MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION -

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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

Computer simulations of processes related to radiation damage have provided deep insight into atomistic processes at the origin of all changes that irradiation produces on mechanical properties of materials. However, as progress continues and more and more complex materials are developed, like the nanostructured Oxide Disperse Strengthened (ODS) ferritic steels, the simulations are confronted with the necessity to capture intricate thermodynamic and kinetic effects. The work reported here is an attempt to bring simulation capabilities to new domains where such effects are accurately described. In this report we present our recent results on the nature of the phase diagram of FeCr in the low Cr region, where finite solubility together with the existence of new intermetallic phases may be at the origin of the explanation of embrittlement and swelling under irradiation, with their intricate dependence on Cr composition.

Our work in the last few years has followed a systematic approach to model this alloy that started with a methodology to generalize many-body classic potentials to incorporate complex formation energy curves. Application to Fe-Cr allowed 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. In this period we report on the consequences of the negative heat of formation at low Cr composition on the <u>formation of new phases at low T</u>, in particular ordered intermetallic phases, whose existence have been the subject of speculation in recent years.

PROGRESS AND STATUS

Short-range order (SRO) in Fe-rich Fe-Cr alloys is an anomaly originated in the negative heat of formation of this alloy for Cr content below about 5at%. In this region of composition, the mixture is expected to have ordered phases.

To describe the energetic origin of the order in FeCr we notice first that the heat of solution of a single Cr impurity in Fe is large and negative; i. e. the mixture is exothermic with a strong tendency to form compounds. However, as the Cr composition increases, a strong Cr-Cr repulsion, originated in magnetic effects and explained in detail by the work of P. Klaver in Belfast, prevents further incorporation of Cr turning the mixture into an endothermic, or positive heat of formation, i. e. an alloy with tendency to segregate into heterogeneous solid solutions, rich in Fe and rich in Cr. The question that arises then is whether this repulsion is able to stabilize long range ordered structures.

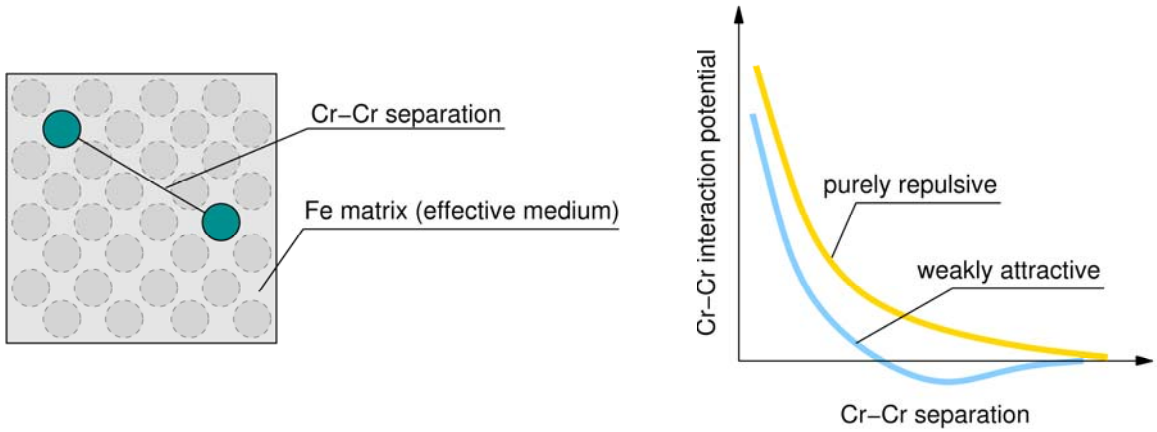

Figure 1: (left) Scheme of the effective Cr-Cr interaction in dilute FrCr alloys. (right) With an effective interaction potential repulsive at all distances, the system exhibits short range order. If the potential has a negative value at some distances, then possibly new long range order, or intermetallic phases, may exist.

Figure 1 (left) schematizes this topic: for the purpose of the argument, Cr-Cr interaction can be thought of as an effective interaction in a medium represented by the Fe matrix. If this interaction is purely repulsive, then short range order, SRO, appears as a consequence of the tendency of the effective interaction to maximize Cr-Cr separation. This issue has been extensively studied by us and has been reported in the July 2007 Semiannual Report. The corresponding publication is in press in Phys. Rev. B. However, if the effective interaction has a range of distances where it becomes negative, as schematized in Fig. 1 (right), then in addition to SRO, long range order, i. e. true new crystallographic phases may exist. This has been the subject studied in the period covered by this report, and the corresponding publication in under review in Appl. Phys. Lett.

