

Entropies and enthalpies for various defect processes in Al

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Abstract. Very recent first principle calculations for vacancy migration enthalpy and entropy for Al, considering local density approximation and generalized gradient approximation, have been reported by making use of the transition theory. Here, we discuss these calculated values along with those obtained from independent experiments focused on two other defect processes, i.e. vacancy formation and self-diffusion activation. We show that these values are compatible with those expected from aspects developed on the basis of thermodynamics of point defect in solids. In particular, we find that the ratio entropy/enthalpy for all these three processes (formation migration and self-diffusion activation) is practically the same and in addition it is governed by the bulk expansivity and elastic data.

Index Terms- entropy, enthalpy, defect processes, Al

1 INTRODUCTION

ALUMINIUM is the second most abundant metallic element in the Earth's crust after silicon. It is ductile, easily machined and cast and has excellent corrosion resistance and durability. Although it doesn't conduct electricity as well as copper it is used in electrical transmission lines because of its light weight. Aluminium and its alloys are vital to the aerospace industry and are used in wide variety of products as railcars, marine vessels, cans, foils and other items that require a strong, light material.

Diffusion is a basic and important factor for materials design and understanding of many important phenomena, such as solidification, precipitation, homogenization of alloys, re-crystallization, grain boundary migration, creep, etc. Several studies [1], [2], [3], [4] have been focused on predicting self-diffusion and impurity diffusion coefficients using the transition state theory and first-principles calculations. Vacancy migration enthalpy and entropy for pure aluminium based on first-principle calculations considering local density approximation (LDA) and generalized gradient approximation (GGA) have been recently reported [1].

The scope of the present short paper is two fold: First, to point out that these two thermodynamic parameters i.e. defect enthalpy and entropy, which can be deduced from independent experiments and in particular for vacancy formation and self-diffusion activation, have a ratio equal to that resulted from the aforementioned microscopic calculations for the migration process. Second, we show that the value itself of this ratio for all these three defect processes (formation migration and self-diffusion activation) is comparable to the one obtained by means of bulk expansivity and elastic data.

According to a thermodynamical model, termed as $cB\Omega$ model, the defect Gibbs energy g is interconnected to the isothermal bulk modulus B through the relation [5], [6], [7], [8]:

$$g^i = cB\Omega \quad (1)$$

where 'i' stands for the different process mechanism, (formation, migration and activation), Ω is the mean atomic volume per atom and c^i is a dimensionless constant which can be considered as independent of temperature and pressure. Recent successful applications of the $cB\Omega$ model to various categories of solids as to metals (e.g. Na) [9], ionic superconductors (e.g. α -PbF₂ and β -PbF₂) [10], [11], diamond [12] are available. The defect entropy s^i can be derived by inserting (1) into the relation $s^i = -(dg^i/dT)_P$ as:

$$s^i = -c^i\Omega \left[\beta B + \frac{\partial B}{\partial T} \right]_P \quad (2)$$

On the other hand from a combination of (1) and (2) and the thermodynamic formula $h^i = g^i + Ts^i$ the defect enthalpy h^i can be expressed as:

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$$h^i = c^i \Omega \left[B - T\beta B - T \frac{\partial B}{\partial T} \Big|_P \right] \quad (3)$$

At the temperature $T=0K$ the defect enthalpy is $h_0 = cB_0\Omega_0$ and hence $c = h_0 / B_0\Omega_0$. Thus we get:

$$h^i = \frac{h_0^i}{B_0} \frac{\Omega}{\Omega_0} \left[B - T\beta B - T \frac{\partial B}{\partial T} \Big|_P \right] \quad (4)$$

and

$$s^i = - \frac{h_0^i}{B_0} \frac{\Omega}{\Omega_0} \left[\beta B + \frac{\partial B}{\partial T} \Big|_P \right] \quad (5)$$

In most of the cases experimental enthalpy h_{exp} is described as an almost linear Arrhenius plot with a single value and it is usually obtained in a middle temperature range. If we consider that B varies linearly with T , the intercept of the straight line on the vertical axis of the relation $B=f(T)$ gives the quantity $B_0^{SL} = B - T \frac{\partial B}{\partial T} \Big|_P$. Assuming now that $B_0^{SL} \gg \beta BT$ and $\Omega/\Omega_0 \approx 1$, (4) becomes

$$h_{exp}^i = h_0^i \frac{B_0^{SL}}{B_0} \quad (6)$$

From (5) and (6) we have

$$\frac{s^i}{h_{exp}^i} = - \frac{(\beta B + \frac{\partial B}{\partial T} \Big|_P) \Omega}{B_0^{SL} \Omega_0} = A \quad (7)$$

Thus the quantity $A = s^i / h_{exp}^i$ given by (7) depends only on the bulk properties of the host material and it is independent of the process mechanism.

