MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION

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SUMMARY

This report is the final of a series started in 2005, when I became the PI of this project. All along these years, this research has followed a path towards a quantitatively accurate atomic scale description of metallic alloys. The progress in the description of Fe alloys in its bcc phase has been important. Our work, together with those of several other groups in the world, has achieved a certain degree of success.

However, the atomic scale description for ferromagnetic alloys has reached a barrier that seems quite difficult to overcame, that of the finite temperature behavior of the magnetic excitations: Our work, as well as all other models for the atomic scale interactions in ferritic alloys, is valid for temperatures well below the Curie temperature (~ 1000 K). Going beyond these temperatures, a necessary objective for nuclear applications at 500 C and above requires a new approach to the problem. This new approach is being worked out right no by a few groups around the world and hopefully will provide new ways to describe these alloys.

Within the restriction just mentioned, i. e. a description valid for T < 1000 K, our work has made significant progress in the last year, by producing results in the developments of both tools and algorithms.

- We implemented the formalism of the composition dependent embedded atom model for ternary alloys (CD-EAM) into Lammps, a freely distributed code for molecular dynamics. We also implemented a 'variance constrained' Metropolis Monte Carlo, MMC, algorithm into Lammps, also for ternary alloys. This work has been the result of a fruitful collaboration with a Ph D student of Prof. K. Albe from Darmstadt, Germany, A. Stukowsky.
- 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. This has been the result of P. Erhart's work.
- 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. This is the result of A. Caro's work.
- We started simulation of He bubbles in FeCr alloys, determining the pressure versus size relation for the 1He/vacancy ratio and the mechanisms of bubble growth at varying density. This has been the result of the collaboration with M. Caro, L. Zepeda-Ruiz and a student of Prof. Srinivasan from UNT, J. Hetherly.

It is important to mention that these tools are free for distribution. Some of them are already part of the Lammps official download package, some others are at the Stukowski web page and the last one, the parallel variance constrained Metropolis Monte Carlo within Lammps is soon being release after submission of the corresponding paper (under B. Sadigh's responsibility).

PROGRESS

In the period covered by this report, we evaluated some properties of He bubbles in ferritic alloys. These results are the subject of a publication that will be ready before my departure from LLNL, at the end of February 2010.

Advances in the improved understanding of the energetics of Fe-Cr alloys have provided the basis for the development of accurate interatomic potential models, which enable large scale simulations of the microstructural evolution. Two approaches were developed, known as the two band model \cite{OlsWalDom05} and the composition dependent model, \cite{CarCroCar05} which both address the complex shape of the heat of formation curve at 0 K as determined from first-principles calculations.

Development of the ternary FeCrHe potential

In a recent paper we proposed a simple scheme to construct composition dependent interatomic potentials for multicomponent systems that can reproduce the heat of mixing of every binary in the system over the entire compositional range [see publications below]. The methodology, a formal extension of our previous composition-dependent interatomic potentials model published in 2005, provides a systematic approach to modeling arbitrarily complex multicomponent alloys.

The case of FeCrHe is a particularly simple ternary because the addition of a chemically inert element such as He to the binary FeCr can be done with interactions based on pair potentials alone, reducing the complexity of the composition dependence to the FeCr binary alone.

A ternary potential is constructed from the potentials for the three pure element Fe, Cr, He, plus the elements needed for the description of the three binaries Fr-Cr, Fe-He, Cr-He.

He has been studied for a long time and the present state of the art for the classical potential description of its energetics and thermodynamics is highly accurate. We have taken the He-He potential derived by Beck with the cut off and short-range behavior adapted by Morishita, the Fe-Fe potential derived by Ackland in 2004 and the Cr potential derived by Terentyev in 2009.

For the Fe-He and Cr-He cross potentials we used the recent results by Juslin and Terentyev. The Fe-Cr potential is a new derivation similar to the original CDM but here based on state-of–the-art pure element potentials (Fe from Ackland 2004, instead of Mendelev 2003, and Cr from Terentyev in 2009. The mixed interaction has been constructed to reproduce the mixing enthalpy curve obtained from first-principles calculations by Olsson in 2004.

He EOS

We start analyzing results for pure He in the (ρ, T) region of interest of Fe alloys for nuclear applications, i. e. for densities around 1 He/vacancy and temperatures $300 < T < 800$ K. This value is the result of the fact that He as created by nuclear transmutations sits initially at interstitial sites in the Fe matrix, and converts into a substitutional impurity as soon as it encounters a vacancy. This reaction is energetically highly favorable. It has been proven that He-V complexes have a tendency to coalesce into larger clusters that further evolve by capturing/emitting additional He atoms, vacancies, and interstitials, thus evolving from $\rho = 1$ to nearby values.

