Thermodynamic assessment of Fe-Ti-S ternary phase diagram by using cluster variation method

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1. Introduction

Fe-Ti-S ternary system

- High-precision thermodynamic assessment is desired about the equilibrium of FCC and (Fe,Ti)S for ultra low carbon steel.

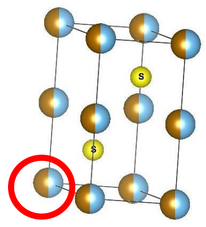
Previous work [1)]

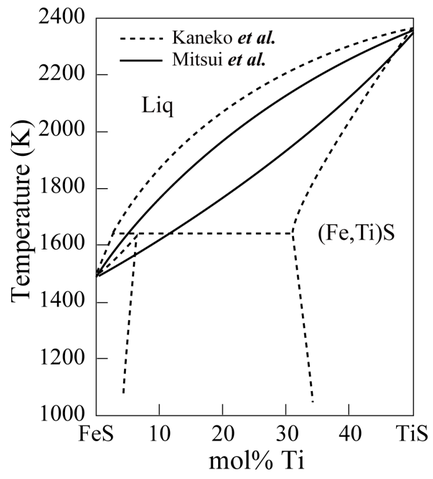
System	Phase	Free energy
Ti-S	Solid solution	The interaction parameter is not evaluated
	Compounds	First principles calculations and Debye-Grünaizen model
Fe-S,Fe-Ti	Solid solution, Compound	Calculated by *Lee et al.* and *Kumar et al.*
Fe-Ti-S	Off-stoichiometric compounds	The interaction parameter is not evaluated
	Stoichiometric compound	First principles calculations and Debye-Grünaizen model

1) H.Ohtani *et al.* the 171st ISIJ Meeting (March , 2012)

(Fe,Ti) S phase

NiAs type crystal structure





Phase decomposition ? Isomorphic solid solution [2)]

2) H. Mitsui *et al*, *ISI Int.*,**49**(2009)936-941

Purpose

①Ti-S binary system : To determine the free energy of solid solutions.

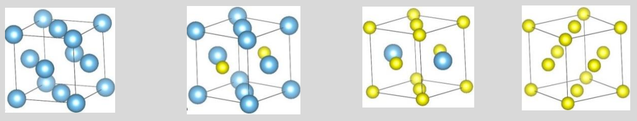
②Fe-Ti-S ternary system: To determine the free energy of (Fe,Ti)S
→To distinguish between phase decomposition and isomorphous of (Fe,Ti)S.

2. Calculation method

First-principles calculation

・ ATAT(Alloy Theoretic Automated Toolkit)
Searching ordered structures on various concentrations.

・ VASP(Viena ab-initio simulation package)
Calculating the formation energy of ordered structures.

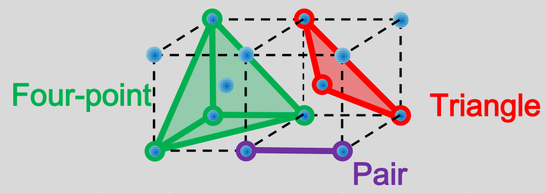


Cluster expansion method (CEM)

Total Energy = Sum of energy of clusters

$$E^{(m)} = \sum_i \upsilon_i \cdot \xi_i^{(m)}$$

υ_i : Effective cluster interaction
$\xi_i^{(m)}$: Cluster correlation function



Determine the most relevant clusters which can reproduce the results of fist-principles calculations.

Cluster variation method (CVM)

$$F(\xi) = E(\upsilon,\xi) - T \cdot S_{\mathrm{conf}}$$

$$S_{\mathrm{conf}} = k_B \ln W$$

W : Configration combination of clusters

k_B : Boltzman constant

Evaluate the configurational entropy against the cluster correlation function.

