

MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION - A. Caro, P. Erhart, M. Serrano de Caro, B. Sadigh (Lawrence Livermore National Laboratory), S.G. Srinivasan (UNT), A. Stukowski (Germany).

OBJECTIVE

This research has two main objectives:

- The development of computational tools to evaluate alloy properties, using the information contained in thermodynamic functions. We aim at improving the ability of classical potentials to account for complex alloy behavior, and
- The application of these tools to predict properties of alloys under irradiation, in particular the FeCr system.

SUMMARY

This semester has been very productive in the developments of both tools and algorithms.

- With the visit of a A. Stukowsky, a graduate student from Prof. K. Albe (Germany) we implemented the formalism of the composition dependent embedded atom model (CD-EAM) into Lammmps, a freely distributed code for molecular dynamics. We also implemented a 'variance constrained' Metropolis Monte Carlo, MMC, algorithm into Lammmps.
- We developed a modified version of the CD-EAM, that we call 'one site' CD-EAM that significantly improves the performance of a MMC algorithm without affecting the accuracy of the interatomic potential.
- We developed a ternary FeCr-He potential based on data obtained from Prof. K. Nordlund's group in Finland. We validate this potential against *ab initio* data on He in FeCr obtained from within a collaboration with Chu Chun Fu at CEA-Saclay, France.
- We started simulation of He bubbles in FeCr alloys, determining the pressure versus size relation for the 1He/vacancy ratio

BACKGROUND

Our work aims at developing theoretical and numerical methodologies that are directly applicable to multi-scale modeling addressing the specific issues related to multi-component, multi-phase systems in non-equilibrium states, such as solid-solution hardening, point defect-solute interactions, stoichiometry effects, static and dynamic strain aging, dislocation-solute interactions, and in general the aspects of microstructure evolution that are affected by irradiation. At its present stage of development, we have been able to predict numerous thermodynamic properties of FeCr mainly related to ordering and precipitation; we have found new intermetallic phases and suggested the existence of a dependence of the solubility limit on the degree of order of the alloy. At present, we are studying dislocation mobility in the solid solution and the heterogeneous phase, and we are developing a new algorithm to perform Monte Carlo simulations inside the miscibility gap, a technique that will allow us to study interfacial energies and nucleation sizes.

We develop a strategy to model radiation damage in FeCr alloys, system in which magnetism introduces an anomaly in the heat of formation of the solid solution that is at the basis of its unique behavior. Magnetism has implications for the precipitation of excess Cr in the α' phase in the presence of heterogeneities. These complexities pose many challenges for atomistic (empirical) methods. To address such issues we develop a modified, many-body potential by rigorously fitting thermodynamic properties, including free energy. Multi-million atom displacement Monte Carlo simulations in the transmutation ensemble, using both our new potential and our new MC code, are able to predict properties of non equilibrium processes like heterogeneous precipitation, and dislocation – precipitate interactions, enabling the study of hardening and embrittlement under irradiation.

PROGRESS AND STATUS

In the period covered by this report, we developed a first version of a ternary empirical potential that adds He to the binary FeCr potential we developed a few years ago. We also developed the numerical codes that solve this model both in molecular dynamics and in Metropolis Monte Carlo.

Multicomponent alloy potentials can be build in different ways, depending on the particular scheme adopted for the interactions. Our FeCr binary potential is based on a standard EAM embedding part plus a pair potential that has an extra many body contribution in the form of a polynomial that depends on local composition. This methodology, which is similar to the CALPHAD strategy for binary and multicomponent alloys, is readily generalized to multicomponent systems. For a ternary, what needs to be done is to develop the composition dependent polynomials corresponding to the two new binaries generated when a third element is added to FeCr, namely FeHe and CrHe. These polynomials are closely related to the heats of formation of these new binaries.

Fortunately for us, He is a chemically inert noble gas that does not form alloys or compounds with any other element; its low solubility is a consequence of elastic interactions not compensated by any chemical attraction. As a result, He solubility is very small in both metals, leading to precipitation of He in the form of bubbles. From the modeling perspective then the only parameter that needs to be fitted is the heat of solution of a single impurity, in both host metals, i. e. the equivalent to the derivative of the heat of formation of FeHe and CrHe at vanishing He compositions.

The strategy we followed was to take advantage of a recent development of FeHe and CrHe binary potentials developed by our colleague at Helsinki University, Prof. K. Nordlund, who made these developments available to us before publication.

The properties that are used as target are summarized in Table 1.

Fe-He	Subs.	Octa.	Tetr.
DFT Seletskaja	4.08	4.60	4.37
Fu	4.22	4.57	4.39
This potential:	4.10	4.51	4.39
Cr-He	Subs	Oct.	Tetr.
DFT Norlund:	5.00	5.37	5.20
This potential:	5.01	5.34	5.25

Table 1: Selected properties of substitutional He as obtained from ab initio calculations and by the classical potential

An empirical ternary potential is in fact a collection of six potentials: Fe, Cr, He, FeCr, FeHe, and CrHe. In the process of constructing the ternary potential, we re-fitted the Fe potential from the Mendeleev-2003 to the newest version Ackland-2004, which has better self-interstitials and dislocation core properties. In this way, the ternary potential is based on what is considered today the most accurate Fe and Cr potentials.

The potential was also fitted to configurations of relaxed He_N (a-c) and He_NV_1 (d-f) clusters in pure Fe used to fit the potential, as shown in Figure 1. [From K. Nordlund, FI]. The potential has not yet been published, as many more tests are needed to certify its accuracy.

