First principles calculation of phase diagrams of V-Nb, V-Ta and Nb-Ta alloys

C. Ravi, B. K. Panigrahi, M. C. Valsakumar, and A. Van de Walle

Citation: AIP Conference Proceedings **1447**, 839 (2012); doi: 10.1063/1.4710264
View online: http://dx.doi.org/10.1063/1.4710264
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1447?ver=pdfcov
Published by the AIP Publishing

First Principles Calculation of Phase Diagrams of V-Nb, V-Ta and Nb-Ta Alloys

C. Ravi*, B. K. Panigrahi, M. C. Valsakumar, and A. van de Walle†

Materials Physics Division, Indira Gandhi Centre for Atomic Research, Kalpakkam-603102, India
**E-mail: ravic@igcar.gov.in*
†Engineering and Applied Science Division, California Institute of Technology, Pasadena, California 91125, USA

Abstract. We report the solid state phase diagram of V-Nb, V-Ta and Nb-Ta alloys computed by combining the density functional theory total energies with the cluster expansion and Monte Carlo techniques. From the computed phase diagrams, we find that V-Nb and Nb-Ta alloys form continuous series of solid solutions and the solid solution phase is stable down to ambient temperatures, consistent with experiments. The calculated bcc V-Ta phase diagram exhibits complete miscibility. Since the current cluster expansion ignore V_2Ta phase, the chemical interaction due to relatively large electronegativity difference, which cause the ordering of V_2Ta phase from the bcc solid solution, appears to manifest by making the solid solution phase remain stable for the complete concentration range, down to ambient temperatures, perhaps with some short-range-order. This work further demonstrates the dominant role of constituent strains in the accurate calculation of phase diagram of alloys of constituents with significant size mismatches.

Keywords: V-Nb, V-Ta, Nb-Ta alloys, Phase equilibrium, Cluster expansion and Monte Carlo techniques.
PACS: 64.75.-g, 61.66.-f

INTRODUCTION

Theoretical study of phase diagram requires calculation of the free energy as a function of composition and temperature. Calculation of free energy and ground-state structure of an $A_{1-x}B_x$ binary alloy requires, in principle, calculation of the total energy for all possible configurations of placing atoms A and B at the N different sites of the underlying Bravais lattice. As the number of possible configurations 2^N becomes enormous even for a modest N, it is difficult to calculate the energy quantum mechanically for the complete set of configurations. The cluster expansion method constructs an Ising-like Hamiltonian for the energies of the different atomic configurations [1].

CLUSTER EXPANSION METHOD

The cluster expansion method consists of considering the alloy being made of geometric objects such as points, pairs, triplets, and associating a characteristic energy with each of these objects. For a given underlying Bravais lattice, cluster expansion then expresses the energy $E(\sigma)$ of any configuration σ of the alloy as a linear combination of the characteristic energies and correlation functions of each figures, like a generalized Ising Hamiltonian. For accurate calculation of thermodynamic properties, it is essential that the cluster expansion Hamiltonian include the strain energies, due to lattice constant mismatch of the constituents [2], and the phonon contributions, besides the chemical interactions. Current cluster expansion is constructed to include both these contributions.

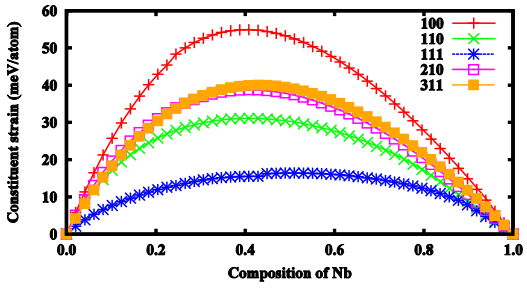

FIGURE 1. Constituent strain energy of V-Nb system is shown as a function of composition *x* for different interface orientations *k*. The constituent strain energy is defined as the energy required to main coherency along an interface between bulk crystals A and B.

Solid State Physics: Proceedings of the 56th DAE Solid State Physics Symposium 2011
AIP Conf. Proc. 1447, 839-840 (2012); doi: 10.1063/1.4710264

Finite temperature properties are calculated by resorting to Monte Carlo simulations using the cluster expansion Hamiltonian E(σ) [3]. We apply these techniques for computing the phase diagrams of V-Nb, V-Ta and Nb-Ta alloys. V-Nb and V-Ta have size mismatch of 8.5%. Nb-Ta is a size matched system. Figure 1 show, as an example, the calculated constituent strain energies of V-Nb alloy.

