doi:10.1017/S143192761300665X
Microsc. Microanal. 19 (Suppl 2), 2013

Tracing the Solute Distribution and Effects in Materials by Combining Atom Probe Tomography and Atomistic Simulation: Summary of Recent Results

Anna V. Ceguerra[1, 2], Xiang-Yuan Cui[1, 2], and Simon P. Ringer[1, 2]

[1.] Australian Centre for Microscopy & Microanalysis, The University of Sydney, NSW 2006, Australia
[2.] School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, Australia

Chemical modification by doping or alloying solute atoms into solid solutions is widely used for tuning the properties of both structural and functional materials. Precise determinations of the spatial distribution of the solute atoms is essential for understanding the structure-property relationships and material design.

Three-dimensional atom probe tomography (APT) is a powerful microscopy technique that possesses the unique capacity to reveal both composition and crystallographic structure at the atomic scale[1]. However, like all microscopy techniques, APT has limitations in the form of a finite detector efficiency (37-57%), and tomographic reconstruction issues including anisotropy. In addition, there are occasional limitations arising from the overlap of mass-to-charge peaks.

Such spatial limitations can be partially overcome by atomistic simulation by the so-called Generalised Multicomponent Short-Range Order (GM-SRO)[2] developed in 2010. The equations for the GM-SRO parameters were derived to fill the need for describing multicomponent interactions between sets of elements. The theory was applied to measure GM-SRO from the real-space chemical information obtained in atom probe data, and a Monte Carlo method was adapted to generate 100% complete data with the requisite chemical complexity[3]. This is in contrast to attempting to measure the n-component pair-wise SRO from diffraction patterns, which are both notoriously difficult to measure and difficult to interpret[4]. APT is combined with Monte Carlo and first principles density functional theory (DFT) simulations for the purposes of exploring the above-mentioned structure property relationships (Figure 1).

APT and DFT are two atomic-scale techniques which are intrinsically complementary to each other. Firstly, as a self-consistent electronic structure method, the DFT results heavily depend on the starting structural model. We have adapted the APT data to provide the starting geometrical structure for DFT calculations. Via analysis of the many-body interactions, DFT provides valuable insights into the energetic origins of the effects of dopants in affecting material properties. Here we briefly highlight three recently completed projects.

Case 1: Co doped ZnO grown on different substrates[5]. In contrast of a pure DFT predication that Co dopants prefer to form embedded clusters in ZnO matrix[6], our APT study revealed that such proposed Co clustering can be safely ruled out in the samples grown by MBE on a ZnO substrate, thus cannot be responsible for the controversial origin of room-temperature ferromagnetism. Instead, our DFT simulation disclosed that the unintentional H contamination can be attracted to Co dopants and play a key role in mediating ferromagnetism. Such a mechanism was subsequently confirmed experimentally by magnetic measurements on hydrogen-treated ZnO:Co[5].

Case 2. Mg site occupancy in an Al-Mg-Li alloy[7]. By combining APT and DFT simulation, we conclusively showed that Mg partitions to site normally occupied by Li in the δ' Al_3(Li, Mg) precipitate phase. DFT calculations provide direct insights into the energetic origins of our atomic

resolution APT observations. First, it is energetically favourable for Mg partitions to the Li sites. Secondly, between the matrix and the precipitates there is a small difference in the Mg substitutional formation energy. This is in line with the small difference in the amount of Mg detected by APT between the matrix and the precipitates.

Case 3. Effects of K-clustering in $BaFe_2As_2$ superconductors[8]. The Coexistence and competition of superconductivity and magnetism has been a recurring theme in the study of unconventional superconducting materials. In the new Fe-based superconductors, the local fluctuations in the distribution of dopant atoms are thought to be responsible for the nanoscale electronic disorder or phase separation in pnictide superconductors. Indeed, APT enabled the first direct observations of dopant species clustering in a K-doped 122-phase pnictide. DFT calculations suggest the coexistence of static magnetism and superconductivity on a lattice parameter length scale over a wide range of dopant concentrations. Collectively, our results provide evidence for a mixed scenario of phase coexistence and phase separation, depending on local dopant atom distributions.

Such advances in the field of nanoscale characterisation and simulation allow us to understand and interpret images at atomic scale. This opens the door to rational design of materials from the bottom-up, where nanotechnology is only starting to realise its full potential today.

References

[1] B. Gault, et al., Mater. Today **15**, (2012) p 378.
[2] A. V. Ceguerra, et al., Physical Review B **82**, (2010) p 132201.
[3] A. V. Ceguerra, et al., Acta Crystallogr. Sect. A **68**, (2012) p 547.
[4] D. de, Journal of Applied Crystallography **4**, (1971) p 15.
[5] L. Li, et al., Physical Review B **85**, (2012) p 174430.
[6] D. Iusan, et al., Physical Review B **79**, (2009) p 125202.
[7] B. Gault, et al., Scr. Mater. **66**, (2012) p 903.
[8] W. K. Yeoh, et al., Phys. Rev. Lett. **106**, (2011) p 247002.

https://doi.org/10.1017/S143192761300665X Published online by Cambridge University Press