Development of an effective interatomic potential for transition metals and alloys: Modified Wills–Harrison model

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Abstract. This paper deals with the development of an effective interionic interaction for transition metals and alloys in the spirit of a hybridized pseudopotential tight-binding formalism, developed among others by Wills and Harrison. Stated briefly, the recipe consists in writing the total interionic interaction as a sum of contributions arising from nearly free s-electrons and that of tightly bound d-electrons. The s–d hybridization is also accounted for by allowing for the relative change in the occupancy of s and d electron counts. This potential, although not taking into account the magnetic contribution, contains otherwise all the essentials of a physically meaningful interatomic interaction. In this paper, a modified version of the Wills–Harrison model is used to calculate the structural and cohesive properties of transition metals at 0 K. The calculated values are in reasonable agreement with the experimental ones. This method is also used to derive an effective interatomic interaction for γ -TiAl. The use of this potential in obtaining an estimate of point defect energetics in TiAl is discussed.

Keywords. Interatomic potentials; Wills–Harrison model; TiAl; vacancy properties.

1. Introduction

The availability of simple and physically appealing interatomic potentials is rather crucial for meaningful modelling studies of condensed systems (Gehlen *et al* 1972). In the realm of physical metallurgy, the use of empirical and semi-empirical pair potentials has a long history in that diverse issues ranging from alloy phase stability to defect structure modelling have been tackled using the so-called fitted potentials (Gehlen *et al* 1972; deHosson 1981). In spite of easy applicability, the empirical potentials lack a strong theoretical basis, making thereby the results obtained from them rather difficult to be interpreted (Carlsson 1990). In brief, it may be said that empirical interatomic potentials are neither transparent nor transferable (deHosson 1981; Carlsson 1990).

2. Wills–Harrison model

2.1 Genesis

In the realm of metal physics, the use of pseudopotential theory has provided a simple and neat picture of simple metal cohesion (Harrison 1970). The effective interionic interaction in this case may be approximated (Harrison and Wills 1982) to be consisting of a net Coulombic repulsion, modified by a screening factor. It follows that to a first-order approximation, no explicit introduction of a structure-dependent term is necessary to account for the bulk properties (Harrison 1970; Harrison and Wills 1982). Thus the failure to hold the Cauchy relation ($C_{12} = C_{44}$) is directly explained from the volume-dependent repulsive ion–ion interaction. Of course, it is necessary and

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desirable to include the structure-dependent term when it comes to calculating, say the relative structural stabilities (Hafner 1987). But this point does not concern us here. On the other hand, it was generally ascribed that owing to strong scattering d -electron potential a perturbative treatment of the total energy of transition metals is impractical (Ashcroft and Mermin 1976). But the crux of the point is that if one could separate somehow the free electron like s -state from the deeply bound d -state and describe their coupling as a perturbation in an appropriate expandable parameter (Harrison and Froyen 1980), meaningful and useful simplifications of the transition metal band structure can still be achieved on lines similar to the development of pseudopotential formalism (Wills and Harrison 1983). Starting from early seventies to the present time, the torrent of developments in the theory of transition metal cohesion has taken the field far beyond the aforementioned simple description. The readers are referred to the reviews (Harrison 1980; deHosson 1981, 1989; Pettifor 1983) for further details. However, it is sufficient to mention that the genesis of the Wills–Harrison Model (WHM) (Wills and Harrison 1983) is strongly rooted in the multifarious developments concerning the electronic structure of transition metals. In this paper a modified version of the original WHM is adopted to probe a few structural metallurgical issues. A brief account of the basics of WHM is presented below.

2.2 Basic description

The total potential energy of a condensed system consisting of ions (nucleus + core electrons) and the outer valence electrons is generally given by (Gehlen *et al* 1972)

$$\phi = \phi_s(V) + \frac{1}{2} \sum \dot{V}_{\text{eff}}(r; V), \quad (1)$$

where, the summation is carried over to all $\{r_i\}$, the set of lattice positions. The first term in RHS is basically a many body effective ion–ion interaction term. In WHM (Wills and Harrison 1983), the s - and p -electron contributions to cohesion are treated in a nearly free electron pseudopotential. The contribution from the d -band broadening and s - d hybridization are treated in the framework of linear muffin tin orbital (LMTO) formalism. By superposing these two contributions to the total energy, an effective real space ion–ion potential is derived in a form, which is similar to (1). The V_{eff} may further be explicitly split into two contributions as given by

