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A summary of the CALPHAD XXXVIII conference

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ABSTRACT

CALPHAD XXXVIII was held in Prague on 17–22 May 2009, organized jointly by Masaryk University and the Institute of Physics of Materials ASCR. There were 149 active participants who presented 63 oral contributions and 87 posters. A "Young Scientists Session" was organized on the evening of 18 May with L. Kaufman and Y.M. Muggianu as invited speakers. The presentations and posters covered a broad spectrum of topics: besides CALPHAD-type thermodynamic modeling and related experimental work, a significant number of contributions on first-principles calculations were presented. The use of the information that can be obtained by first-principles calculations using different techniques, together with traditional thermodynamic and phase diagram data was highlighted in the first sessions. Important advances in the calculation of magnetic properties were also presented. Phonon spectra, all-electron and other vibration/relaxation calculation techniques that include dynamic features and temperature effects were themes of presentations, together with *ab initio* modeling of diffusion processes. Hydrogen-containing systems were discussed and databases for specific problems were presented. During the presentations, several examples of CALPHAD predictions compared with experimental results confirmed the power of the CALPHAD method for industrial applications. A cultural program (including a concert in Aula Carolina, sponsored by the Charles University, and an excursion to the medieval Karlštejn castle) completed the program of the conference.

The abstracts of all oral contributions and titles of posters are also listed in the present Summary.

1. Oral presentations

1.1. *Ab initio* modeling

Thermodynamics of actinide alloys — Results and challenges

P.E.A. Turchi, A.I. Landa, P. Söderlind, L. Kaufman

The prediction of phase stability trends and phase diagrams of multi-component complex alloys is undoubtedly the Holy Grail of alloy physics and materials properties simulation, and this is particularly true for actinide-based materials. On the one hand, it was recently shown that first-principles results of alloy energetics and phase diagrams could advantageously supplement phenomenological modeling of alloy thermodynamics although there are limitations in terms of structures and number of alloy components [1]. On the other hand, CALPHAD is successful in modeling complex materials but the accuracy of the output obviously depends on the quality of the thermodynamic database on which this phenomenological approach relies [2]. Several classes of applications will be discussed after a brief critical review of the quantum-mechanical-based approaches that are available to interface with CALPHAD modeling, and of the challenges faced by *ab initio* formalism to describe f-electron systems. First, we show that enough experimental information for U–Zr is available to perform an accurate phase diagram assessment with a CALPHAD approach, and to test the validity of an *ab initio* approach to reproduce important features of the phase diagram and gain knowledge on phase stability, especially regarding the co-existence of the bcc (γ) and C32 (δ) phases [3,4]. Second, with limited phase diagram information, we show that the phase diagram of Am–Pu can be assessed with a CALPHAD approach, and identify specific *ab initio* calculations [5,6] and experimental data that would clearly validate one of the two proposed phase diagrams. Third, with very limited information on the location of the melting line, we show that the phase diagrams of Pu–X (X = Ta, V) can be assessed with a CALPHAD approach, and show that *ab initio* results on the location of the bcc miscibility gap would confirm the phenomenological results. Finally, for other systems such Am–X (X = U, Np, Cm), no results are available, and since experiments are difficult and costly, an *ab initio* approach is the only viable route to guide the selection of critical experiments for validation purposes.

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Modeling the Fe–Cr phase diagram: The first-principles magnetic cluster expansion formalism versus CALPHAD data analysis

