

Gibbs free energy difference between the undercooled liquid and the β phase of a Ti-Cr alloy

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The heat of fusion and the specific heats of the solid and liquid have been experimentally determined for a $\text{Ti}_{60}\text{Cr}_{40}$ alloy. The data are used to evaluate the Gibbs free energy difference, ΔG , between the liquid and the β phase as a function of temperature to verify a reported spontaneous vitrification (SV) of the β phase in Ti-Cr alloys. The results show that SV of an undistorted β phase in the $\text{Ti}_{60}\text{Cr}_{40}$ alloy at 873 K is not feasible because ΔG is positive at the temperature. However, ΔG may become negative with additional excess free energy to the β phase in the form of defects.

In a series of papers, Blatter, von Allmen and their colleagues have reported the spontaneous vitrification (SV) of Ti-Cr alloys when a metastable β phase was annealed at a subeutectoid temperature.¹⁻⁴ The β phase (bcc) is a disordered solution which is stable only at high temperatures but can be retained at low temperatures with a moderate quenching rate. Phase decomposition studies^{5,6} and a thermodynamic model⁷ indicate that the quenched β phase is within the spinodal lines and is strongly subject to decomposition. However, Blatter *et al.* found that the β phase was transformed into an amorphous phase upon annealing at 873 K for 6 h. Although the experimental evidence is not totally convincing (to our knowledge, only one independent confirmation has been reported⁷), the possibility of SV in Ti-Cr alloys has been sought on the basis of a thermodynamic criterion.^{1,8,9} The thermodynamic criterion dictates that the free energy of the amorphous phase must be lower than that of the β phase at the SV temperature. However, the conclusions are not conclusive because the analyses heavily rely on models and assumptions. The Gibbs free energy difference, $\Delta G(T)$, between the liquid and the β phase at the temperature, T , is formally written as

$$\Delta G(T) = \left(\Delta H_f + \int_{T_m}^T \Delta C_p dT \right) - T \left(\Delta S_f + \int_{T_m}^T \Delta C_p / T dT \right), \quad (1)$$

where ΔH_f and ΔS_f are the enthalpy and the entropy of fusion, respectively, T_m is the melting point (a congruent melting for the present case) and $\Delta C_p = C_p^l - C_p^\beta$ is the difference in specific heats of two phases. In this letter, we calculate $\Delta G(T)$ using the experimentally determined ΔH_f , C_p^β and C_p^l and evaluate the feasibility of SV in Ti-Cr alloys from a thermodynamic point of view without getting into the kinetic aspect of the transition.

We used a Perkin-Elmer DSC 4, a high temperature SETARAM DSC 2000 K and a drop calorimeter for calorimetric measurements. A detailed description of the drop

calorimeter has been provided elsewhere.¹⁰ Buttons of the $\text{Ti}_{60}\text{Cr}_{40}$ alloy were prepared by induction melting of 99.7% pure Ti and 99.9% pure Cr on a silver boat in an Ar atmosphere. X-ray diffraction showed that the as-prepared alloys were predominated by the metastably retained β phase. The diffraction lines were narrow, indicating very little distortion of the lattice. We first determined T_m and ΔH_f using the high temperature DSC. The results are 1688 ± 10 K and 15.7 ± 3.7 kJ/mol, respectively, which are in good agreement with the assessed phase diagram.¹¹

We next measured the enthalpy of the $\text{Ti}_{60}\text{Cr}_{40}$ liquid alloy as a function of temperature using the drop calorimeter. The result is shown in Fig. 1. The enthalpy of the β phase at 298 K is assigned to zero. The enthalpy of the liquid, H^l , (presented as the solid circles) is fitted with two commonly used empirical equations for the enthalpy by a regression method. The results are

$$H^l(T) = -26.3 + 5.10 \times 10^{-2} T \quad (\text{kJ/mol}) \quad (2)$$

and

$$H^l(T) = 9.98 + 0.0405T - 3.12 \times 10^4 / T \quad (\text{kJ/mol}). \quad (3)$$

Equation (3) is drawn in Fig. 1. By definition, C_p^l is given by

$$C_p^l = dH^l/dT = 51.0 \quad (\text{J/mol K}) \quad [\text{using Eq. (2)}] \quad (4)$$

and

$$C_p^l = 40.5 + 3.12 \times 10^7 / T^2 \quad (\text{J/mol K}) \quad [\text{using Eq. (3)}]. \quad (5)$$

For comparison with the specific heat of the β phase, Eq. (5) is drawn in Fig. 2.

For the β phase, at low temperatures (< 700 K) where the retained β phase was stable for the duration of the measurement, we directly measured C_p^β using the DSC 4. The result is shown in Fig. 2. as the open circles. At high temperatures (> 1400 K) where the β phase could be retained in the dropped sample, we measured the enthalpy of

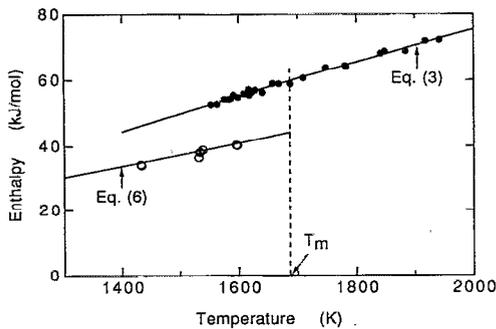


FIG. 1. The enthalpy of the $\text{Ti}_{60}\text{Cr}_{40}$ alloy measured by a drop calorimeter. Equations (3) and (6) are fitted equations. Equation (6) is determined by taking into account the specific heat data shown in Fig. 2.

