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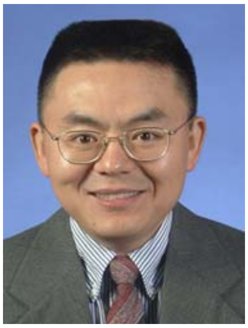
Editorial



In this editorial, I would like to touch upon three topics, namely the increasing interplay of modeling and experiments, phase diagrams for multifunctional materials, and the intermediate temperature phase diagrams.

Interplay of Modeling and Experiment

A very positive and important trend in phase diagram determination is the ever-increasing interplay of modeling and experiment. Chang and his students illustrated the application of CALPHAD modeling in efficient determination of phase diagrams (Ref 1, 2). By putting together an approximate thermodynamic description based on the constituent binary systems, an approximate ternary or high order phase diagram can be calculated with assumptions that the solubilities of the third or higher order elements in the binary intermetallics are negligible and there are no ternary or higher order compounds. A few selected alloys can be strategically selected to provide key experimental information to maximize the importance of these data points in improving the thermodynamic parameters of the system (Ref 1, 2). The key experiments are designed to find out whether ternary and higher order compounds exist and to examine the solubility of the third or higher order elements in binary or ternary intermetallics. Such information is used as input for the next iteration of thermodynamic modeling. I think this approach will become more widely used in the future. This methodology has the advantage of higher efficiency in obtaining a thermodynamic description of a multicomponent system with limited alloys. The users are cautioned that only the composition space that has experimental data are considered to be validated—other composition space still needs to be validated in the future for reliable prediction.

CALPHAD modeling has also helped to reveal/predict phase diagram features that otherwise would be hard to be aware of or could be easily missed during experimental investigations. A defining case is the magnetic-transition-induced miscibility gap (so-called Nishizawa horn), and an example is shown in the Co-V binary system. Such a miscibility gap was predicted from thermodynamic modeling long before definite experimental confirmation was made (Ref 3). Without thermodynamic modeling, it would have been hard to imagine such a miscibility gap and to understand the phase diagram features and materials behavior around such a region.

The coupling of theoretical modeling and experimental investigations has also been very important in understanding complex phase diagram features involving both ordering and magnetic transitions. The Fe-Si example clearly illustrates this point (Ref 4). Without the modeling insight, it would have been difficult to pinpoint the phase diagram features.

Phase Diagrams of Multifunctional Materials

Multifunctional materials such as magnetic, magnetocaloric, magnetoelastic, spintronic, thermoelectric, piezoelectric, and dielectric materials are becoming an increasingly important part of our daily life for sensing, actuation, computing, energy conversion, communication, and so on. These materials take advantage of their unique physical, chemical, and structural properties and very often involve complex interlays of structural, magnetic, and electronic transitions with external or induced stress field, magnetic field, electrical field, and thermal field. It is not surprising that their related phase diagrams are often very complex. One can take a look at the phase diagrams of $LaMnO_3$-$SrMnO_3$ and $LaMnO_3$-$CaMnO_3$ to appreciate the complexity of such systems (Ref 5, 6). Since such systems are becoming increasingly important to our modern society, the phase diagram community needs to position itself to face the challenges of measuring such complex systems.

Many multifunctional materials are used in the thin film format in real applications. In this case, a non-equilibrium state and/or constrained state very often exist, and the substrate on which the film is deposited can have a very strong effect on the phase formation in the film. This opens new opportunities for fine-tuning the structure-property relationships of thin-film functional materials; at the same time it complicates the phase diagram studies. One needs to consider the effects of the substrate, especially the coherence strain. One example is the work of Li et al. (Ref 7) on the $PbTiO_3$-$PbZrO_3$ system. The phase diagrams are significantly different under none, positive, or negative strain constraint conditions relative to the substrate. A more detailed "phase diagram" under different substrate strain conditions for the $PbZr_{0.53}Ti_{0.47}O_3$ composition was constructed by Choudhury et al. (Ref 8). Phase field modeling greatly helps to define the overall topology of these phase diagrams (These serve as more examples of the importance of the interlay of theory and experiment).

Intermediate Temperature Phase Diagrams

There have been sporadic reports of *room temperature* phase diagrams for high melting point elements. The practice started several decades ago [e.g., (Ref 9) for Co-Fe-W], but unfortunately it still persists nowadays [e.g., (Ref 10) for Co-La-Ti]. Individual alloys were usually melted and homogenized at a very high temperature, which is a good practice. They were subsequently step-wise heat treated to, or simply heat treated at, an intermediate temperature, e.g., 650-800 °C for 45 days for the Co-La-Ti alloys, and then slowly furnace cooled to room temperature. Then XRD or other techniques were used to identify the phases in the alloys to establish the phase equilibria. Phase diagrams determined in this way should not be called "room temperature phase diagrams"; instead, they should be regarded as phase diagrams at the temperatures of the final heat treatments. In addition, it is always a better practice to quench the samples from the temperatures of final heat treatments to room temperature to avoid the complication of further phase transformations during the slow furnace cooling. All the "room temperature phase diagrams" reported in the literature for systems containing elements with melting points higher than 1000 °C should be regarded with suspicion and should actually be considered as phase diagrams at the temperatures of the respective final heat treatments. Slow diffusion and phase transformation kinetics would never allow alloys made up of high melting point elements (e.g., Co-Fe-W) to reach equilibrium at ambient temperature. For Co-Fe-W alloys, even equilibria at 500 °C are already extremely difficult to achieve in bulk samples, not even mentioning at ambient temperature.

There may be a way to reach intermediate temperature phase equilibria for high melting point alloys. The formation of nano-scale intermetallic compounds and solid solutions at ambient temperature using the so-called "metallurgy in a beaker" (Ref 11, 12) methodology is very encouraging. This method can be tracked back to at least 45 years ago (Ref 13) when Kulifay synthesized 28 compounds including intermetallics, antimonides, arsenides, tellurides, and a few ternaries and non-stoichiometric compounds. His method consists of the reduction of aqueous solutions containing the elements by addition to aqueous hydrazine or hypophosphorous acid solutions at 100 °C and atmospheric pressure. The recent work of Schaak et al. (Ref 11, 12) demonstrated similar synthesis of several high melting-point binary and ternary intermetallic compounds such as $AuCu_3$, $FePt_3$ and CoPt as well as solid solutions such as Ni-Pt. They synthesized the compounds and alloys at room temperature in a solution and then crystallized them at 300 °C. It is remarkable to be able to form such high melting-point *equilibrium* intermetallics and solid solutions at 300 °C. A benchmark study using this methodology for low-temperature phase diagram determinations will be very valuable to see whether wider composition spaces can be explored. The methodology may provide critical data for intermediate temperature phase stability for CALPHAD modeling.

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