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# Solution-based thermodynamic modeling of the Ni–Ta and Ni–Mo–Ta systems using first-principle calculations

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ABSTRACT

Solution-based thermodynamic descriptions of the Ni–Ta and Ni–Mo–Ta systems are developed with supporting first-principles calculations and reported experimental data for parameter evaluation. For the Ni–Ta system, the liquid, bcc and fcc phases are described with a random solution model, $D0_{22}$–$Ni_3Ta$ is treated as a stoichiometric compound, and the remaining compounds are modeled as solid solutions on multiple sublattices. The resulting model for the Ni–Ta system is integrated with reported treatments of the Ni–Mo and Mo–Ta systems, and a thermodynamic model for the ternary Ni–Mo–Ta system is developed. The zero-Kelvin enthalpies of formation for the intermetallic compounds in the Ni–Mo–Ta system and the enthalpies of mixing for the bcc and fcc special quasirandom structures (SQS) in the binary Ni–Ta system are computed using the Vienna Ab-initio Simulation Package (VASP). Phase equilibria modeling results for the ternary Ni–Mo–Ta system are summarily presented in the form of isothermal sections and liquidus projections, with appropriate comparisons with available experimental data.



## 1. Introduction

High temperature performance is a critical issue for power generation and transportation applications of Ni-based superalloys, and considerable effort has been devoted to the development of the thermodynamic models required to describe phase stability at elevated temperatures in these materials [1–9]. Specifically, it is necessary to understand the thermodynamic effects of alloying elements, such as Ta and Mo, which play an important role in strategies for increasing the high temperature stability of $\gamma/\gamma'$ microstructures. To this end, we focus here on the development of reliable thermodynamic models for the Ni–Ta and Ni–Ta–Mo alloy systems.

Thermodynamic modeling of the Ni–Ta binary system was reported by Kaufman [4] and by Ansara and Selleby [5]. In each of these approaches, a total of eight phases were considered. The liquid, fcc, and bcc phases were treated as single-sublattice solutions, while the C16-$NiTa_2$, $\mu$-NiTa, C11$_b$-$Ni_2Ta$, $\kappa$-$Ni_3Ta$, and $\zeta$-$Ni_8Ta$ phases were treated as stoichiometric compounds. Subsequently, in order to model the solubility ranges exhibited by certain intermetallic phases, Cui and Jin (CJ) [6] described the $\kappa$-$Ni_3Ta$ and C16-$NiTa_2$ phases with two-sublattices and the $\mu$-NiTa phase with four-sublattices. Pan and Jin (PJ) [7] further refined the model by adding a two-sublattice treatment for the C11$_b$-$Ni_2Ta$ phase and reassessing the system, reducing the total number of thermodynamic parameters. The Ni–Ta binary phase diagrams associated with these modeling efforts are shown in Fig. 1, along with relevant experimental data [6,7,10–16]. In addition, Figs. 2 and 3 show that the calculated enthalpy of formation for the compounds at 298 K and enthalpy of mixing for liquid at 1873 K using both the CJ [6] and PJ [7] models differ substantially from reported measurements.

For the Ni–Mo–Ta ternary system, CJ also reported [9] an assessment based on the binary model parameters for the Ni–Mo [9], Mo–Ta [9], and Ni–Ta [6] systems. In their treatment, they model the $D0_a$-$Ni_3Mo$ and $\kappa$-$Ni_3Ta$ phases as a single phase. While this approach is reasonable since the two structures differ only in layer packing sequence, the phases are clearly distinct, and we treat them separately here. In addition, the present model incorporates a more recent description of the Ni–Mo system [8] as shown in Fig. 1(d) and a new assessment of the Ni–Ta binary. In subsequent sections of this paper, we will discuss these differences further and present the refined model, which offers better agreement with the experiment.

