Formation energy of κ-carbide using *ab initio* calculations

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Introduction

The compound $Al(Fe,Mn)_3C$ with an anti-perovskite structure, known as κ-carbide, is easily found in strong, low-density steels containing substance concentrations of aluminium and manganese. The strength of Mn-Al-C steels is enhanced by the precipitation of κ-carbide, which is coherent with austenite, causes a shear band induced plasticity effect (SIP effect) [1]. The formation of κ-carbide in the austenite is an important method of controlling the final properties of these high-performance steels. However, there are a few calculations about formation energy by theoretical approach. In this research, we calculated the formation energy of Fe_3AlC in term of first-principles calculation by using the total-energy all-electron full-potential linearized augmented plane wave (FLAPW) method within the generalized gradient approximation (GGA).

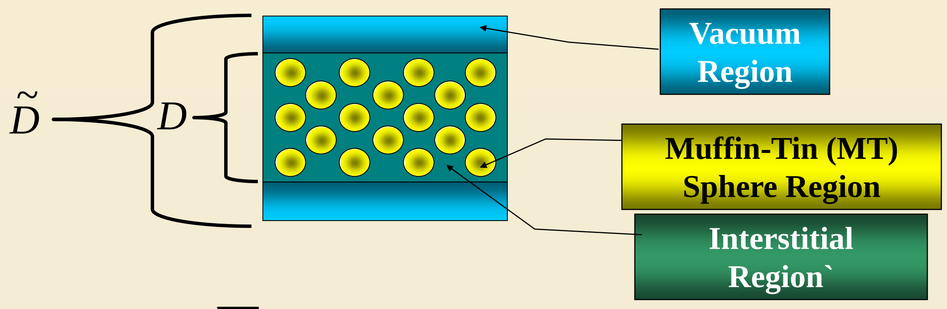
Method

Ab-initio calculation

A method of calculating atomic and molecular structure directly from the first principles of quantum mechanics, without using experiment data as parameters

FLAPW method

An all-electron method which within density functional theory is universally applicable to all atoms of the periodic table and to systems with compact as well as open structures



$$\psi_n(\mathbf{k}_n,\mathbf{r}) = \sum_j c_{nj}\chi(\mathbf{K}_j,\mathbf{r})$$

$$\chi(\mathbf{K}_j,\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i\mathbf{K}_j\cdot\mathbf{r}}, & \mathbf{r}\in \text{Interstitial} \\ \sum_j \left[A_L(\mathbf{K}_j)u_l(E_l,r) + B_L(\mathbf{K}_j)\dot{u}_l(E_l,r)\right]\times Y_L(\hat{\mathbf{r}}), & \mathbf{r}\in \text{MT sphere} \\ \sum_q \left[A_q(\mathbf{K}_j)u_q(E_v,z) + B_q(\mathbf{K}_j)\dot{u}_q(E_v,z)\right]\times e^{i\mathbf{K}_q\cdot\mathbf{r}_\parallel}, & \mathbf{r}\in \text{Vacuum} \end{cases}$$

$$\mathbf{K}_j = \mathbf{k} + \mathbf{G}_j \qquad \mathbf{K}_q = \mathbf{K}_{j\parallel} + \mathbf{G}_j$$

Formation energy (Formation enthalpy)

$$\Delta H(Al_aC_bMn_cFe_d) = U(Al_aC_bMn_cFe_d) - a\,U(\text{fcc Al}) - b\,U(\text{Graphite C}) - c\,U(\alpha\text{-Mn}) - d\,U(\text{bcc Fe})$$

Where, ΔH is formation enthalpy and U is internal energy of specimen.

