

The kinetics of pressure-induced polymorphic transformations

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Abstract. The various methods of obtaining the kinetics data in pressure-induced transformations have been briefly reviewed. Some of the recent results obtained for the pressure-induced alpha-omega transformation in titanium, and fcc-bcc transformation in ytterbium have been discussed. The general features of the kinetics data have been compared with those for other transformations available in literature.

Keywords. High pressure; kinetics; phase transformation; titanium; ytterbium

1. Introduction

The study of the kinetics of phase transformation often plays an important role in understanding the mechanism of the phase transformation. The kinetics of the pressure-induced transformations have not been studied as extensively as the kinetics of temperature-induced transformations mainly because of the difficulties in high pressure experiments. The transformations studied in the past were mostly of reconstructive type (a classification introduced by Buerger 1953) which require high temperature and high pressure. Some of the transformations studied in detail are: calcite \rightleftharpoons aragonite (Davis and Adams 1965; Brar and Schloessin 1979); GeO_2 (α -quartz) \rightleftharpoons GeO_2 (rutile) (Zeto and Roy 1969; Brar and Schloessin 1981); PbO_2 (I) \rightleftharpoons PbO_2 (II) (Dachille and Roy 1964); $\gamma \rightarrow \alpha$ transformation in Fe_2O_3 (Goto 1964); graphite \rightleftharpoons diamond (Hanneman 1969; Bundy 1969). The earlier studies on the kinetics of pressure-induced phase transformations have been reviewed by Onodera (1971), and Osugi *et al* (1975). In this paper the discussion is restricted to the polymorphic transformations which occur at room temperature. The results obtained under isobaric conditions for alpha-omega transformation in titanium and fcc-bcc transformation in ytterbium have been discussed.

2. General considerations

The relative stabilities of the various phases (of the same chemical composition) can be conveniently discussed with reference to a diagram showing the variation of Gibbs free energy, G , as a function of the thermodynamic variable. Such a diagram for a system which exhibits two phases A and B as the pressure is varied, is shown in figure 1. The lines marked 1 and 2 depict the variation of G with pressure for respectively phases A and B . The point of intersection of the two lines represents the pressure, p_0 , at which the free energies of the two phases are equal; p_0 is termed thermodynamic equilibrium pressure. The phase A is stable below p_0 whereas phase B is stable above p_0 . The symbols A_m and B_m indicate metastable phases.

In practice the transformation $A \rightarrow B$ does not take place at p_0 , but often a pressure

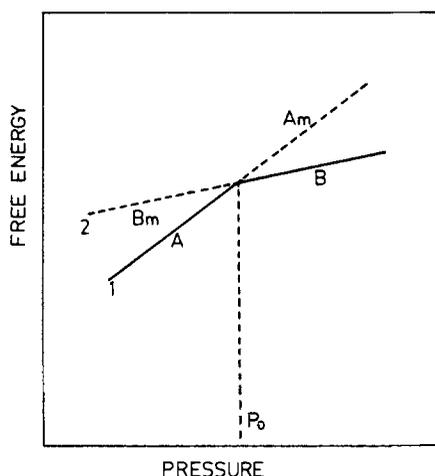


Figure 1. Variation of Gibbs free energy with pressure of phases *A* and *B* in the vicinity of p_0 . Phase *A* undergoes a first order transformation to phase *B* above p_0 .

well above p_0 has to be applied to drive the transformation. This is because the transformation faces an activation barrier (figure 2). The activation free energy ΔG^* is often very large compared to the free energy difference between the two phases *A* and *B*. Phase *A* which may be present above p_0 is, in fact, a metastable phase A_m . Similarly, when the pressure is reduced from well beyond p_0 where only phase *B* is present, phase *A* does not reappear until the pressure is reduced well below p_0 . Phase *B* which persists below p_0 is also a metastable state. The difference between p_0 and the pressure required to observe $A_m \rightarrow B$ transformation[†] is called over-pressure, and depends on the magnitude of ΔG^* . The larger the ΔG^* the higher will be the over-pressure required for a given rate of transformation.

