

Precise determination of isomorphous and eutectoid transformation temperatures in binary and ternary Zr alloys

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Differential thermal analysis (DTA) was used to accurately determine the phase boundary temperatures in the binary and ternary phase diagrams of Zr alloys containing Fe, Cr and O. The effects of heating and cooling rates on the onset temperatures of allotropic, isomorphous and eutectoid phase transformations were investigated both experimentally and theoretically. The phase boundary temperatures were determined by extrapolating the heating or cooling rate to 0 K min^{-1} using a predictive equation derived in this work. Comparison of theoretical calculation with experimental data showed good agreement.

1. Introduction

DTA is faster, more economical and more accurate than conventional metallographic techniques for determining phase transformation temperatures [1, 2]. In Zr alloys, a major obstacle to accurate determination of transformation temperatures is their extreme chemical reactivity. For example, during a DTA cycle at elevated temperature, oxygen contamination increases the α - β phase boundary temperature.

Although DTA has been used to determine phase transformation temperatures and to construct phase diagrams [1–5], no investigation has been reported on how to determine the equilibrium phase transformation temperature, which is essential to the accurate determination of phase diagrams. Since the atomic diffusion rate is very slow in solid phases of Zr alloys, which is common for most solid state diffusion, the equilibrium conditions in the samples of Zr alloys can not be obtained in practical DTA experiments. Overheating or overcooling always exists in actual experiments, which makes it impossible to measure the equilibrium solid phase transformation temperature.

The objectives of this study were (1) to develop a procedure to minimize the oxygen contamination so that the transformation temperature of crystal bar Zr and binary and ternary Zr alloys may be measured accurately and (2) to derive a predictive equation which will accurately determine the equilibrium phase transformation temperatures of Zr alloys.

2. Experimental procedure

The differential thermal analyser used in this study is a Du Pont 9900 DTA analyser with the high temperature 1600 cell. The cell was purged with ultra high purity argon (research grade), whose oxygen content

was further reduced with a high capacity hot gas purifier, to protect the sample from oxidation, which is a severe problem for Zr alloys. The DTA system was maintained leak-proof to prevent air contamination. Any residual air in the system had to be removed before the start of a DTA cycle. This was accomplished by purging with pure argon for 2 h prior to the start of a test.

The compositions of samples representing allotropic, isomorphous and eutectoid phase transformations are listed in Table I. These alloys were chosen because they represent typical Zr alloys systems and have typical phase transformation which may be encountered in determining Zr alloy phase diagram.

3. Results and discussion

After optimizing the furnace assembly for minimum possible oxygen contamination, excellent DTA results were obtained. A typical DTA curve in heating of crystal bar Zr is shown in Fig. 1. This very smooth curve with no noise could only occur when the environment around the Zr specimen was free of oxygen contamination. The onset phase transformation temperature for the given heating rate was easily determined by a standard method [6] as illustrated in Fig. 1. This onset temperature is for the “non-equilibrium” phase transformation for a given material. The finish temperature of the phase transformation is not, however, well pronounced in the curve [7], thus, only the onset phase transformation temperature can be used to construct the phase diagram.

Since the onset temperature changes as a function of heating and cooling rate, a method to predict the true (equilibrium) transformation temperature is needed. The effects of heating or cooling rate on the onset

TABLE I The chemical compositions of experimental alloys

| Sample | Compositions (wt %) | | | | Transformation type |
|------------|---------------------|---------|---------|-----------|---------------------|
| | Fe | O | Cr | Zr | |
| Crystal Zr | < 0.005 | < 0.005 | < 0.005 | remainder | Allotropic |
| Zr-Fe | 0.938 | 0.091 | 0 | remainder | Eutectoid |
| Zr-Fe-O | 0.928 | 0.210 | 0 | remainder | Eutectoid |
| Zr-Fe-Cr | 0.232 | 0.104 | 0.232 | remainder | Isomorphous |

