MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION—A. Caro (Lawrence Livermore National Laboratory) (Work done in collaboration with B. Sadigh, P. E. A. Turchi, and M. Caro, Lawrence Livermore National Laboratory)

OBJECTIVE

The research has two main lines. On one side is the development of computational thermodynamic tools to evaluate alloy properties, in particular, free energies, and from these to assess the phase stability and microstructure evolution of model systems under irradiation; with them, to use the information on thermodynamic functions to improve the potentials to the extent that it can be done within the classic approach. On the other hand, to use the tools so developed to predict properties of alloys under irradiation.

SUMMARY

The real problem of microstructure evolution of steels under irradiation involves complex thermodynamics of non-equilibrium and kinetic processes in multicomponent–multiphase alloys. Empirical simulations have a long history addressing Fe and, in particular, with one impurity relevant in fission reactor pressure vessels steels: Cu. However no realistic assessment of the accuracy of the model predictions has been available until very recently. The classic computational approach deals with an oversimplified description of alloys.

The aim of the proposed work is to develop 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.

In recent times, several new algorithms appeared showing procedures to numerically evaluate free energies, using both *ab-initio* and empirical descriptions for the total energy, either in molecular dynamics (MD) or Monte Carlo frames (MC). Frenkel and Ladd introduced a method to calculate absolute free energies of arbitrary solids based on the construction of a reversible path from the solid phase under consideration to a reference system whose free energy is known through an analytic expression. Their reversible path method, with some modifications, is one of the most common methods used today, either in MC and MD. This is the method we have implemented in the first phase of this work and applied it to the study of several model systems, Au-Ni, Fe-Cu, and Fe-Cr. In recent papers we reported on the phase diagram calculations for some of these systems. We found they show unexpected differences with the known assessed one.

We concluded from this study that alloys in the framework of empirical potentials require a different treatment of the hetero-atomic interactions if the concentrated cases are to be correctly described. The cases we studied show that adjusting the heat of solution of a single impurity is not enough to describe the complex behavior of concentrated systems. This problem can be addressed by further modifications to the EAM formalism to incorporate concentration dependent interactions that will reproduce the magnitude of excess enthalpy of mixing, as well as the asymmetry around equi-atomic composition.

PROGRESS AND STATUS

We have completed the development of a numerical tool that allows us to study alloys microstructure. In particular, we finished a quite unique code to perform Monte Carlo calculations in multimillion-size samples that would allow us to uncover and explore the microstructure of alloys, either in bulk, as well as in the presence of defects like grain boundaries, isolated dislocations, dislocations cells, etc. It is important to mention that it is not a lattice Monte Carlo code, but a fully relaxed one in the transmutation ensemble. It will provide size, shape, and composition of precipitates, as well as interface energies and structure.

Early examples of application are reported in Figs. 1 and 2.

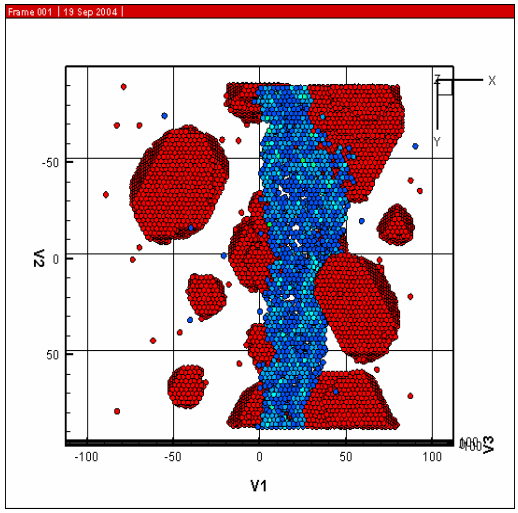

Fig. 1. As an example of application of the newly developed Monte Carlo code, this figure shows a perfect dislocation in fcc Cu (characterized by the ribbon of stacking fault, blue atoms) and nanometer size Fe precipitates, in a dilute $Cu_{99}Fe_1$ alloy.

