THERMODYNAMIC STUDY OF PURE TITANIUM ALOTROPY

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ABSTRACT

Titanium is a lightweight metal highly resistant to mechanical impacts and heat exposure, making it suitable as a refractory metal (heat-resistant). Titanium exhibits allotropy. Its allotropes are alpha phase (compact hexagonal), beta phase (body-centered cubic). This article is devoted to the analysis of the Gibbs Free Energy against temperature curves and Enthalpy against Temperature curves for the comprehension of how the formation of the allotropes contributes to the minimization of Gibbs Free Energy and for using the data for determining the transition temperatures.

Keywords: *Gibbs Free Energy, Titanium, Allotropy.*

INTRODUCTION

Titanium is a lightweight metal highly resistant to mechanical impacts and heat exposure, making it suitable as a refractory metal (heat-resistant). Pure titanium is a ductile metal, easy to manipulate, and despite forming an oxide layer when exposed to atmospheric air, these oxides do not degrade the metal. It also possesses a white, metallic, and lustrous appearance.

Titanium exhibits allotropy. At room temperature, it has a compact hexagonal crystal structure called the alpha phase, which remains stable until 1155 °C; above this temperature, the structure changes to a body-centered cubic phase, an allotrope called the beta phase. Alpha titanium refers to pure titanium or titanium with increased strength due to the addition of small amounts of phase-stabilizing elements like Al, Sn, Ni, and Cu.

In this context, a concept that can explain these pure iron allotropic changes well is Gibbs energy (G), a thermodynamic quantity indicating the available free energy for a reaction or process in a thermodynamic system. It is defined as the difference between the enthalpy (H) and entropy (S) of the system, multiplied by the absolute temperature (T).

The GxT curve illustrates how Gibbs free energy varies with temperature in a thermodynamic system. This curve can be used to determine the relative stability of titanium allotropes at different temperatures and predict phase changes during system cooling or heating. For instance, in the titanium GxT curve, it is possible to observe that alpha titanium is the most stable phase at lower temperatures, while beta titanium is more stable at higher temperatures.

The temperature at which both phases have the same Gibbs free energy is called the transformation temperature or critical temperature.

Additionally, enthalpy is associated with the amount of thermal energy involved in phase changes within the system. For example, during the fusion of beta titanium, an amount of energy equal to the fusion enthalpy is required for the phase change to liquid titanium. Similarly, during the solidification of liquid titanium, energy equal to the solidification enthalpy is released. These relationships between Gibbs energy, enthalpy, and the GxT curve are fundamental for understanding phase changes and the stability of titanium allotropes.

This work aims to plot the variation of the Gibbs free energy and the enthalpy with the temperature for the different phases of pure titanium. Through this, it is possible to understand that the minimization of the Gibbs free energy gives the most stable phase in a specific temperature range.

MATERIALS AND METHODS

To plot the variation of the Gibbs free energy and the enthalpy with the temperature, it will be necessary to use materials thermodynamics principles applied to empirical equations obtained from a trustworthy database.

Thermodynamic data

The database used in this work was taken from NASA’s CAP (Coefficients and Properties) program report [1]. The program uses a 9-constant representation given by the following equations, respectively for the specific heat at constant pressure (C_p), the enthalpy (H), and the entropy (S) as a function of temperature (T):

$$\frac{C_p(T)}{R} = \frac{a_1}{T^2} + \frac{a_2}{T} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4 \qquad (1)$$

$$\frac{H(T)}{R} = -\frac{a_1}{T} + a_2 lnT + a_3T + \frac{a_4T^2}{2} + \frac{a_5T^3}{3} + \frac{a_6T^4}{4} + \frac{a_7T^5}{5} + b_1 \qquad (2)$$

$$\frac{S(T)}{R} = -\frac{a_1}{2T^2} - \frac{a_2}{T} + a_3 lnT + a_4T + \frac{a_5T^2}{2} + \frac{a_6T^3}{3} + \frac{a_7T^4}{4} + b_2 \qquad (3)$$

As described in NASA’s report, the coefficients were generated by least-squares fits to empirical or calculated thermodynamic functions for condensed and gas-phase species. R represents the universal ideal gas constant. The coefficient values are shown in table 1 below:

Table 1: Empirical thermodynamic coefficients from NASA’s CAP program [1] used in equations (1), (2) and (3).