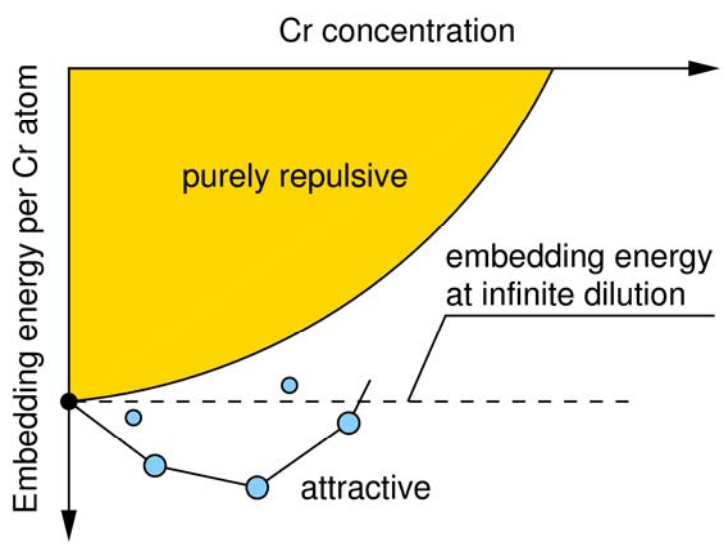

Figure 2: Schematic representation of the energetics of FeCr as a function of composition. For a purely repulsive potential, all possible configurations of Cr atoms must lay below the energy at infinite dilution.

The search for intermetallic phases is equivalent to the search for long range ordered structures whose energy is below the embedding energy at infinite dilution, as shown in Figure 2. For a purely repulsive Cr-Cr interaction, the energy per Cr atom of a given LRO structure can only be larger or equal to the energy at infinite dilution, region marked yellow in Fig. 2. However, for an attractive interaction, some compositions commensurate with long range order, points blue in the figure, must lay below the energy at infinite dilution.

The *ab initio* data by P. Klaver et al., Figure 3, unequivocally shows that no such structures have been found so far, since for every composition, the energy per Cr atom is above the value at the lowest composition (infinite dilution limit). It is important to point out that the structures explored where not the result of a systematic search of possible minimum energy configurations.

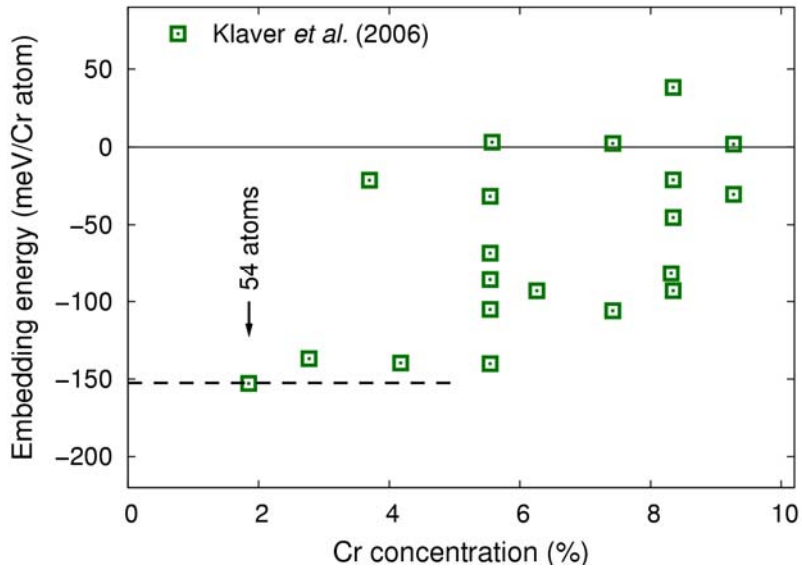

Figure 3: Energy per Cr atom of several long range order compounds in the FeCr system reported by Klaver (2006).

In our work we used the results of short range order described in the previous semiannual report to guide the search of ordered structures by distributing Cr atoms along particular crystallographic directions which minimize or maximize the number of Cr-Cr pairs. Since we have calculated the SRO layer by layer up to 4th neighboring shells, we can reverse-engineering the structures in search of those configurations more akin to produce long range order.

