The kinetics of pressure-induced $\alpha \rightarrow \omega$ transformation in Ti

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The kinetics of the pressure-induced $\alpha \rightarrow \omega$ transformation in titanium is reported in the pressure range 5–9 G Pa. The occurrence of this transformation under shock loading has been discussed using the observed pressure dependence of the kinetics.

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The α phase (hcp) of titanium, which is stable at normal conditions of temperature and pressure, transforms to ω phase[1] (hexagonal) at high pressures. On release of pressure, ω phase is retained metastably at 1 atm. The transformation is known to be martensitic in nature.[2]

In experiments conducted under static pressures, the $\alpha \rightarrow \omega$ transformation is found to be time dependent, wherein the fraction of transformed ω phase increases with time.[3,4] The $\alpha \rightarrow \omega$ transformation is also found to occur under shock loading.[5] For any transformation to occur under shock loading, its kinetics should be fast enough for the system to respond to loads of short duration, typically a few microseconds. The kinetics of the $\alpha \rightarrow \omega$ transformation in Ti as a function of pressure have been reported in this paper with a view to predict the kinetics under very high pressures. The change in the electrical resistance occurring at the $\alpha \rightarrow \omega$ transformation has been recorded as a function of time. From this, the fraction $\zeta_p(t)$ of the transformed ω phase as a function of time has been calculated. The $\zeta_p(t)$-t data at $26 \pm 2°$ C and at pressures ranging between 5 and 9 G Pa have been obtained. The occurrence of the transformation under shock loading has been discussed using the pressure dependence of the kinetics obtained in this study.

A tungsten carbide opposed anvil device capable of going up to 10 G Pa, wth pyrophyllite gasket and talc as the pressure transmitting medium, was used to pressurize the specimen. The Bi-I→II (2.54 G Pa) and Bi-III→V(7.7 G Pa) transitions were used to determine the relation between the specimen pressure and the load applied on the anvils. To take into account the run-to-run variation in the load-versus-specimen pressure relation, a Bi specimen was placed at right angles to the Ti specimen in each run; a thin sheet of mica was used to insulate Bi and Ti specimens. A four-lead arrangement was used to measure the resistance of the Ti specimen, while a simple two-lead measurement was found adequate to detect the two transitions in Bi. The starting material for the Ti specimen was Marz grade Ti wire (0.125 mm in diam) from Materials Research Corporation, USA. The major impurities are listed in Table I. These wires were flattened and specimens measuring approximately $5 \times 0.5 \times 0.05$-mm cutoff. The grain size was nearly 2μ. The Bi specimens, also of the same dimensions as the Ti specimens, were prepared from Bi lumps of 99.999% purity.

The pressure was increased up to 6 G Pa at a rate nearly 0.1 G Pa per min. In this pressure range the sample was predominantly in α phase. The resistance of the α phase was found to decrease with the increase in pressure. Above 6 G Pa, the α phase transformed to ω phase with appreciable speed and, therefore, the desired pressure P (6 G Pa$\leqslant P \leqslant$9 G Pa) was reached by rapid pressurization (nearly 0.5 G Pa s^{-1}). The pressure was held constant at P and the resistance of the sample monitored as the $\alpha \rightarrow \omega$ transformation progressed with time. The resistance of the sample increased during the $\alpha \rightarrow \omega$ transformation. In the ω phase the sample resistance decreased with the increase in pressure. The $\alpha \rightarrow \omega$ transformation was considered complete when the sample resistance showed no detectable increase with time. That the $\alpha \rightarrow \omega$ transformation was complete at this point was further confirmed by slightly increasing the pressure, which resulted in a decrease in the sample resistance. If untransformed α phase was present, then an increase in pressure would cause this α phase to transform to ω phase causing an increase in the sample resistance. Such experiments were done at several pressures between 6 and 9 G Pa. The fraction $\zeta_p(t)$ of the ω phase was calculated from the resistance data using the following relation[6]

$$\zeta_p(t) = \frac{\Delta r}{r} \times \frac{1 + \frac{2}{3}(r/R_{\alpha P}) + \frac{1}{3}(\Delta r/R_{\alpha P})}{1 + (\Delta r/R_{\alpha P})}, \tag{1}$$

with $r = R_{\omega P} - R_{\alpha P}$, and $\Delta r = R_P(t) - R_{\alpha P}$, where t denotes time, and $R_{\alpha P}$ and $R_{\omega P}$ are, respectively, the resistances of the α and ω phases at pressure P. $R_P(t)$ is the resistance of the sample at a time t after the pressure P was reached; the time dependence of the resistance indicates the progress of the $\alpha \rightarrow \omega$ transformation. $R_{\alpha P}$ and $R_{\omega P}$ were determined experimentally in each run. $R_{\alpha P}$ was obtained from the extrapolation to P of the α-phase resistance versus the pressure data up to 6 G Pa. The estimated decrease in the

TABLE I. The major impurities in Ti.

