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Review

Materials Science

High-throughput experimental tools for the materials genome initiative

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Abstract The materials innovation infrastructure in the materials genome initiative (MGI) consists of three major components: computational tools, experimental tools, and digital data. This article will review experimental tools for high-throughput, high spatial resolution measurements of several materials properties such as elastic modulus, thermal conductivity, specific heat capacity, and thermal expansion. Application of these tools on composition-varying samples such as diffusion multiples can be used to quickly and efficiently obtain composition–phase–structure–property relationships for materials property database establishment. They can also be used in conjunction with theoretical modeling to find and explain unusual effects to improve the predictability of models. More micron scale resolution experimental tools are in development. These high-throughput tools will be an essential part of MGI.

Keywords High-throughput experiment · Diffusion multiples · Micron-scale analysis · Materials property · Database

1 Introduction

U.S. President Barack Obama introduced the Materials Genome Initiative (MGI) in June 2011 during his speech at the Carnegie-Mellon University announcing the Advanced Manufacturing Partnership. He clearly defined the goal of MGI as "to discover, develop, manufacture, and deploy advanced materials at twice the speed than is possible today". The pertinent whitepaper "Materials Genome Initiative for Global Competitiveness" released by the White House Office of Science and Technology Policy outlines a Materials Innovation Infrastructure (MII) as consisting of three platforms: computational tools, experimental tools and digital data. This article will review some of the important experimental tools that will significantly accelerate the establishment of composition–phase–property relationships for rapid establishment of digital databases and for validation of theoretical models.

High-throughput experimental tools and bioinformatics are two key enablers for the "Human Genome Project" [1], similarly high-throughput experimental tools and materials informatics will be essential parts of MGI. About 15 years ago, the author developed a diffusion-multiple approach for rapid determination of phase diagrams and diffusion coefficients [2–5]. He had a very simple idea of rapid establishment of composition–phase–property relationships by performing micron-scale localized property measurements on composition gradients/variations of solid solutions and compounds created in diffusion multiples through thermal interdiffusion. To enable such measurements, a new set of experimental tools for property measurements at micron-scale resolution must be developed. Over the past several years, he and his collaborators have developed femtosecond laser based thermoreflectance tools to accurately measure several physical properties such as thermal conductivity [6–8], coefficient of thermal expansion (CTE) [9], and specific heat capacity (C_P) [10] in micron-scale spatial resolution. These property measurement tools together with diffusion multiples or combinatorial

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materials libraries [11] can accelerate the property measurements by orders of magnitude, thus enabling rapid establishment of composition–structure–property relationships to accelerate materials research and development. Such research will also provide vast amounts of experimental results for the establishment and validation of predictive theories linking compositions to phases to structures to properties. The systematic measurements/mapping on continuous composition gradients can also effectively discover unusual effects. Detailed analysis of samples locally extracted using focused ion beam (FIB) from regions where the unusual effects are observed during property mapping together with theoretical analysis can effectively establish new theories to explain the observed unusual effects, thus improving the accuracy and reliability of property predictions.

Many different kinds of experimental tools have been employed by the materials research community to study compositions, crystal structures, defects, microstructures, and various properties. This article will not be able to cover all the tools in detail due to the space constraint. A brief review will be given on high-throughput experimental tools for effective establishment of composition–phase–property relationships and for validation of theoretical models. The systematic nature of these tools in materials research and discovery will be shown to demonstrate the effectiveness in revealing and studying unusual effects, which will be very important for the improvement of models, especially for inclusion of unusual effects into the models. After this introduction, the diffusion-multiple approach will be briefly introduced. The method can be used to effectively determine phase diagrams which are "maps" that the materials scientists often use during alloy and process design/development. Binary and ternary phase diagrams are also essential input to the calculation of phase diagram (CALPHAD) modeling [12–15] which is one of the most widely used tools in alloy design. Effective extraction of diffusion coefficients from many binary diffusion couples inside diffusion multiples will be very significant for the establishment of diffusivity/mobility databases and for simulating diffusion-driven processes in materials. Ultrafast laser based measurement techniques will then be introduced to show their effectiveness in establishing composition and phase dependent thermal conductivity, thermal expansion, and specific heat capacity. These tools can also be used to study ordering, site preference/elemental substitution, and solid solution effects. Recent development in digital three-dimensional (3D) microstructure characterization and their implication in understanding complex mechanisms in materials will be briefly reviewed. Efforts on localized measurements of mechanical properties will also be discussed. Model-driven experimentation is another very important research direction; examples will be used to show its effectiveness in model validation. Integration of experimental tools with computational tools and digital databases will be discussed before the final summary.