Having finished in FY04 the development of codes to obtain free energy of alloys, and having studied several potentials available in the literature, highlighting their strength and limitations, we entered the second stage of this research, i.e., the development of improved EAM potentials for alloys with the right thermodynamic behavior. In this goal, we are doing substantial progress in the Fe-Cr system.

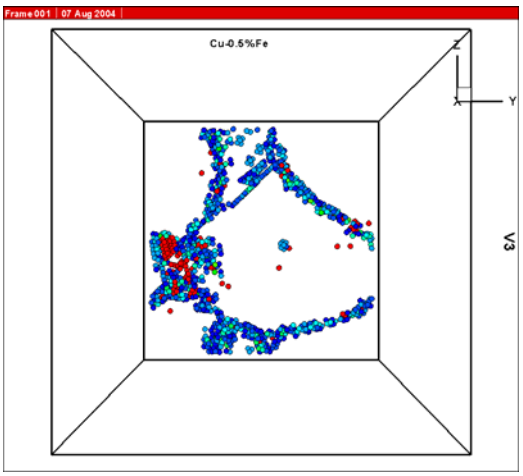

Fig. 2. In polycrystalline materials solute segregation to grain boundaries plays a significant role in affecting the mechanical properties. In this figure we observe Fe precipitation (red atoms) in a nanocrystalline Cu sample where only atoms at grain boundaries (blue circles) are shown. A segregation tendency is clearly observed.

The ability to predict microstructures would be of significant value to effectively make progress in the field of alloys under irradiation. For the particular problem of Fe-Cr alloys, experimental evidence suggests the presence of a negative heat of mixing for concentrations below the solubility limit. This would imply an

ordering tendency in the ferromagnetic phase, a feature which is hard to model simultaneously with the presence of a miscibility gap.

We have developed a generalization of the EAM formalism for concentrated alloys that allows reproducing an arbitrarily complex heat of solution. This was achieved by further modifying the EAM formalism to incorporate concentration dependent interactions that reproduce the magnitude of excess enthalpy of mixing, as well as the asymmetry around equi-atomic composition. Figure 3 shows the agreement between the reported heat of solution of Fe-Cr and the values obtained with the modified EAM scheme. Both curves are indistinguishable. Bulk modulus and lattice parameters, predicted by the model, are not available in the literature for comparison purposes.

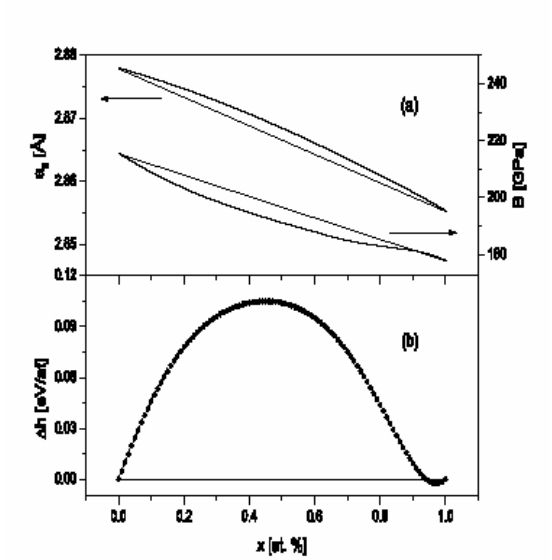

Fig. 3. Variations of bulk modulus B, lattice parameter (a), and formation energy of the Fe-Cr alloy (b), predicted by the modified EAM description of Fe-Cr alloys. Thin straight lines represent the linear interpolation corresponding to the ideal solution. Maximum departures for B and a0 from ideal behavior are 0.25% and 0.1 %, respectively.

The numerical tool we developed and this new potential combined are expected to help us in studying the complex behavior of this alloy in a unique way.

The strategy that we follow is that as new and better potentials for Fe are developed, and new properties for the Fe-Cr system are characterized, either by *ab initio* or experiments, we then focus into their incorporation on better classic potentials for the alloy.

References

[1] A. Caro, P. E. A. Turchi, M. Caro, and E. M. Lopasso, Thermodynamics of an empirical potential description of Fe-Cu alloys, J. Nucl. Mater. 336 (2005) 233–242.
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