MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION—A. Caro, M. Caro, J. Marian (Lawrence Livermore National Laboratory), E. Lopasso (Centro Atomico Bariloche, Argentina), and D. Crowson (Virginia Polytechnic Institute)

OBJECTIVE

This research has two main objectives:

- The development of computational tools to evaluate alloy properties, using the information contained in thermodynamic functions to improve the ability of classic potentials to account for complex alloy behavior, and

- The application of these to predict properties of alloys under irradiation.

SUMMARY

Atomistic simulations of alloys at the empirical level face the challenge of correctly modeling basic thermodynamic properties. In this work we develop a methodology to generalize many-body classic potentials to incorporate complex formation energy curves. Application to Fe-Cr allows us to predict the implications of the ab initio results of formation energy on the phase diagram of this alloy and to get a detailed insight into the processes leading to precipitation of α' phase under irradiation.

PROGRESS AND STATUS

Four main activities were developed in the period covered by this report.

1. Continuing the work described in the previous report, namely the procedure to build a classic model for Fe-Cr alloys from the perspective of thermodynamics, we derived the phase diagram of that system that has been sent for publication and accepted in applied Physics Letters. This diagram provides an explanation to several experimental observations that were at odds with the traditional phase diagram.

2. We started the study of precipitation of α' phase, using the recently developed Monte Carlo code and the potential for the alloy. We explore homogeneous nucleation first and determine some properties of the precipitates.

3. We started the study of point defects in the alloy, with a careful comparison with ab initio results from P. Klaver – M. Finnis group in UK.

4. We started the study of radiation damage in the alloy with a new collaboration with S. Srini from Los Alamos National Lab.

In what follows, we briefly describe the achievements.

<u>Phase Diagram of the Fe-Cr Empirical Potential</u>

We analyzed the implications of the recently reported results of *ab initio* calculations of formation energies of the Fe-Cr alloy. The formation energies show a change in sign from negative to positive as CR composition increases above ~ 10%. By developing a classic potential to evaluate the thermodynamic properties [1], we determine the location of the solubility limit and compare it with earlier results. A significant difference appears in a region of temperature and composition that is relevant for the nuclear applications of this alloy. Experimental results seem to confirm the validity of the location of the new *solvus* line.

The Phase diagram we obtained is shown in Fig. 1 below. It shows the low T - low x region of interest $0K < T < 1000K$ and $0\% < x_{Cr} < 20\%$. A continuous followed by a dotted line is our results for the *solvus* in the FM phase, while the dashed line is the *solvus* as it appears in SSOL, the database of Thermocalc.

Our *solvus* is plotted with a solid line only for temperatures below the invariant line suggested by the experiments, that we report in the figure as a horizontal solid line; above it, the *solvus* is shown with a dotted line, indicating that other effects determine the diagram at those T-x values, namely, the σ phase and the magnetic transition.

In Fig. 1 we have added the experimental results of Kuwano et al. [2] and those of Mathon et al. [3]. The discrepancy between the SSOL [4] *solvus* and the *solvus* implied in the *ab initio* results is obvious, as is the agreement between the experimental results and our prediction. The most striking difference is the fact that the *solvus* line, if extrapolated to zero temperature, does not cross the x-axis at x = 0, as explicitly assumed in the CALPHAD treatment. This fact can easily be understood if one considers a very low T, where excess free energy is essentially equal to the excess heat of formation (hof); then the solid line in Fig. 2, that shows the formation energy of the alloy, can be reinterpreted as a free energy curve and the common tangent construction would show that the miscibility gap at $T = 0K$ closes at x ~ 0.04, i.e., the location of the minimum of that curve. This fact can be considered as the main consequence of the *ab initio* result giving a change in sign in the hof.

The implications of this are as follows: Fig. 1 shows how the phase diagram at low T and low x is modified if one considers the heat of formation predicted by *ab initio* calculations. This diagram is calculated using a classic potential that reproduces the energetics (in particular the change in sign at some low Cr concentration), and by doing the thermodynamics exactly via switching Hamiltonians and thermodynamic integration techniques. The fact that the miscibility gap closes at finite x and that the maximum in the hof is higher than the SSOL value implies that the location of the *solvus* is significantly affected.