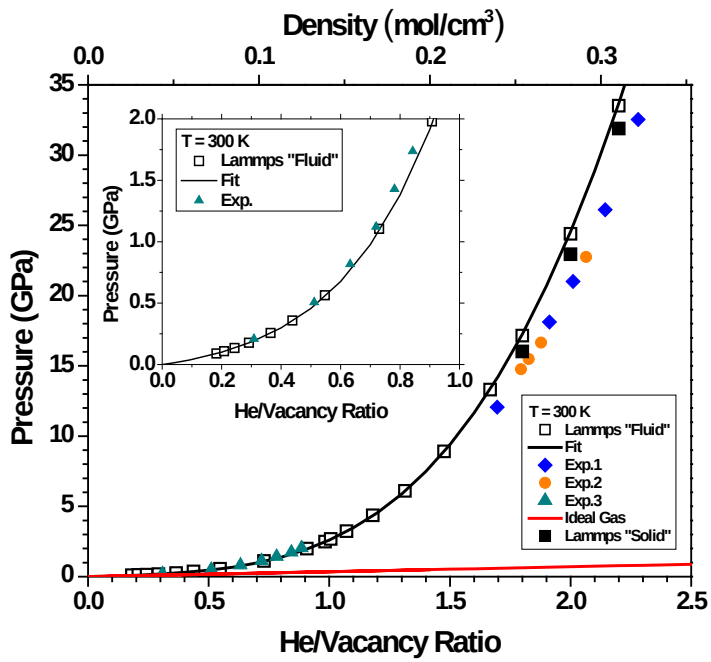

Figure 1: Pressure - density relation at 300 K as obtained by MD in the region of interest for nuclear materials studies. Inset shows the low density region magnified. Branching at around r = 1.7 reflects the solid-fluid transition. Red line is the pressure of an ideal gas (kinetic contribution alone). Lammps fluid refers to simulations done increasing pressure, where finite size effects delays solidification. Lammps solid is the result of solidification with the presence of defects (see Figure 2).

At densities and temperatures in this range He has solid–liquid phase transition. Figure 1 shows the results for MD simulations for the P-ρ relation at T = 300 K. Starting at low densities ($\rho < 1$) the agreement with experimental results from is excellent, see inset in Fig.1. As density approaches 1.7 He/vacancy we observe a branching corresponding to the two phases fluid and solid, as measured experimentally and by MD simulations. We mention here that the fluid phase is retained in the simulation in regions where equilibrium indicates a solid phase, as a result of finite size effects. We come back to this point later, when discussing Fig. 2.

The discrepancy between the MD simulations for the solid phase (indicated by solid squares as Lammps "solid' in the figure, and the experimental results is due to the rapid solidification and finite size effects in the simulation that freeze a highly defective solid. The red line corresponds to the pressure of an ideal gas at similar densities (kinetic contribution alone), showing that most of the pressure in He at these densities comes from the finite size of the He atoms and their He-He repulsion.

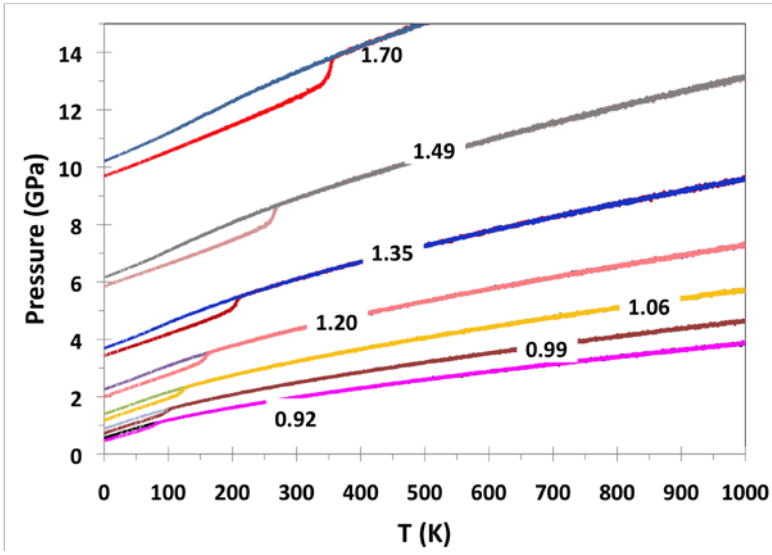

Figure 2: Pressure – Temperature relation for different densities for He. Curves are labeled by density, in units of He/Vacancy. Simulations start at 0K with an fcc solid phase, rise T up to 1000 K and then decrease T to 0K. Branching reflects the solid-fluid transition. Significant hysteresis is due to finite size effects.