2 The diffusion-multiple approach

The idea of the diffusion-multiple approach [2–5, 16] can be illustrated with a simple Co–Cr diffusion couple shown in Fig. 1. After a piece of Co and a piece of Cr were placed together and annealed at 1,100 °C for 1,000 h, interdiffusion took place and an intermetallic compound, σ phase, formed between the face centered cubic (fcc) and body centered cubic (bcc) solid solutions (Fig. 1b). Composition profiles across the diffusion zone obtained using electron probe microanalysis (EPMA) are shown in Fig. 1c. The local equilibrium at the fcc/σ and σ/bcc interfaces gave the equilibrium tie-lines (big circles in Fig. 1a). This is the basis for using diffusion couples for phase diagram determination and has been used successfully for several decades.

It can be seen that interdiffusion has created a complete series of compositions at the temperature of annealing (1,100 °C) for all the single-phase regions in the Co–Cr phase diagram: from 0 at.% to ~39 at. % Cr in the Co-based fcc phase, from ~54 at.% to ~66 at.% Cr for the σ phase, and from ~78 at.% to 100 at.% Cr for the Cr-based bcc phase. The diffusion-multiple idea is basically to take advantage of the compositional variations and the phase formation in diffusion experiments to perform localized property measurements to effectively obtain composition–phase–property relationships. Such measurements require a new set of property measurement tools with a spatial resolution on a micron scale, but they will greatly increase the efficiency of property measurements by reducing the need of making many individual alloys and measuring them one at a time.

To increase efficiency, diffusion multiples were designed to include several diffusion couples and triples to map several binary and ternary phase diagrams from a single sample and also to create large composition variations in both solid solution phases and intermetallic compounds for property measurements [2–5]. A good example is a Ti–Cr–$TiAl_3$–$TiSi_2$ diffusion multiple shown in Fig. 2 [18, 19].

The tri-junction regions (diffusion triples) allow ternary isothermal section phase diagrams to be mapped very effectively. This method is following the pioneer work of Jin [20]. The applicability of the diffusion-multiple approach to the determination of very complex phase diagrams has been demonstrated for many systems [18]. A comparison of the phase diagrams determined using

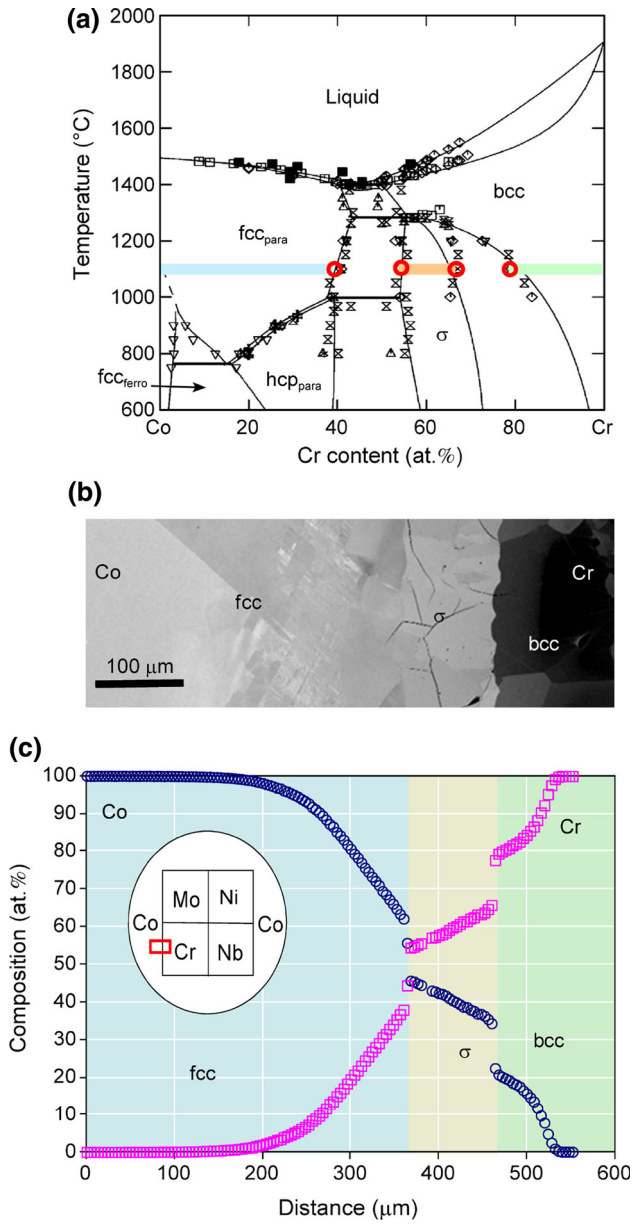

Fig. 1 (Color online) A diffusion couple of Co and Cr annealed at 1,100 °C for 1,000 h showing the formation of phases and complete composition variations of the single phase regions. **a** The Co–Cr binary phase diagram [17]; **b** SEM backscattered electron image showing the phases; **c** composition profiles obtained from EPMA analysis. Copyright 2011, Springer

diffusion multiples and those using equilibrated alloys has been made for both simple and very complex ternary systems [18]. The Ti–Al–Cr example is shown in Fig. 2b in comparison with the results obtained using more than a hundred alloys (Fig. 2c), demonstrating both high efficiency and high reliability of the diffusion-multiple approach. This method will greatly help meet the demands of experimental ternary phase diagrams for establishing multicomponent thermodynamic databases. No reliable multicomponent thermodynamic databases can be established without reliable binary and ternary phase diagram data from experimental measurements.

