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An Empirical Many-Body Potential for B2 FeAl

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Abstract. Studies of grain boundaries may be helpful in understanding the brittleness of the B2 ordered alloy FeAl. To this end, an interatomic potential is proposed, lying on a modified Embedded-Atom Method. This method, rather similar to that used for semiconductors, involves a 3-body non central term in the energy, making it possible to describe the strongly directional effects in FeAl. A great number of zero temperature bulk and defect properties are correctly reproduced for Fe and Al as well as for the alloy, indicating that the potential is probably a good tool for molecular statics simulations. As a first application, the structure of the $\Sigma 5$ [100] 37° tilt grain boundary is determined.

1. INTRODUCTION

Intermetallic compounds, owing to their potential ability to replace other materials, form the subject of an increasing amount of studies. Among these, FeAl takes up an interesting place, in regard of its quite high specific stiffness. Unfortunately, it is impaired by a strong intergranular brittleness making its elaboration uneasy and its industrial use hazardous. As is the case for many intermetallics, addition of a small amount of boron changes its fracture mode into transgranular cleavage [1]. Therefore, current researches aim at understanding the reasons for this brittleness and the role of B. Within the scope of these researches, the present paper describes the fitting of an interatomic potential for the Fe-Al system, the final purpose being the study of grain boundaries.

2. CHOICE OF POTENTIAL

The Fe-Al system is described by such a complexe phase diagram that it is totally hopeless to attempt to determine a potential that could describe the properties of compounds with any composition. Our final aim being to calculate the properties of grain boundaries in nearly stoichiometric FeAl (in the range of compositions between 38 and 50 at. % Al), it seems natural to focus the fit on the characteristics of this precise monocrystalline compound. However, the segregation phenomena occurring at interfaces are bound to change the local composition dramatically. In such conditions, the potential should be able to describe these pure elements too.

Moreover, the Fe-Al system displays strongly directional bonds, which is exemplified by a negative Cauchy discrepancy $C_{12}-C_{44}$. This feature rules out any as-such use of the Embedded Atom Method (E.A.M.) for our purpose, since this procedure cannot allow for it [2]. This roughly means that E.A.M. cannot properly describe covalent effects, in which the electronic charge density is concentrated on particular directions. In fact, classical E.A.M.-type expressions can be derived in two ways, the first of which [3] makes it valid for normal metals (with very little directional bonding) and the second one [4] rests on a simple tight-binding method well suited for transition metals. The case of FeAl is situated quite intermediately between the two preceding ones: it is a mixture of a simple and a transition metal, and the electronic structure shows a strong s-d hybridization, responsible for its quite unusual behaviour. Faced with such a system, the most satisfactory attitude would doubtlessly be to get an analytical expression on a

theoretically firm basis. To this aim, a potential based on the tight-binding bond model has recently been derived [5]. But the calculation of configurational energy and forces is too heavy for us to use it in our grain boundaries calculations. Thus we have to confine to a much simpler semi-empirical model, which is more easily tractable.

Keeping in mind the inefficiency of the classical E.A.M., we turned to potentials designed for semi-conductors, although it has not been so far a very usual procedure to describe metallic systems. The most simple ones involve an additional 3 body non-central term [6], which was initially introduced as an angularly dependent correction for the density over a site [2,7]. However, as the system of interest is metallic, we preferred to confine to a form of potential already successfully tested in such a context and chose an expression first proposed on more empirical grounds [8] and already known to be efficient for several elements (among which Cr also displays a negative Cauchy discrepancy). Following these authors, we thus write the energy of an assembly of atoms i as:

$$E_i = \sum_i \left[F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} V_{ij}(r_{ij}) + \alpha_i Y_i^2 \right], \text{ where } \rho_i = \sum_{j \neq i} f_j(r_{ij}).$$

F_i can be regarded as the so-called embedding function (although its significance is quite dubious), ρ_i is the induced density over site i , V_{ij} is a pair potential classically collecting elsewhere ill-described interactions (exchange and correlation,...) and α_i is a parameter supposed to depend in a complex way on the local composition of the alloy and to contain all that information about directionality which is not taken into account by the first two classical terms.

Moreover, $Y_i^2 = \sum_{\alpha, \beta} (\lambda_i^{\alpha\beta})^2 - \frac{1}{3} \text{tr}(\overline{\lambda_i})^2$ is the second invariant of $\overline{\lambda_i}$, with:

$$\lambda_i^{\alpha\beta} = \sum_{j \neq i} f(r_{ij}) \frac{(r_\alpha^j - r_\alpha^i)(r_\beta^j - r_\beta^i)}{(r_{ij})^2}$$

In fact, Y_i^2 can be recast to yield a more explicit 3-body expression:

$$Y_i^2 = \sum_{\substack{j \neq i \\ k \neq i}} f(r_{ij}) f(r_{ik}) (\cos^2 \theta_{ijk} - \frac{1}{3})$$

The physical interpretation of $\overline{\lambda_i}$ rests on Kanzaki forces [9], but it is also possible to notice that its form mimics that of a d orbital.