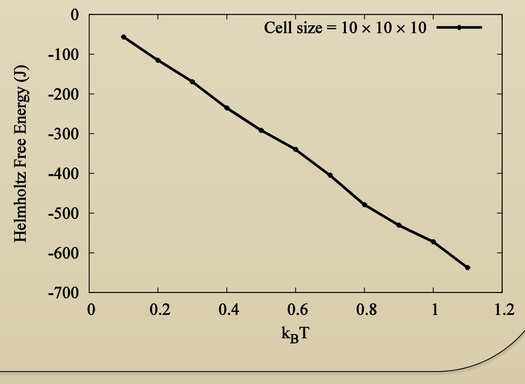
Conclusion

The calculated equilibrium lattice parameters are 3.736 Å and 3.761 Å for the nonmagnetic (NM) and ferromagnetic (FM) cases, respectively, which are comparable to the measured one of FM Fe_3AlC, 3.781 Å [2]. The formation enthalpies of Fe_3AlC are calculated to be –26.1 and –28.2 kJ/atom-mol, for the NM and FM cases, respectively. These values are little smaller than the results of Ohtani *et al.* [3], but the formation enthalpy difference between the NM and FM cases are the same.

For Fe_2MnAlC, which has three octahedral site for carbon, we also calculated formation enthalpy with and without carbon. Clearly, these three types have higher energy than Fe_3AlC.

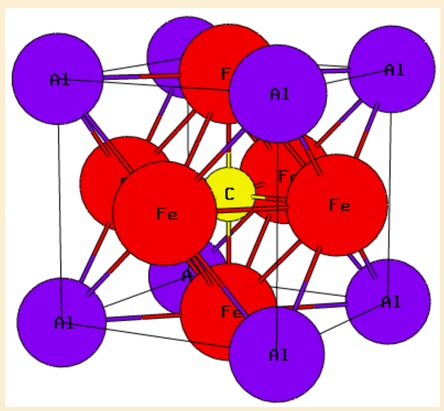
With these formation enthalpy, we assume that Fe_2MnAlC with carbon in body center is only κ-carbide and the others are austenite. Then, set 10×10×10 matrix which has κ-carbide or austenite in each cell and calculate Helmholtz free energy with changing temperature by Monte Carlo. However, we cannot see any sign of phase transformation.

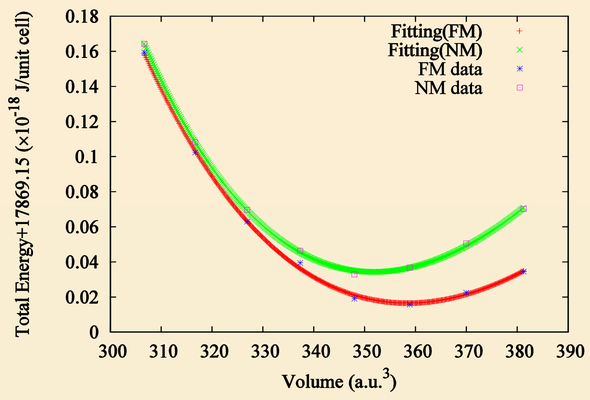
In future, we will calculate the Gibbs free energy with calculated enthalpy. Also, we will improve this Monte Carlo method.



Calculations

κ-carbide ($AlCFe_3$)



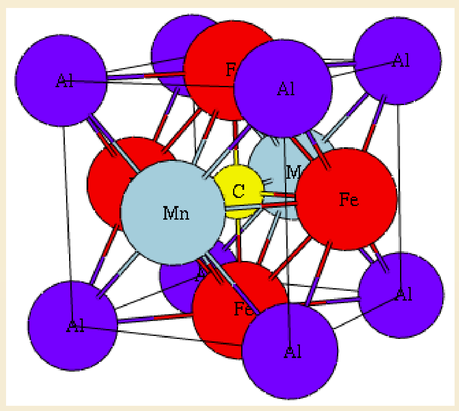


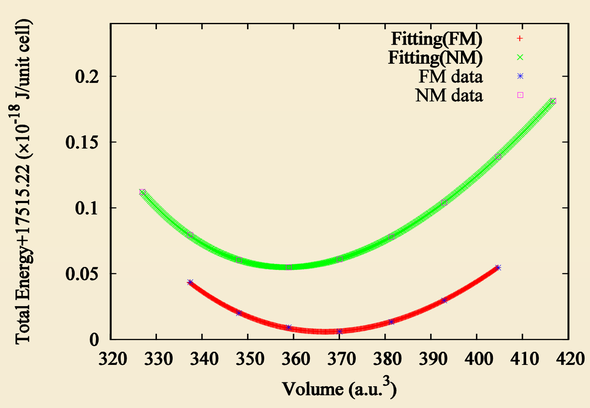
Equilibrium lattice parameter is 3.761 Å