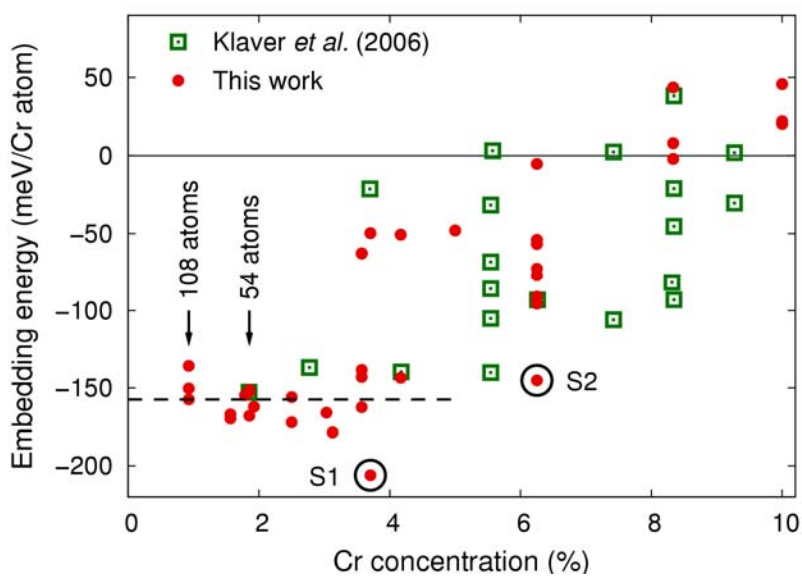

Figure 4: *Energy per Cr atom of several long range order compounds in the FeCr system reported found by us (red dots) and those by Klaver (2006) (green swuares). Clearly seen are*

configurations with energy below the infinite dilution limit, reflecting the existence of a positive Cr-Cr interaction and therefore new intermetallic phases.

The *ab initio* calculations were done using VASP; details can be found in the corresponding publication. The results of our calculations are presented in Figure 4. Clearly seen are numerous long range ordered structures with energies below the dilute limit. These are candidates to be stable intermetallic compounds. One of them, marked S1 in the figure has the absolute minimum energy, at a composition of x_{Cr}= 0.0385 or $Fe_{26}Cr$. Figure 5 shows the superstructure, with Cr atoms located in a bcc lattice with $a_{supercell} = 3\ a_{bcc}$. Cr's are located in the 10th shell of another Cr atom, filling it at ¼ with Cr and ¾ Fr. The crystallography is shown in figure 5.

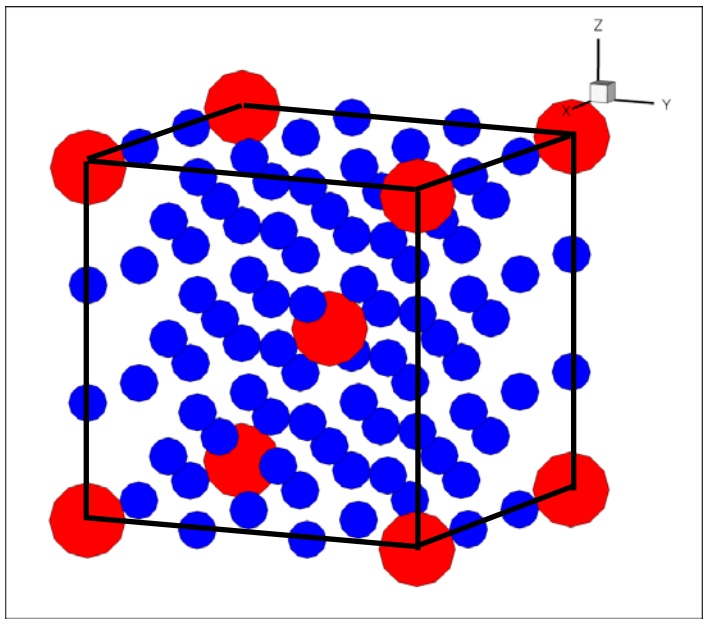

Figure 5: Lowest energy structure (S1 in Fig. 4).Red atoms are Cr, blue atoms are Fe. Cr atoms sit on a bcc super lattice with $a_{super\ lattice} = 3\ a_0$

If data in Figure 4 are presented in the conventional energy per atom plot, we can use common tangent construction to trace the phase diagram at 0 K. Figure 6 shows those results. The line connecting points S1 and S2 with x=0 and x=1 represents the lowest energy configurations and therefore identify the stable phases, namely: the Fe rich solid solution (bcc), the intermetallic $Fe_{26}Cr$ (bcc superlattice), the intermetallic $Fe_{15}Cr$(base centered monoclinic), and the Cr rich solid solution (bcc). Additionally we know that the Cr rich solid solution has a miscibility gap and therefore the Cr rich solution may be heterogeneous.

These results represent the most detailed study of the energetics of FeCr in the region of interest for nuclear applications. Even if the ordering energies of these intermetallic phases are probably very low and therefore they are not expected to be observed or to be developed under irradiations, they are the true equilibrium at low T; the remnant order measured experimentally can be considered as originated in them.