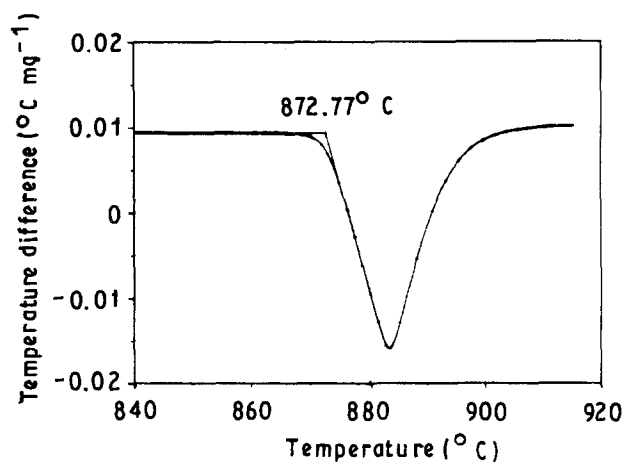


Figure 1 DTA curve for crystal bar Zr with heating rate of $14^{\circ}\text{C min}^{-1}$ and onset temperature of 872.8°C .

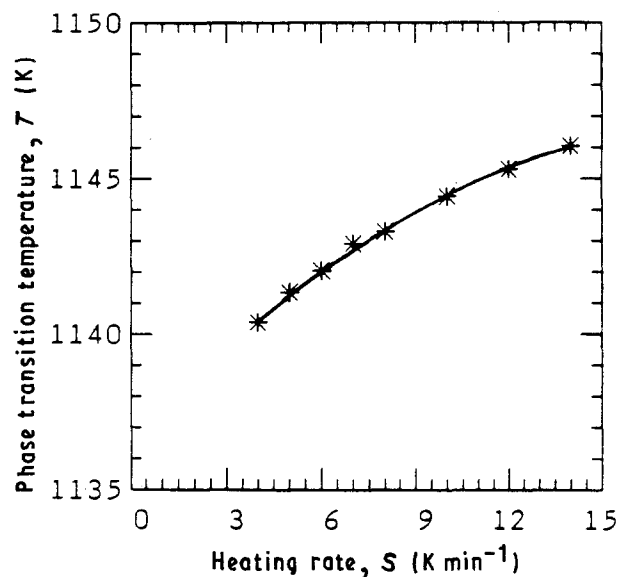


Figure 2 Allotropic transformation temperature plotted against heating rate for crystal bar Zr.

phase transformation temperature for the alloys tested are shown in Figs 2 to 5. It is obvious that the onset phase transformation temperature increases with increasing heating rate and decreases with increasing cooling rate. The relationship between the onset phase transformation temperature and the heating or cooling rate is not, however, linear.

If the relationship between the onset temperature and the heating or cooling rate (shown in Figs 2 to 5) can be derived from fundamental thermodynamics principles, then, it will be possible to determine the equilibrium phase transformation temperature by extrapolating the heating or cooling rate to 0 K min^{-1} .

To derive a predictive equation for the equilibrium transformation temperature, one must consider the formation of the first critical nucleus of new phase as the commencement of a phase transformation. The incubation time of the phase transformation is thus virtually the incubation time of nucleation. Since nucleation occurs more readily on grain boundaries than in the crystal matrix [8], only nucleation on grain boundaries is considered in this derivation.

Russell [9] showed that, for a binary system consisting of components A and B, the incubation time of nucleation on grain boundaries is

$$\tau(T) = C_1 T n_k^2 / \beta_k \Delta G_k^0 \quad (1)$$

where $\tau(T)$ is the incubation time at temperature T , C_1 a constant, n_k the number of solute atoms in a critical size nucleus, β_k the frequency factor, ΔG_k^0 the free energy of nucleus formation. Substituting quantities of n_k , β_k and ΔG_k^0 , which is given also by Russell [9], into