The presence of an activation barrier (and hence the requirement of an over-pressure to drive the transformation) implies that any physical property measured with increasing and decreasing pressure around p_0 will exhibit a hysteresis. This hysteresis is inherent to the transformation and is different from the hysteresis arising from the friction in high pressure set-up. A hypothetical plot of a physical property against pressure exhibiting a hysteresis is shown in figure 3. The different phases and the pressure range over which they exist are also indicated. It may be noted that the magnitude of the property of phase *A* measured with decreasing pressure does not always coincide with that obtained with increasing pressure. The properties such as electrical conductivity which may depend on the grain size and the plastic strains in the specimen show a value, on cycling through the transformation, which differ from the starting value. However, some other properties, such as volume change under pressure, show reproducible values with increasing or decreasing pressures in the region where either phase *A* or *B* alone is present.

[†]In commonly used notations this transformation is simply denoted by $A \rightarrow B$, but strictly speaking it is $A_m \rightarrow B$. The $A \rightarrow A_m$ involves only an increase in G along the line 1 in figure 1, and does not represent a phase transformation. The suffix *m* is therefore just a reminder that phase *A* is already in the region where *B* is stable.

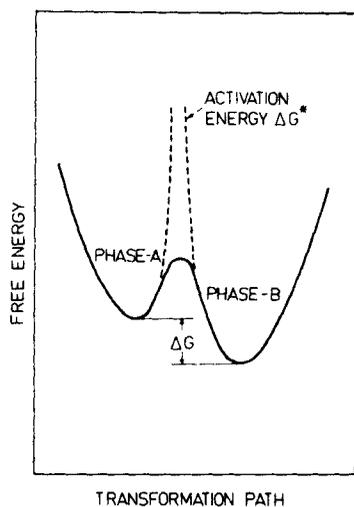


Figure 2. A section at $p > p_0$ indicating the variation of free energy along the transformation path.

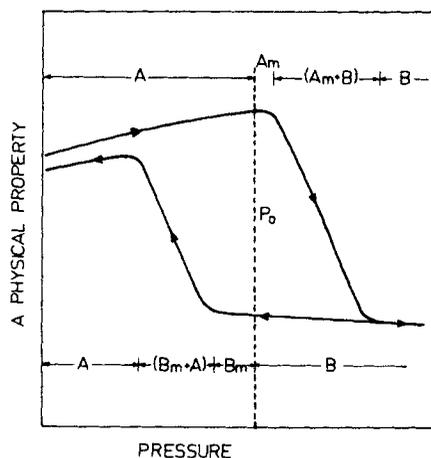


Figure 3. Intrinsic hysteresis when a physical property is measured with increasing and decreasing pressure enclosing $A \rightleftharpoons B$ phase transformation.

It is seen from figure 3 that p_0 lies within the hysteresis loop. The position of p_0 with respect to the hysteresis loop is important because this knowledge can be used to experimentally determine p_0 which is an important parameter. It is often assumed that p_0 is located at the midpoint of the hysteresis loop. Thus, p_0 in these experiments have been taken as the average of the pressures at which $A_m \rightarrow B$ and $B_m \rightarrow A$ are observed to start. However, there is no *a priori* justification for this. As discussed earlier, the overpressure required to produce an observable rate of transformation depends on the activation free energy for the transformation. Thus, p_0 can lie at the midpoint of the

hysteresis loop only if the activation barriers for the $A_m \rightarrow B$ and $B_m \rightarrow A$ transformations are identical. In general, the position of p_0 remains to be determined by more elaborate experiments.

