Temperature dependence of formation entropy in α-Zr

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Abstract- A recent article on the calculation of elastic constants for alloy systems at different concentrations with the aid of a thermodynamic model gave us the motivation to propose an alternative application of this model. Here, we study the temperature dependence of formation entropy of α-Zr in a wide range of values, using a slight modification of the same model which interrelates bulk properties and point defect parameters. The resulting formation entropy values are found to be in good agreement with those recently obtained by detailed microscopic calculations, when errors are considered.

Index Terms- formation entropy, α-Zr, Gibbs energy, bulk modulus, thermal expansion coefficient, defect, thermodynamic model.

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1 INTRODUCTION

IN a recent article [1] the elastic constants for different alloy systems have been calculated through a method proposed by [2] according to the formula :

$B=[1+x\ (V_2/V_1)\ -1)/\ 1+(B_1/V_2/B_2/V_1-1)]\ B_1$

where x is the molecular fraction of compound 1 with bulk modulus and molar volume B_1 and V_1, respectively, while B_2 and V_2 are the bulk modulus and the molar volume for compound 2. Considering that each molecule added to a homogeneously mixed crystal represents a defect, the above formula can be also derived from a thermodynamic model, termed cBΩ, which interrelates bulk properties to defect parameters. This model has been successfully used in various cases i.e. from mixed alkali halides [3], [4] to various categories of solids [5] as well as to precursory seismic electric signals (SES) [6], [7] ,[8] [9].

Here, as another application of the this model, we

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will investigate the temperature dependence of the formation entropy in *α-Zr* and we will compare our results with recently published ones. Zirconium belongs to Group IV transition metals which attract the scientific interest due to their widespread use such as in aerospace industry, nuclear reactors and biochemistry, where the corrosion resistance, the heat stability, the low density (light weight), the static stress and stiffness are of benefit. Zirconium has a bcc structure (β-phase) at high temperatures and undergo a martensitic phase transition into the hexagonal closed pack (hcp) structure (α-phase) at lower temperatures. Under pressure it transforms into another hexagonal structure called the ω-phase as the titanium and hafnium [10], [11], [12].

2 DATA ANALYSIS AND RESULTS

According to the cBΩ model the Gibbs formation energy g^f is related to the bulk modulus B and mean atomic volume per atom Ω through the formula [13],[2]:

$$g^f=c^f B\Omega \tag{1}$$

where c^f is a constant and it is considered as independent of pressure and temperature.

In order to calculate the formation entropy s^f we combine (1) with the relation $s^f = -\dfrac{\partial g^f}{\partial T}\ \Big|_P$ and we get:

$$s^f = -\ c^f \Omega\ (\beta B + \frac{\partial B}{\partial T}\ \Big|_P) \tag{2}$$

where β is the volume thermal expansion coefficient and T is the temperature. Considering that at T=0 the Gibbs formation energy g^f becomes equal to the formation enthalpy h_0^f we have:

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$$c^f = h_0^f / B_0 \Omega_0. \qquad (3)$$

Now, by inserting the value c^f into (2) we can estimate s^f according to the formula:

$$s^f = -\frac{h_0^f}{B_0}\left(\beta B + \frac{\partial B}{\partial T}\Big|_P\right)\frac{\Omega_T}{\Omega_0} \qquad (4)$$

where Ω_T is the mean atomic volume per atom at temperature T.

Here, we calculate the formation entropy s^f for α-Zr in the temperature range (0-1050)K by using (4). We consider $\Omega_T/\Omega_0 = \exp\int_0^T \beta dT = 1 + \beta_{mean}T$, where the volume thermal expansion coefficient β is derived from the formula of Zhao et al. [14] $\beta = \alpha_T = \alpha + bT$ with [=(1.5 ± 0.8) x 10^{-5} K^{-1}, b=1.7(± 1.4) x 10^{-8}K^{-2} and β_{mean} = 2.38$10^{-5}$ K^{-1} for the temperature range (0-1050)K. The values of the isothermal bulk modulus B are taken from the relevant diagram for α-zirconium of fig.8 of Hu et al. [15], while the temperature derivative $\frac{\partial B}{\partial T}\Big|_P$ = -0.014 GPa K^{-1} is obtained from the mean slope at the two ends of this diagram and only for T=0 it is estimated as $\frac{\partial B}{\partial T}\Big|_P$ =-0.013 GPa K^{-1}. The value h_0^f =1.782 eV is derived from fig.8a of Wen and Woo [16] while for the bulk modulus we considered B_0=93.4GPa [17]. The latter value also agrees with the obtained one at T=0 from fig.8 of Hu et al. [15]. The calculated s^f values and their errors, arising from the uncertainties in the estimation of β, along with the bulk modulus B at different temperatures are shown in Table 1.

TABLE – 1
FORMATION ENTROPY s^F AND
BULK MODULUS B AT
DIFFERENT TEMPERATURES T
FOR A-ZR

T (K)	B (GPa)	s^f (k)
0	93.4	2.39 ± 0.3
300	90.9	2.64 ± 0.3
450	88.8	2.66 ± 0.3
600	87.0	2.68 ± 0.3
750	85.0	2.70 ± 0.3
900	83.2	2.72 ± 0.3
1050	81.1	2.74 ± 0.3

A plot of calculated s^f versus temperature is depicted in fig.1 (red dots) with a vertical red line marking the error while

blue triangles and associated error (blue vertical line) represent the temperature dependence of formation entropy found by Wen and Woo [16] by means of tedious microscopic calculations.
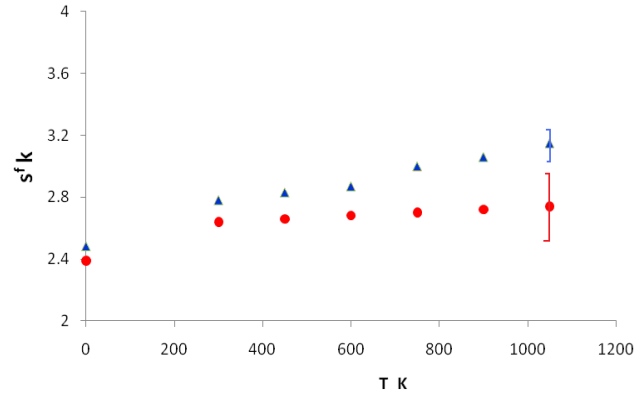

Fig.1 The formation entropy s^f versus temperature for α-Zr. Red dots denote our results and blue triangles those obtained by Wen and Woo [16]. Vertical bars depict the relevant errors.

An inspection at fig.1 shows that at lower temperatures the calculated values of formation entropy are in satisfactory agreement with those found by Wen and Woo [16], when errors are considered, while at higher temperatures the observed discrepancy is almost at the error margins.

3 CONCLUSIONS

The temperature dependence of formation entropy in α-Zr in a broad range of values (0-1050)K has been investigated with the aid of a thermodynamical model which interrelates bulk properties and point defect parameters. The resulting values are in good agreement with those obtained by recent microscopic calculations when errors are considered.

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