Computational Thermodynamics and Kinetics-Based ICME Framework for High-Temperature Shape Memory Alloys

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Abstract Over the last decade, considerable interest in the development of High-Temperature Shape Memory Alloys (HTSMAs) for solid-state actuation has increased dramatically as key applications in the aerospace and automotive industry demand actuation temperatures well above those of conventional SMAs. Most of the research to date has focused on establishing the (forward) connections between chemistry, processing, (micro)structure, properties, and performance. Much less work has been dedicated to the development of frameworks capable of addressing the inverse problem of establishing necessary chemistry and processing schedules to achieve specific performance goals. Integrated Computational Materials Engineering (ICME) has emerged as a powerful framework to address this problem, although it has yet to be applied to the development of HTSMAs. In this paper, the contributions of computational thermodynamics and kinetics to ICME of HTSMAs are described. Some representative examples of the use of computational thermodynamics and kinetics to understand the phase stability and microstructural evolution in HTSMAs are discussed. Some very recent efforts at combining both to assist in the design of HTSMAs and limitations to the full implementation of ICME frameworks for HTSMA development are presented.

Keywords HTSMAs · CALPHAD · ICME · Phase field modeling · Precipitation modeling

Introduction

High-temperature shape memory alloys (HTSMAs) undergo large recoverable shape changes at high stresses as a result of reversible martensitic transformations that occur at temperatures higher than 100 °C [1]. Recently, HTSMAs have attracted significant interest due to their potential use in high-temperature solid-state actuation [1–4] in a wide range of applications in the automotive and aerospace industries. Despite their promise and potential, significant challenges must be overcome in order to facilitate the large-scale deployment of HTSMAs.

First, our understanding of the effects of chemistry and microstructure on the transformation behavior and performance of HTSMAs is still incomplete, particularly when considering performance metrics related to the long-term functional reliability of HTSMA-enabled devices. Furthermore, despite the fact that there is significant research activity [5] on different aspects related to the development of HTSMAs, most of the efforts have focused on a rather limited number of systems (such as NiTi–Hf/Zr [6, 7], Co–Ni–Ga [8, 9], NiTi–Pd/Pt [10], Ti–Ta [11], etc.). While computational and theoretical tools at multiple scales, ranging from the electronic structure level [12] to the continuum [13], have contributed to a better understanding of specific phenomena related to the phase-stability or phase-transformation behaviors of HTSMAs, there are only a few efforts that have sought to integrate models at multiple scales [14]. Finally, and perhaps more importantly, while there is increased connectivity between the state-of-the-art characterization and simulation approaches, the

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problem of identifying optimal chemistries and processing routes to achieve the application-driven performance requirements remains largely unsolved.

Integrated Computational Materials Engineering (ICME) [15] has emerged as an all-encompassing framework for the accelerated development of materials. Although implementation of ICME has already been (tentatively) demonstrated in a wide range of industries and material classes [16], a cursory literature search yielded only a handful of cases in which ICME approaches were employed in the development of SMAs. While ICME is truly a multidisciplinary endeavor that involves a wide range of experimental and computational techniques, this paper focuses on computational thermodynamics and kinetics as two of the essential tools in the toolkit for the use of ICME to develop HTSMAs.

The paper is organized as follows: First, unique challenges associated with the design of HTSMAs are discussed. Second, ICME is properly defined, and the connection with computational thermodynamics and kinetics is made. This is followed by an introduction to the CALPHAD approach. Different examples of work involving the use of CALPHAD methods to describe the phase stability in SMAs are presented. This is followed by a discussion of the use of computational kinetics approaches to predict the microstructural evolution in SMA systems, particularly those modified through nanoprecipitation [7, 17]. We then briefly discuss some very recent attempts to combine computational thermodynamics and kinetics into a design framework for precipitate-engineered HTSMAs [18]. The paper then concludes by outlining some of the major challenges that need to be overcome for ICME approaches to become widely used in the HTSMA community.

Unique Challenges of High-Temperature Shape Memory Alloys

Practical applications of HTSMAs require much more beyond sufficiently high transformation temperatures. Compared to conventional SMAs, the greater availability of thermal energy generates additional challenges associated with HTSMA's mechanical strength, phase stability and interactions with surrounding (extreme) environments. Unfortunately, computational efforts targeting such issues in HTSMAs have been scarce. In light of this, we outline a number of challenges unique to the HTSMAs, and later in the paper, we propose several potential ways in which an ICME approach may be used to address those challenges.