3. FITTING PROCEDURE

Firstly, two potentials were calculated for pure elements: they reproduce well-known zero temperature properties: sublimation energy, lattice parameter and the three cubic elastic constants. The next step consisted in fitting a FeAl potential, derived from those calculated for the pure metals, through the addition of an Fe-Al pair potential. This alloy potential was tested relatively to perfect lattice and defect properties of FeAl. Finally, we also briefly studied the behaviour of the potential in an Fe₃Al structure.

We only give here the analytical expressions used. The corresponding graphs are presented on fig.1. Numerical values of parameters for pure elements as well as for the alloy are collected in appendix.

3.1 Pure elements

The pair potential is taken from [10]: $V(r) = \psi(r) - \psi(D_p) + \frac{D_p}{20} \left[1 - \left(\frac{r}{D_p} \right)^{20} \right] \psi'(D_p)$,

where $\psi(r) = \psi_0 [\exp(-2\gamma(r-t)) - 2 \cdot \exp(-\gamma(r-t))]$ is a Morse potential. D_p is the cut-off distance and t , γ are adjustable parameters.

For the density function, we choose an exponential form: $f(r) = f_0 \exp(-\beta (\frac{r}{a_0} - 1))$.

The immersion function is chosen to have the following properties : $F(0)=0$, $F^{(p)}(\rho_0) = F_0^{(p)}$ ($p=0,1,2$). Moreover, F has to always be convex for $\rho > \rho_0$; if $\rho < \rho_0$, this property depends on F_0 , F_0' , F_0'' . Thus, the immersion function has a twofold expression:

$$F(\rho) = \frac{A}{2\rho} + \frac{[(\rho_0)^4 F_0'' - A\rho_0]}{6\rho^2} + \left[F_0' + \frac{A}{6(\rho_0)^2} + \rho_0 F_0'' / 3 \right] \rho + F_0 - \rho_0 F_0' - (\rho_0)^2 F_0'' / 2 - \frac{A}{2\rho_0}$$

if $\rho > \rho_0$ (ρ_0 is the density over a site of monocrystal at equilibrium).

$$F(\rho) = \rho^2 F_0'' / 2 - [F_0' - \rho_0 F_0''] \rho + (F_0 - \rho_0 F_0' + F_0'' (\rho_0)^2 / 2) \left[1 + \left(\frac{\rho}{\rho_0} - 1 \right)^3 \right] \text{ otherwise.}$$

The parameter A governs the slope for strong densities. It plays no role in the fitting procedure because all densities appearing there are lower than the equilibrium value. It however influences grain boundaries energies.

The 5 equations expressing the 5 properties mentioned above depend on F_0 , $f_0 F_0'$, $(f_0)^2 F_0''$, ψ_0 and $(f_0)^2 \alpha$ linearly. This feature makes it possible to calculate exactly these five parameters so as to reproduce systematically these properties. Strictly speaking, the fitting was performed by a limited manual adjustment of the parameters γ , t , β et D_p in order to get plausible values for the vacancy formation energy as well as the (001) surface energy and structure and energies of several simple tilt grain boundaries. Since it is only a scaling parameter (which nevertheless influences α , F_0' and F_0''), f_0 is chosen arbitrarily. It should again be emphasized that for fixed γ , t , β and D_p , the physical properties are not modified by varying f_0 at constant F_0 , $f_0 F_0'$, $(f_0)^2 F_0''$, $(f_0)^2 \alpha$ and A/f_0 . A class of physically equivalent models can thus be generated. Moreover, subtraction of a linear function yp (y is a constant) from the immersion function $F(\rho)$ of an element does not modify the configurational energy, if this operation is balanced with the addition of $2yf(r)$ to the corresponding pair potential.

3.2 FeAl

The usual method to get an E.A.M. alloy potential rests on the above mentioned properties of the energy of pure elements and on the fact that only f_0^{Al}/f_0^{Fe} has a physical meaning for a binary alloy [10]: as in the case of a single element, it is possible to determine equivalent models by varying one f_0 at constant ratio. Thus we kept f_0^{Al} equal to 10^{-3} and calculated f_0^{Fe} . The Fe-Al pair potential is also chosen to be a Morse potential.

The value of α depends on the local environment of an atom. Thus, the fitted value of α for FeAl would be valid strictly speaking only for the perfect stoichiometric monocrystal. Nevertheless, by lack of satisfying as well as easily tractable procedure to calculate this parameter for a given environment, we simply assumed a constant value for the calculation of defect properties (A.P.B. for example), which amounts to regarding α as determined by the global composition. The values obtained that way show that the directionality of bonding is indeed much stronger in the alloy than in the pure elements: the amount of directional bonding is roughly two orders of magnitude higher in the alloy for each element. Direct comparison is allowed by the fact that the scaling parameters f_0 are (respectively almost) identical for Al (for Fe) when shifting from components to alloy.