The method of determining p_0 was suggested by Bridgman (1940). The pressure is increased in small steps and the progress of the transformation is monitored by observing the change in specimen resistivity for a fixed interval of time after each increase. If $A_m \rightarrow B$ transformation is observed, then the pressure is decreased in steps with a waiting period after each decrement of pressure, until $B_m \rightarrow A$ transformation is observed. The process is repeated until a region is obtained within which no perceptible $A_m \rightarrow B$ or $B_m \rightarrow A$ transformation takes place. This region was termed "region of indifference" by Bridgman. It is then assumed that p_0 lies in the middle of the region of indifference. This method requires that the pressure be truly hydrostatic and be measured *in situ* by suitable method, for example with the help of a manganin gauge. This method is time-consuming and has been used only for a few transformations which are used as pressure standards (Zeto *et al* 1968; Zeto and Vanfleet 1969). This method poses serious experimental problems at pressures above 6 GPa. As a result it is customary in high pressure work to quote the pressure at which the transformation is detected with increasing pressure. The transformation pressure thus obtained is termed 'start pressure'. The start pressure is not related to p_0 in any definite manner. The next best that has been done is to assume that p_0 is located at the midpoint of the hysteresis.

The determination of p_0 by the above method breaks down in case of transformations which exhibit such large hysteresis that the high pressure phase is metastably retained at atmospheric pressure. In such cases, the width of the hysteresis can be reduced by intentionally increasing the shear component of stress while pressurizing the specimen. The determination of p_0 of $\alpha \rightarrow \omega$ transformation in titanium is one such example (Zil'Bershteyn *et al* 1976). As the temperature of the specimen is increased the hysteresis in $\alpha \rightarrow \omega$ transformation decreases. Taking advantage of this fact Zil'Bershteyn *et al* (1974) determined p_0 at higher temperatures by taking the average of the $\alpha \rightarrow \omega$ and $\omega \rightarrow \alpha$ transformation pressures. The value of p_0 at room temperature was obtained from these measurements by extrapolation of the p_0 versus temperature data. The p_0 for $\alpha \rightarrow \omega$ transformation in titanium obtained by the two methods agrees well. Both the methods, however, assume that p_0 is located at the midpoint of the hysteresis loop.

The high pressure transformations may occur from one stable to another stable phase, stable to metastable phase, or even from one metastable phase to another metastable phase. A number of interesting examples are given by Roy (1969). In this paper the discussion will be confined to transformations from one stable phase to another stable phase; this may, however, involve a metastable phase as an intermediate step.

The pressure-induced transformations which have been studied for their kinetics aspects fall under two categories. In the first category are polymorphic transformations which are displacive transformations (Buerger 1953). These transformations usually have low activation energy and are relatively rapid. Since polymorphic transformations can occur at relatively lower temperatures (room temperatures or lower), any diffusion process is unlikely to take place. The second category of transformations are the reconstructive type. These have large activation energy and are generally sluggish. The transformation rates become appreciable only at higher temperatures. Such transformations are often diffusion-controlled.

3. Experimental methods

The study of the kinetics of phase transformations requires information on the fraction transformed as a function of time. The change in a physical property such as volume or the electrical resistance of the specimen is recorded as a function of time as the transformation progresses. The fraction transformed at various time intervals are calculated from such data. It is desirable to obtain the kinetics data under isobaric conditions because the interpretation of the data is simpler. However, it is not uncommon to find in literature studies made under the conditions of varying pressures. The methods commonly used to obtain the kinetics data are described in some detail.

The measurement of volume change associated with a first order transformation offers a simple method of obtaining the kinetics data. The fraction transformed is proportional to the volume decrease; the constant of proportionality is obtained by noting the volume decrease for complete transformation. A piston-cylinder high pressure set-up is ideally suited for such measurements. The sensitivity of the measurements is considerably improved in these experiments because a relatively large-sized specimen (volume $\approx 1 \text{ cm}^3$) can be used. As the transformation progresses and the volume decreases, the piston moves inward. For a properly designed set-up the volume change is proportional to the piston displacement. Thus, complete kinetics data can be obtained by recording the piston displacement as a function of time. This method however, has a serious drawback; the large size of the specimen, which results in an increased sensitivity in the measurement of volume changes, leads to a large drop in pressure when transformation takes place. It is difficult to maintain a constant pressure during the transformation. For this reason, studies under isobaric conditions cannot be made. In spite of this drawback, the method has been used to obtain interesting results (Livshitz *et al* 1960, 1969; Lacam *et al* 1973; Leliwa Kopystynski *et al* 1975).