A first observation from this figure is that at densities around and above 1 He/V the pressures are above 1 GPa, which is the order of magnitude of the strength of a metal, suggesting that these densities will probably induce plastic deformation of the matrix. A second observation is that at the T-ρ of interest, He presents a solid-fluid phase transition.

Figure 2 shows P-T relationship at different densities. The solid-fluid transition is clearly visible, although it is not at the thermodynamic equilibrium transition temperature due to finite size effects. Upon quenching, a defective solid forms in all cases.

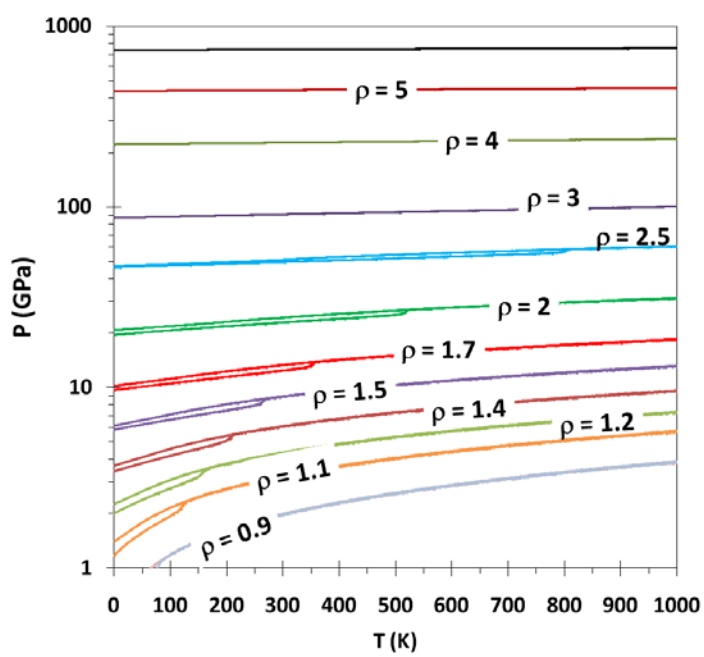

Figure 3: P-T relation at high densities for the fluid phase of He.

At densities higher than 1, the main contribution to the pressure comes from the He-He repulsion, being only slightly dependent on T. Figure 3 shows that regime for densities up to 6 He/V and pressure in the hundreds of GPa

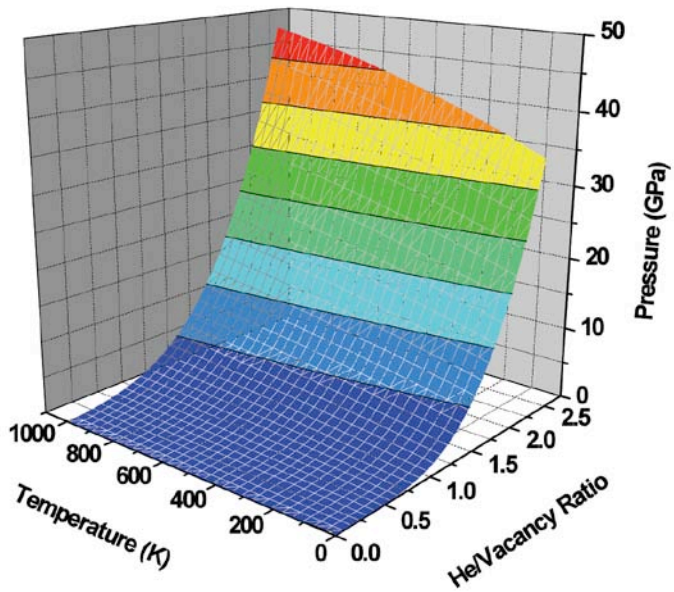

Figure 4: Equation of State for the fluid phase of He.