Impurity elements	C	H	O	N	Al	Cr	Cu	Fe	Hf
Content ppm	78	4	63	6	15	25	8	50	12
Impurity elements	Mg	Mn	Mo	Nb	Ni	S	Si	Sn	V Zr
Content ppm	15	1.2	5	6	5	1.5	3.5	5	1 20

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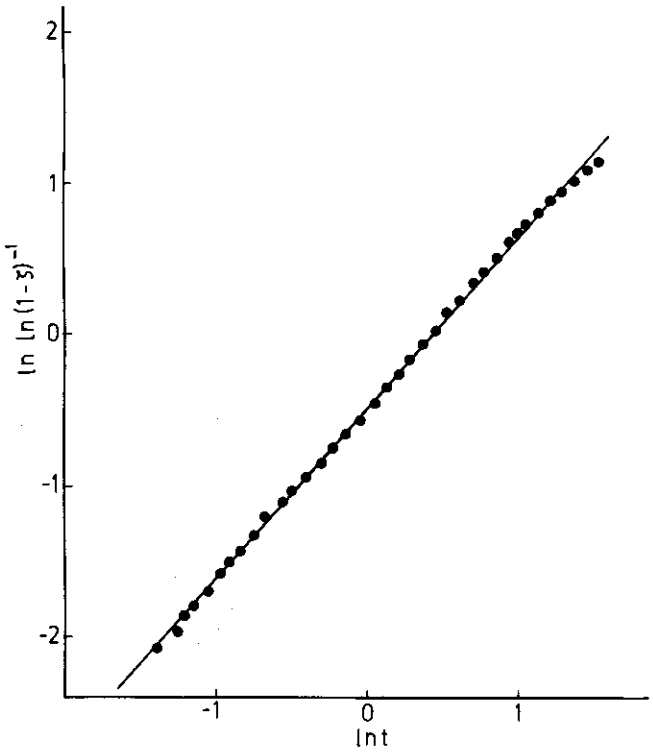

FIG. 1. Typical plot showing the variation of $\ln \ln(1-\zeta)^{-1}$ with $\ln t$.

resistance of α phase between 6 and 9 G Pa was nearly 2%. The resistance of the sample after the completion of the transformation was taken as $R_{\omega P}$.

A $\zeta_p(t) - t$ plot was found to be sigmoidal. Further, when $\ln \ln(1-\zeta)^{-1}$ was plotted against $\ln t$, a straight line was obtained. A typical plot is shown in Fig. 1. This indicates that $\zeta_p(t)$ and t are related through an equation,

$$\zeta_p(t) = 1 - \exp - K(P)t^{n(P)}, \tag{2}$$

where $K(P)$ and $n(P)$ are constants at a pressure P. This equation has been derived for a nucleation and growth process.[7,8] The $\alpha \rightarrow \omega$ transformation in Ti is martensitic; the validity of Eq. (2) in such a case is difficult to justify. The $\zeta_p(t) - t$ data are *found* to fit Eq. (2). In general, the kinetic features of a martensitic transformation can resemble those of a nucleation and growth process when termally assisted nucleation (pressure-assisted nucleation in the present case) controls dominantly the overall transformation rate (Ref. 7, p. 10). For further discussion, Eq. (2) was rearranged as follows:

$$\zeta_p(t) = 1 - \exp - [t/t_0(P)]^{n(P)}, \tag{3}$$

where $t_0(P) = [K(P)]^{-1/n(P)}$. At $t = t_0(P)$, $\zeta_p(t_0) = 1 - e^{-1} \simeq 0.63$. Thus, $t_0(P)$ is the time required for 63% conversion, and can be used conveniently as a measure of the "speed" of the transformation. From the experimental $\zeta_p(t) - t$ data, $t_0(P)$ and $n(P)$ can be obtained by plotting $\ln \ln(1-\zeta)^{-1}$ against $\ln t$; $n(P)$ is given by the slope of the line, and $t_0(P)$ can be calculated from the intercept on the $\ln \ln(1-\zeta)^{-1}$ axis. The values of $t_0(P)$ obtained at various pressures is shown in Fig. 2. It is seen that $\ln t_0(P)$ decreases linearly with the increase in pressure. A least-squares fit gave the following result:

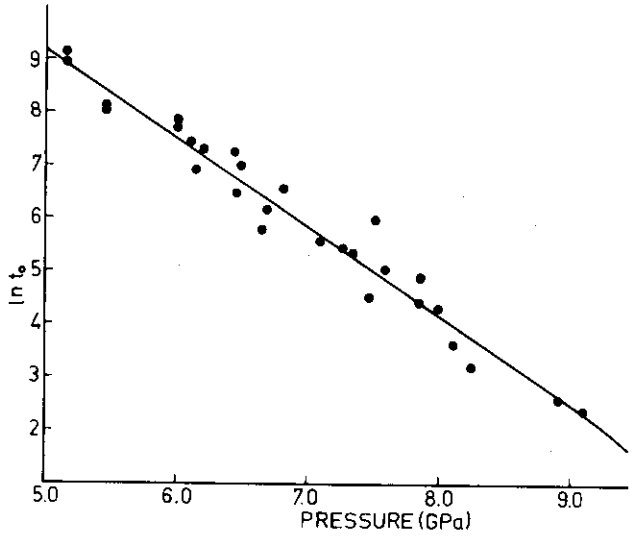

FIG. 2. Variation of $\ln t_0$ with pressure.

$$\ln t_0(P) = 17.56 - 1.674P, \tag{4}$$

where t_0 and P are, respectively, in the units of s and G Pa. The coefficient of determination was 0.96. $n(P)$ was found to decrease slightly with increasing pressure. Assuming that a second-degree polynominal in P describes the pressure dependence of $n(P)$, a least-squares fit gives the following result

$$n(P) = 3.324 - 0.242P - 0.0023P^2. \tag{5}$$

Equation (3) together with Eqs. (4) and (5) describe completely the kinetics of the $\alpha \rightarrow \omega$ transformation in Ti. The temperature-induced martensitic transformations are known to depend on the grain size.[9] By analogy, the pressure-induced martensitic transformations are also likely to depend on the grain size. No attempt has been made here to study this aspect of the transformation.

It is seen from Eq. (4) that $t_0(P) \simeq 1\ \mu$s at $P = P_s = 19$ G Pa. P_s denotes the pressure at which $t_0(P) \simeq 1\ \mu$s. Thus, at 19 G Pa the kinetics of the transformation become so fast that the transformation can proceed appreciably in the short duration (a few μs) of a shock wave impulse.

The occurrence of the $\alpha \rightarrow \omega$ transformation in Ti under shock loading was established by Kutsar *et al.*[5] The x-ray examinations of the samples, shock loaded to 35 G Pa at 293° K, showed the presence of ω phase in small quantities. At this pressure the estimated shock residual temperature exceeded the temperature of $\omega \rightarrow \alpha$ transformation resulting in a poor yield of ω phase. When the residual temperature was lowered by cooling the specimen in liquid nitrogen down to 120° K, before loading it to 35 G Pa, nearly 60% ω phase was detected.

The present kinetics data suggest that the transformation under shock loading should occur around 19 G Pa while the experimental value is 35 G Pa. This difference may arise from various sources: (i) A linear relation [Eq. (4)] has been assumed in extrapolating to high pressures the $\ln t_0$ vs P data. It may be noted that this extrapolation is over six orders of magnitude. This would give an underestimate of P_s if $\ln t_0$ is not truly linear in P but contains a positive term in P^2. (ii) The $\alpha \rightarrow \omega$ transformation in Ti is sensitive to the presence

of impurities, especially oxygen, which is known to raise the transition pressure. A closer comparison of the values of P_s is not meaningful because the data in two studies (Ref. 5 and the present) are on samples of different purities. (iii) Above all, the occurrence of $\alpha \rightarrow \omega$ transformation in Ti does not appear to have been studied under shock loading to various pressures. It is likely that 63% transformation occurs at pressures significantly lower than 35 G Pa. In fact, a discontinuity in shock Hugoniot of Ti was observed[10] at 17.5 G Pa which could be attributed to the $\alpha \rightarrow \omega$ transformation.

The shock residual temperature has to be taken into account while attempting to extend the results of the static pressure measurements to the shock wave conditions. If the residual temperature is more than the $\omega \rightarrow \alpha$ transformation temperature, the amount of ω phase in the shock-loaded sample may be reduced. An estimate of residual temperature in Ti indicates[5] that below 20 G Pa, it is less than transformation temperature, and therefore this factor need not be considered in the present discussion.

The kinetics of the $\alpha \rightarrow \omega$ transformation in Ti is sensitive to the deviatoric component of stress present in the pressurizing system. In shock wave experiments large deviatoric stresses are likely to be present. A detailed discussion of this aspect is not possible because the quantitative estimates of the deviatoric component and its effects on kinetics are not known. Qualitatively, the presence of deviatoric stresses larger than those present in the static pressure experiments will have a tendency to reduce P_s.

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