2 DATA AND ANALYSIS

In the case of pure aluminium we consider at $T=850 K$ the volume thermal expansion coefficient [13], $\beta=1.05 \times 10^{-4} K^{-1}$. The quantity $B_0^{SL} = 84 \text{ GPa}$ and the slope $dB/dT = -0.0301 \text{ GPa/K}$ are estimated from a least square fitting to the data of the temperature dependence of B of Tallon and Wolfenden, [14], in the temperature range (673-873)K while $B=58.5 \text{ GPa}$ at $T=850 K$. The ratio Ω/Ω_0 is calculated from (6) of Guerard et al. [15], (i.e. $\Omega/\Omega_0 = 1 + \Delta V/V_0 \approx 1 + 3(\Delta\alpha/\alpha_0)$) where $\Delta V/V_0$ and $\Delta\alpha/\alpha_0$ are the relative volume and lattice parameter changes, respectively. An extrapolation to $T=850K$ of the data listed in Table 1 of Guerard et al. [15], results to $\Delta\alpha/\alpha_0=0.026$ and thus $\Omega/\Omega_0 = 1.08$. Inserting now in (7) all the appropriate above values we get $A=3.08 \times 10^{-4} K^{-1} \approx 3.6 k/eV$. Fig.1 shows a

plot of defect entropies versus enthalpies where the blue dots denote the activation and formation data deduced from independent experiments as follows: the self-diffusion activation data from Lundy and Murdock [16] and the vacancy formation data from Guerard et al. [15] and Simmons and Balluffi [17] (see Table 1).

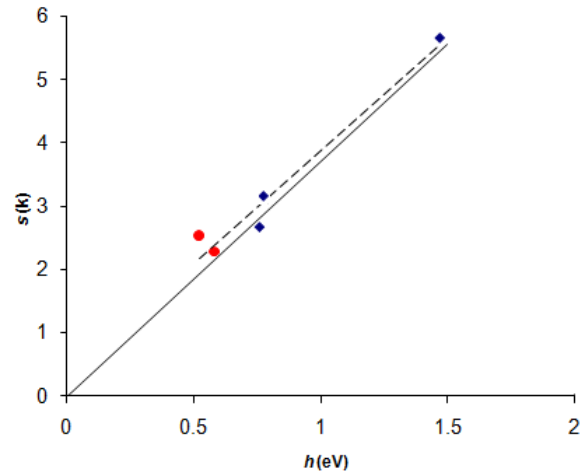


Fig.1 Plot of defect entropies versus enthalpies where the blue dots denote the activation and formation data and the red circles the migration defect parameter data obtained by Mantina et al.[1] (in their Table 1). The dashed line corresponds to the least square fitting to the above data which are also presented in our Table 1 while the solid straight line with slope A to the $cB\Omega$ model.

The red circles denote the migration defect parameter data obtained by Mantina et al. [1] (see their Table 1) from first-principles calculations for pure Al with two different methods; the local density approximation (LDA) and the generalized gradient approximation (GGA). The solid straight line with slope A corresponds to the $cB\Omega$ model and the dotted one to the least square fitting to the above data which are also presented in our Table 1.

There are two important points emerged from Fig.1. First, it is obvious that all data for the three defect processes are more or less aligned along a straight line. In other words, the entropy values for various defect processes (formation migration and self-diffusion activation) seem to scale with the corresponding enthalpy values. Second, the slope of the straight line (dotted) resulted from the values that correspond to these three processes seems to agree well with the slope A of the solid straight line predicted from the $cB\Omega$ model. Hence, the application of the above thermodynamic model in pure Al shows that defect parameters of different mechanism processes i.e. formation migration and activation deduced either from microscopic or macroscopic calculations obey the $cB\Omega$ model.

TABLE – 1.

DEFECT ENTROPIES AND ENTHALPIES FOR PURE AL FOR DIFFERENT PROCESSES

s (k)	h (eV)	process
3.12	0.81 ^a	(formation)
2.40	0.76 ^b	(formation)
5.55	1.47 ^c	(activation)
2.53	0.52 ^d	(migration)
2.28	0.58 ^d	(migration)

^a from [15] Guerard et al. [15].

^b from [17] Simmons and Balluffi [17].

^c from [16] Lundy and Murdock [16]

^d from Table 1 of Mantina et al. [1]

3 CONCLUSION

In the present work we show that defect parameters of pure aluminium of different mechanism processes (formation, migration, activation) deduced either from microscopic or macroscopic calculations are in good agreement with a linear relation of bulk properties of Al predicted by a thermodynamical model.

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