The mechanical strengths of HTSMAs are complicated by the intersection of inherently higher dislocation mobility at higher temperatures and high internal stresses generated

during the motion and interaction of martensite phase front. Suppression of defect generation during transformation cycles becomes increasingly more challenging as operating temperature increases, which leads to incomplete shape recovery particularly during superelasticity or stress-biased shape memory response (actuation). Furthermore, the loss of dislocation barriers creates a number of associated problems such as cyclic instability and creep [4]. At moderately high temperatures, the effectiveness of work hardening is quickly exhausted. Instead, for HTSMAs designed to operate at temperatures below 400 °C, focused research efforts in the last 5 years has produced highly effective precipitation-strengthening protocols utilizing nanometer-sized precipitates in a number of NiTi-based HTMSA systems [1, 7, 10]. However, the phase stability of these precipitates limit the ability to achieve similar strengthening at higher transformation temperatures where precipitate coarsening begins to occur [19]. Because of this, there have been increased interest recently in microalloying to achieve solid-solution or interstitial strengthening [20, 21]. Nevertheless, HTSMA systems designed to operate at temperatures above 400 °C seldom show appreciable shape memory and superelastic behavior at the present time, and even in alloys that do, full recovery at any applied strain level is rarely observed.

The aforementioned challenges in phase stability are not limited only to precipitation hardening. In the majority of HTSMA systems, the transforming phases are metastable. Given sufficient time at high temperature, the equilibrium phase or an intermediate metastable phase will form. A typical example would be, for example, the Ti–Ta system in which its functional stability is compromised by the precipitation of the ω phase during aging [22]. The decomposition of the matrix through uncontrolled precipitation or the second-phase formation causes major shift in both the transformation temperatures and the mechanical strength of the alloy. Chemical modification can be used in this case to suppress the formation of detrimental phases, as is the case of Ti–Ta-based HTSMAs in which Al additions suppress the formation of the ω phase [11]. Finally, water quenching required after homogenization of many HTSMA systems causes disordered crystal structures and high levels of nonequilibrium point defect concentrations. If self-diffusion is fast enough, the re-ordering process can drastically change the transformation temperatures, such as in the case of copper-based HTSMAs [23].

HTSMAs exposed to the atmosphere at high temperatures will likely react with oxygen and other gaseous species, forming metal-oxide products at the surface. In uncontrolled atmosphere, the alloy will continue to convert more of its mass to oxide products unless a robust and dense protective oxide layer is formed [24]. A unique

problem to HTSMAs is their high sensitivity of transformation temperatures to matrix composition. Frequently, the oxide layer of an alloy is composed of mostly the oxide of a single element, thus reducing its concentration in the matrix. For example, Ni–Ti-based SMA and HTSMAs form oxide layers that are largely titanium-rich (i.e., TiO_2). Consequently, a nickel-rich layer forms immediately below the surface followed by a larger sub-surface region of titanium-depleted region and significantly reducing local transformation temperatures.

Beyond compositional changes, shape change associated with the phase transformation may also cause cracking in the brittle oxide layer, making the development of a stable oxide layer difficult even in alloys normally with good oxidation resistance. Even if this problem were to be resolved, full oxidation resistance HTSMAs are likely to require the careful selection of the oxide layer forming element as different oxides have much different growth rates. For example, Al_2O_3 tends to form the most effective passivating layers and in structural alloys alumina-forming compositions are being actively sought [25].

Integrated Computational Materials Engineering

As the cost of experimentation and the demand for high-performance materials rise, there is increasing pressure to accelerate the cycle for the discovery and development of materials. In the context of alloy design, Olson's pioneering work [26] has shown a viable methodology that integrates simulation and experiments to accelerate the optimization of engineering alloys (see Fig. 1). The underlying principle of this approach is based on the fact that goals associated to technology-driven performance metrics enable the identification of relevant properties of materials, the (micro)structures that are necessary to achieve said properties and, finally, the required processing (and chemistry) schedules to arrive at (micro)structures

optimality of which is defined directly in terms of engineering design goals. This is essentially an inverse problem.

A formal framework to address the performance–property–structure–processing inverse problem has been realized through the concept of ICME, which has emerged as a powerful framework that “integrates science and engineering as well as the results of theory, experiments, and simulations into computational tools that can be used directly in engineering of new products or manufacturing processes” [15]. An update to this concept has come more recently (in the US) in the form of the Materials Genome Initiative [27], which aims to accelerate the discovery, development, and deployment of materials through the integration of experiments, simulation, and data.