Formation energy for NM = – 26.1 kJ/atom-mol

for FM = – 28.2 kJ/atom-mol

κ-carbide ($AlCMnFe_2$)



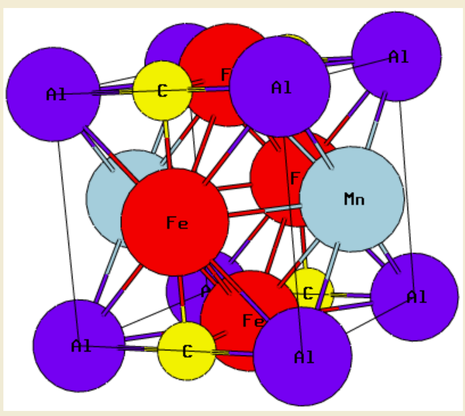


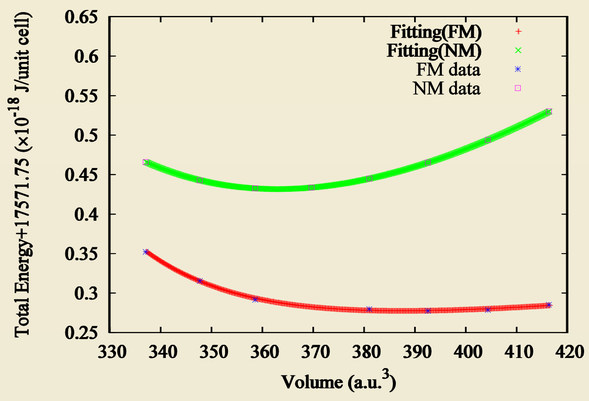
Equilibrium lattice parameter is 3.788 Å

Formation energy for NM = 456.8 kJ/atom-mol

for FM = 450.5 kJ/atom-mol

$AlCMnFe_2$ with another octahedral site



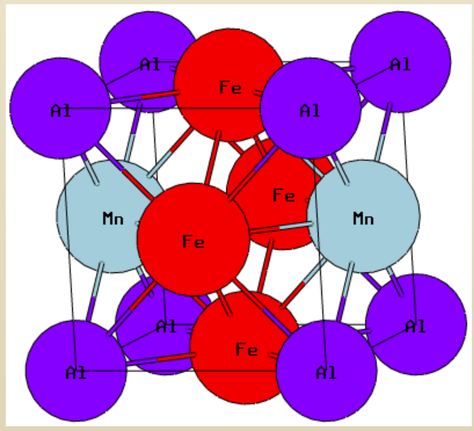


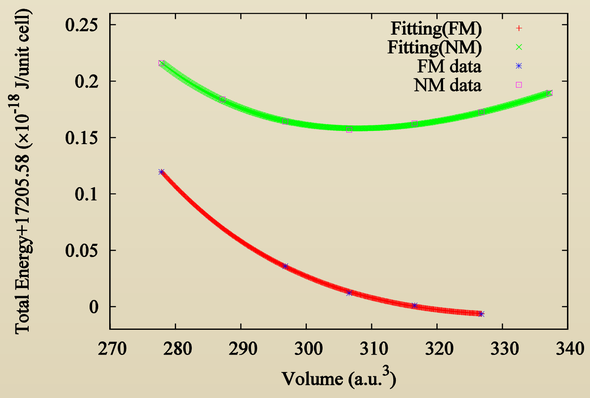
Equilibrium lattice parameter is 3.854 Å

Formation energy for NM = 505.0 kJ/atom-mol

for FM = 483.8 kJ/atom-mol

$AlMnFe_2$





Equilibrium lattice parameter is 3.674 Å

Formation energy for NM = 586.2 kJ/atom-mol

for FM = 561.3 kJ/atom-mol

References

[1] G. Frommeyer and U. Brüx, *Steel Res. Int.* **77**, 627 (2006).
[2] L. S. Palatnik, I. A. Tananko and Yu. G. Bobro, *Kristallografiya* **9**, 163 (1964).
[3] H. Ohtani, M. Yamano, and M. Hasebe, *ISIJ International* **44**, 1738 (2004).