In addition to effective mapping of phase diagrams, diffusion multiples allow large amounts of diffusion profiles of binary systems to be collected efficiently, which allow composition-dependent diffusivity data to be extracted for the construction of mobility databases for the simulation of precipitation growth and interfacial interactions in materials. New algorithms [21] have been developed to allow automated extraction of diffusion coefficients from multiple-phase binary diffusion profiles such as those shown in Fig. 1c. The result of the Co–Cr binary system at 1,100 °C is shown in Fig. 3.

3 High-throughput measurements of thermal conductivity

As mentioned before, an important feature of diffusion multiples is their ability to create complete single-phase composition ranges of solid solutions and intermetallic compounds of binary and ternary systems [2–5]. In this sense, diffusion multiples serve as an efficient way to synthesize many compositions and compounds in parallel in a single sample, allowing many properties to be mapped as a function of composition, phase and crystal structure. The enabling technology for such property mapping is micron-scale property measurement tools.

An important tool developed in recent years is time-domain thermoreflectance (TDTR) for thermal conductivity measurements using a femtosecond laser in a pump–probe configuration [6–8]. Such measurements can achieve ±8 % accuracy and a spatial resolution of 2–4 microns. In a sense, the technique behaves like a femtosecond laser based scanning microscope and it can collect a 100 grid point by 100 grid point digital thermal conductivity map in 1 h.

For metals and most intermetallic compounds, heat conduction is carried predominantly by free electrons. Therefore, the thermal conductivity of these materials is sensitive to elemental substitution, point defect formation, and ordering; and can be used to study these phenomena. Both elemental substitution and point defect formation decrease the thermal conductivity, since both increase the electron scattering. Ordering in crystals decreases the electron scattering and thus increases the thermal conductivity.

The systematic and effective nature of the thermal conductivity mapping technique is demonstrated in Fig. 4 for thermal conductivity mapping of a Ni–$Ni_{45.5}Al_{54.5}$ diffusion couple [22]. Clearly, the thermal conductivity values obtained from the diffusion couple using localized measurements are in excellent agreement with those

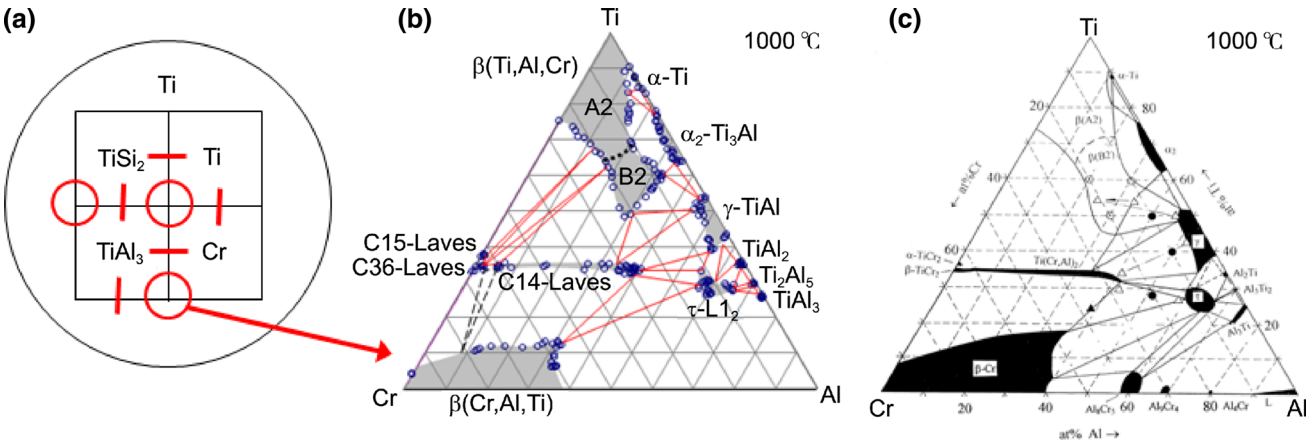

Fig. 2 (Color online) Application of a diffusion-multiple approach to the study of Ti-base phase diagrams. **a** A Ti–Cr–$TiAl_3$–$TiSi_2$ diffusion multiple; **b** the 1,000 °C isothermal section of the Ti–Al–Cr system (Copyright 2004, Springer) obtained from a tri-junction region in the diffusion multiple sample shown in **a**; **c** the isothermal section at the same temperature of the Ti–Al–Cr system based on more than 100 equilibrated alloys [19]. Copyright 1999, Elsevier