The change in electrical resistance of the specimen can be used to monitor the progress of the transformation. A typical resistance-pressure data for titanium is shown in figure 4. As the pressure is increased the resistance of α -titanium decreases, and with

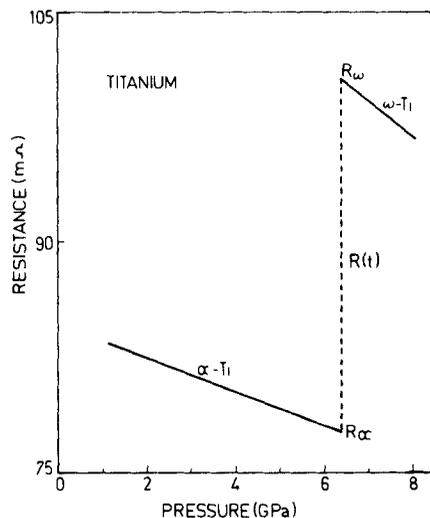


Figure 4. The resistance of titanium specimen as a function of pressure.

sufficiently high over-pressure the transformation to ω -phase starts. The resistance of the specimen $R(t)$ becomes time-dependent, and is recorded as a function of time. The resistances of the specimen in α - and ω -phase at a constant pressure are respectively R_α and R_ω . In general, α and ω -phase may be taken to denote respectively the low and high pressure phase in a pressure-induced transformation. The fraction of ω -phase formed at any instant t can be calculated from the knowledge of $R(t)$, R_α and R_ω . In fact $R(t)$ represents the resistance of an intimate mixture of α and ω phases. If it is assumed that resistances of the α and ω phases lie in series, then it turns out that the fraction of ω -phase is proportional to the change in resistance. This approximation has often been used to calculate the fraction transformed. Clearly, this assumption represents an extreme case, and is not likely to have a general validity. It can as well be assumed that the α and ω -phases provide a parallel resistive path, and in such a case the fraction transformed is proportional to the change in electrical conductivity. A rigorous expression for the effective resistance of a two-phase random mixture is given by Landauer (1952). This expression, instead of a series or parallel approximation, has been used in recent studies to estimate the fraction transformed (Singh *et al* 1982a, 1982b). More complicated models have been used in other studies (Lombos and Mahdaly 1977).

The resistometric method of determining the fraction transformed has an advantage that a small specimen ($0.5 \times 0.05 \times 5$ mm) is used. The volume change of transformation is a very small fraction of the volume of the high pressure cell, and therefore the pressure does not drop as the transformation progresses. This makes it possible to obtain data under isobaric conditions.

The transformations resulting in quenchable phases can be studied by x-ray diffraction technique. This involves holding the specimens at a given temperature and pressure for different times and quenching them to room temperature and one atmosphere. The fraction of the high pressure phase is determined at one atmosphere by x-ray diffraction technique. The high intensity x-ray sources, such as rotating anode x-ray generators and synchrotron radiation source, make it possible to record diffraction patterns from specimen under pressure in a few minutes. Thus, it is possible now to determine the fraction transformed by pressurizing the specimen and carrying out *in situ* x-ray diffraction analysis. This method has been recently used to study the $B1 \rightarrow B2$ transformation in KC1 (Hamaya and Akimoto 1981). The precision with which the fractions of the phases can be determined is rather limited.