Phase	$\boldsymbol{\alpha_1}$	$\boldsymbol{\alpha_2}$	$\boldsymbol{\beta}$	**Liquid**
Temperature range (K) **Coefficients**	**200-900**	**900-1156**	**1156-1944**	**1944-6000**
a_1	3,59860135E+04	-2,87623591E+06	-1,69874057E+06	0
a_2	-8,27230596E+02	0	6,57660124E+03	0
a_3	7,68909777	45,7315342	-8,55618295	5,628714139
a_4	-1,143968449E-02	-7,69238160E-02	9,78958583E-03	0
a_5	1,392105464E-05	3,79991949E-05	-3,99241876E-06	0
a_6	-4,69105716E-09	0	1,123642773E-09	0
a_7	-9,85213040E-13	0	-1,20104805E-13	0
b_1	2,936621421E+03	-2,038023972E+04	-3,92991829E+04	-2,37735462E+03
b_2	-39,813801	-2,516270281E+02	65,0659019	-30,79443471

Development of the equations

As explained by DeHoff [2], the Gibbs free energy is an extensive property and a state function given by:

$$G \equiv U + PV - TS \equiv H - TS \tag{4}$$

Where *U* is the internal energy, *P* is the pressure, *V* is the volume, *T* is the temperature, *S* is the entropy and *H* is the enthalpy.
At constant pressure, the enthalpy, in its differential form, can be written as:

$$dH = C_p dT \tag{5}$$

Appling the empirical equation (1) to equation (5) and integrating from the standard point at $T_0 = 298{,}15K$ and $P_0 = 1\ atm$ to a certain temperature *T* at the same pressure, one can obtain:

$$\Delta H_p = R * \int_{T_0}^{T} \frac{a_1}{T^2} + \frac{a_2}{T} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4 dT \tag{6}$$

Where the subscript “*p*” points that the integration was done at constant pressure.
Developing equation (6) with the constant values in Table 1 for the alpha phase in the range from 200 K to 900 K as an example:

$$\begin{aligned}\Delta H_p = R * \Bigg[\left(-\frac{a_1}{T} + a_2 lnT + a_3T + \frac{a_4T^2}{2} + \frac{a_5T^3}{3} + \frac{a_6T^4}{4} + \frac{a_7T^5}{5}\right) \\ - \left(-\frac{a_1}{298{,}15} + a_2\, ln\, ln\, (298{,}15)\ + a_3(298{,}15) + \frac{a_4(298{,}15)^2}{2} \right. \\ \left. + \frac{a_5(298{,}15)^3}{3} + \frac{a_6(298{,}15)^4}{4} + \frac{a_7(298{,}15)^5}{5}\right)\Bigg]\end{aligned}$$

$$\Delta H_p = R * \left(-\frac{a_1}{T} + a_2 lnT + a_3T + \frac{a_4T^2}{2} + \frac{a_5T^3}{3} + \frac{a_6T^4}{4} + \frac{a_7T^5}{5}\right) - R * (-2936{,}62) \tag{7}$$

It is evident from equation (7) that the last numerical term is equal to the constant b_1. This shows that equation (2) is simply the integration of equation (1) from the standard point.

The same can be shown for the entropy function, which is given by:

$$dS = \frac{C_p}{T} dT \tag{8}$$

Integrating equation (8) from the same standard point discussed before, it is obtained:

$$\begin{aligned} \varDelta S_p = R * \Bigg[& \left(-\frac{a_1}{2T^2} + \frac{a_2}{T} + a_3 lnT + a_4 T + \frac{a_5 T^2}{2} + \frac{a_6 T^3}{3} + \frac{a_7 T^4}{4} \right) \\ & - \left(-\frac{a_1}{2 * 298{,}15^2} + \frac{a_2}{298{,}15} + a_3 ln(298{,}15) + a_4 9298{,}15) + \frac{a_5 (298{,}15)^2}{2} \right. \\ & \left. + \frac{a_6 (298{,}15)^3}{3} + \frac{a_7 (298{,}15)^4}{4} \right) \Bigg] \end{aligned}$$

$$\varDelta S_p = R * \left(-\frac{a_1}{2T^2} + \frac{a_2}{T} + a_3 lnT + a_4 T + \frac{a_5 T^2}{2} + \frac{a_6 T^3}{3} + \frac{a_7 T^4}{4} \right) - R * (-39{,}81) \tag{9}$$

Again, the last numerical part of equation (9) is equal to the constant b_2, which shows the origin of equation (3)

The Gibbs free energy or chemical potential is obtained by connecting equations (2) and (3) through the definition in equation (4).

