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# Modelling Thermodynamics of Alloys for Fusion Application

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**MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION** - A. Caro, B. Sadigh, P. E. A. Turchi, and M. Caro, (Lawrence Livermore National Laboratory), E. Lopasso (Centro Atomico Bariloche, Argentine), and D. Crowson (Virginia Polytechnical Institute)

## OBJECTIVE

This research has two main objectives.

- On one side is 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.
- On the other hand, to apply the tools so developed 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.

## PROGRESS AND STATUS

We address the problem of alloy description with atomistic models from the perspective of thermodynamics. We derive the phase diagram of a model Hamiltonian, namely, the embedded-atom EAM potential for Fe-Cr.

To do so, we follow the procedure described in [1-2] and apply it to Iron alloys with different Chromium concentrations. The same computational thermodynamics tools developed in [3] were applied with success in the case of Fe-Cu alloys to predict the phase diagram of such a system.

Gibbs free energies for the solid and liquid phases are calculated using MD simulations for pure elements and for several Fe-Cr alloys. In this work, we use the Fe potential reported in [4] and the Cr potential reported in [5]. For the cross potential we use the methodology described in [6] that incorporates the complex formation energy curve for Fe-Cr. The cross potential is derived so that it reproduces the calculated *ab initio* formation energy  $Dh$  of Olsson et al. [7]. The formation energy of bcc ferromagnetic Fe-Cr alloys given in [7] can be reproduced by a Redlich-Kister expansion to 4<sup>th</sup> order in  $(1-2x)$  as follows:

$$\Delta h = x(1-x) \sum_0^n L_p (1-2x)^p \quad (1)$$

As we see in Fig.1  $Dh$  is highly non-symmetric and even changes sign at low Cr composition.

## Phase Diagram of the Fe-Cr Empirical Potential

We calculate the free energy per particle at a given temperature  $T$ ,  $f(T)$ , through thermodynamic integration between the state of interest and a reference state at temperature  $T_0$  with known free energy  $f(T_0)$ . The free energy per particle is given by the Gibbs-Duhem integral:

$$f(T) = f(T_0) \frac{T}{T_0} - T \int_{T_0}^T \frac{h(t)}{t^2} dt \quad (2)$$

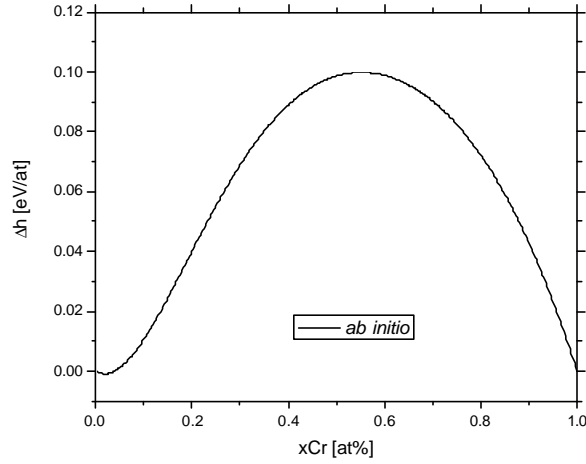


Fig. 1: Calculated mixing enthalpy for ferromagnetic bcc Fe-Cr alloys, corresponding to Fe-Cr in the low temperature range ( $T < 1000$  K)

Second-order polynomials are adjusted to the simulation results of the internal enthalpy for solid and liquid Fe-Cr alloys, and the integral of Eq. (2) is solved analytically.

The resulting Gibbs free energies and enthalpy per particle are computed as:

$$\begin{aligned} g(T) &= A + B T + C T^2 + D T \ln(T) \\ h(T) &= A + 2DT + 2CT^2 \end{aligned} \quad (3)$$

We can also express the free energy of a random solid solution phase of an alloy with composition  $x$  at temperature  $T$  as:

$$g(x, T) = g_{ref}(x, T) + g_{mix}(x, T) + Dg(x, T) \quad (4)$$

where  $g_{ref}$ ,  $g_{mix}$  are given by ( $k$  is Boltzmann constant equal to  $8.617385 \times 10^{-5}$  eV/K):

$$\begin{aligned} g_{ref}(x, T) &= (1-x) g_{Cr}(T) + x g_{Fe}(T) \\ g_{mix}(x, T) &= kT [(1-x) \ln(1-x) + x \ln(x)] \end{aligned}$$

The excess Gibbs energy of mixing can also be conveniently expressed by a Redlich-Kister expansion [8] as:

$$\Delta g(x, T) = x(1-x) \sum_0^n L_p(T) (1-2x)^p \quad (5)$$

where  $L_p(T)$  is the  $p$ th-order binary interaction parameter.

