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Editorial

Recently, [2007Tur] presented a comprehensive review on the use of ab initio methods in calculating the thermodynamic properties of solids. This excellent paper is essential reading, even for those not involved directly with theoretical calculations. It is well known that the basic Schrödinger wave equation is not amenable to solution for a many body problem such as a crystal containing $\sim 10^{23}$ atoms. [2007Tur] discusses the various approximations and theories, which reformulate the equation as a one-electron problem, which is simpler to solve. The range of properties that can be obtained from ab initio calculations is very impressive: crystal stability, structural energy differences, lattice parameters, elastic properties, magnetic properties, alloying effects like enthalpy of mixing, enthalpy of transformation, and ordering energy, surface and interfacial energies, and also properties relevant to kinetic processes such as the enthalpy of formation and migration of vacancies in elemental and alloy crystals. The most immediate application of the ab initio results on the energetics of known and hypothetical compounds is as direct input data selected for CALPHAD optimization. This ensures that acceptable values result after optimization. Simple binary phase diagrams can also be calculated directly by conversion of the ab initio results to the Redlich-Kister format. This will be particularly useful in cases, where no binary experimental data exist for use in the optimization of higher order systems.

On the experimental front, two recent papers on multicomponent phase diagrams are worth mentioning. [2008Yan] made a detailed experimental study of the *C*14 Laves phase and its equilibrium with the adjoining phases in the Al-Fe-Ni-Ti quaternary system. At high temperatures, the *C*14 Laves phase originating along the Ti-Fe edge of the composition tetrahedron forms a continuous solid solution with the *C*14 phase that lies as a ternary phase on the Al-Ni-Ti face. At 900 °C, a miscibility gap arises in this phase. Through detailed experimental investigation, [2008Yan] characterized the complex shape of the two *C*14 regions at 900 °C. Figure 1 is a schematic projection of the *C*14 phase that originates on the Ti-Fe edge. The line marked 15 is its binary homogeneity range. It extends on both sides on the Ti-Fe-Al and Ti-Fe-Ni faces and also into the quaternary region. Plane 123451 lies on the Ti-Fe-Al face. Plane 567815 lies on the Ti-Fe-Ni face. These planes are in contact with two-phase regions in the quaternary space. The lines joining two-phase regions and the corner points *A, B, C*, and *D* represent three- and four-phase equilibria. [2008Yan] presented projections of the *C*14 phase along the Ni-Fe and Al-Fe directions, which are quantitative data based on the experimental results. [2008Yan] presented a similar description of the Laves phase that originates on the Al-Ni-Ti face and extends into the quaternary region by Fe substitution. Also, a listing of the measured compositions of the co-existing phases in four-phase equilibria was presented for 11 tie-tetrahedra. Data such as these are vital to understanding the phase relationships in this technologically-important quaternary system. Currently, such data cannot be generated by theoretical calculations.

Another innovative idea in designing key experiments based on preliminary thermodynamic calculations was reported by [2009Jan]. Understanding the phase equilibria of the Al-Mg-Ca-Sr-Mn quinary system is essential for improving the mechanical properties of Al-Mg alloys which have Ca, Sr, and Mn as additives. [2009Jan] performed preliminary calculations using ternary descriptions to identify the quinary invariant reactions. The centroid composition of an invariant reaction, which *fully* converts the reacting phases to the product phases and thereby yields the *maximum* heat effect, is also found by calculation. Experimental alloys are then designed to correspond to the calculated centroid composition. The thermal arrests found by DTA are matched with the calculated data. The temperatures of such reactions are among the most decisive input data for the final optimization.

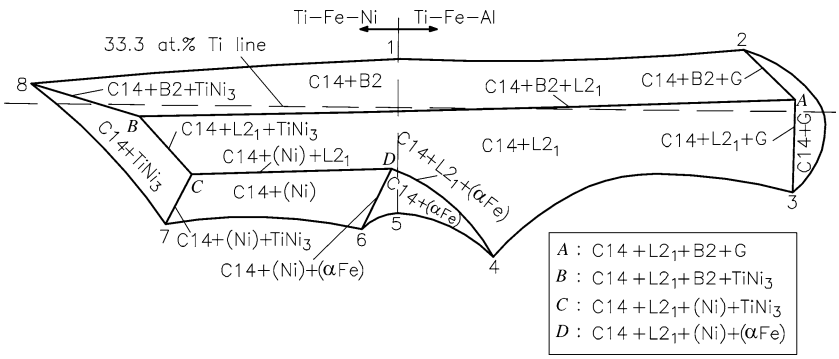

Fig. 1 Schematic projection of the *C*14 Lave phase region at 900 °C in the Al-Fe-Ni-Ti system [2008Yan]

In conclusion, ab initio calculations have made spectacular progress in recent decades and will continue to do so in future. The theoretical results will be used increasingly in conjunction with experimental data for the calculation of complex phase equilibria. However, we are not in a position presently to design multicomponent industrial alloys on the basis of theoretical calculations alone. It is a matter of great concern that experimental work is becoming sparse. It is imperative that good and innovative experimental projects get all-round encouragement and support, till the ultimate goal of ab initio designing of alloys for industrial applications is in sight.

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