While MGI provides a goal (reduced time and cost associated with the discovery and development of materials), ICME provides a framework that focuses not only on problems associated with the material space, but that instead makes the discovery/development process of the materials an integral component of product design and development, as shown in Fig. 2. While there is already a significant collection of successful case studies of ICME implementation (in the automotive, aerospace, and maritime industries), the types of applications have been almost exclusively (at least within the metal and alloy material families) structural in nature [16]. Deployment of ICME frameworks for the development of (high-temperature) SMAs thus remains an open field.

Figure 2 also highlights the importance of (computational) thermodynamics and kinetics to the overall ICME framework as one of the necessary, albeit not sufficient, conditions to use ICME approaches to accelerate the development of materials. Material development must start first with an understanding of their phase stabilities, that is, the phases that exist at (possibly metastable) equilibrium under relevant thermodynamic conditions. As the synthesized materials rarely exist in their true equilibrium state, kinetics provides the theoretical framework to elucidate how the materials change under different driving forces that arise during processing/operating conditions.

While experiments—the advent of novel high-throughput approaches [28, 29] is especially promising—can potentially be used to explore the phase stability space of material systems, a truly predictive framework (necessary within the ICME context) requires the use of theoretical and computational methods that enable the systematic encoding of thermodynamic information about a given system of interest. Understanding of the evolution of materials (during processing as well as operation) requires in turn computational techniques capable of describing the evolution of microstructural degrees of freedom as the materials evolve toward equilibrium. Only by combining

Fig. 1 The central paradigm in the science and engineering of materials. Adapted from Olson [26]

Fig. 2 The ICME flow chart in which the direction of the arrows has been inverted to reflect the fact that ICME is ultimately about the development of goal-oriented materials. The role of computational

thermodynamics and kinetics in the establishment of quantitative processing-structure relationships has been highlighted. Adapted from Allison [14]

computational thermodynamic and kinetic it is possible to develop predictive modeling frameworks that connect initial composition and processing to microstructure but that can also account for material evolution during operation.

The CALPHAD Method

Since the work by Gibbs, thermodynamics has played a preeminent role in improving our understanding of the phase stability of materials. Initial efforts were focused on determining the equilibrium state of material system and measuring thermodynamic properties of phases without much regard for the integration of this information into a coherent, self-consistent knowledge base. With the advent of the CALculation of PHase Diagrams (CALPHAD) method [30] pioneered by Kaufman et al. [31, 32], it became possible to systematically encode the thermodynamic properties of phases through relatively simple mathematical models that described how the Gibbs energies (or other potentials) of individual phases changed with composition, temperature, pressure, and any other internal/external degree of freedom.

The CALPHAD approach prescribes a systematic construction of thermodynamic models from lower-order (unary, binary) to higher-order systems, and this allows the extrapolation of thermodynamic models to multicomponent, multiphase systems. This makes CALPHAD-based thermodynamic databases and related software some of the primary tools in ICME approaches, at least when it comes to the development of metals and alloy systems [33]. The parameterization of CALPHAD models is carried out through the minimization of the (square of) the difference between experiments and model predictions [34], and takes into account uncertainties associated with experimental observations. With the dramatic improvement in methods and hardware infrastructure, it has become possible to

supplement experimental data through ab initio calculations [35–39] (see Fig. 3).

Once the thermodynamic models for all the phases likely to take part in equilibrium has been encoded in a thermodynamic (CALPHAD) database, the thermodynamic equilibrium is arrived at through the minimization—through Newton–Raphson, convex hull [40] or other numerical optimization techniques—of the Gibbs energy of the entire system (comparing all the possible linear combinations of phases) subject to constraints, such as global mass conservation, conservation of mole fractions of constituents in individual phases, etc. (Fig. 4). Equilibrium calculations can in turn yield other thermodynamic quantities of interest, such as enthalpies, heat capacities, equilibrium population of intrinsic defects, chemical activities, etc.