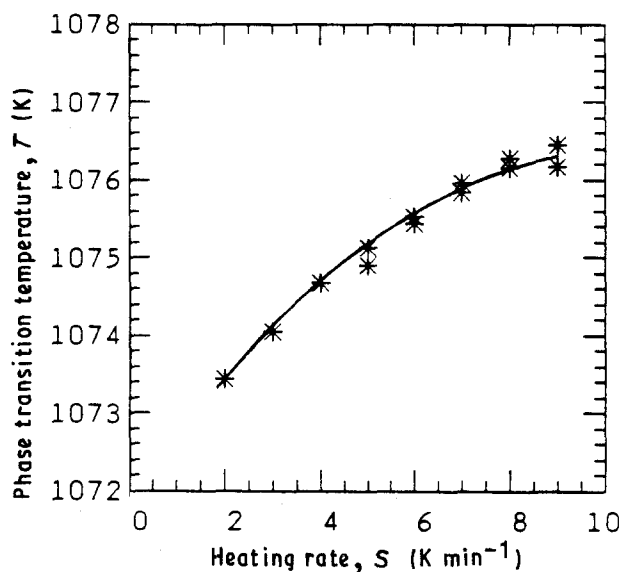


Figure 3 Eutectoid transformation temperature plotted against heating rate for Zr-0.938 Fe alloy.

Equation 1 and integrating all constant terms into constant C_2 yields

$$\tau(T) = C_2 T r_k^4 (\Delta G_v + \varepsilon)^2 (X_A / D_B^b + X_B / D_A^a) \quad (2)$$

where r_k is the critical nucleus radius, ΔG_v the free energy change on creating a unit volume of stress free nucleus phase, ε the strain energy, D_A^a and D_B^b boundary diffusivities and X_A and X_B the average mole

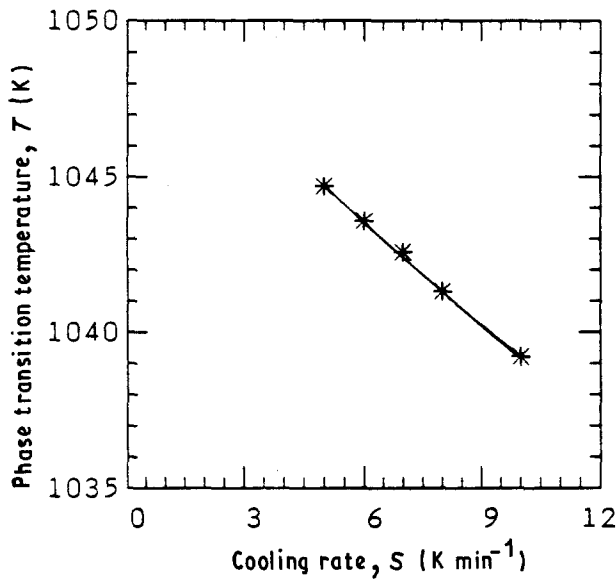


Figure 4 Eutectoid transformation temperature plotted against cooling rate for ternary Zr alloy containing 0.928 Fe and 0.210 O.

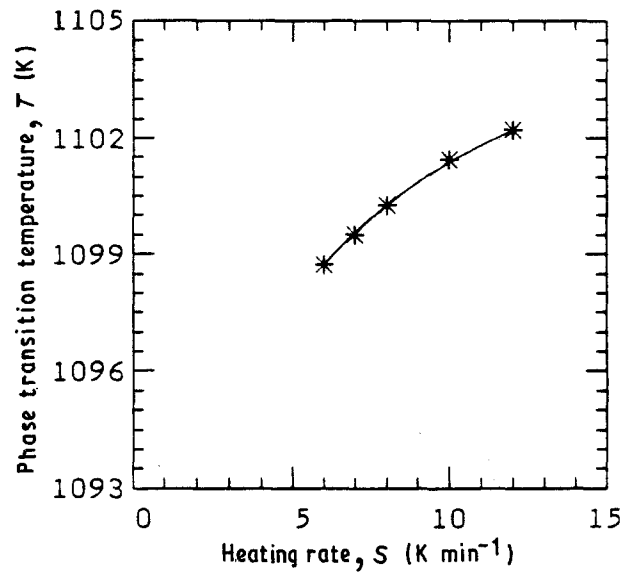


Figure 5 Isomorphous transformation temperature plotted against heating rate for ternary Zr alloy containing 0.232 Fe and 0.232 Cr.

fractions of components A and B, respectively.

