EFFECT OF LATTICE VIBRATIONS ON SILICON DISTRIBUTION IN SI-LOW-CONCENTRATION TI-SI SYSTEM

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Abstract

In this paper we calculate the vibrational free energies of Ti_5Si_3, Ti_3Si, Ti_5Si_4, TiSi and Si solid solution phases and include them in our thermodynamic model in order to estimate the effect of lattice vibrations on precipitation thermodynamics and distribution of silicon in Si-low-concentration Ti-Si system.

Keywords: Titanium silicides, precipitation, lattice vibrations

1. INTRODUCTION

Silicon is a promising alloying element for nanostructured titanium alloys because it stabilizes their structure. Titanium alloys containing even small amounts of Si show better corrosion resistance and mechanical properties compared with Si-free commercially pure titanium [1–3] and can be used as promising materials for medical implants [1]. Silicon in such alloys can exist in different states, such as dilute solid solution or titanium silicide precipitates. Dispersions of the silicide particles can be very effective for strengthening and improving the structural stability of Si-doped titanium alloys [4–6]. On the other hand, silicon is well-known solid solution strengthener. Therefore, it is important to know the distribution of silicon between silicide particles and solid soluion in Si-doped titanium alloys for estimation of its influence on their strength characteristics. In our recent work [7] we theoretically predicted the distribution of silicon between precipitations of titanium silicides and dilute solid solution in α-Ti. For this purpose we used the thermodynamic model [8], which is based on precipitation energies of the silicide phases and the law of mass action. We have found that silicon is mainly distributed between dilute solid solution and two precipitating phases (Ti_5Si_3 and Ti_3Si) at the temperatures from 200 K to the temperature of polymorphic α/β-Ti transformation and that Ti_5Si_3 is the most favorable precipitating phase in this temperature interval. However, in that work [7] we have not included the vibrational free energy term in the expression for the Gibbs free energy change during precipitation. In present work we calculate the vibrational free energies of Ti_5Si_3, Ti_3Si, Ti_5Si_4, TiSi and Si solid solution phases and include them in our thermodynamic model in order to estimate the effect of lattice vibrations on precipitation thermodynamics and distribution of silicon in Si-low-concentration Ti-Si system.

2. DETAILS OF CALCULATIONS

Vibrational free energies were calculated within harmonic approximation in the framework of the supercell approach using a small displacement method as implemented in the PHONOPY code [9]. Supercell calculations were performed in the framework of the density functional theory (DFT) [10, 11] within the generalized gradient approximation (GGA) using Perdew et al. functional [12, 13] for description of exchange-correlation energy and projected augmented wave (PAW) method [14] as implemented in ABINIT code [15]. The calculations were performed using an energy cutoff of 700 eV for the plane-wave basis set and converged with respect to the k-point integration. Brillouin-zone (BZ) integrals were approximated using the special k-point sampling of Monkhorst and Pack [16]. The 7x7x6 grid was used for Ti_5Si_3 supercell with 32 atoms, 5x5x10 grid was used for Ti_3Si supercell with 32 atoms, 7x7x4 grid was used for Ti_5Si_4 supercell

with 36 atoms and 4x6x5 grid was used for TiSi supercell with 64 atoms. The integration over the BZ was made using the Methfessel–Paxton smearing method [17] with 0.136 eV smearing width. Such choice of main parameters ensures energy convergence to 1 meV/atom. Forces in supercells were calculated with accuracy of 0.03 eV/A. For determination of the free energy of Si atom in dilute solid solution, supercell of 47 α-Ti atoms with 1 Si atom in substitutional position was used.