Bearing Eqs. (4-5) in mind we choose to express the functional form of each coefficient  $A$ ,  $B$ ,  $C$ , and  $D$  in Eq.(3) as:

$$Coeff = C_{Fe} (1-x) + C_{Cr} x + x (1-x) S L_p^{Coeff} (1-2x)^p$$

With these values we build up a database for Fe-Cr and use the software package Thermo-Calc [8] to calculate the phase diagram shown in Fig. 2.

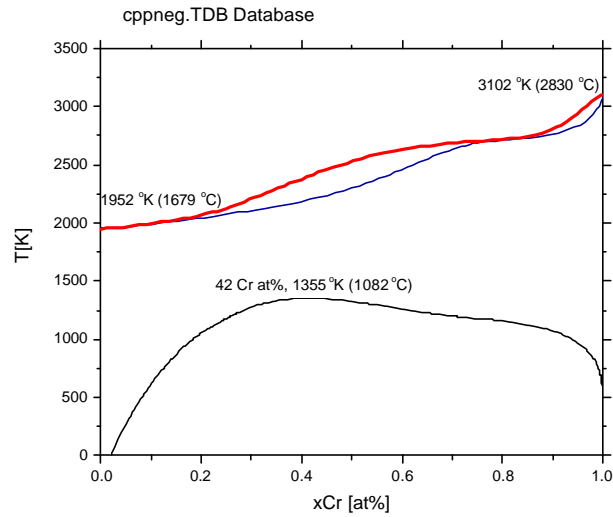


Fig. 2: Predicted phase diagram obtained from the application of the Thermo-Calc software to the database *cppneg.TDB* generated using the Fe-Cr empirical potential.

### The Heat of Formation

Experimental points have been reported at  $T = 1600$  K. The SSOL library in Thermo-Calc (CALPHAD) package reproduces these points very well.

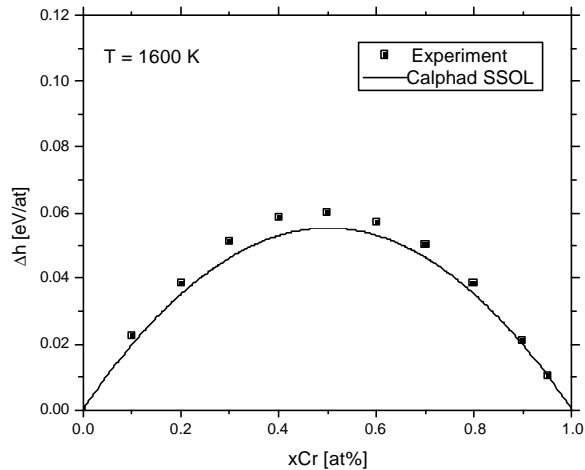


Fig. 3: Heats of formation of Fe-Cr as described in the database of Calphad and experimental measurements..

Our database *cppneg.TDB* based on the Fe-Cr empirical potential reproduces well the calculated *ab initio* formation energy at low temperature.

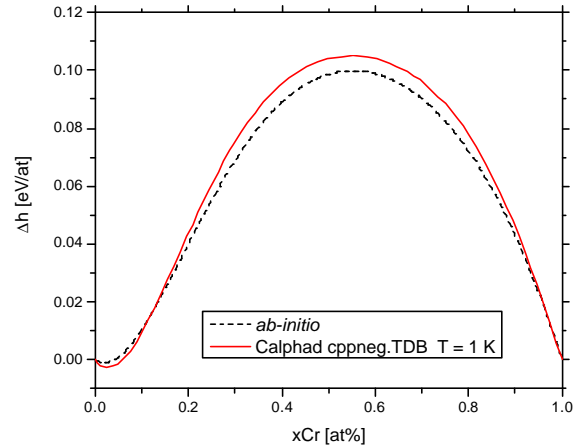


Fig. 4: Heats of formation of Fe-Cr as described in the database built upon our potential and the *ab initio* results.

The point of controversy is the difference in the formation enthalpy of the ferromagnetic solid solution between *ab initio* calculations and CALPHAD SSOL, see graph below:

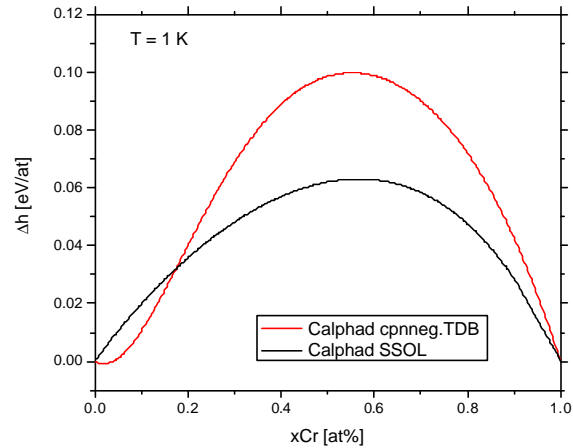


Fig. 5: Heats of formation of Fe-Cr as described in the database of Calphad and our own based on the *ab initio* results.