Considering

$$r_k = -2\sigma_c/(\Delta G_v + \epsilon) \quad (3)$$

where σ_c is the surface energy,

$$\int_{T_0}^T \frac{(T - T_0)^2 dT}{T[X_A D_A^0 \exp(Q_B^b/RT) + X_B D_B^0 \exp(Q_A^b/RT)]} = C_4 S \quad (10)$$

$$\Delta G_v = \Delta H_v(T_0 - T)/T_0 \quad (4)$$

where ΔH_v is the reaction enthalpy, T_0 the equilibrium transformation temperature,

$$D_A^b = D_A^0 \exp(-Q_A^b/RT) \quad (5)$$

$$D_B^b = D_B^0 \exp(-Q_B^b/RT) \quad (6)$$

where D_A^0 and D_B^0 are diffusion constants, Q_A^b and Q_B^b activation energies for boundary diffusion, R the gas constant, and ignoring the strain energy term, ϵ , for simplicity, Equation 2 may be rearranged as

$$\frac{1}{T[X_A D_A^0 \exp(Q_B^b/RT) + X_B D_B^0 \exp(Q_A^b/RT)]} = aT^2 + bT + c \quad (11)$$

$$\tau(T) = \frac{C_3 T}{(T - T_0)^2 [X_A D_A^0 \exp(Q_B^b/RT) + X_B D_B^0 \exp(Q_A^b/RT)]} \quad (7)$$

where C_3 is a constant.

Simulating the calculation of the CCT diagram from TTT diagram [10], the following equation may be obtained

$$\int_0^{\tau_s} \frac{dt}{\tau(T)} = 1 \quad (8)$$

where τ_s is the incubation time of phase transformation for continuous heating or cooling and t time. In a typical DTA experiment, a constant heating or cooling rate through the transformation temper-

ature range is usually used, thus,

$$T = T_0 + St \quad (9)$$

where S is the constant heating or cooling rate. Substituting Equations 7 and 9 into Equation 8 yields

Some approximation has to be made in order to overcome the difficulty in integrating the left-hand side of Equation 10. In actual DTA experiments to determine the near-equilibrium phase transformation temperature, the heating or cooling rate used would not be very large. The temperature range $T - T_0$, over which the integration is made, thus should not be large either, e.g. less than 20 K. Over such a small temperature range, substituting

$1/T[X_A D_A^0 \exp(Q_B^b/RT) + X_B D_B^0 \exp(Q_A^b/RT)]$ with a parabolic function should not cause a substantial inaccuracy, therefore, let

Substituting Equation 11 into Equation 10 and integrating the left-hand side of Equation 10 yields

$$\frac{1}{3}(T - T_0)^3 T^2 \left[a + \frac{b}{T} + \frac{c}{T^2} - \frac{T - T_0}{4T} \left(\frac{2aT + b}{T} \right) + \frac{a}{10} \left(\frac{T - T_0}{T} \right)^2 \right] = C_4 S \quad (12)$$

Considering $(T - T_0)/T \ll 1$ for most solid phase transformations, Equation 12 may be approximated as

$$(T - T_0)^3 (aT^2 + bT + c) = C_5 S \quad (13)$$

where C_5 is a constant. Substituting Equation 11 into

Equation 13 and rearranging Equation 13 yields

$$T = C\{ST[X_A D_A^0 \exp(Q_B^b/RT) + X_B D_B^0 \exp(Q_A^b/RT)]\}^{1/3} + T_0 \quad (14)$$

With the phase transformation temperature obtained under different heating or cooling rates, S , in the DTA experiments, the equilibrium phase transformation temperature, T_0 , may be obtained by extrapolating S to 0°C min^{-1} using Equation 14. There are, however, some difficulties in using Equation 14 since the boundary diffusion data, D_A^0 , D_B^0 , Q_A^b and Q_B^b are not available in most cases. To overcome this difficulty in actual calculations, Equation 14 may be approximated by

$$T = C[ST \exp(Q_b/RT)]^{1/3} + T_0 \quad (15)$$

where Q_b is Q_A^b or Q_B^b , whichever is larger, and Q_A^b or Q_B^b may be estimated as $0.25\text{--}0.6 Q_A$ or Q_B [11], where Q_A and Q_B are lattice diffusion activation energies, which can be easily found in reference [12]. Equation 15 may also be applied to unary or more complex ternary systems, provided that Q_b is estimated from the largest lattice activation energy among those of all elements which participate in the transformation.