While the CALPHAD method was initially developed to encode in a systematic manner the thermodynamics and kinetics of multicomponent systems, it has already been extended to represent the compositional dependence of other thermodynamic properties [41, 42], such as molar volumes, thermal expansion, bulk modulus, etc. In CALPHAD modeling, properties in multicomponent material systems can be written in a general form as follows [43]:

$$\phi = {}^{\circ}\phi + \Delta\phi,$$

where ϕ is the property of the multicomponent phase ${}^{\circ}\phi = \sum x_i {}^{\circ}\phi_i$ represents the mechanical mixing of individual constituents, and $\Delta\phi$ denotes the (nonideal) interactions among the constituents commonly written as

$$\Delta\phi = \Delta\phi_{\text{conf}} + \sum \sum x_i x_j \sum_{k=0}^k \phi_{ij} (x_i - x_j)^k + \sum \sum \sum x_i x_j x_k \phi_{ijk},$$

where $\Delta\phi_{\text{conf}}$ is the configurational contribution, and ϕ_{ij} and ϕ_{ijk} are the binary and ternary interaction parameters, respectively (Fig. 3).

Fig. 3 General CALPHAD approach as a way to encode the compositional dependence of properties of materials

Fig. 4 Phase-stability predictions through the CALPHAD approach

Applications of the CALPHAD Approach to Shape Memory Alloys

The CALPHAD method has been widely applied to a large number of material systems, although its application to shape memory alloys (SMAs) has been rather modest. In fact, most CALPHAD works on SMAs have focused on NiTi-based systems [44–48]. These trends seem to be changing, though, as there has been an increase in the number of investigations on the phase stability and thermodynamic properties of SMAs. In this section, we will present some examples in which CALPHAD methods and ancillary techniques, including electronic structure calculations, have been used to elucidate the factors that control phase stability in some important SMA systems.

Thermodynamic Modelling

With a few exceptions, not much work has been done on the application of CALPHAD methods to the investigation of the phase stability in SMAs, and still much less work has been done in HTSMAs. Perhaps one of the first (and most important) works that make use of the CALPHAD method to understand the phase stability in SMAs is the work by Tang [45] and Tang et al. [44] on the thermodynamics of the Ni–Ti binary system over the entire relevant composition-temperature space. In their work, Tang et al. considered all the possible phases in the Ni–Ti system, including the monoclinic B19' martensite [49]. Contrary to the usual approach by CALPHAD practitioners to ignore the products of martensitic transformations as they are usually metastable—and their presence is greatly affected

by cooling rates—Tang et al. considered B19' as one of the phases that competed for stability in the low-temperature region of the phase diagram. This was justified in light of the fact that the B2 austenite is truly unstable with respect to the martensitic transformation and it is only (entropically) stabilized at high temperatures due to anharmonic phonon–phonon interactions [50]. In addition to the incorporation of order–disorder transformation and the inclusion of anti-site defects and vacancies, magnetic contributions [51] to the free energy were taken into account.

One of the major features of Tang's work was the use of the so-called compound energy formalism (CEM) [52] to describe the Gibbs energies of all intermetallic phases in the system. The austenite phase B2 was modeled in turn as a two-sublattice system $((\text{Ni,Ti,Va})_{0.5}(\text{Ni,Ti,Va})_{0.5})$ in which anti-site and vacancy point defects could be present to account for deviations from stoichiometry at elevated temperatures. The model also accounted for possible $\text{B2} \rightarrow \text{bcc}$ order/disorder transformations, although in Ni–Ti, the B2 phase melts before it experiences disorder [44, 48]. In other systems [53], however, it is necessary to consider $\text{B2} \rightarrow \text{bcc}$ order/disorder due to the stability of bcc solid solutions in binary constituents. In the Ni–Ti–Nb system, as recently assessed by Santhy and Kumar [53], for example, the bcc solid-solution phase is stable over wide composition–temperature regions in the Ti–Nb and Ni–Nb systems.

Figure 5a shows the low-temperature phase diagram in the Ni–Ti binary system resulting from the assessment by Tang et al. [44]. At equilibrium, the B2 (and B19') would coexist with either the NiTi_2 or the Ni_3Ti intermetallic compounds. Under metastable conditions, one would expect to have extended B2 + B19' two-phase regions. The figure also shows the predicted T_0 curve, which would correspond exactly to M_S if there were no barriers and irreversibilities associated to the transformation [44]. Within the thermodynamic framework of Tang, the steep decrease of M_S in Ni-rich Ni–Ti SMAs is merely a consequence of thermodynamic competition between B2 and B19'.