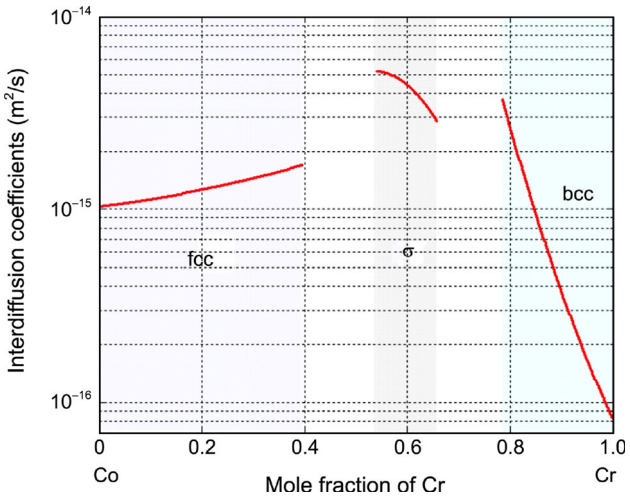

Fig. 3 (Color online) The composition-dependent interdiffusion coefficients of all the phases of the Co–Cr binary system at 1,100 °C extracted from the diffusion profile shown in Fig. 1c [21]

reported by Terada et al. [23, 24] from bulk samples of twenty individually cast alloys. The result definitively shows that accurate thermal conductivity-composition relationship can be established using thermal conductivity mapping on graded compositions in diffusion samples without the need of making many individual alloys. The effects of solid solutioning in the fcc phase, ordering–disorder transition in the Ni_3Al phase and compositional point defect in the β-NiAl phase on thermal conductivity are also clearly shown.

By taking advantage of this new thermal conductivity measurement tool and many diffusion couples in several diffusion multiples, we have now collected more composition-dependent thermal conductivity data than all prior studies combined. Thermal conductivity mapping can be used to study the compositional point defects in solid solutions and intermetallic compounds. It can also be used to study elemental substitution (site preference) as a third element is added to a binary intermetallic compound [22, 25].

4 High-throughput measurements of thermal expansion

Very recently we developed a high spatial resolution technique for localized measurement of the CTE using the same laser system as that for the thermal conductivity measurement [9, 26]. By moving the probe beam a few microns away from the pump beam and examining the deflection of the probe beam by the localized surface bulging as a result of thermal expansion from the heating of the pump laser, we can back out the CTE using a time-domain probe beam deflection (TD-PBD) method. The accuracy can reach ±6 % which is very impressive for localized CTE measurements (Fig. 5b).

One can appreciate the effectiveness of this new measurement technique from a Fe–Ni diffusion couple which was diffusion annealed at 1,100 °C for 1,000 h and then water quenched to ambient temperature. The composition profile from EPMA analysis clearly shows a complete solid solution from pure Fe to pure Ni in about 800 μm distance (Fig. 6a). TD-PBD measurement was performed on the diffusion couple and the results are superimposed onto Fig. 6a. Since the composition at each location is obtained from EPMA, Fig. 6a can be converted to Fig. 6b which shows the composition-dependent CTE of the Fe–Ni binary