In the present work, the thermodynamic properties of the Ni–Ta and Ni–Mo–Ta systems and the associated phase equilibria are

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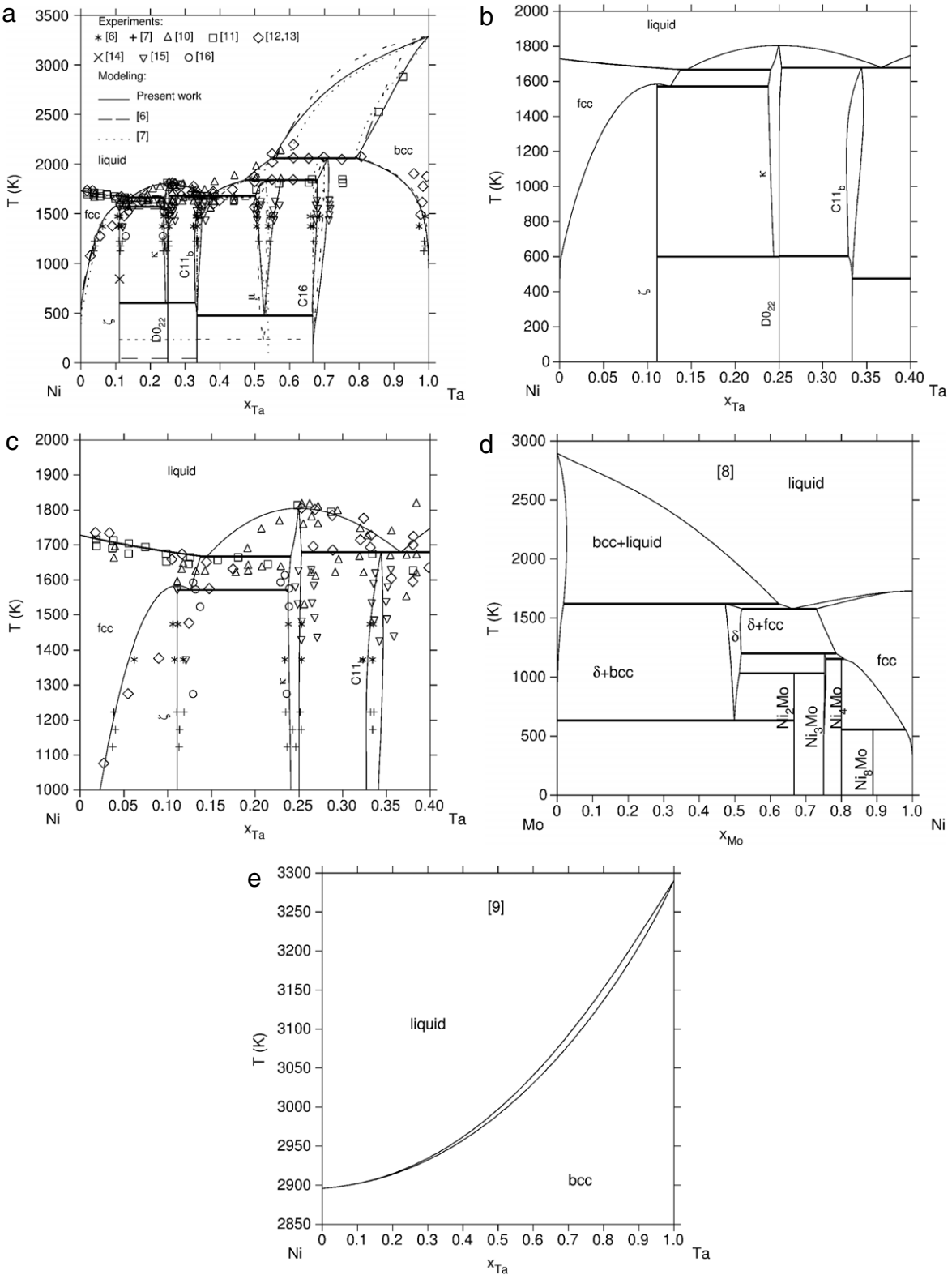


**Fig. 1.** The Ni–Ta phase diagram computed from the current model (a) shown over the full range of composition, compared with previous models and reported experimental data and shown over the Ni-rich portion of the binary range, without (b) and with (c) relevant experimental data. The Ni–Mo and Mo–Ta phase diagram plotted in (d) and (e) respectively.

described by incorporating the first-principles calculations into a general CALPHAD [17,18] approach. The evaluation starts with the binary Ni–Ta system, for which the thermodynamic parameters are evaluated with the first-principles calculated enthalpies of formation and all available experimental data [6,7,10–16,19–22]. Special quasirandom structures (SQS) [23,24] are used to calculate the enthalpies of mixing for the bcc and fcc phases from first-principles, and the results are incorporated into the comprehensive model.

For the ternary Ni–Mo–Ta system, a distinguishing feature of our approach, in comparison with that reported in Ref [9], is