It is instructive to compare the various methods discussed above and point out their merits and drawbacks. The method based on the measurement of volume change directly gives the fraction transformed, but it is difficult to maintain the pressure constant. Further, since a piston-cylinder apparatus is used, the highest pressure is limited to about 4.5 GPa. The resistometric methods are most convenient in practice. Since the specimen size is small, the progress of transformation does not result in a drop in pressure. Since the specimen size is small, it is possible to use opposed anvil devices to pressurize the specimen. These devices using tungsten carbide anvils can easily go up to 15 GPa. This method however can be used only with conducting or semiconducting specimen. The calculation of the fraction transformed assumes that specimen is an intimate random mixture of two phases. Any departure from this in actual case is likely to introduce errors. The x-ray methods are more cumbersome in general, and less precise when used with high pressure x-ray cameras.

The study of kinetics under isobaric conditions requires that the specimen be

pressurized to a desired level before any transformation can take place. For sluggish transformations the loading rates available in conventional high pressure set-up are adequate. However, for fast transformations a specially designed loading set-up is required. A method for rapidly loading an opposed anvil set-up was developed, and is shown schematically in figure 5. The bomb, the hydraulic ram and the reservoir can be isolated by closing respectively V_1 , V_2 and V_3 . The pump has a built in non-return valve. The hydraulic ram which loads a tungsten carbide opposed anvil set-up is first pressurized to a desired initial pressure by closing V_3 and opening V_1 and V_2 . The ram is isolated by closing V_2 . The bomb is pressurized to a higher pressure. The pressure in the hydraulic ram jumps to a higher value when V_2 is suddenly opened. The final ram pressure is a function of initial pressure and the bomb pressure. The rise time of the pressure pulse is nearly 200 msec. Such a rapid pressurization results in a temperature rise of the specimen but it is small and can be neglected. The details of this method are given elsewhere (Singh *et al* 1983a).

The change in other physical properties associated with the transformation, has been occasionally used to follow the progress of the transformation. Samara *et al* (1967) studied the rate of orthorhombic to cubic transformation in thallium iodide by monitoring the change in the specimen capacitance. The changes in optical absorption of transparent specimen can be used to study the kinetics of transformations. Takano *et al* (1982) used the diamond anvil cell to this effect.

4. Results and discussion

The literature on the kinetics of pressure-induced transformations is rather limited. The first measurements of the rates of solid-solid transformations were made by Bridgman (1916) by following the rate of decrease in pressure caused by the decrease in volume associated with the transformation. It was observed that the rate of transformation increased with increasing over-pressure. More recently, while characterizing accurately BiI \rightarrow II transition for the purpose of pressure calibration, Davidson and Lee (1964), and Zeto *et al* (1968) studied the kinetics aspect. It became clear that the transformation was not a fixed-strain transformation, but involved a thermally activated nucleation process. Further, the transformation was isobaric in that it ran to completion as the

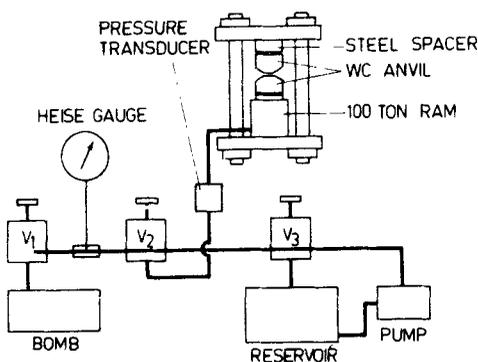


Figure 5. A method for step-loading an opposed anvil set-up.