The study of order that we have performed during 2007 is the basis for the next step in our work that is the study of dislocation mobility in presence of order. As it is well know, order hinders dislocation motion since dislocation glide disrupts order across the glide plain, generating

a source of hardening. Our next objective is therefore to quantify the influence of order on the mobility functions of screw dislocations in FeCr alloys.

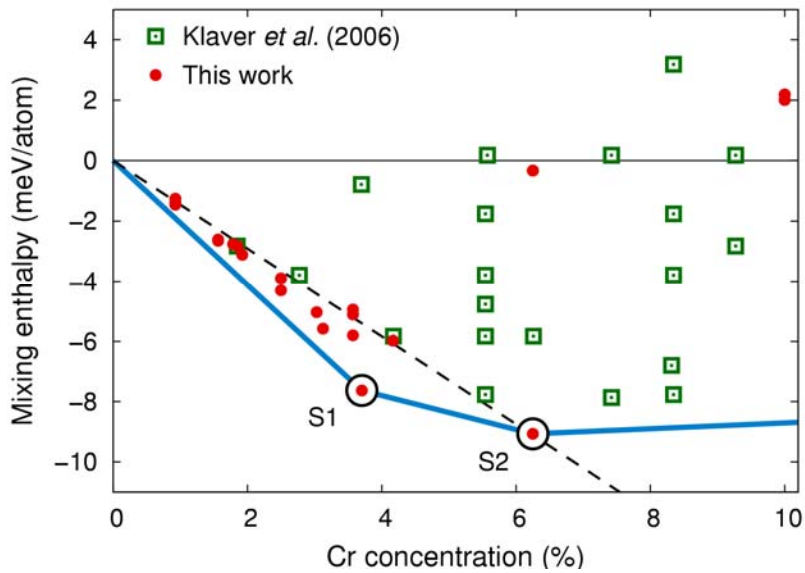

Figure 5: Mixing enthalpy per atom of several long range order compounds in the FeCr system reported found by us (red dots) and those by Klaver (2006) (green squares). The blue line connecting points labeled S1 and S2, being lower in energy that any other configuration, identifies the phases existing at 0 K in FeCr.

Conclusions:

In the period reported here, We have concluded the study or order in FeCr with the discovery of two intermetallic phase that represent the ground state of this system at low T. The compounds $Fe_{26}Cr$ and $Fe_{15}Cr$ with bcc and bc monoclinic structures respectively represent the lowest energy structures for this system and their existence confirms the presence of an attractive effective Cr-Cr interaction, whose origin is still to be determined.

Publications

P. Erhart, B. Sadigh, A. Caro, M. Serrano de Caro, "Intermetallic phase in FeCr alloys". Submitted Appl. Phys. Lett.

P. Erhart, A. Caro, M. Serrano de Caro, B. Sadigh, "Short-range order and precipitation in Fe-rich Fe-Cr alloys", Accepted Phys. Rev. B

A. Caro, D. Farkas, E. M. Bringa, G. H. Gilmer, and L. A. Zepeda-Ruiz. ”Mobility and mechanical response of dirty interfaces in nanocrystalline Cu”. Submitted to Acta Mater

C. Jiang, S. G. Srinivasan, A. Caro, and S. A. Maloy. “Structural and elastic properties of Cementite from first-principles calculations”. Submitted to Phys. Rev. B.

P. Bellon, R.S. Averback, S. Odunuga, Y. Li, and a. Caro. “Crossover from superdiffusive to diffusive mixing in plastically deformed solids”. Phys. Rev. Lett **99**, 110602 (2007).

L. Malerba, A. Caro, and J. Wallenius. “Multiscale modeling of radiation damage and phase transformations: the challenge of FeCr alloys”. Submitted to Jr. Nucl. Mat. 2007.

Conference Presentations

Paul Erhart, Alfredo Caro, Babak Sadigh, Magdalena Caro “Short-Range Order, Precipitation, and Intermetallic Phases In Fe-rich Fe-Cr Alloys**”**. **Invited Talk**, MRS Fall meeting Boston Nov 2007.

M. Caro, A. Caro, P. Erhart. “Precipitation, Segregation, and the Origin of Corrosion Resistance of FeCr Alloys”. MRS Fall meeting, Boston Nov 2007

Alfredo Caro. “The Computational Modeling of Alloys: From *ab initio* and Thermodynamics to Precipitation in Fe-Cr. **Invited talk**, Materials for Generation IV Rectors. NATO Advanced Study Institute Cargese, Corsica, Sept 24 – Oct 6 2007.