Theoretical studies of energetic and structural properties of bulk and nanoparticles of FePt alloy

R. V. Chepulskii, W. H. Butler
Phases of FePt

Temperature (°C)

Fe          Atomic Percent Platinum          Pt

L1₂(FePt₃,Fe₃Pt)

L1₀(FePt)

(αFe) (~65)

(γ₁(Fe₃Pt),γ₂(FePt)) (~50)

(γ₃(FePt₃)) (~1350°C)

(γFe,Pt) (~1300°C)

(δFe) (~770°C)

1538°C

1394°C

1769°C

912°C

770°C

0 10 20 30 40 50 60 70 80 90 100

Fe          Atomic Percent Platinum          Pt
LATTICE GAS MODEL

Atoms of different types in different quantities

1. Crystal lattice

2. Atoms are permitted to be situated only within the crystal lattice sites

3. Atoms interact through the lattice potential

4. Atoms exchange the positions in accordance with Gibbs statistics

\[ W(\text{state}) \propto \exp \left[ - \frac{E(\text{state})}{k_B T} \right] \]
ENERGY of a TWO-COMPONENT LATTICE GAS

\[ \text{state} = \left\{ C_\alpha^R \right\} \]

\[ \alpha = A, B \ (A = \text{Fe}, B = \text{Pt}) \quad R - \text{radius - vector of sites} \]

\[ C_\alpha^R = \begin{cases} 1, \text{if } \alpha - \text{atom is at site } R \\ 0, \text{otherwise} \end{cases} \]

\[ E(\text{state}) = E_0 + \sum_{\alpha, R} E_\alpha^R C_\alpha^R + \frac{1}{2} \sum_{\alpha_1, \alpha_2 R_1, R_2} E_{\alpha_1, \alpha_2}^{R_1, R_2} C_\alpha^R C_\alpha^R C_\alpha^R \]
Two-component: \( C_R^A + C_R^B = 1 \Rightarrow C_R^B = 1 - C_R^A \)

\[
E\text{(state)} = V^{(0)} + \sum_R V_R^{(1)} C_R^A + \frac{1}{2} \sum_{R_1, R_2} V_{R_1, R_2}^{(2)} C_{R_1}^A C_{R_2}^A
\]

Mixing potentials:

\( V^{(0)} \) - only B-atoms

\[
V_R^{(1)} = E_{R_1}^A - E_{R_1}^B + \sum_{R_2} \left[ E_{R_1, R_2}^{A,B} - E_{R_1, R_2}^{B,B} \right]
\]

\[
V_{R_1, R_2}^{(2)} = E_{R_1, R_2}^{A,A} - 2E_{R_1, R_2}^{A,B} + E_{R_1, R_2}^{B,B}
\]
Assume: \[ V_R^{(1)} = V^{(1)} \]

\[
E(\text{state}) = V^{(0)} + V^{(1)} N_A + \frac{1}{2} \sum_{R_1, R_2} V_{R_1, R_2}^{(2)} C_A^{R_1} C_A^{R_2}
\]

\[
W(\text{state}) \propto \exp \left[ - \frac{\sum_{R_1, R_2} V_{R_1, R_2}^{(2)} C_A^{R_1} C_A^{R_2}}{2k_B T} \right]
\]
Monte Carlo (MC) simulation

Fe and Pt are placed on a fcc lattice $N(\text{Fe})=N(\text{Pt})$

Metropolis sampling: $P = \exp \left[ -\frac{\Delta E + E_b}{k_B T} \right]$

$\Delta E$ energy difference between configurations

$E_b$ energy barrier if particle-particle exchange

$E_b = 0$ : for study of equilibrium, not kinetics
If the totally disordered configuration is chosen as initial state, after simulation the final configuration contains anti-phase domains shifted relative to each other by $a/2$ along z-axis. These anti-phase boundaries cost zero energy in model which has only nearest neighbor interactions.
Connolly-Williams method

The mixing potentials are assumed to have the symmetry of the crystal lattice

\[ E(\text{state}) = V^{(0)} + V^{(1)} N_A + \frac{1}{2} \sum_{R_1,R_2} V_{R_1,R_2}^{(2)} C_A^{R_1} C_A^{R_2} \]

\[ E(\text{state}) = V^{(0)} + V^{(1)} N_A + \sum_{\text{shell}=1}^{N} V_{\text{shell}} \Pi(\text{state}) \]

1. Choose a set of linearly independent periodic structures.

2. Perform first principles calculations of their energies (VASP)

3. Fit the mixing potentials to calculated values of the total energies of these structures
21 structures were accurately fit using 3 shells of interactions.

Relative Average Error = 1.14%
Absolute Average Error = 0.12 eV
(per one structure)
PAIR MIXING POTENTIAL
(Connolly Williams method)

Distance in units of FCC lattice parameter
Monte Carlo simulation started with totally ordered state
### PHASE TRANSITION TEMPERATURES

<table>
<thead>
<tr>
<th></th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>To (bulk)</td>
<td>1510 K</td>
<td>1572 K</td>
</tr>
<tr>
<td>To (d=5.94 nm)</td>
<td>1440 K</td>
<td></td>
</tr>
<tr>
<td>To (d=3.5 nm)</td>
<td>1100 K</td>
<td></td>
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<tr>
<td>T curie (bulk)</td>
<td></td>
<td>710 K</td>
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CONCLUSIONS

1. In the case of \( d=3.5 \text{ nm} \) and \( T=600 \text{ C} \), we are below the phase transition (within the error of theoretical model 60 K).

2. The absence of the order means the kinetic problems.

3. Even if there is no phase transition, we should have an order in equilibrium.