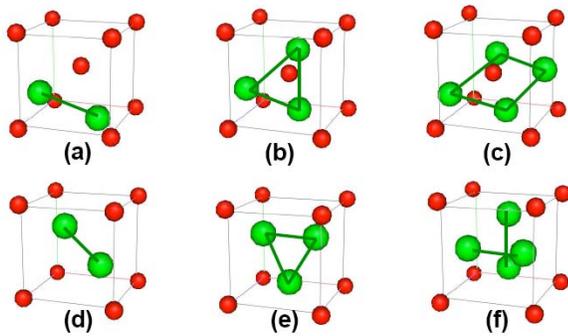


Figure 1: Configurations of relaxed HeN (a-c) and HeNV1 (d-f) clusters in pure Fe

This new ternary potential needs special codes to run. With the visit of A. Stukowski from Darmstadt, Germany, Ph D student of K. Albe, we first incorporated our CD-EAM for FeCr (composition dependent embedded atom model) into Lammmps, a free MD code developed at Sandia. We then developed the routines for the ternary alloy. We formulated an improved version of this potential model that is more efficient for large-scale Monte-Carlo and molecular dynamics simulations, while retaining the complexity implicit in its three-body interactions. The paper describing code and this improvement is in press, and it is available upon request to the authors. This code enables the simulation of large alloy systems for which the CD-EAM is the optimal choice. Its performance is reported in Figure 2.

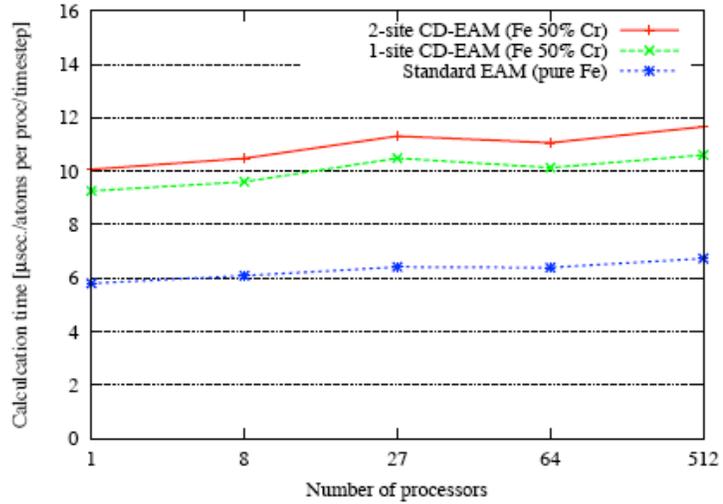


Figure 2: Comparison of the computation times for the CD-EAM models and the standard EAM model in a parallel molecular dynamics simulation. The benchmark simulation consists of a bcc crystal at 300K with 16,000 atoms per processor.

To study precipitation of He into bubbles in single crystals as well as in the presence of heterogeneities such as grain boundaries, free surfaces or dislocations, we also developed a Metropolis Monte Carlo code based on the backbone of LAMMPS. Its first test runs indicate that it is ready to be used.

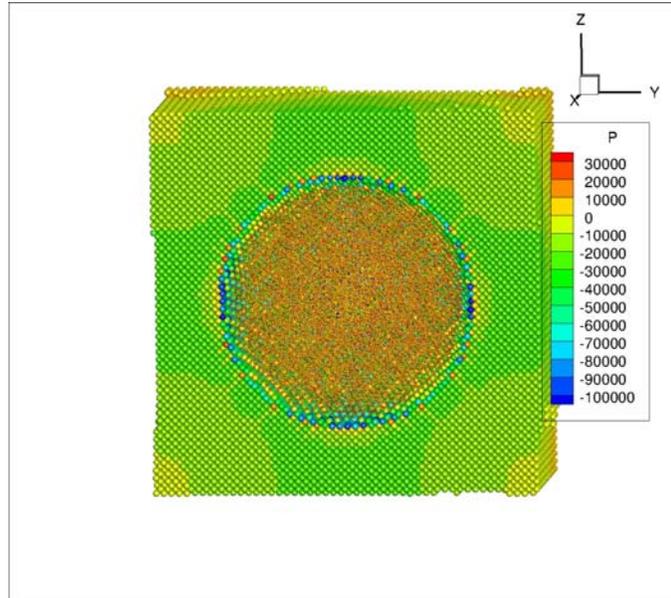


Figure 3: A 4.5 nm He bubble in Fe. The He/vacancy ratio is 1. At this density, He is a fluid under compression. Results obtained with the new Md-MC code Lammps and the new FeCr-He interatomic potential.

With the ternary potential and the MD and MC codes, we are starting the study of thermodynamics and kinetic properties of He in FeCr alloys. Figure 3 shows a 4.5 nm radius He bubble in Fe in a pressure color code. He is a fluid under a ~ 2 GPa of pressure, while the surrounding matrix shows levels of stress from -10 GPa in tension to 3 GPa in compression.

Conclusions

We derived the analytic force expression for the concentration-dependent embedded atom method (CD-EAM) potential and showed that the forces for this advanced many-body model can be calculated in a computationally efficient manner, at a cost which is only slightly larger than for standard EAM potentials. This facilitates the application of the CD-EAM model in large-scale molecular dynamics simulations of concentrated alloys.

The CD-EAM model in its original form is not suitable for Monte-Carlo simulations since its effective pair interaction range is twice as large as the cutoff radius of the potential. By introducing a slight modification of the analytic form of the CD-EAM model it is, however, possible to reduce the effective interaction radius to be equal to the cutoff radius. This renders massively-parallel Monte-Carlo simulation based on the new CD-EAM model possible while preserving all of the qualities of the original CD-EAM model. Energy and force calculation routines for the two-site and the new one-site CD-EAM model have been implemented in the massively-parallel molecular dynamics code LAMMPS [10] and are available upon request from the authors.

Publications

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