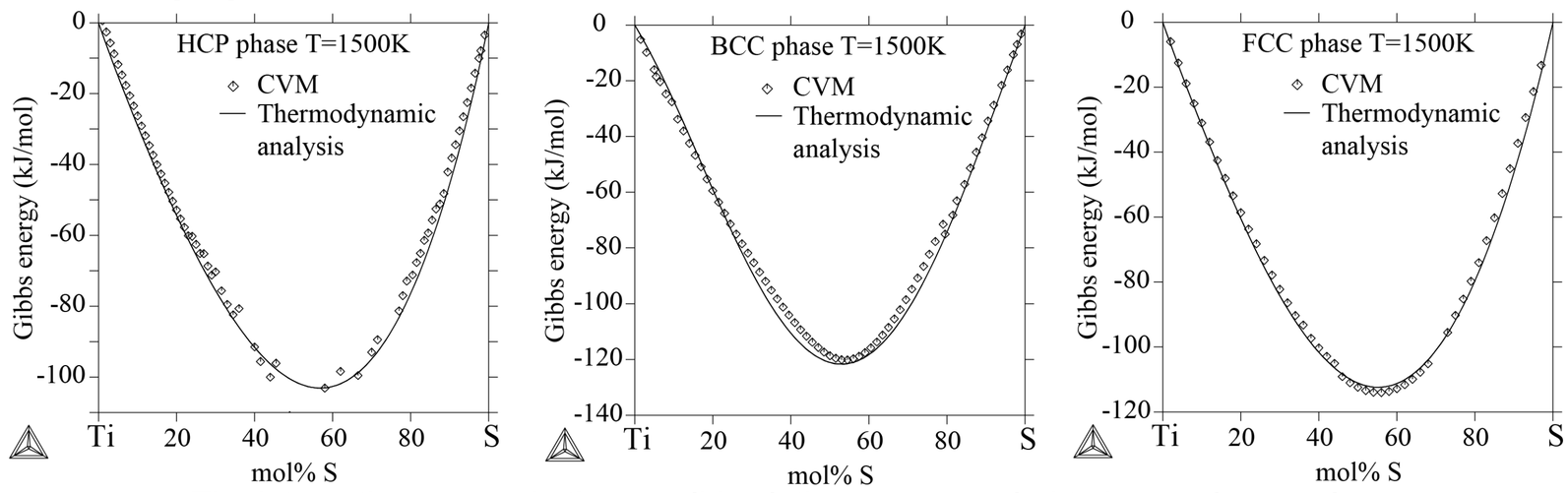
Calculation of phase diagrams

Fit regular solution and sub-lattice models to the results of CVM

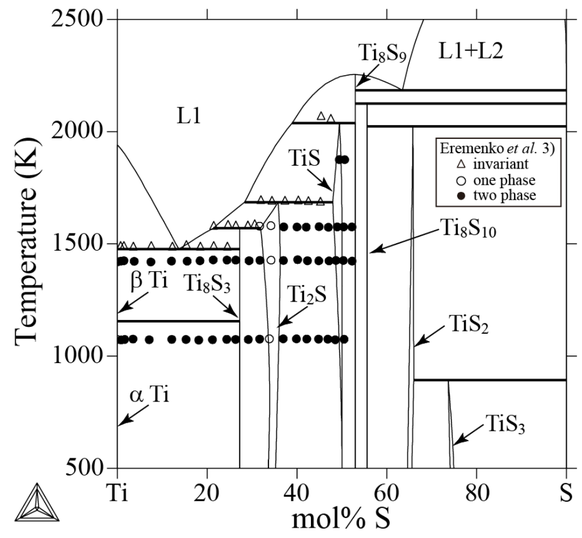
Solid solution phase : Regular solution model
Compound phase : Sub-lattice model