RESULTS AND DISCUSSION

The equations developed in the previous section were used to calculate the variation of Gibbs free energy and enthalpy by applying the values obtained in the developed equations. The enthalpy curve concerning the temperature of Ti, along with the Gibbs free energy curves of each phase of Ti, is displayed in Figure 1. When examining the enthalpy curve, the presence of steps at phase transition temperatures is notable, which is related to the latent heat of phase transformations. Furthermore, as can be observed, the intersection of the Gibbs free energy curves of the Ti phases was used to determine the phase transition temperatures. In other words, the temperatures at which the curves intersect were identified as the phase transition temperatures.

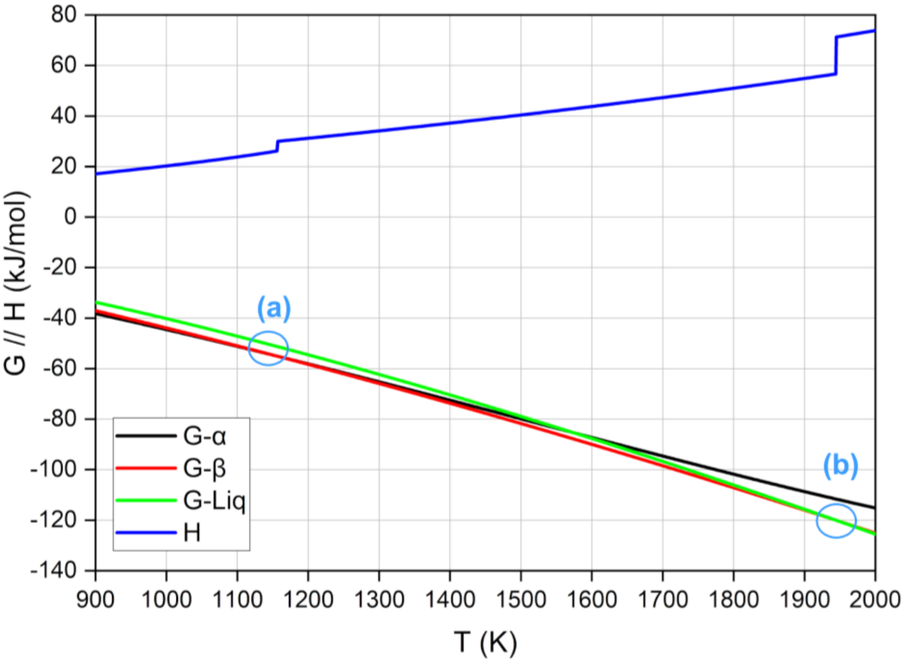

Fig. 1 - Curves of the Variation of Gibbs Energy (*G*) and Enthalpy (*H*) of the solid and liquid phases of Titanium as a function of Temperature.

In Figure 2a, the phase transition from α phase to β phase can be observed occurring at 1156 K, resulting in a transformation. In Figure 2b, this transition is shown for the phase transition from *β* phase to *L* phase, resulting in a transformation that occurs at 1944 K. It is noteworthy that during the phase transition temperatures, there is an increase in enthalpy values as the temperature rises, forming a kind of "step," as mentioned earlier. This is precisely caused by the latent heat of phase transformations, and these "steps" are formed during the phase transition temperature from one phase to another.