3. RESULTS AND DISCUSSION

Vibrational formation free energies $\Delta F_{vib}(T)$ of titanium silicides from solid solution in dependence of temperature were calculated as follows:

$$\Delta F_{vib}(T) = [F_{vib}^{Ti_xSi_y}(T) - xF_{vib}^{Ti_{hcp}}(T) - yF_{vib}^{Si_{sol}}(T)]/y, \qquad (1)$$

where $F_{vib}^{TixSiy}(T)$, $F_{vib}^{Tihcp}(T)$ and $F_{vib}^{Sisol}(T)$ are temperature dependencies of vibration free energies of the silicide Ti_xSi_y, pure α-Ti and Si in solid solution, consequently. Temperature dependencies of silicon atoms distribution calculated within our model without and with inclusion of vibrational formation free energies are shown on Fig.1 and Fig. 2.
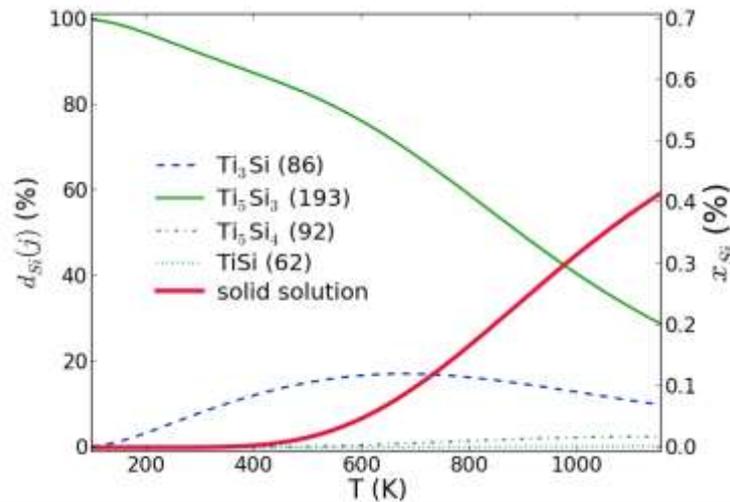

Fig.1. Temperature dependence of silicon distribution between Ti–Si precipitates and Si solid solution without inclusion of lattice vibrations. Total silicon concentration x_{Si} is 0.7 wt.%.
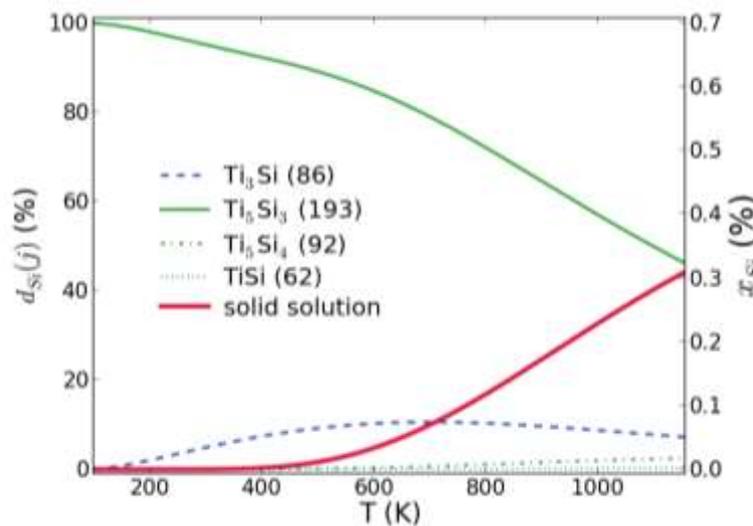

Fig.2. Temperature dependence of silicon distribution between Ti–Si precipitates and Si solid solution with inclusion of lattice vibrations. Total silicon concentration x_{Si} is 0.7 wt.%.

It can be seen that lattice vibrations do not change qualitatively the temperature dependence of silicon distribution between Ti-Si phases. However, they make Ti_5Si_3 precipitating phase more preferable for silicon, while Ti_3Si and Si solid solution phases become less preferable.

CONCLUSION

We have calculated the vibrational free energies of Ti_5Si_3, Ti_3Si, Ti_5Si_4, TiSi and Si solid solution phases and included them in our thermodynamic model. We have found that lattice vibrations make Ti_5Si_3 precipitating phase more preferable for silicon, while Ti_3Si and Si solid solution phases become less preferable.

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