Ground-States and Phase Diagrams

Figure 2 shows the cluster expansion calculated ground-state search in V-Nb alloy. No intermediate ground-states are predicted, which is in agreement with experimental absence of ordered phases. In Fig.3, we compare the computed phase diagrams of V-Nb, V-Ta and Nb-Ta alloys with experiments. Experimental phase diagram of V-Nb exhibits a continuous series of solid solutions and the solid solution phase is stable down to ambient temperatures. V-Ta exhibits complete miscibility in the solid state above 1583 K and a miscibility gap between the solid solution and the V_2Ta Laves phase that form from the solution phase. Nb-Ta phase diagram shows complete miscibility. The computed V-Nb and Nb-Ta phase diagrams form continuous series of solid solutions and the solution phase is stable down to ambient temperatures. The bcc V-Ta phase diagram exhibits complete miscibility. Since the current cluster expansion ignores the known V_2Ta phase, the chemical interaction causing its ordering appears to manifest by making the solution phase remain stable for the complete concentration range, down to ambient temperatures, perhaps with some short-range order.

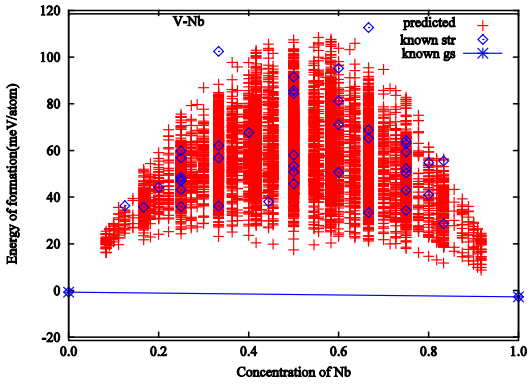

FIGURE 2. Cluster expansion calculated ground-state search of V-Nb alloy covering all bcc supercells having up to 12 atoms obtained with a Hamiltonian that includes constituent strain interactions. The current cluster expansion predicts no intermediate ground-states, which is in agreement with experiments.

These results further demonstrate the important role of constituent strains for the accurate calculation of phase diagram of alloys of constituents with significant size mismatches. The phonon free energy computed with the transferable force constants, is found to have moderate effect on the phase stability of these alloys.

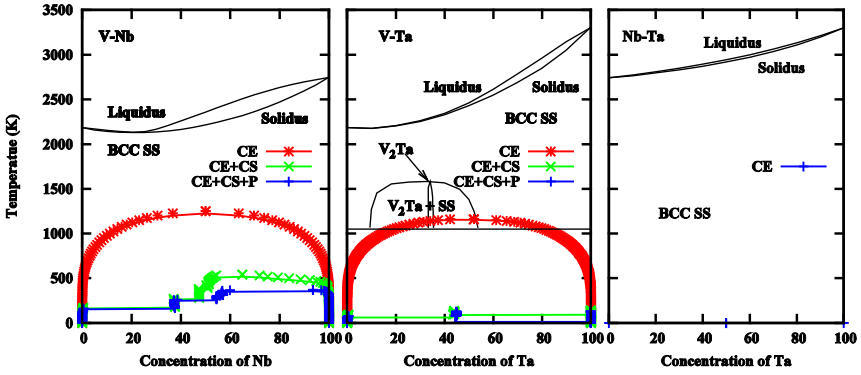

FIGURE 1. Calculated phase diagrams of V-Nb, V-Ta and Nb-Ta alloys compared with experiments. Liquidus, solidus and V_2Ta phase boundaries are experimental results. Curves with label CE represent conventional cluster expansion. CS and P represent constituent strain and phonon contributions. Conventional cluster expansion predicts large miscibility gap for V-Nb and V-Ta alloys. Constituent strain lowers the miscibility gap temperature significantly, which makes the computed phase boundaries to be consistent with experiments.

REFERENCES

1. G. Ceder, Comp. Mater. Sci., **1**, 144 (1993).
2. D. B. Laks, L. G. Ferreira, S. Froyen and A. Zunger, Phys. Rev. B **46**, 12587 (1992).
3. A. van de Walle and G. Ceder, J. Phase Equil., **23**, 348 (2002).