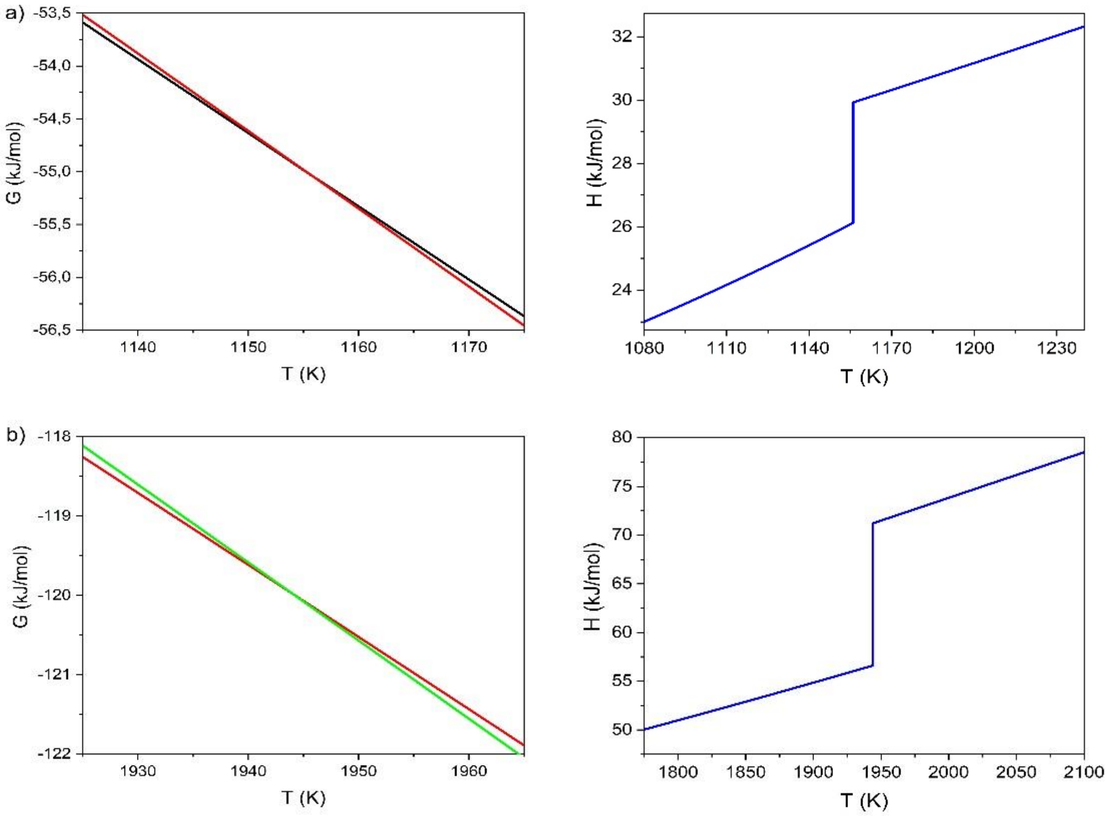

Fig. 2 – Intersection of the Gibbs Energy Variation (*G*) and Enthalpy Variation (*H*) for the $\alpha \rightarrow \beta$, $\beta \rightarrow L$ phase transations.

As can be observed in Table 2, the values of Gibbs Free Energy and some temperature intervals are provided, including the phase transition temperatures. It is possible to notice that the Gibbs Energy values are exactly equal at the phase transition point. Consequently, the phase transition temperatures will also be equal. The calculated data can be compared with the temperature values provided by DeHoff [2], as shown in Table 3, where it is possible to notice a minimal discrepancy of only 1 K for each phase. One possible explanation for this could be the number of constants used in the calculations, as some constants are equal to zero, preventing a more refined adjustment for the calculations, for example. In [3] values identical to those in the literature for Pure Iron were found, using the same database. However, the constant values are more refined to obtain these data. For Pure Titanium, the results obtained were nearly identical between the phase transitions, as demonstrated by the *G x T* and enthalpy (*H*) curves elaborated, where it is possible to highlight the intersection point near the phase transition temperature.

Table 2: Calculated values of Gibbs Free Energy, highlighting the phase transition temperature values.

Temperature (K)	**Gibbs Free Energy (J/mol)**		
	Alpha	**Betha**	**Liquid**
1050	-47817,97011	-47400,15713	-
1100	-51181,32409	-50976,13662	-
1150	-54634,01857	-54614,03144	-
1156	**-55054,67798**	**-55054,67795**	-
⋮	-	⋮	⋮
1500	-	-81721,90962	-78888,81765
1700	-	-98435,67551	-96729,31868
1800	-	-107112,9904	-106071,3418
1900	-	-116000,5718	-115673,4828
1944	-	**-119977,2476**	**-119977,2475**
⋮	-	⋮	⋮

Table 3: Phase transition temperatures for pure titanium.

Transformation	**Temperature (K)**	
	Calculated	**DeHoff [2]**
Ti-α ➔ Ti- β	1155	1156
Ti- β ➔ Ti-Liq.	1944	1943
Ti-Liq. ➔ Ti-Gas.	-	3558

CONCLUSIONS

This paper discussed the allotropy of pure Titanium studying the evolution of the minimization of the Gibbs free energy to explain how the allotropes evolved. The coefficients for the specific heat were taken from NASA's CAP report and using the definition of Gibbs free energy and literature equations the curves were plotted and the data was compared with the literature showing very good accuracy for the determination of the transition temperatures, despite a difference of 1 K.

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