Figure 4 shows the equation of state, EOS, for the fluid phase of He obtained from a fit to the ensemble of data presented in Figures 2 and 3. The surface P(ρ,T) is described by,

$$P(\rho,T) = a_0(\rho) + a_1(\rho) * T + a_2(\rho) * T^2$$

$$a_0(\rho) = -5.98E\text{-}01 * \rho^5 + 3.29E+00 * \rho^4 - 1.76E+00 * \rho^3 + 3.76E\text{-}01 * \rho^2 - 1.10E\text{-}02 * \rho$$

$$a_1(\rho) = 1.02E\text{-}03 * \rho^5 - 4.24E\text{-}03 * \rho^4 + 4.66E\text{-}03 * \rho^3 + 2.19E\text{-}03 * \rho^2 + 1.07E\text{-}03 * \rho$$

$$a_2(\rho) = -6.49E\text{-}07 * \rho^5 + 2.39E\text{-}06 * \rho^4 - 2.09E\text{-}06 * \rho^3 - 9.56E\text{-}07 * \rho^2 + 1.20E\text{-}07 * \rho$$

This expression will be used to estimate the density inside He bubbles in FeCr.

He bubbles in FeCr

Experiments and simulations show that solid He exists in three different stable crystallographic structures, namely hcp, fcc, and bcc depending on temperature and pressure. When embedded in a matrix, the behavior of He bubbles will reflect the influence of the surroundings, most probably transforming from a fluid at low density to an amorphous solid.

A full EOS of He bubbles in metals P(ρ, R, T, μ_{He}) with R the radius of the bubble and μ_{He} the He chemical potential is still missing. In what follows we explore some aspects of this problem, namely the P-ρ relation for bubbles.

We use two computational techniques for these studies. One is a Metropolis Monte Carlo in the semi grand canonical ensample that allows us to randomly swap the chemical identity of an atom between Fe, Cr or He, according to user-determined chemical potentials for each species. The Metropolis algorithm controls acceptance or rejection of the swap. The displacement component of the ensemble is accomplished by molecular dynamics. Alternating MC and MD the system evolves towards equilibrium via nucleation and growth of He bubble and eventually α' precipitates.

Figure 5 shows several He bubbles, form very small to a 7 nm one, containing several thousand He atoms. Pressures measures on He and matrix atoms are in a range of several GPa, being larger for the smaller clusters. The lower figure shows the interesting fact that α' precipitates (in green) do not attract He bubbles (in blue).

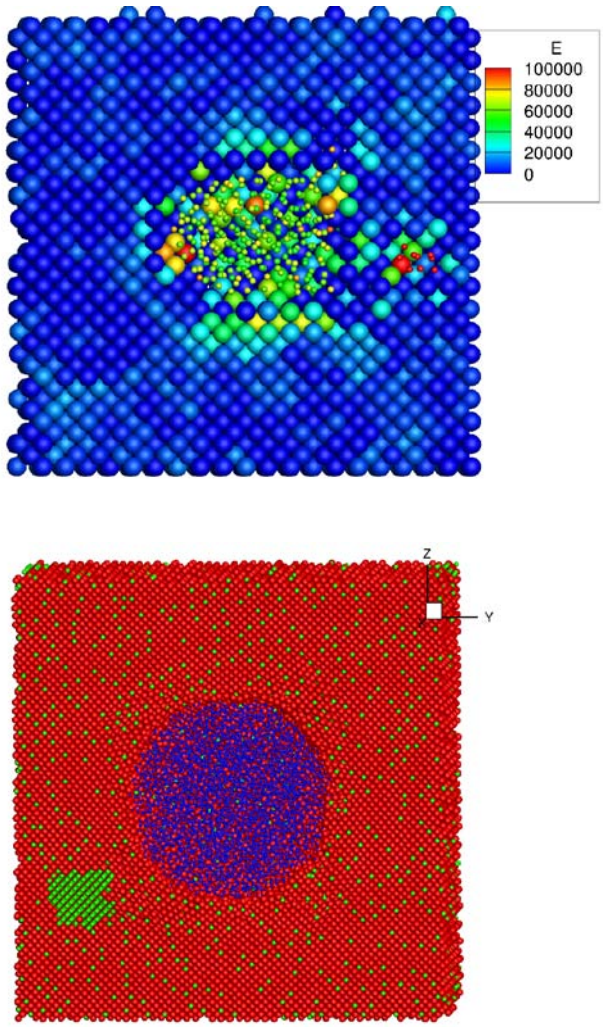

Figure 5: (upper figure) Two small He bubbles at density = 1 He/V showing the pressure range, from 10 GPa for He atoms in a small (~ 0.5nm) bubble to about 5 GPa in a medium (~ 2nm) bubble.(lower figure) A 7 nm He bubble in a 15% FeCr alloy showing that Cr rich α' phase (shown in green) does not make contact with the He bubble (blue). Suggesting that precipitation of α' is not providing sites for heterogeneous he precipitation.