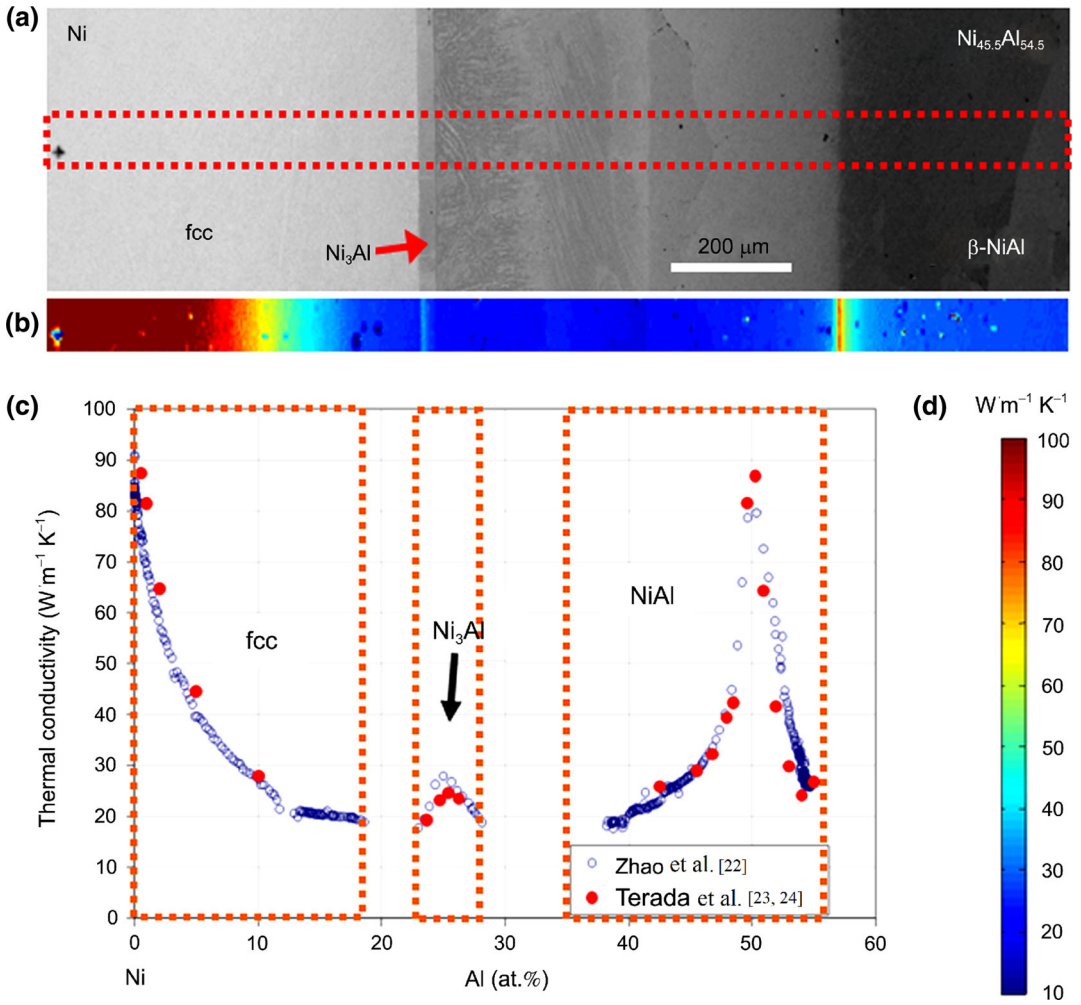

Fig. 4 Thermal conductivity mapping of a Ni–$Ni_{45.5}Al_{54.5}$ diffusion couple [22]. **a** SEM image of the diffusion couple; **b** thermal conductivity map/image of the region enveloped by the *dotted line* in **a**; **c** composition-dependent and phase-dependent thermal conductivity values obtained from the diffusion couple in comparison with those obtained measurements on individual alloys using bulk sample measurements by Terada et al. [23, 24]; **d** color code for the thermal conductivity values in **b**. Copyright 2012, Elsevier

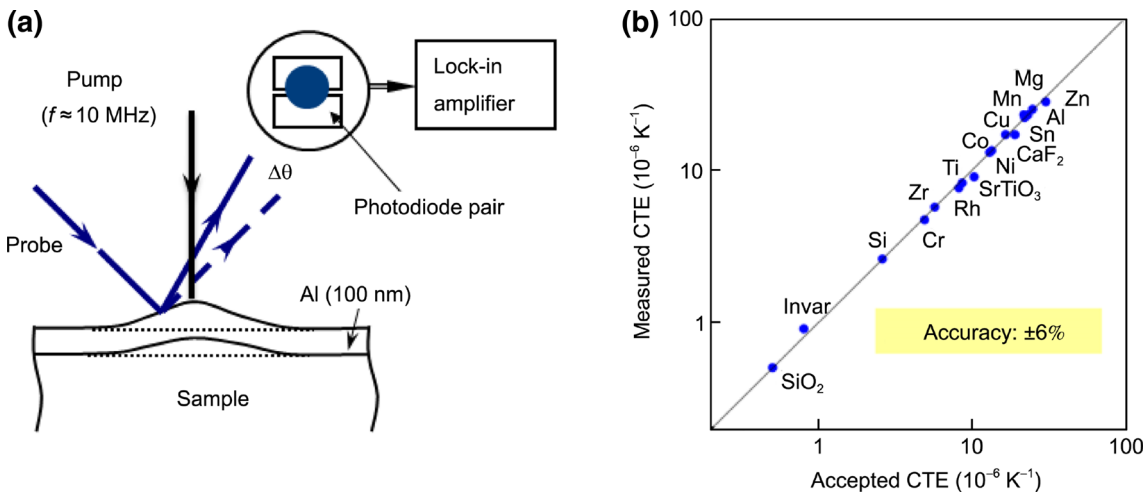

Fig. 5 Localized measurement of CTE using time-domain probe beam deflection. **a** Schematic of the technique; **b** accuracy of the technique showing with a benchmark study [9]. Copyright 2008, American Institute of Physics