pressure was held constant. Though these studies were significant in establishing the nature of the transformation, no quantitative kinetics studies were made. Kopystynski *et al* (1975) studied the B1-B2 transformation in rubidium chloride by measuring the pressure drop in the high pressure cell as the transformation progressed. The rate of pressure drop could be explained on the basis of a nucleation and growth model. Hamaya and Akimoto (1981) studied the B1-B2 transformation in potassium chloride by pressurizing the specimen in a cubic press and using *in situ* x-ray diffraction analysis. They showed clearly that the kinetics data satisfied Avrami equation. Then appeared the results of the studies on kinetics of $\alpha \rightarrow \omega$ transformation in titanium (Singh *et al* 1982b; Murali Mohan *et al* 1982; Singh *et al* 1983a), and fcc-bcc transformation in ytterbium (Singh *et al* 1982b). These studies reveal some interesting features of the displacive transformations, and will be discussed further. The isobaric conditions were achieved either by a rapid pressurization or by a special loading technique (Singh *et al* 1983a). The progress of the transformation was followed by monitoring the resistance of the specimen. The fraction of the high pressure phase as a function of time was calculated from the specimen-resistance versus time data. The following features were observed in both titanium and ytterbium transformations.

(i) The transformations started with a definite incubation (induction) period. The incubation period decreased rapidly with increasing over-pressure. A similar behaviour was observed by Onodera (1971) in cadmium chalcogenides. Onodera (1971) suggested that the observed incubation period could be the intrinsic property of the transition or could arise as a result of time delay in pressure transmission by solid pressure transmitting medium. The results on titanium and ytterbium transformations indicate that the observed incubation period is the inherent property of the transformation.

(ii) The transformations are isobaric-isothermal type in that these run to completion as the pressure is held constant. This is in agreement with the earlier observation (Vohra *et al* 1977) that the transformation progressed with time as the pressure was held constant. Similar behaviour was observed in bismuth (Davidson and Lee 1964) and potassium chloride (Hamaya and Akimoto 1981). In cadmium chalcogenides the transformation was found to start under isobaric conditions initially (Onodera 1971) but tailed off after some time; either a change in temperature or pressure was required to drive the transformation to completion.

(iii) The kinetics data satisfied Avrami equation (Christian 1975);

$$\zeta = 1 - \exp - \{t/\tau(p)\}^{n(p)}, \quad (1)$$

where ζ is the fraction of the high pressure phase at an instant t , and τ and n are constants at a given pressure, but in general are functions of pressure. At $t = \tau$, $\zeta = 1 - \exp(-1) \approx 0.63$. Thus, τ is the time required for nearly 63% transformation. This equation is derived assuming that the transformation involves the steps of nucleation and growth. In the case of homogeneous nucleation which decreases with time, $3 < n < 4$, $2 < n < 3$ and $1 < n < 2$ for, respectively, a three-, two-, and one-dimensional growth. The case $n = 1$ represents a homogeneous rate equation. In polymorphic transformations, the lowest value of n that can arise is unity, and occurs for growth of nuclei formed on grain boundaries after site saturation (Christian 1975).

In the case of α - ω transformation in titanium $n = 3 \pm 1$ at 5 GPa and decreases to $n = 1 \pm 0.2$ at 9 GPa. For fcc-bcc transformations in ytterbium, $n = 1.1 \pm 0.2$ at 3.4 GPa and decreases to $n = 0.3 \pm 0.1$ at 4.8 GPa. As mentioned above, the lowest value of n predicted from theoretical models in polymorphic transformation is unity.

However, experimentally, $n < 1$ has been observed. Obviously, an improved model of nucleation is required to deal with this situation.

The parameter τ in (1) is found to decrease rapidly with increase in pressure. The pressure dependence of τ is shown in figure 6. The $\ln \tau$ versus pressure data is linear for ytterbium, but shows a small curvature in titanium. In terms of the activation free energy for the combined process of nucleation and growth, τ is given by

