

Editorial



2008 was my 20th year as editor of this journal. During those 20 years, there has been a great deal of development and change. Initially, the journal was published with the title *Bulletin of Alloy Phase Diagrams* and, together with the *Indian Journal of Alloy Phase Diagrams*, it published the critically compiled summary of published information on phase diagrams together with crystallographic and thermodynamic information pertinent thereto. As time progressed and the compilation program was completed for the more important systems, the emphasis shifted and resulted in the merger of the two journals to become the *Journal of Phase Equilibria*, which published papers that, for the most part, were concerned with the utilization of the compiled material. While a large fraction of this utilization involved Calphad-type assessments of phase equilibria, there were many other diverse utilizations. An example is the series of papers authored by Nai-Yong Tang concerning the thermodynamic and phase relationships in galvanizing baths which control the quality of the galvanized product. The most recent of this series of papers was published in 2008, Vol. 29, pp 337-344.

Certainly during these last 20 years the Calphad method for calculating phase equilibria has matured and flowered. Calculations for ternary systems such as the one for the Nb-Ni-Y system by N. Mattern et al., 2008, **29**(2), pp 141-155, are frequently done groups scattered across the world, and calculations for quaternary systems such as the Ti-Fe-Ni-Al system by Xinlin Yan et al., 2008, **29**(5), pp 414-428 are not uncommon. However, for the ternary and quaternary systems cited, the authors in both cases made supplementary experimental measurements to generate data needed for their calculations, and that makes their work above average. Assessment of quinary and higher order systems have been done, but their interpretation with validation of the calculated results is a bit more difficult; however, progress is being made. Two papers generated by the group at Clausthal, authors A. Janz et al., are included in this issue. The second of these two involves the calculation of the phase equilibria for the quinary Mg-Al-Ca-Sr-Mn system. The report proposes and experimentally tests a relatively straightforward procedure for verifying the validity of the predictions of the quinary equilibria. This represents progress.

Diffusion was added to the title of the journal when it was recognized that many alloys are utilized in metastable states, and diffusion is one of the factors that controls the achievement of such a metastable state. Diffusional information has been successfully treated via the Calphad approach, and we are now seeing diffusion papers being regularly published in the journal.

In looking toward the future, I foresee expansion of the journal's coverage into new areas. As an example, I found an intriguing paper in the first issue of JPED 2008 Vol. **29**, entitled *Thermodynamic Study of Liquid, Crystalline, and Quasi-Crystalline Al-Mn Phases*, by A.I. Zaitsev et al., **29**(1), pp 20-29. Quasi-crystals have five-fold symmetry, but do not exhibit translational repetition as do normal crystals. However, they have all atoms on defined sites, so they do conform to Boltzmann's definition to conform with the Third Law, and they can contain mismatches which are analogous to dislocations albeit a bit more complex. There is currently a great deal of interest in these materials, and I am glad to see that papers like this take us into a new and developing area. This paper followed a well planned set of experiments, and hopefully more papers of this type will appear in the future to open other new research areas. Research such as this will take us further into the unknown, and once the unknown becomes known, the knowledge can frequently be put to practical use to suit mankind's needs.

I can think of several areas which might be constructively explored. For example, let us take isotopic abundance and the Third Law and ask the question, "Are we always justified in neglecting isotopic ratios in computing configurational entropy?" Certainly in most cases the neglect is unquestionably valid, because the isotopic ratio is unchanged by many normal interactions. However, in the development of nuclear power, it was found that isotopes could be separated by diffusional processes. If one looks at the hydrogen isotopes, (hydrogen, deuterium, and tritium), one finds that the V-H system is significantly different from the V-D and V-T systems. This can be rationalized as being due to vibrational entropy differences, but if the vibrational amplitudes of the three hydrogen isotopes are significantly different, may the difference not significantly affect the jump frequencies of the isotopic species to effect isotopic redistribution during diffusion?

Another area in need of exploration is the surface energy due to grain boundaries, and the effect of this energy on the equilibrium state of a material. With the increasing importance of nanotechnology, this seems to be a significant area to explore. The approach could well start by examining the extensive data that were generated during the development of the understanding of point, line, and planar imperfections during the third quarter of the 20th century. The geometry of the grains of materials was extensively studied by Fred Rhines and his students. The results of their studies should allow a reasonable evaluation of total surface area per mole of material as a function of grain size. The work of others has shown that relative energies of grain boundaries could be determined from the surface tension balance among three grains at their junction; the determination involves the angles between the grain boundaries. This requires an accurate determination of the orientation of the three conjoining grains, and the interface between any two adjacent grains will have a surface energy, provided the atoms on the two sides of the interface do not meet coherently. If the atoms are coherent, there is no boundary, and this provides a zero point for grain boundary energy.

However, if there is only a slight tilt angle or slight twist angle between the two sides of the boundary, an orderly array of dislocations is produced, edge with tilt and screw with twist. If both very slight tilt and very slight twist are combined, the dislocation array is a mixture of edge and screw dislocations. As the slight angles of tilt and/or twist incrementally increase, experiments have shown that the interface energies increase very rapidly and rise to a plateau at relatively small angles of mismatch. Thus the large majority of interface area in a polycrystalline material has a constant energy per unit area. Thus, if the total area of interface can be reasonably estimated from the work of Rhines, and the energy per unit area can be approximated as constant, the remaining task is to evaluate the value of the constant. This task will involve some precision calorimetry on materials of interest with various grain sizes. The results of such measurements could be extrapolated downward in grain size (increasing interface area) to determine the grain size at which the interface energy becomes an important contribution to the enthalpy and thus important to defining phase equilibria. Continuing the extrapolation to still smaller grain sizes may reveal a point beyond which grain boundary energies may dominate the definition of phase equilibria.

Man is blessed with an avid curiosity, and the foregoing discussion illustrates that my curiosity is still active. What I hope to see in the future is that a normal flow of competently crafted papers will continue, but that this flow is occasionally spiced with an additional submission of a paper that explores a new field or introduces a new idea into a well explored field.

J. F. (Jack) Smith
Editor
Journal of Phase Equilibria and Diffusion