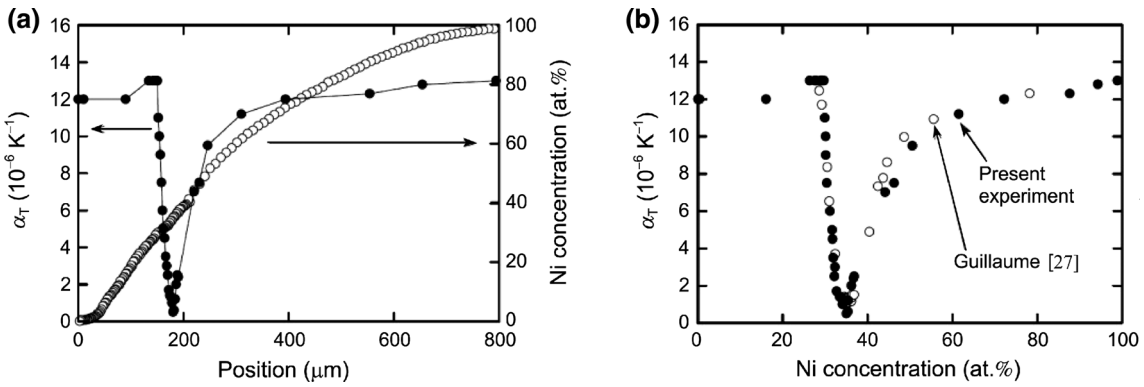

Fig. 6 Localized measurement of CTE (α_T) using time-domain probe beam deflection on an Fe–Ni diffusion couple [12]. **a** EPMA Ni concentration profile (*open circles*) and measured CTE values (*black dots*); **b** composition-dependent CTE measured from TD-PBD (*black dots*) in comparison with results measured from individual alloys (*open circles*) reported by Guillaume in his 1920 Nobel-prize winning paper [27]. Copyright 2008, American Institute of Physics

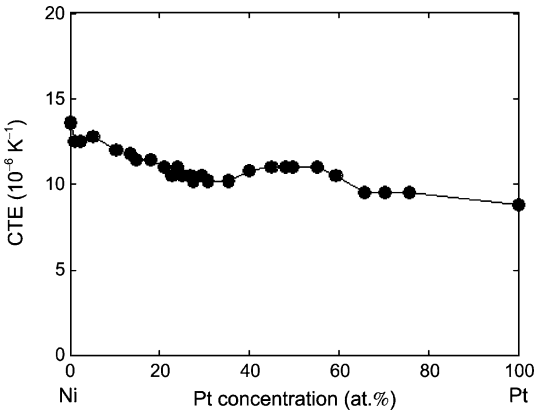

Fig. 7 Localized CTE measurement results from a Ni–Pt diffusion couple [26]. Copyright 2010, Taylor & Francis Group

system [9]. These data clearly reveal the Invar effect around the 35 at.% Ni composition from the diffusion couple without using any individual alloys. The localized measurement results agreed well with those reported using individual alloys by Guillaume [27] who was awarded the 1920 Nobel Prize in physics for the discovery of the Invar effect.

The complete composition variation created in the Fe–Ni diffusion couple also allowed us to perform a systematic and combinatorial study of the mechanism of the Invar effect [28]. By performing low-dose MeV Ar^+ irradiation, we find an increase in the CTE of Fe–Ni alloys in the Invar region (i.e. 30 at.%–37 at.% Ni) while the rest of the Fe–Ni compositions do not show any change. At an Invar composition of $Fe_{65}Ni_{35}$, the CTE increases from 0.5×10^{-6} K^{-1} before irradiation to 4.3×10^{-6} K^{-1} at the highest ion dose of 1.2×10^{14} ions cm^2—an eightfold increase. The result indicates that atomic short range order played a significant role in the Invar effect [28].

The PD-PBD CTE measurement result in a Ni–Pt diffusion couple is another good example that shows the power of combining a complete composition variation with localized property measurement in both systematically studying a system and revealing unusual effects [26]. A small increase in CTE in the concentration region between ~32 at.% and 63 at.% Pt can be clearly seen (Fig. 7) [26]. Such a small increase would be lost in the measurement variations/noise if one would use several (e.g. ten) individual alloys to evaluate the composition-dependent CTE. It should also be mentioned that the thermal conductivity and thermal expansion values reported here are not just trends, they are values of archival quality and they are as good as measurements from bulk samples made from individual alloys.

5 High-throughput measurements of other properties

The above examples show high-throughput measurement/extraction of phase diagrams, diffusion coefficients, thermal conductivity, and thermal expansion. Several other properties such as elastic modulus [29–31], specific heat capacity [10, 32] and Curie temperature [25] as a function of composition can also be measured very effectively. Nanoindentation has been used to perform micron-scale measurements of hardness and elastic modulus [2–5, 29, 30]. Optical ellipsometry can be used to perform accurate micro-scale measurements of optical properties [33, 34]. An evanescent microwave probe was developed to measure dielectric constants of ceramic materials [35, 36]. Micro-scale, four-point probes were used to measure electrical conductivity [37, 38], but they are not very robust when the spatial resolution requirement goes down to a few microns. A detailed review of the state-of-the-art tools can be found in [25].