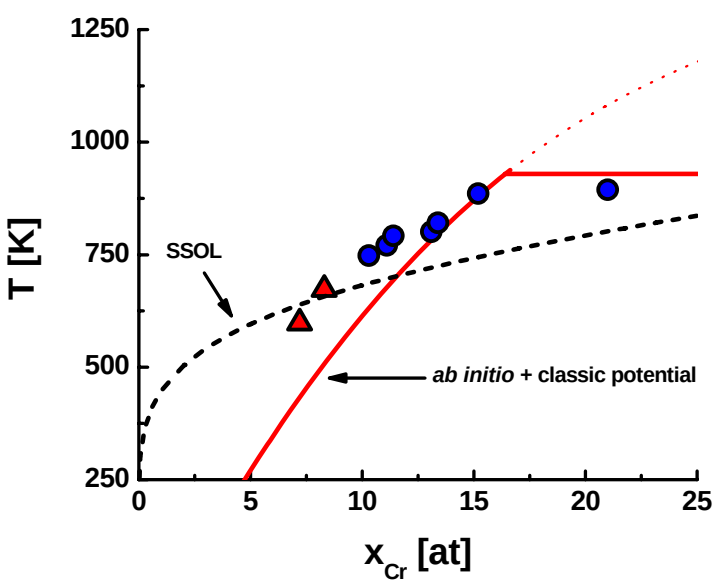

Fig. 1. Portion of the phase diagram as predicted by our methodology, showing the location of the solvus, together with experimental results from Ref [2, 3], and the solvus as appears in SSOL, the database of CALPHAD [4].

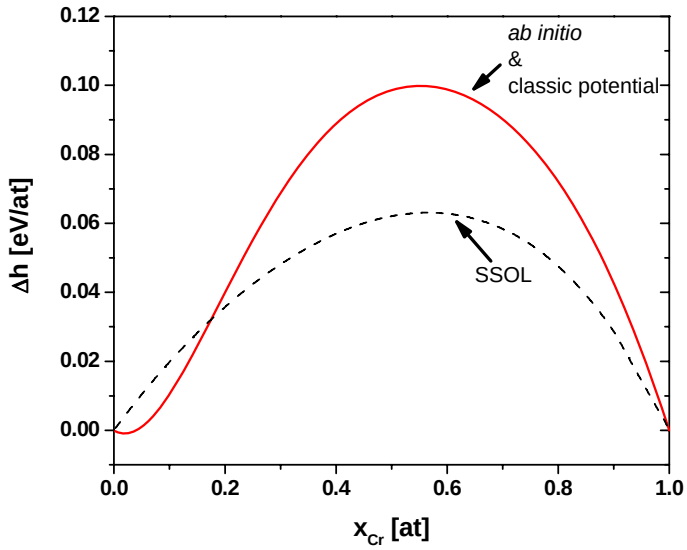

Fig. 2. Formation energy of the alloy as predicted by ab initio calculations (solid line) and as reported in the database of CALPHAD.

In summary, we observe that the change in sign of the heat of formation at about 6% Cr modifies the location of the *solvus* in the phase diagram by making it much steeper than the SSOL value. The solubility limit above ~ 700K is much less that the value in SSOL and conversely, below ~ 700K it is much higher. In particular, at low temperature, even at 0 K, there is a finite Cr solubility because the *solvus* does not go to *xCr* = 0 at *T* = 0 but to *xCr* ~ 0:04.

As we pointed out above, the finite Cr solubility at 0 K is a result that is not affected by the controversy regarding the value of the hof around equiatomic composition. However how steep the *solvus* is at both ends of the diagram strongly depends on that value. The solubility of Fe in the α' phase, as we predict it, is too low compared to experiments [3] and SSOL [4], a result also related to the high hof predicted *ab initio*.

<u>Precipitation of α' Phase</u>

The predictions of the Fe-Cr alloy potential regarding segregation of supersaturated solid solution can be assessed by using the Monte Carlo code with displacements developed in this work. Figure 3, below, shows the phases α and α' with a flat interface in a heterogeneous sample during a MC run used to determine the equilibrium composition of the two coexisting phases. By averaging in time the composition profiles, we determine the composition shown in Fig. 4.

In addition to composition, Fig. 4 also shows that the nature of this particular interface between coherent α and α' precipitates is quite sharp, only about one lattice parameter.