To sum up, ψ_{FeAl} , γ_{Al} , γ_{Fe} , α_{Al} , α_{Fe} are determined by solving a linear system so as to reproduce the same five properties as for a pure element. A manual fitting of f_{Fe}^0 , γ_{FeAl} , t_{FeAl} and D_{pFeAl} was performed to provide correct values of extra defect energies.

Figure 1: Graphs of the potential used for FeAl: a) density functions, b) immersion functions, c) pair potentials.

4. RESULTS

4.1 Tests of the potential

For pure elements as well as for FeAl, the experimental values of cohesion energy [11,12], lattice parameter [13] and elastic constants [14,15] are reproduced with a precision better than 0.1%. Other properties are detailed in the following table.

Table 1: Calculated values for pure elements and alloy.

Property	Al		Fe		FeAl			
	calculated	experim.	calculated	experim.	calculated		experim.	
Antiphase boundary (1-10)1/2[111](mJ/m ²)					370		300 [15]	
Vacancy (eV)	0.6	0.7 [16]	2.0	1.9 [4]	Al 2.8	Fe 0.8	Al	Fe 0.7
(001) surface (mJ/m ²)	1280	1200 [17]	2220	2200 [4]	1380	2150		
Antisite defect (eV)					0.78	0.76		

Experimental data relative to point or planar defects in FeAl are quite rare. The main available ones concern the vacancy formation energy which must be regarded as an apparent energy taking into account the influence of all types of defects. However, there is some evidence for believing that Al vacancies are almost inexistant, at least for temperatures below 1000 K. This is the reason why we put down the corresponding measured value to Fe vacancies. Such an assumption is also backed up by ab initio calculations only providing the Fe vacancy energy, without referring to the Al one.

We also successfully checked the validity of the potential by comparing the relative stabilities of the three classical crystallographic structures. The results are reported below:

Table 2: Stability of metastable structures.

Structure	b.c.c.		f.c.c.		h.c.p.		
	a(Å)	E _{coh} (eV)	a	E _{coh}	a	c(Å)	E _{coh}
Al	3.16	-3.25	4.04	-3.34	2.67	5.42	-3.32
Fe	2.86	-4.29	3.59	-4.20	2.52	4.26	-4.20

The last test performed up to now concerned Fe_3Al , the equilibrium lattice parameter and formation energy of which were calculated: $5.78 \text{ \AA}$ (exp. value: $5.7923 \text{ \AA}$ [13]) and -16.88 eV for 3 Fe and 1 Al (exp. value: -16.86 eV [12]).

4.2 Application to a grain boundary structure

With this model, we studied by molecular statics the local composition of the $\Sigma 5$ $[100]$ 37° tilt grain boundary in stoichiometric B2 alloy. We compared the energies of structures differing by rigid translations and composition in the interface plane: we find the energy minimum for the Fe-rich structure (fig.2b), more stable than the most favourable stoichiometric model (fig.2a): thus the grain boundary displays an intrinsic (non thermal) enrichment.

Figure 2: Local Fe enrichment on the $\Sigma 5$ $[100]$ 37° tilt boundary.

5. CONCLUSIONS

We have developed a Modified Embedded Atom Method potential for B2 FeAl alloys. It proved to be quite satisfactory in the description of pure elements and of this compound, characterized by strong directional bonds. The procedure was firstly to fit two separate models for Fe and Al, and then to determine a cross-potential and an angular parameter specific to the B2 alloy. The negative Cauchy discrepancy could thus be allowed for.

The potential gives quite plausible values for defect energies (vacancies, antisites and antiphase boundary), which is an essential feature for future studies of grain boundaries. In this perspective, we tested the model by determining the local enrichment in the $\Sigma 5$ $[100]$ 37° tilt grain boundary, and reached the conclusion that an Fe-plane at the interface is needed to get the energy minimum.

APPENDIX

Table 3: Interatomic potentials for Fe, Al and FeAl : values of parameters.

	Pure elements		FeAl alloy		
	Al	Fe	Al	FeAl	Fe
f_0	10^{-3}	10^{-3}	10^{-3}		$9.21 \cdot 10^{-4}$
$\beta(\text{\AA}^{-1})$	5.8	6.0			
$\gamma(\text{\AA}^{-1})$	0.3	0.9		0.35	
$t(\text{\AA})$	3.45	2.8		2.5	
ψ_0 (eV)	0.8663	1.3152		0.961	
A(eV)	0.8	0.08			
y(eV)			-7.42		-84.35
α (eV)	89	1992	7467		108064
$F_{\text{equilibrium}}$ (eV)	1.46	-3.6			
$F'_{\text{equilibrium}}$ (eV)	68.2	-144.6			
$F''_{\text{equilibrium}}$ (eV)	4647.0	2866.9			
$D_p(\text{\AA})$	5.65	3.5		4.4	
$D_d(\text{\AA})$	5.4	4.4			

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