$$\ln \tau(p) = b_0 + \Delta G^*(p)/RT, \quad (2)$$

where b_0 is a constant, $\Delta G^*(p)$ is the pressure-dependent activation free energy, and R is gas constant. Equation (2) suggests that $\Delta G^*(p)$ can be obtained from the measurement of $\tau(p)$ if b_0 is known. The calculation of b_0 from first principles is complicated. The following arguments can be used to estimate the value of b_0 . For a given value of b_0 , $\ln \tau$ decreases with decreasing $\Delta G^*(p)$, and assumes a minimum value when $\Delta G^*(p) = 0$. It may be noted that negative value of $\Delta G^*(p)$ has no physical significance in the present context. In the absence of any energy barrier, the transformation will propagate with velocity of sound. The velocity of sound in solids is typically a few km/sec. This suggests that $\tau \approx 10^{-6}$ sec when $\Delta G^*(p) = 0$, and $b_0 = -13.8$. This is the largest value of b_0 for which $\tau = 10^{-6}$ sec can occur. For b_0 less than -13.8 , $\tau = 10^{-6}$ sec can occur for a positive value of $\Delta G^*(p)$.

It is seen from (2) that the pressure dependence of $\Delta G^*(p)$ is essentially the pressure dependence of $\ln \tau$, for a constant b_0 . The variations of ΔG^* with pressure as obtained from (2) with $b_0 = -13.8$ are shown in figure 7 for titanium and ytterbium. The activation free energy is nearly 15 kcal/mol at 5 GPa for $\alpha \rightarrow \omega$ transformation in titanium, and at 4 GPa for fcc-bcc transformation in ytterbium. In both cases activation free energy decreases with increasing pressure.

The experimentally obtained values of activation free energies are significantly lower than the activation energy for self diffusion. This suggests that diffusion process is not involved in these transformations. In diffusion-controlled transformations, the activation free energy is expected to increase or remain relatively unaltered when pressure is increased. The fact that activation free energy decreases with increase in pressure in the present case, also suggests the absence of any diffusion process in the transformation.

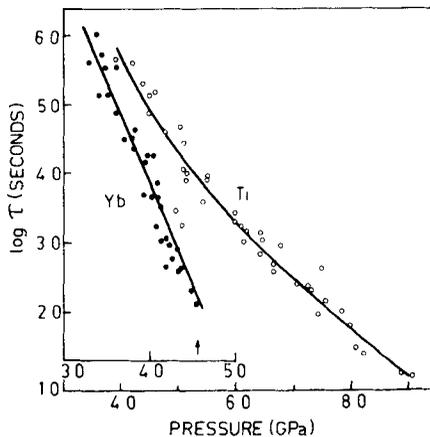


Figure 6. The pressure dependence of τ for titanium and ytterbium.

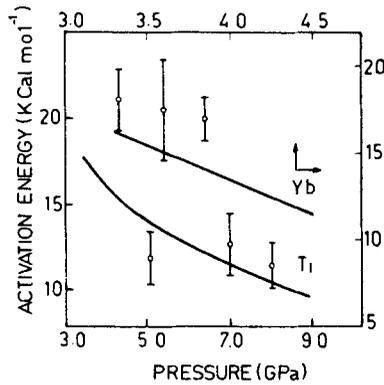


Figure 7. The activation free energy for the total process as a function of pressure. The dots indicate measured activation enthalpies.

Similar conclusions have been drawn in case of transformation in potassium chloride (Hamaya and Akimoto 1981) and cadmium chalcogenides (Onodera 1971).

The experiments were also carried out at elevated temperatures and τ -values determined. The activation enthalpies were determined from $\ln \tau$ versus $1/T$ plot. The values of activation enthalpies thus obtained together with the error bars are marked in figure 7. From the differences between the activation free energies and the corresponding enthalpies, the activation entropies were estimated, and found to be 4 cal/mol/K for titanium and 8 cal/mol/K for ytterbium.

It is seen from figure 6 that the transformations in both cases occur over a wide range of pressures. In principle transformation can occur at any pressure above equilibrium pressure. The present data indicate that $p_0 < 4.0$ GPa for $\alpha \rightarrow \omega$ transformation in titanium, since experimentally the transformation has been found to occur even at 4 GPa. This is consistent with the experimental value of $p_0 = 2$ GPa, as obtained by Zil'Bershteyn *et al* (1976). For the same reasons, the present data suggest that $p_0 < 3.4$ GPa for ytterbium. No measurement of p_0 for fcc-bcc transformation in ytterbium seems to have been made.