3. Results and discussion

①Ti-S binary system

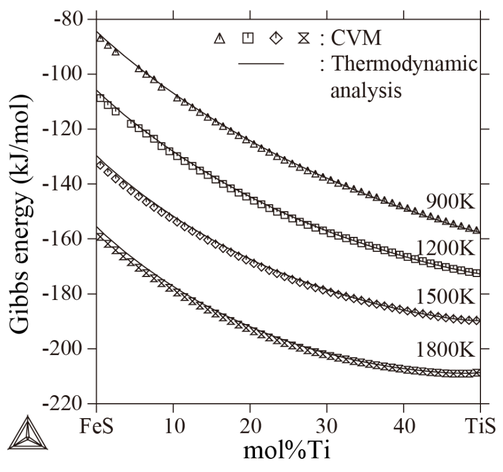


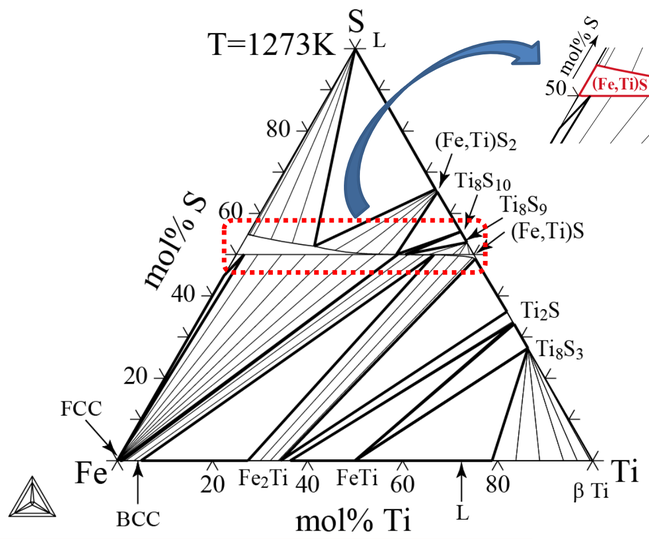
・ The interaction energy in these solid solutions are revealed to have a large value.
・ The calculated phase diagram has good agreement with experimental results in the Ti-rich side. The phase decomposition of liquid phase is predicted in the calculated phase diagram.

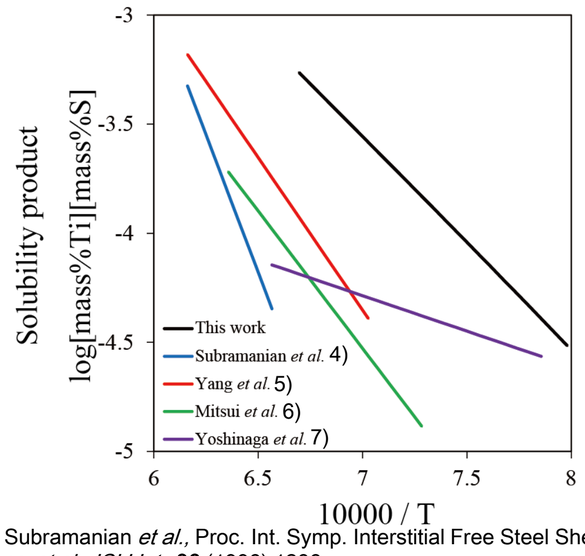


3) V. N. Eremenko *et al*, *Khal'kogenidy*(Kiev), (1967) 69-78

②Fe-Ti-S ternary system







・ The free energy curve is convex downward, which indicates the behavior of an isomorphic solid solution due to the attractive interaction between Fe and Ti in (Fe,Ti)S.

・ The calculated phase diagram has good agreement with experimental results.

The thermodynamic parameters of this study determined the gradient of solubility product of TiS and can reproduce the experimental values reported by Yang *et al.* and Mitsui *et al.*

4) S. V. Subramanian *et al.*, Proc. Int. Symp. Interstitial Free Steel Sheet (1991) 15.
5) X. Yang *et al.*, *ISIJ Int.*, **36** (1996) 1286.
6) H. Mitsui *et al.*, *CAMP-ISIJ*, **17** (2004) 1275.
7) N. Yoshinaga *et al.*, *ISIJ Int.*, **34**(1994) 24.

4. Summary

The phase equilibria in the Fe-Ti-S system were determined by using various calculation techniques. The calculated Ti-S and Fe-Ti-S phase diagrams had good agreement experimental results. The behavior of an isomorphic solid solution in (Fe,Ti)S is expected by CVM calculation.