M.Y. Lavrentiev, D. Nguyen-Manh, S.L. Dudarev

Developing predictive models for ferritic/martensitic steels exhibiting higher resistance to irradiation than other steels represents one of the fundamental challenges for multi-phase and multi-scale fusion materials modeling. In the case of binary FeCr alloys, where radiation damage effects are similar to those occurring in ferritic steels, first-principles spin-polarized electronic structure calculations have recently provided a fundamental explanation for the negative-mixing-enthalpy anomaly characterizing the alloy in the 0%–10% Cr concentration range, for example the formation of compounds not predicted by CALPHAD [1]. To understand the thermodynamic and magnetic properties of FeCr alloys, a new magnetic cluster expansion (MCE) formalism [2] was proposed and developed as means for *ab initio* based modeling the α–γ and γ–δ phase transitions in the finite temperature domain of the Fe–Cr phase diagram. Benchmarking calculations for pure iron show that the predicted Curie temperature T_c and the $T_{\alpha\gamma}$ and $T_{\gamma\delta}$ transition temperatures agree well with experimental data, a genuinely significant advance given the exceedingly small Gibbs free energy differences between the bcc and fcc phases. Extending our MCE-based investigation to the Fe-rich region in Fe–Cr alloys, we show that the Curie temperature of the alloy is maximal in the range of small Cr concentrations, resulting from anti-ferromagnetic ordering of moments of Cr atoms with respect to the ferromagnetically ordered environment of Fe atoms. This prediction is in agreement with experimental observations and with the CALPHAD data analysis [3]. We also discuss the γ-loop formation and the role of vibrational contribution to the free energy, driving magnetic phase transformations in Fe–Cr alloys.

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Lattice relaxation effects on the phase equilibria investigated by CVM

T. Mohri

First-principles phase diagram calculations have been attracting broad attention. One of the deficiencies of CVM-based first-principles calculations, however, is the fact that the order–disorder transition temperature is overestimated due to the neglect of local lattice relaxation effects. In order to circumvent such an inconvenience, two schemes have been developed. One is to introduce lattice thermal vibration effects into the free energy formula, and the other is to explicitly consider the local relaxation by an improved entropy formula termed Continuous Displacement CVM (CDCVM). In the present study, we compare the results of two kinds of calculations on a two-dimensional square lattice. One is to introduce the lattice vibration effects within Debye–Gruneisen approximation and the other is CDCVM. It has been pointed out that the lattice vibration effects reduce the transition temperature through the lattice softening at elevated temperatures which is manifested by the reduction of the curvature of a binding energy curve. However, we propose that an opposite case may take place when the Debye temperature of an ordered phase is lower than that of the constituent pure phases. CDCVM, on the other hand, always results in the reduction of the transition temperature.

1.2. Ab initio and atomistic modeling

Stability domain of the intermetallic phases in the Ga–Ti system

C. Colinet, J.-C. Tedenac

The total energies of intermetallic compounds in the Ga–Ti system have been calculated using the Vienna Ab Initio package [1,2] making use of the projector augmented waves technique [3,4] in the generalized gradient approximation [5]. In the PAW potentials, the 3d and 4s orbitals as well as the semicore 3p orbitals are treated as valence orbitals for Ti, while 3d, 4s and 4p orbitals are used as valence orbitals for Ga. The calculations have been performed for the experimentally observed compounds [6,7] at their ideal stoichiometry. The calculated formation enthalpy of the hexagonal $B8_2$–$GaTi_2$ compound is in excellent agreement with the value obtained by direct reaction calorimetry [8]. The composition dependence of the enthalpies of formation is slightly asymmetric, the values of the enthalpies of formation being slightly more negative in the Ga-rich side. The calculated zero-temperature lattice parameters agree well with those obtained experimentally at ambient temperature. Vacancy and antisite defect formation energies in $D0_{19}$–$GaTi_3$, $B8_2$–$GaTi_2$, filled $D8_8$–Ga_4Ti_5, and $L1_0$–GaTi have been calculated. Based on statistical-thermodynamic models [9–11], the defect concentrations have been calculated as function of temperature and deviation from stoichiometry in each of the phases. The Gibbs energy as well as the Ga and Ti chemical potentials has been obtained as a function of composition for various temperatures, allowing us to discuss the equilibrium between the intermetallic phases and to explain their domains of off-stoichiometry. Relationships between *ab initio*, experiment and CALPHAD assessment will be discussed.

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An energetic study of transition metal silicides by DFT

G. Shao

Transition metal silicide-based refractory composite alloys have been extensively studied due to their potential for applications as the next-generation turbine airfoil materials, as their operating temperatures are significantly higher than those of advanced Ni-based superalloys. Most research work has been directed towards studying multi-component alloying in order to develop alloys of a good balance of creep resistance, fracture toughness, oxidation resistance, and room-temperature ductility. Refractory composite alloys based on transition metal (M) silicides are mainly