The Entropy calculated for the classic potential appears to be remarkable close to the Calphad values indicating a good over-all reproduction of the dynamics of the system.

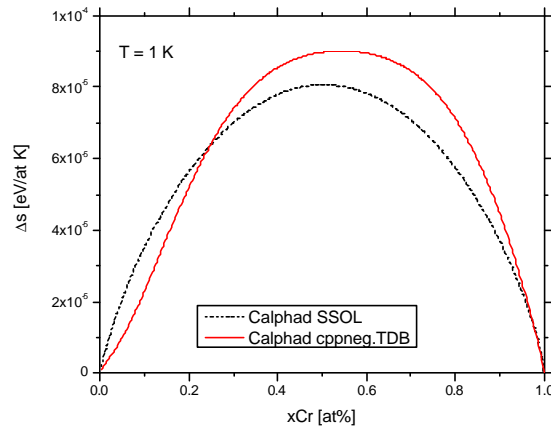


Fig. 6: Entropy of formation of Fe-Cr as described in the database of Calphad and our own database based on *ab initio* results.

### Comparison with the Experimental (CALPHAD) Phase Diagram

The experimental phase diagram is obtained using the SSOL library in Thermo-Calc. Melting points are shown in the table below:

	Fe	Cr
SSOL	1810 K (1537 C)	2180 K (1907 C)
Cppneg.TDB	1952 K (1679 C)	3102 K (2830 C)

Pure Cr is poorly described, as its melting point is significantly above the experimental value. The phase diagram obtained using Thermo-Calc appears in the graph below. Note that BCC, FCC, Sigma and Liquid phases of the SSOL database are included.

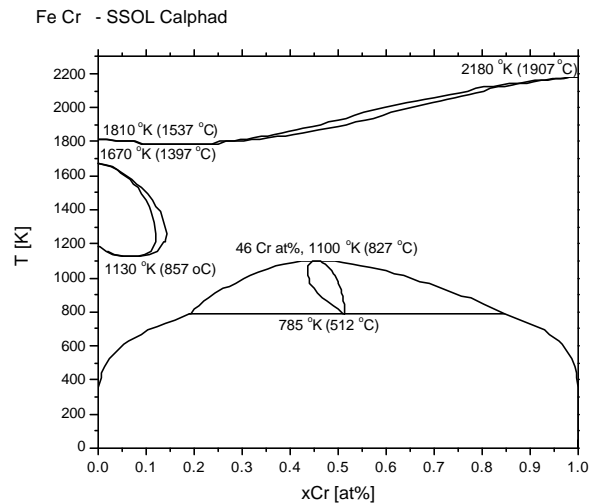


Fig. 7: Experimental phase diagram of the Fe-Cr system.

Neglecting all phases but Liquid and BCC, we obtain the phase diagram shown below .

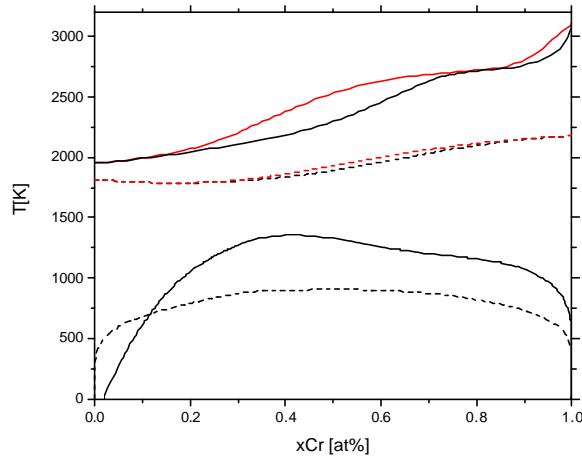


Fig. 7: Phase diagram reporting only liquid and bcc phase of the Fe-Cr system as measured experimentally (dotted lines) and as implied by the ab initio results (solid lines)

Solid lines correspond to the results obtained in this work. Dash lines correspond to SSOL CALPHAD database. The “experimental” (CALPHAD) miscibility gap has a maximum at 904.7 K ( $x_{Cr} \sim 0.515$  at%) and is quite symmetric as compared to the highly nonsymmetrical miscibility gap is found in our work. The miscibility gap has a different shape at low concentration, the solid curve goes to zero at  $x_{Cr} = 0.0197$  at%.

These results prove on one side the ability of our approach to go from ab initio results to classic potentials, and to go from classic potentials to thermodynamics. From here on, we can reliably use the potentials so developed to evaluate non equilibrium processes induced by radiation.

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