$$V_{\text{eff}}(r) = V_s(r) + V_d(r), \quad (2)$$

where $V_s(r)$ is the nearly free electron contribution and is given by (Harrison and Wills 1982)

$$V_s(r) = \frac{(Z_s e)^2}{r} \cosh^2(\kappa r_c) e^{-\kappa r}, \quad (3)$$

where $\kappa^2 = 4k_f me^2/\hbar^2 \pi$ is the square of the Thomas–Fermi screening length, r_c the Ashcroft's empty core pseudopotential radius and Z_s the number of valence s -electrons. This potential is derived using the Thomas–Fermi linear screening approximation (Harrison 1970; Harrison and Wills 1982). The purely repulsive form of $V_s(r)$ derives from this assumption. On the other hand, if one employs a Lindhard approximation for the Hartree dielectric function, a potential with a long-range oscillatory behaviour is obtained (Harrison 1970).

The effective d -band contribution ($V_d(r)$) is obtained by coupling d -orbitals on different sites with the conduction s -electrons. In WHM, this is evaluated in the spirit of LMTO theory and Hartree–Fock free atom wave functions. The tight-binding matrix elements are represented in this model by a quantity r_d called the d -orbital radius of the free atom. Thus, we get

$$V_d(r) = V_d^b(r) + V_d^r(r), \quad (4)$$

where in $V_d^b(r)$, the bonding d -contribution is given within the framework of Friedel's rectangular density of d -states model as (Wills and Harrison 1983)

$$V_d^b(r) = -Z_d(1 - Z_d/10)\sqrt{12/n} (28.1/\pi)\hbar^2 r_d^3/mr^5, \quad (5)$$

where n is the first coordination number. The repulsive $V_d^r(r)$ due to the hybridization shift in the centre of gravity of the d -states is given by (Wills and Harrison 1983)

$$V_d^r(r) = -Z_d(225/\pi^2)\hbar^2 r_d^6/mr^8, \quad (6)$$

where Z_d is the number of bonding d -electrons. Barring Z_s , Z_d , r_c , n and r_d , there are no other adjustable parameters. In fact all these values are available from standard sources (Harrison 1980; Harrison and Froyen 1980; Wills and Harrison 1983). Further r_c can also be determined using the familiar zero pressure condition $((\partial E/\partial V)_{V_{\text{eq}}} = -p = 0)$. In table 1, the input parameters needed for calculating $V_{\text{eff}}(r)$ are presented for selected transition metals.

2.3 Modified Wills–Harrison scheme

The values of bulk modulus at zero pressure (B_0) calculated *vide* (1)–(6), show rather poor agreement with the experimental values. This is partly due to the neglect of magnetic interactions in late $3d$ metals and spin–orbit coupling in heavier transition metals. Since a rigorous description of both of these is beyond the scope of the original WHM, we choose to modify the WHM prescription in an *ad hoc* manner by incorporating two additional parameters, k_1 and k_2 such that

$$V_{\text{eff}}(r) = V_s(r) + k_1 V_d^b(r) + k_2 V_d^r(r). \quad (7)$$

The constants k_1 and k_2 are determined by requiring $V_{\text{eff}}(r)$ to simultaneously satisfy B_0 and B'_0 , the pressure derivative of bulk modulus at equilibrium volume. B'_0 is given by

$$B'_0 = \frac{1}{B_0}(-V dB/dV)_{V=V_0}. \quad (8)$$

The values of k_1 and k_2 obtained are listed in table 1.

Table 1. List of input parameters.

Metal	Z_s	Z_d	n	r_c	r_d	r_0	$B_0(\text{exp})$	k_1	k_2
Ti	1.5	2.5	12	0.91	1.08	1.61	1051	2.07	4.85
V	1.5	3.5	8	0.87	0.98	1.49	1619	2.22	5.53
Cr	1.5	4.5	8	0.82	0.9	1.42	1901	2.15	5.04
Mn	1.5	5.5	8(α -Mn)	0.78	0.86	1.43	596	0.657	0.632
Fe	1.5	6.5	8	0.71	0.8	1.41	1683	2.274	4.96

Note: all r values are in 10^{-10} m. B_0 , the experimental bulk modulus values are in 10^2 MPa.