the β phase, H^β , using the drop calorimeter. The result is shown in Fig. 1 as the open circles. The two sets of data are well fitted simultaneously by

$$H^\beta(T) = -7.17 + 0.0227T + 4.59 \times 10^{-6} T^2 \quad (\text{kJ/mol}) \quad (6)$$

and

$$C_p^\beta(T) = 22.7 + 9.18 \times 10^{-3} T \quad (\text{J/mol K}). \quad (7)$$

Equations (6) and (7) are drawn in Figs. 1 and 2, respectively. The heat of fusion calculated by taking the difference between Eqs. (3) and (6) at T_m is 15.5 kJ/mol, which is in very good agreement with the result from the DSC measurement.

We are now able to calculate ΔG of the $\text{Ti}_{60}\text{Cr}_{40}$ alloy using the experimentally determined ΔC_p and ΔH_f . However, C_p^l is only determined at the limited undercooling level (< 135 K). Thus, we assume that Eqs. (4) or (5) can be extrapolated into low temperatures. The extrapolation of Eq. (4) underestimates ΔC_p because C_p^l of glass-forming alloys generally increases as undercooling increases due to the decrease in configurational entropy of the liquid.¹² The extrapolation of Eq. (5) is more realistic but may overestimate ΔC_p . We also have a fairly large uncertainty in ΔH_f (12.0 – 19.0 kJ/mol) measured by DSC. Considering these uncertainties in C_p^l and ΔH_f , we decided to calculate ΔG with several combinations of ΔC_p and ΔH_f . The results

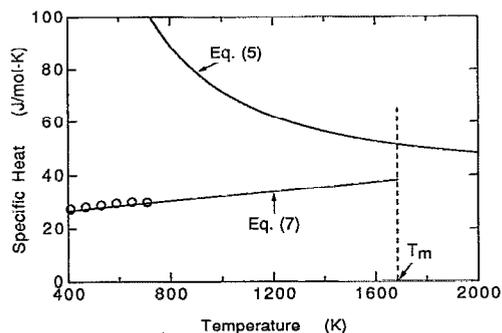


FIG. 2. The specific heats of the $\text{Ti}_{60}\text{Cr}_{40}$ alloy calculated from Eqs. (5) and (7). The open circles are values measured by DSC.

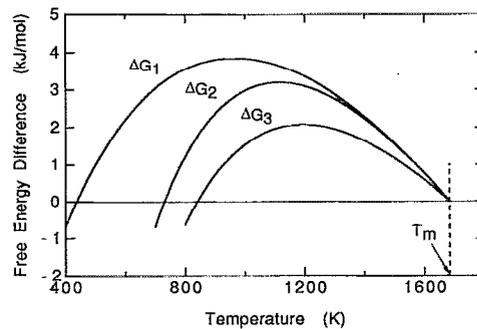


FIG. 3. The free energy difference between the liquid and the β phase for the $\text{Ti}_{60}\text{Cr}_{40}$ alloy.

are shown in Fig. 3: ΔG_1 is obtained with Eqs. (4) and (7) and $\Delta H_f = 15.5$ kJ/mol; and ΔG_2 is obtained with Eqs. (5) and (7) and $\Delta H_f = 15.5$ kJ/mol; and ΔG_3 is obtained with Eqs. (5) and (7) and $\Delta H_f = 12.0$ kJ/mol. The temperatures, T_c , where $\Delta G = 0$, are 430, 735, and 840 K for ΔG_1 , ΔG_2 , and ΔG_3 , respectively.

In Fig. 3, the temperature at which ΔG reaches a maximum represents the Kauzmann temperature, T_K .¹³ Below T_K , the entropy of the undercooled liquid becomes smaller than that of the β phase. This situation seems paradoxical but is feasible if we assume that the liquid is topologically ordered and the β phase is disordered. Thus, the liquid may be undercooled below T_K , but is eventually transformed into glass (amorphous phase) at the glass transition temperature, T_g (which has not been determined in the present system). The specific heat of glass is generally slightly larger than that of its corresponding crystalline phase; therefore, the ΔG 's in Fig. 3 are not valid below T_g . Consequently, if $T_g > T_c$, then the actual T_c becomes much lower than that which is shown in Fig. 3. It is clear that even with the most favorable situation, i.e., ΔG_3 with $T_c = 840$ K, the present results do not predict SV of the undistorted β phase in the $\text{Ti}_{60}\text{Cr}_{40}$ alloy at 873 K. We may add that our β phase sample annealed at 873 K for several hours was decomposed into the stable phases.

Additional excess free energy to the β phase has been suggested in the form of the interstitial-vacancy pairs¹⁴ or lattice distortion,^{9,15} which may raise the free energy of the β phase above that of glass at 873 K. For instance, an additional vacancy concentration of 10^{-3} in the β phase is required to nullify $\Delta G_3 = 0.4$ kJ/mol at 873 K assuming that the enthalpy for vacancy formation is to the order of 1 eV. It has also been suggested that impurities may play a role in SV.¹⁶ We speculate that if this is the case, the role of the impurities is to provide favorable heterogeneous nucleation sites for the amorphous phase rather than to substantially increase the free energy of the β phase.

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