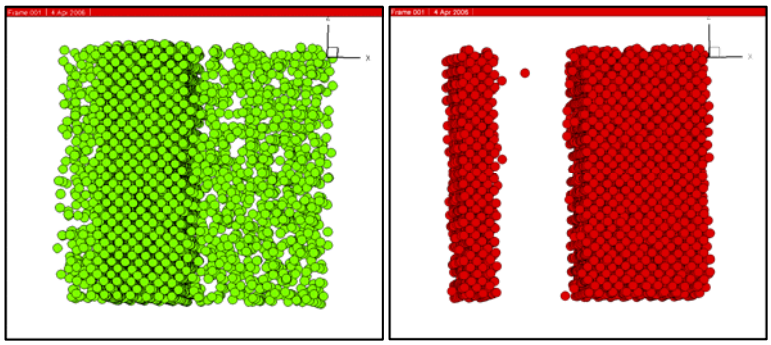

Fig. 3. Composition of a α and α' precipitates in contact in a two phase sample. The figures represent in green the Cr atoms and in red the Fe atoms. In the figure on the left we see α', Cr rich precipitate, and similarly for α on the right.

This result gives an insight on the morphology of α' precipitates. Further studying the mechanisms of precipitation, we are at present analyzing the process of nucleation and growth. Figure 5 shows a precipitate of a few nanometers in a saturated solution at 750K. The precipitate is spherical, coherent and with a sharp interface.

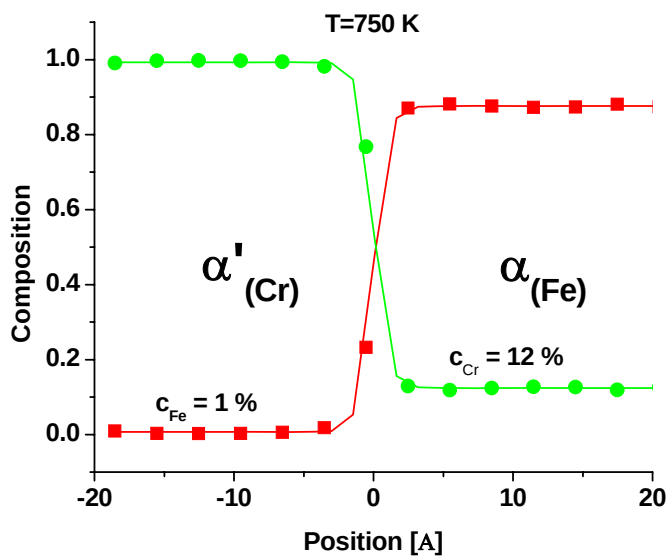

Fig. 4. Composition of a α and α' precipitates in contact in a two phase sample. Comparison of these saturation solubilities with the location of the solvus in Fig. 1 indicates a perfect agreement between the MC result and the prediction of the thermodynamics calculations.

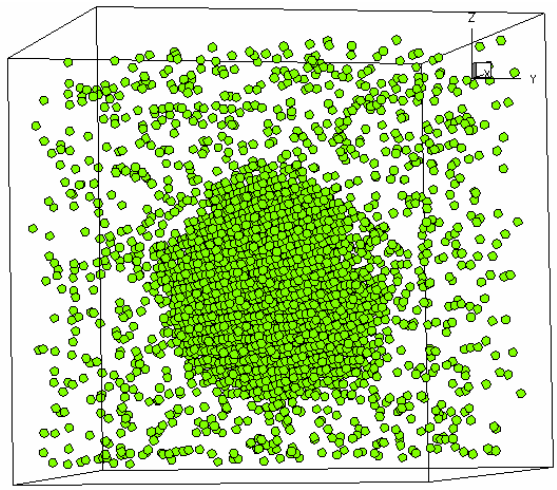

Fig. 5. Homogeneous precipitation of a saturated solution produces spherical precipitates, coherent with the matrix and with sharp interfaces. These are the first results obtained with the MC code developed for this project.

Similarly, we explored precipitation in a solution close to 50% composition where spinodal decomposition instead of nucleation and growth is the precipitation mechanism. Figure 6 shows the microstructure of such precipitation process.