Figure 1. a. Calculated interatomic potential for Ti. Note the cancellation of strong repulsive contribution by the attractive d-band bonding contribution and b. calculated interatomic potential for Cr.

3. Discussion

3.1 General

The calculated potential for titanium taken as a typical example is given in figure 1a. It can be seen that the strong repulsive $V_s(r)$ contribution is more than compensated by the V_d^b term. It is also instructive to note that the minimum in $V_{eff}(r)$ occurs slightly to the right of the actual nn separation. In figure 1b the calculated $V_{eff}(r)$ for chromium is given where in the experimental nn distance and the potential minimum again do not coincide.

This modified WHM potential has been used to calculate the Debye temperature of transition metals (Raju *et al* 1996a). It is sufficient to remark that the calculated values are in reasonable agreement with those obtained by more elaborate scheme (Haglund *et al* 1993).

Regarding its physical content, WHM offers interesting possibilities. In the first it is possible to obtain physically more complete functional forms for $V_{eff}(r)$ by employing better screening scheme and pseudopotentials. Such a potential is actually called for in

Figure 2. $L1_0$ crystal structure of γ -TiAl. Different bond lengths are marked. Note $c/a = d_3/d_2 > 1$.

calculating the relative stabilities among competing crystal structures. Secondly, one can also use the valence partitioning into Z_s and Z_d as an adroitly adjustable tool to obtain optimized $V_{\text{eff}}(r)$, which is appropriate to a given crystal chemical environment (Raju *et al.*, unpublished). Setting aside further discussion, we may briefly concentrate on the application of this potential to γ -TiAl intermetallic (Raju *et al.* 1996b).

3.2 Application to γ -TiAl

γ -TiAl is a layered intermetallic with fct structure ($c/a \sim 1.02$; figure 2). This intermetallic has immense potential as a candidate material for high temperature aerospace applications and has been at the centre of intense research activities. In the present case we are interested in getting a first-order estimate of the point-defect properties by employing the WHM potential in conjunction with the quasi-chemical description of the defect equilibrium. A detailed account of this work has been published elsewhere (Raju *et al.* 1996b).

Briefly the work involves calculating the $V_{\text{eff}}(r)$ for Ti, Al and Ti–Al interactions with reference to the alloyed state. The alloy potential is obtained from the corresponding elemental potential in the following empirical way (Raju *et al.* 1996b):

$$V(r) = V^0(r) [2(r^0/r)^{12} - (r^0/r)^6], \quad (9)$$

where r^0 and r refer to bond lengths in the elemental and alloyed state. Further $V_{ij}(r)$, the interaction potential between unlike atoms is obtained by taking the geometric mean of the respective i and j potentials, i.e.,

$$V_{ij} = \sqrt{V_{ii} * V_{jj}}. \quad (10)$$

Finally, an effective ordering potential for TiAl can be defined as (Raju *et al.* 1996b)

$$V_{\text{ord}} = \left[V_{\text{Ti-Al}} = -\frac{V_{\text{Ti-Ti}} + V_{\text{Al-Al}}}{2} \right]. \quad (11)$$

In figure 3, the ordering potential for equiatomic TiAl is plotted. From the sign of V_{ord} at the observed nn separation distance it is evident, that ordering is definitely favoured in TiAl. Using this calculated potential, the concentration of thermal

Figure 3. Calculated ordering potential for TiAl.

Figure 4. Calculated total thermal vacancy concentration plotted as a function of temperature.

vacancies is calculated within the spirit of a simple quasichemical model restricted to only nn interactions. The result is given in figure 4. Although vibrational contributions to the total vacancy formation enthalpy have not been taken into account, the calculated value of point defect enthalpy of about ~ 1.3 eV agrees well with the reported experimental values of ~ 1.4 eV (Brossman *et al* 1994).

4. Conclusions

A modified WHM has been developed for possible applications in elucidating structural and thermophysical properties of transition metal and their alloys. A preliminary application of this potential to estimate the point defect properties of γ -TiAl is encouraging.

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