Since Equations 14 and 15 are based on fundamental diffusion relationships, these equations may be applied to all diffusion controlled solid state transformations such as isomorphous, eutectoid, peritectoid and monotectoid reactions. They may also be applied to other alloy systems in addition to Zr alloy systems since no special assumption was made referring to Zr alloys in their derivation.

Application of Equation 15 to the experimental data shown in Figs 2 to 5 yielded the results shown in Figs 6 to 9, respectively. It can be seen that, for each alloy used in this study, there is a linear relationship between the phase transformation temperature, T , and $[ST \exp(Q_b/RT)]^{1/3}$, which agrees with Equation 15.

The extrapolated equilibrium α - β transformation temperature, T_0 , for crystal bar zirconium shown in Fig. 6 is 1129.4 K (856.3 $^\circ\text{C}$), which is within the

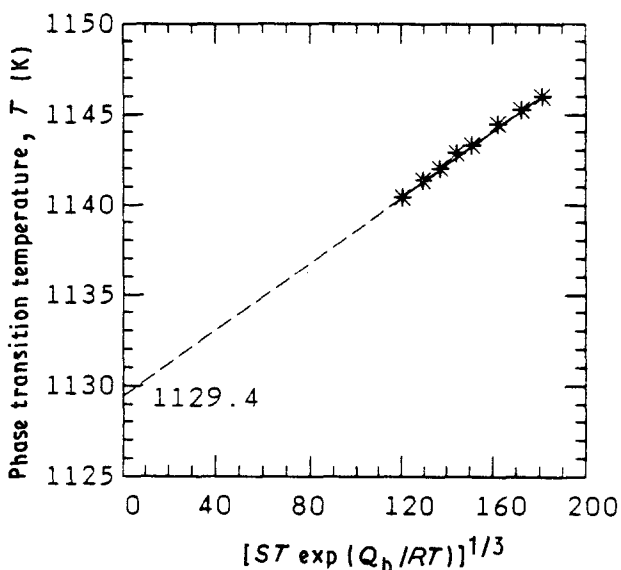


Figure 6 Allotropic transformation temperature plotted against $[ST \exp(Q_b/RT)]^{1/3}$ for crystal bar Zr in heating.

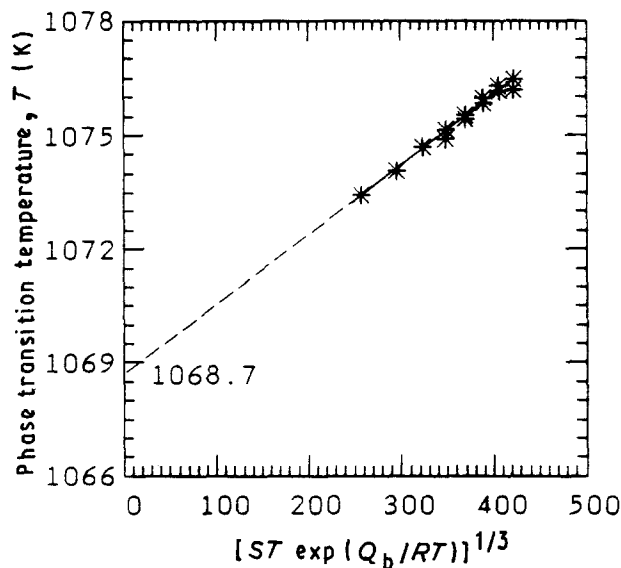


Figure 7 Eutectoid transformation temperature plotted against $[ST \exp(Q_b/RT)]^{1/3}$ for Zr-0.938 Fe alloy in heating.