One most recent development that is worth highlighting is frequency-domain thermoreflectance measurement of C_P

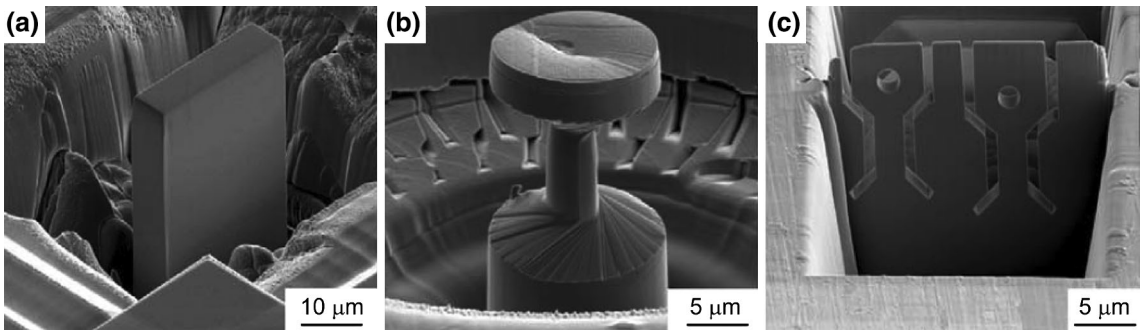

Fig. 8 Micro tensile and bending samples machined using FIB [40]. Copyright 2005, Elsevier

[32]. Its accuracy has not been reported and it is likely similar to the time-domain thermoreflectance method [10]. One can foresee wide applications of these tools, especially for obtaining C_P for thermodynamic modeling and thermodynamic databases and for studying phase transitions.

Uchic et al. [39, 40] have developed methods to machine micropillars/pedestals and even tensile samples with micron dimensions using FIB, as shown in Fig. 8. Microcompression and tension tests have been performed on those micro-samples to obtain information on strength and ductility. A specific size/diameter (which is very materials and microstructure dependent) has to be reached before the tested results match the bulk data. At lower dimensions, dislocation confinement and starvation, stochastic events and other effects dominate the deformation, thus the results can significantly deviate from bulk samples. There is still a lot of work to do to get meaningful, reliable data/information on strength, ductility, and plasticity.

These tools in conjunction with composition-varying and structure/phase-varying samples such as diffusion multiples and combinatorial thin-films [11] would be extremely effective in constructing composition–phase–structure–property relationships. Such effective establishment of these relationships will have a significant impact on materials informatics, testing of materials theories and designing new materials.

6 Digital 3D microstructure characterization and analysis

Digital 3D microstructure characterization and reconstruction have made great progress in recent years. Earlier work started with serial sectioning using mechanical polishing and image reconstruction from two-dimensional (2D) images [41]. Recent progress includes different methods to perform serial sectioning, including FIB [42] and femtosecond laser ablation [43]. Each method has its advantages and shortcomings; and these methods together with 3D atom probe tomography constitute a suite of tools for 3D microstructures across many different length scales. Electron backscatter diffraction (EBSD) [44, 45] is one of the very important tools in this area for orientation imaging and grain size evaluation. The 3D imaging work has also been extended to include not only microstructure information, but also crystal structure and local compositional/spectral information, thus the 3D information is becoming multimodal.

Accurate prediction of properties (especially mechanical properties) needs to take into account the microstructure details, including compositional heterogeneity, microstructure distribution, and anisotropy. The 3D microstructures are much better in validating microstructure evolution models as well as revealing mechanisms that have been puzzling the materials community for decades such as fatigue crack initiation [46].

Digital microstructure is the base for property prediction of engineering materials. The phase distribution and interface properties together with the properties of the phases in the microstructure are required for the prediction of macro properties. The high-spatial resolution experimental tools described above will be very important not only for the establishment of composition-dependent and phase-dependent properties for each phase/crystal structure, but also to provide spatially addressable local properties across the microstructure. Before the development of these "materials property microscopy (MPM)" tools, most materials properties can only be obtained from bulk samples, thus the obtained values are average or minimum results across the entire samples (depending on which properties are being tested). Unless the samples are very uniform and homogeneous (and single-phase), the local properties at a specific composition of a specific phase/crystal structure cannot be obtained unless the MPM tools are employed.

7 Model-driven experiments

Except for high-throughput measurements and digitization, another set of experiments is highly desirable: model-

driven experimentation. Well-designed, critical, and carefully executed experiments are needed to validate and improve models. An elegant example is the carburization experiments to study the transformation mechanisms during diffusion-driven growth [47, 48]. Such direct, effective testing of models shall be highly promoted.

8 Combinatorial materials science

Most multi-functional materials are used in the thin film format; thus, the thin-film based combinatorial materials science approaches are extremely important for the discovery, research, and development of those materials. There are excellent reviews on this subject already [49–55] and the readers are referred to those articles for details.

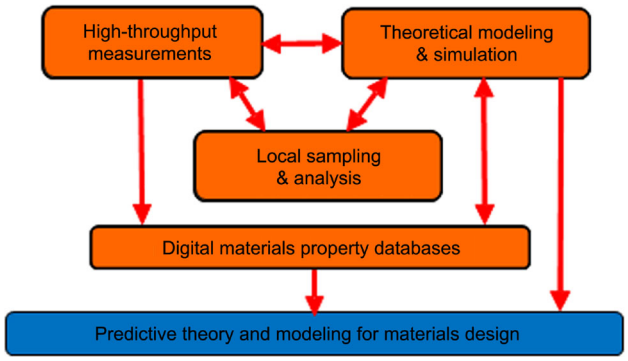

Fig. 9 (Color online) Schematic diagram showing collaborative research between experimentation and computation to effectively provide large amount of property data and discover unusual effects to validate and improve theories and models for physical property predictions