Mobility of the He interstitial

The mobility of a He interstitial atom has been studied with MD in FeCr for composition between 0 and 15 at% Cr, in random solid solutions and in short range ordered solutions. SRO has been established using a Metropolis Monte Carlo code. The details of the simulations are the following: time-step of 0.1 fsec, thermalization of the samples for 10 psec, total run time of 0.2 nsec; sample size is 2000 atoms. The diffusion coefficient is obtained from the < r(t), r(o) > correlation function and the Eisntein formula. An Arhenious plot provides the activation energy, as shown in Figure 6.

As it can be seen form Figure 6, the mobility of He interstitials is only slightly dependent on Cr composition and on the degree of order of the alloys, showing a slight increase of the activation barrier a the Cr content increases. The dispersion of the data is significant and the thermal noise precludes a determination of the interstitial type, namely octahedral or tetrahedral. These results are in qualitative agreement with those reported by Terentev et al. in 2009 using the same potential for Fe-He but a different one for Fe-Cr.

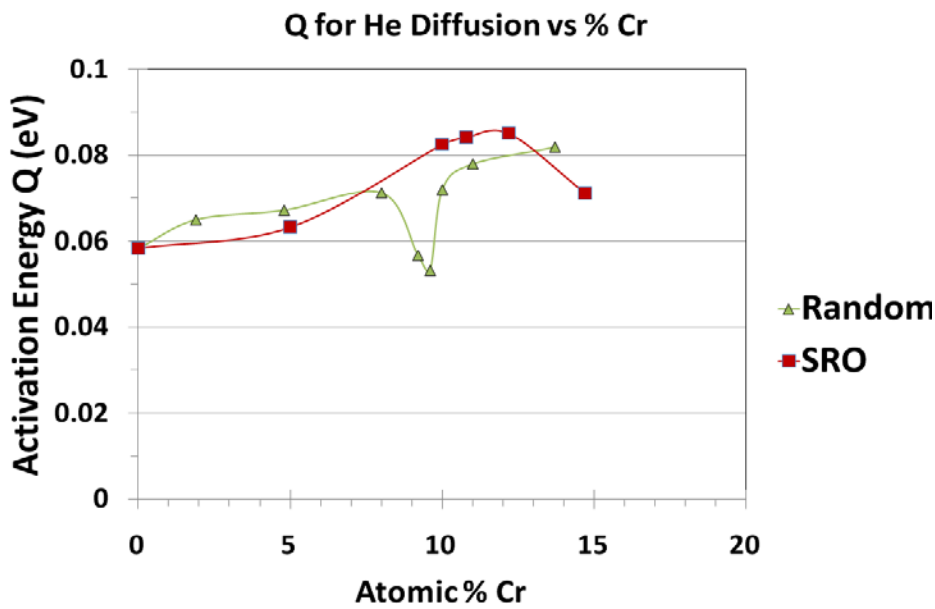

Figure 6: Arrhenious plot of the activation energy for interstitial He diffusion in FeCr alloys in the random solid solution and in the short range ordered solution.

These data is an important input for kinetic Monte Carlo approaches.

Finally, an important results obtained form this work is shown in Figure 7. As a He bubble grows in a Fe sample at 800 K from having 1 atom up to 450 atoms in an initial 27 V cavity, the pressure builds up and induces distortions on the matrix atoms surrounding the bubble. This pressure reaches a peak of about 15GPa, corresponding to a density of about 2 He/V and then starts decreasing reaching a plateau at about 10GPa. During this processes, the matrix yields to accommodate the increasing volume of the bubble and this yielding seems to be accomplished by the emission of <111> interstitial dislocation loops of a dimension comparable with the bubble.

These emissions are not reflected on the pressure vs density curve, which evolves smoothly as the size increases. This simulation suggests that the emission of single interstitials or He interstitials sis not occurring.

To conclude, the present state of this work allows us to define the future direction of work, related to the particular way the bubbles grow via incorporation of He both as interstitial and substitutional, and by the absorption of vacancies. Some of these processes can be studied by direct MD or Metropolis MC, but others, such as the rate of absorption of substitutional He, have to be studied using kinetic MC using off-lattice calculations to incorporate the stress field of around the bubble.