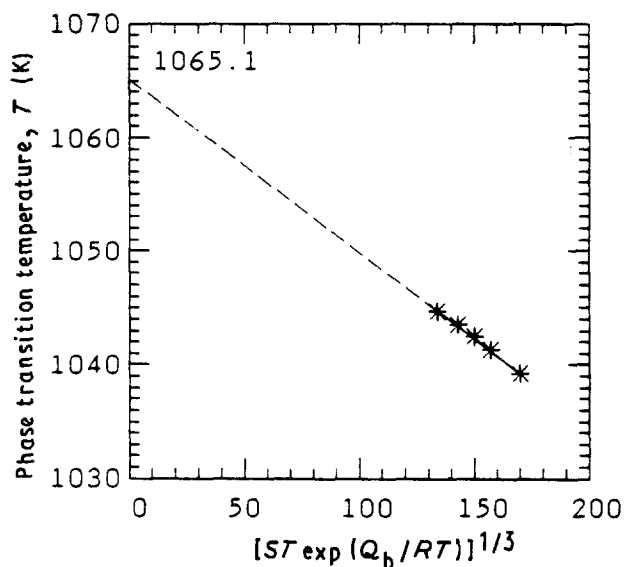


Figure 8 Eutectoid transformation temperature plotted against $[ST \exp(Q_b/RT)]^{1/3}$ in cooling for ternary Zr alloy containing 0.928 Fe and 0.210 O.

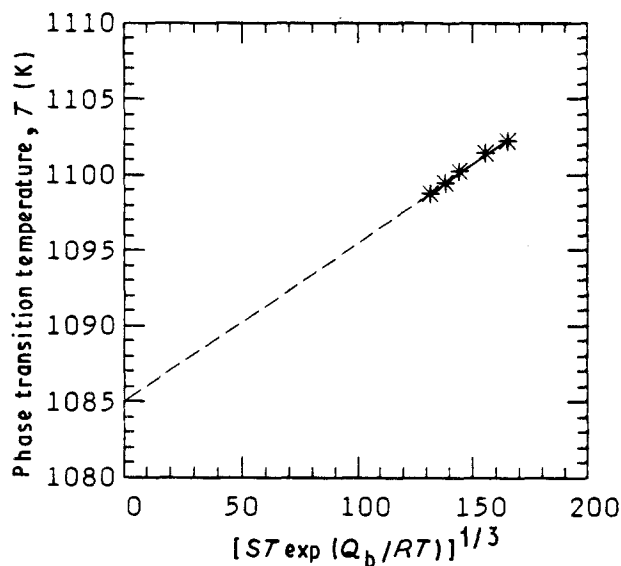


Figure 9 Isomorphous transformation temperature plotted against $[ST \exp(Q_b/RT)]^{1/3}$ in heating for ternary Zr alloy containing 0.232 Fe and 0.232 Cr.

reported temperature range, 854 to 865 °C [13]. The T_0 for Zr-Fe alloy shown in Fig. 7 is 1068.7 K (795.6 °C), which agrees virtually exactly with the established transformation temperature [12]. The values for T_0 for Zr-Fe-O alloy and Zr-Fe-Cr alloy shown in Figs 8 and 9 are 1065.1 K (792.0 °C) and 1085 K (811.9 °C), respectively, which are reasonable with reference to the Zr-Fe, Zr-O and Zr-Cr phase diagrams [12].

Since the effect of thermal stress caused by fast heating or cooling is not considered in Equations 14 and 15, the heating or cooling rate used in the DTA experiment should be below a certain limit, beyond which the linear relationship between phase transformation temperature, T , and $[ST_{\text{exp}}(Q_b/RT)]^{1/3}$ would not be maintained any longer.

4. Conclusions

Excellent DTA results can be obtained for crystal bar Zr and Zr alloys using the experimental procedure described in this paper. The predictive equation derived from fundamental thermodynamics principles in this study is quite accurate in determining the onset equilibrium allotropic, isomorphous and eutectoid phase transformation temperatures in crystal bar Zr and in binary and ternary Zr alloys.

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