In view of these kinetics data one may ask the question: what is the significance of the experimentally determined transformation pressure or often termed start pressure? It appears that start pressure is a function, among many other parameters such as specimen history and the impurity levels, of the rate of loading, and is pressure at which incubation period becomes of the order of the time of loading.

5. Transformation under shock loading

The occurrence of $\alpha \rightarrow \omega$ transformation in titanium under shock loading was clearly established by Kutsar *et al* (1974). The x-ray examination of the specimens, shock-loaded to 35 GPa at 293 K, indicated the presence of ω -phase in traces. The estimated shock residual temperature at such high pressures exceeded the temperature for $\omega \rightarrow \alpha$ transformation, which resulted in a poor yield of the ω -phase. On cooling the specimen down to 120 K before loading it to 35 GPa, nearly 60% ω -phase was detected.

The transformation under shock loading can occur only if its kinetics becomes fast

enough, under the pressure-temperature condition of shock loading, for the system to respond to the loads of short duration, typically a few μsec . Extrapolation of τ - p data suggests that τ becomes of the order of μsec at 20 GPa. Thus, the extrapolation of the present data suggests that nearly 63% ω -phase can be obtained by shock loading the specimens to 20 GPa. This is about half the pressure at which Kutsar *et al* (1974) observed the transformation under shock loading. However, it is not clear from the work of Kutsar *et al* (1974) whether the experiments were systematically conducted at lower shock pressures and the occurrence of ω -phase ruled out. McQueen *et al* (1970) reported a discontinuity in the shock Hugoniot at 17.5 GPa with an associated volume change of about 1%. The specimens recovered after shock loading were stated to be in bcc phase. It may be noted that the first five lines of the ω -phase can be indexed on the basis of bcc lattice. If the shock-recovered specimens were in the ω -phase, then the discontinuity in the shock Hugoniot can be attributed to $\alpha \rightarrow \omega$ transformation, and the pressure of transformation (17.5 GPa) would agree very well with the present extrapolated value of 20 GPa.

The discussion so far was confined to the estimation of lowest shock pressures which will lead to 63% ω -phase. A smaller fraction of ω -phase can be expected at lower pressures. The lowest shock pressure required to produce a given fraction of ω -phase was estimated using $\ln t_\zeta - p$ data (t_ζ is the time for a fraction of transformation ζ) to determine the pressure at which t_ζ becomes 1 μsec . These estimates suggest that detectable fraction of ω -phase, say 10%, can occur at shock pressures as low as 16 GPa.

In these discussions the effect on the $\alpha \rightarrow \omega$ transformation of the temperature which occurs during the shock loading (McQueen and Marsh 1960) has been neglected. If the residual temperature, *i.e.* the specimen temperature after the shock is reduced to zero, exceeds the $\omega \rightarrow \alpha$ transformation temperature (410–430 K) then a reverse transformation may occur resulting in a low fraction of ω -phase in the specimens recovered after shock compression. The estimated residual temperature (McQueen and Marsh 1960) after shock loading to 20 GPa is about 350 K, which is less than the $\omega \rightarrow \alpha$ transformation temperature. For this reason it appears reasonable to neglect the temperature effect in the present discussions. However, even a 20–30 K rise in temperature is found to speed up the kinetics considerably. Thus a temperature rise in front of the shock wave is likely to enhance the kinetics of $\alpha \rightarrow \omega$ transformation and thereby facilitating the formation of ω -phase.

The extrapolation of the $\ln \tau$ versus pressure data for ytterbium suggests that $\tau = 10^{-6}$ sec at 7 GPa, indicating that the fcc-bcc transformation is likely to occur at 7 GPa under shock loading. However, there is no shock wave data for ytterbium available for comparison.

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