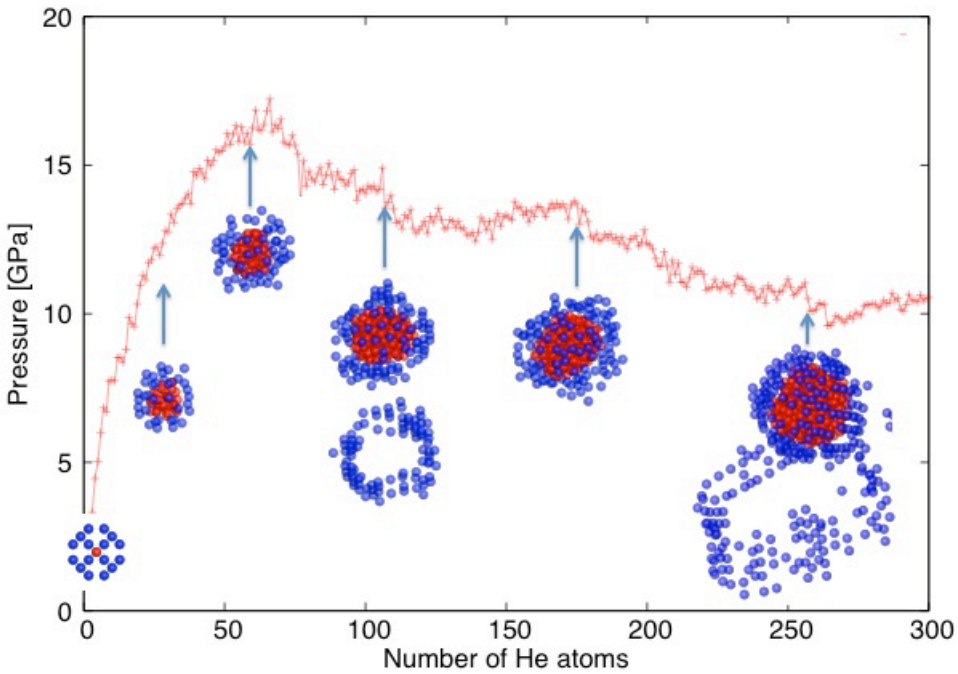

Figure 7: Pressure inside a He bubble as a function of the number of He atoms inside it. Red are He atoms and blue are non-bcc Fe atoms. It can be observed that the bubble grows by emmision of interstitial dislocation loops occurring along the growth path with no particular signature left on the pressure of the bubble.

Publications

Multiscale modelling of radiation damage and phase transformations: The challenge of FeCr alloys
Author(s): Malerba L, Caro A, Wallenius J
Conference Information: Symposium on Microstructural Processes in Irradiated Materials held at the 2007 TMS Annual Meeting, FEB 25-MAR 01, 2007 Orlando, FL
Source: JOURNAL OF NUCLEAR MATERIALS Volume: 382 Issue: 2-3 Pages: 112-125 Published: DEC 1 2008

The influence of short range order on the thermodynamics of Fe-Cr alloys
Author(s): Bonny G, Erhart P, Caro A, et al.
Source: MODELLING AND SIMULATION IN MATERIALS SCIENCE AND ENGINEERING Volume: 17 Issue: 2 Article Number: 025006
Published: MAR 2009

Numerical prediction of thermodynamic properties of iron-chromium alloys using semi-empirical cohesive models: The state of the art
Author(s): Bonny G, Pasianot RC, Malerba L, Caro A. et al.
Conference Information: 3rd Symposium on Nuclear Materials held at the EMRS 2008 Spring Meeting, MAY 26-30, 2008 Strasbourg, FRANCE

Source: JOURNAL OF NUCLEAR MATERIALS Volume: 385 Issue: 2 Pages: 268-277 Published: MAR 31 2009

Efficient implementation of the concentration-dependent embedded atom method for molecular-dynamics and Monte-Carlo simulations
Author(s): Stukowski A, Sadigh B, Erhart P, Caro A. et al.
Source: MODELLING AND SIMULATION IN MATERIALS SCIENCE AND ENGINEERING Volume: 17 Issue: 7 Article Number: 075005
Published: OCT 2009

Composition-dependent interatomic potentials: A systematic approach to modelling multicomponent alloys
Author(s): Sadigh B, Erhart P, Stukowski A, Caro A. et al.
Source: PHILOSOPHICAL MAGAZINE Volume: 89 Issue: 34-36 Pages: 3371-3391 Published: 2009

B. Sadigh, P. Erhart, A. Caro et al., “Heterogeneous nucleation in alloys using MCCask, a parallel Monte Carlo code in the transmutation ensemble with displacements”, in preparation.