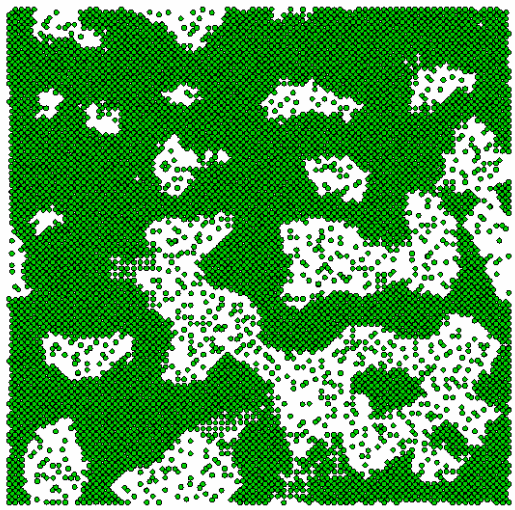

Fig. 6. For compositions inside the spinodal region (i.e., around 50%) the model predicts decomposition by the spinodal mechanism. This result of a MC simulation shows the microstructure after that process took place. Green atoms are Cr atoms.

Point Defects in the Alloy

It has recently been proved by colleagues from the UK that the complex nature of this alloy is due to magnetic effects in competition between ferromagnetic Fe and antiferromagnetic Cr. The ability to capture the essence of these interactions is one of the main challenges for the development of a classic approach to this alloy useful for large-scale molecular dynamics. At the present stage of

our project, we are systematically studying point defects in the alloy and comparing the results with ab initio calculation from P. Klaver – M. Finnis group in UK.

One of the most salient features is the fact that a dilute solution of Cr in Fe is exothermic, i.e., it has a negative heat of formation. However, when the composition rises above ~ 10% the alloy turns into a segregating system with endothermic heat of formation. This property appears in a different scenario when two substitutional Cr atoms in a dilute alloy approach each other. Ab initio calculations show that significant repulsion occurs. Figure 7 shows the excellent agreement between this important feature in the ab initio calculation and in our classic approach, giving a strong support to the validity and utility of the potential developed.

This result is the first step of a series of test we are performing at present to explore diverse configurations of point defects in the alloy, trying to identify the relevant parameters that describe point defects in a concentrated alloy, in view of the future development of approximate methods to treat longer time scales using kinetic Monte Carlo approaches.

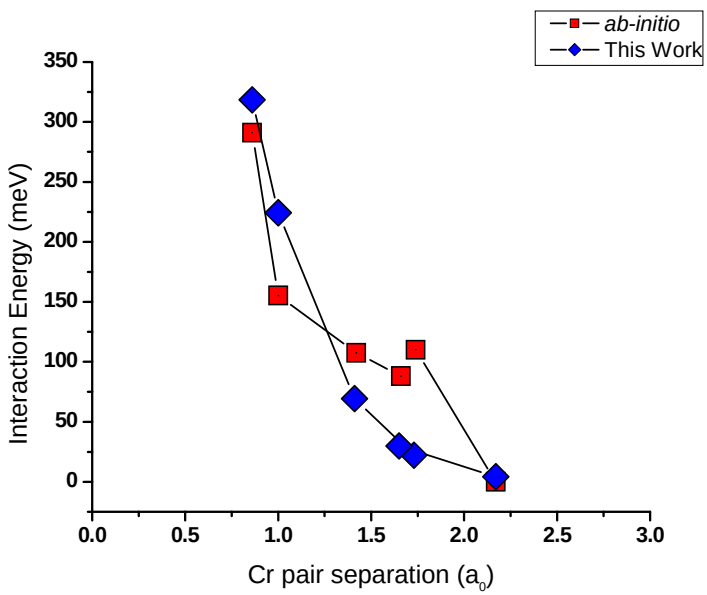

Fig. 7. Interaction energy (repulsion) between two substitutional Cr atoms in an otherwise perfect Fe lattice. Squares represent ab initio results from P. Klaver [Queen's University, Belfast, unpublished] and rhombuses are the predictions of our classic potential. The agreement is remarkable considering that the origin of this repulsion is of magnetic origin, only captured qualitatively in the classic approach.

References

[1] A. Caro, D. A. Crowson, and M. Caro, Classical many-body potential for concentrated alloys and the inversion of order in iron-chromium alloys, Phys. Rev. Lett. 95 (2005) 075702.
[2] H. Kuwano and Y. Hamaguchi, J. Nucl. Mater. 155 (1988) 1071.
[3] M. H. Mathon, Y. de Carlan, G. Geoffrey, X. Averty, and A. Alamo, J. Nucl. Mater. 312 (2003) 236.
[4] N. Saunders and A. P. Miodownki, CALPHAD: A comprehensive guide, Ed., R. W. Cahn, Pergamon Materials Series (Oxford, New York, 1998).