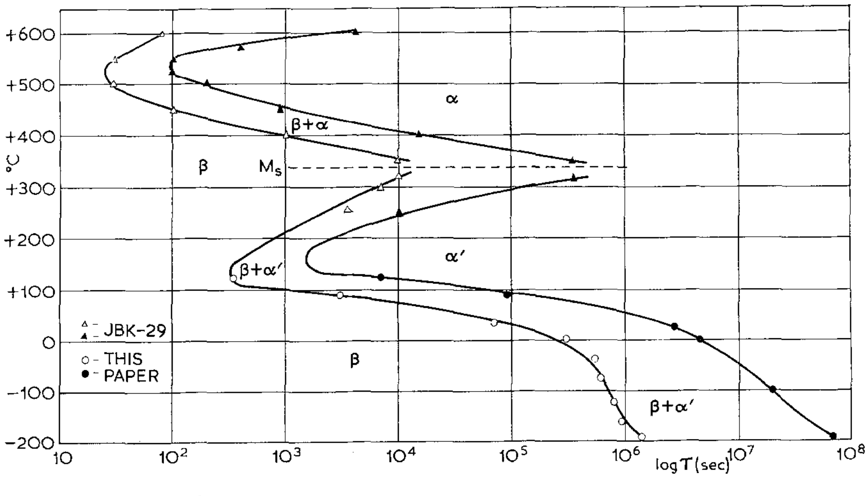


Figure 6 T-T diagram of U — 0, 45% Mo alloy.

Lehman [10], was established. The part of the T—T diagram below the M_s temperature, as far as we know, has not been published in the open literature [11]. By combining our data on the already existing diagram we obtained a complete T—T diagram of the U–0.45% Mo alloy for temperatures ranging from +600 to −196° C (fig. 6). The "C" shape of the curves of the martensitic part of the T—T diagram was to be expected by analogy with other metal systems. The extremity of the "C" curve for the beginning and end of transformation (nose curve) is at about +130° C and at a time of about 300 sec for the beginning, and 1500 sec for the end of transformation. It is interesting to note that the shape of the part of the curves at temperatures close to −196° C suggests that the curves would approach absolute zero (−273° C) asymptotically. This indicates that the beginning of transformation close to absolute zero would approach very great times, i.e. the β—α' transformation would practically stop.

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Received 16 April and accepted 1 September 1970.