9 Integrating high-throughput experimentation with theoretical modeling

Two examples of CTE measurements (Figs. 6b, 7) are used to illustrate another important role that experimental measurements will play in rapid establishment of composition–property relations—to reveal unusual effects. The Invar effect around the Fe-36 at.% Ni composition was clearly revealed during a CTE measurement scan on a Fe–Ni diffusion couple [9] and the data agree well with individual measurements by Guillaume [27]. The CTE measurement result in a Ni–Pt diffusion couple shows an unusual increase in the concentration region between ~32 at.% and 63 at.% Pt (Fig. 7). It is very important to take advantage of the systematic nature of MPM mapping on composition gradients to find such unusual behaviors from experiments. Synergistic collaboration with theoretical analysis can help explain these behaviors (ordering, magnetic transition, point defects, and so on). FIB can be used to extract samples locally from specific locations in the diffusion samples to perform more detailed mechanistic study to validate the theoretical results. Such a collaborative research will lead to predictive theories and models much faster (Fig. 9). Close collaborations between experimental and theoretical research will be essential for making substantial progress in establishing the framework for digital relations and databases for several materials properties, especially those properties key to the prediction of mechanical properties.

10 Summary and concluding remarks

High-throughput experimental tools are one of the key contributors to the success of the Human Genome Project. Similarly high-throughput experiments will also be key to the success of MGI as one of the three platforms for the MII. Not only these experimental tools will be essential to providing digital data for the construction of materials property and structure databases, but also to providing validation of models and theories. In addition, unusual effects discovered through systematic and high-throughput experimentation will also be very important to the improvement of models in order to take into account various effects. Integration of theoretical modeling and experiment will be the most effective way to achieve the best acceleration of materials design. To build reliable physical property databases, we will need large amounts of experimental data not only as inputs to the digital databases, but also as validation of computational tools and methodologies. The diffusion-multiple approach and the associated micron-scale resolution property measurement tools will greatly accelerate the data gathering and reduce the need of making individual alloys for several property measurements.

For some properties such as elastic modulus, computed data from first principles are very reliable and efficient to obtain. In such a case, the experimental measurements are mostly for validation and for discovering unusual behaviors that may not have been taken into account in theoretical models. For other properties such as thermal conductivity, reliable and efficient prediction methodology has not been validated; thus the experimental measurements need to generate large amounts of data for establishing/validating the mathematical equations and also for discovering unusual behaviors so theories can be developed to account for them. In all cases, close collaborations between experimental and theoretical research will be essential for making substantial progress in establishing the framework for digital relations and databases for several physical properties.

An interesting but important question we need to ask is: whether we should bother with the CALPHAD approach at all if calculations of some of the physical properties can be done very effectively using first-principles approaches. Accurate and effective calculations of physical properties for an arbitrary composition (including multicomponent compositions) of a specific crystal structure will require algorithms that: (1) predict the physical properties to the accuracy that can be used in practical applications, (2) handle large number of atoms/unit cells for non-stoichiometric compositions or to develop effective strategy to reduce the number of unit cells while maintaining fidelity/accuracy of the computed properties, (3) take into account the various effects mentioned above (theoretically these effects should have already been "known" after first-principles calculations in a perfect world), and (4) perform accurate calculations at finite (non-0 K) temperatures by including vibrational property calculations. Tremendous progress has been made in this area and with the rapid availability of high speed computers, practical first-principles calculations are on the horizon for most physical properties. Still it will take some time before we see a multicomponent diffusion simulation that gets all the needed data by directly calling first-principles routines. In this regard, the CALPHAD approach still has its legitimacy since it is convenient, fast, and accurate. A marriage of the first-principles calculations with the CALPHAD approach may be the most logical route forward.

Integration of CALPHAD predictions of compositions with predictions from property models and regression-based property databases has proven to be very effective for alloy design. A superalloy GTD262 was developed at GE in about 4 years from concept to production without any composition iterations using this approach; it was cited as one of the two successful examples of integrated computational materials engineering (ICME) demonstrations in a recent National Materials and Manufacturing Board report [56]. This example highlights the essential role of high fidelity property databases and models in accelerated development of new materials.

There is a strong need to develop more micron-scale tools to measure other properties that are not discussed in this article and to apply the tools to establish materials property databases. Also needed are multi-scale measurement techniques for defects and microstructures [57] to satisfy the needs of model development and computational design of materials in MGI. All the tools together will make materials research and discovery more systematic (especially in revealing and studying the unusual effects), and will provide results to improve and validate theoretical models. These tools can potentially be as widely used as SEM, enabling a transition of materials property research and measurement from macro to micro, from ad hoc to systematic, and from discrete to continuous. In brief, the high-throughput materials structure and property measurement tools together with diffusion multiples and combinatorial thin films will greatly accelerate the establishment of composition–structure–property relationships for development of models for accelerated design and discovery of materials.

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