Prediction of Transformation Temperatures

Here we would like to note that the competition between austenite and martensite, and consequently the temperature ranges at which the transformation temperature is likely to be observed can be addressed qualitatively, albeit not quantitatively, within a thermodynamic framework. The T_0 temperature, for example, denotes the condition at which the Gibbs *chemical free energies* of the austenite and martensite phases are equal [54]:

Fig. 5 **a** Low-temperature phase diagram of the Ni–Ti system, taking into account the stabilization of B19' martensite as well as the T_0 line corresponding to the equality in chemical Gibbs energies of B2 and B19'. **b** Site fractions of anti-site and vacancy defects in each of the sublattices of B2 austenite as a function of mole fraction of Ni. y_{Ti}^{a} and y_{Ni}^{b} denote fractions of anti-site defects in 'a' and 'b' sublattices, respectively, while $y_{\text{Va}}^{\text{a,b}}$ denotes the fraction of vacancies. Figures taken with permission from Tang et al. [38]

$$G_{\text{ch}}^{\text{J}}(T_0) = G_{\text{ch}}^{\text{J}}(T_0). \quad (1)$$

At any other temperature, there exists a chemical driving force, ΔG^* , that correspond to the difference in chemical free energies of the two competing phases and is given (in the forward direction) as

$$\Delta G_{\text{mart}}^*(T) = G_{\text{ch}}^{\text{J}}(T) - G_{\text{ch}}^{\text{J}}(T). \quad (2)$$

When cooling, the martensitic transformation starts at M_S , which lies below T_0 as the reaction does not occur instantaneously as there are non-chemical barriers that must first be overcome. Likewise, the reverse transformation starts at A_S , which is (usually) higher than T_0 . Since T_0 is experimentally inaccessible, its determination can only be attained from measurements of M_S and A_S . In the case of non-thermoelastic transformations, when the entropy difference between austenite and martensite is constant and if the critical driving force for the forward and reverse transformation is the same, then it can be shown [55] that T_0 can be estimated as

$$T_0 = \frac{M_S + A_S}{2} \quad (3)$$

On the other hand, in the case of thermoelastic transformations (as in SMAs), it has been recognized that it is better to assume that elastic barriers to the transformation can be expected to become small at both M_S and A_F , that is, the temperatures at which the first martensite plate forms during the forward transformation and at which the last martensite plate disappears during the reverse transformation [54]. In this case,

$$T_0 \approx \frac{M_S + A_F}{2} \quad (4)$$

From the fact that M_S , M_F , A_S , and A_F , rarely coincide, it is evident that nonchemical contributions to the phase transformation must be taken into account. These contributions can be enumerated as (i) the (reversible) elastic stored energy, $\Delta G_{el}^{\gamma \rightarrow \alpha'}$, necessary to accommodate the transformation in both the forward and inverse directions; (ii) the irreversible frictional work, E_{fr} , associated with the motion of interfaces and the (possible) creation of defects during the transformation; and (iii) the interfacial energy contribution, $\sigma \cdot A$, due to the creation of interfaces between austenite and martensite. Taking these contributions into account, at M_S , the following relation can be established [54]:

$$\Delta G_{ch}^{\gamma \rightarrow \alpha'} = \Delta G_{el}^{\gamma \rightarrow \alpha'} + E_{fr} + \sigma \cdot A. \quad (5)$$

From this discussion, it is evident that the determination of T_0 can be easily obtained provided one has the CALPHAD description for the austenite and martensite phases. On the other hand, transformation temperatures associated with non-chemical contributions to the transformation are more difficult to model (and predict), although several groups [56, 57] have attempted to do precisely this in cases in which abundant experimental data and robust thermodynamic models for austenite and martensite are available.

A necessary attribute, although not sufficient, sought after in the quest of the discovery and development of HTSMAs is the identification of compositions with high transformation

temperatures. While CALPHAD, strictly speaking, is not a predictive tool as it requires experimental information to obtain the thermodynamic descriptions of phases, extrapolations can indeed be carried out provided the CALPHAD models are obtained in a consistent manner. Understanding of the chemical contributions to the transformation behavior in SMAs can be used to identify trends in T_0 and thus transformation temperature ranges. Quantitative prediction of observable transformation temperatures, however, is beyond current capabilities, particularly when it comes to estimate irreversible barriers to the transformation—the elastic and surface energy contributions could in principle be estimated from first-principles methods.

Short-Range Orderings and Their Effects on Martensite Stability

Over the past few decades, it has become increasingly apparent that point defects greatly affect the behavior of SMAs. As shown by Ren and Otsuka [58], at equilibrium, point defects' short-range order (SRO) distribution tends to follow the underlying symmetry of the crystal lattice. When the lattice symmetry changes (due to a structural phase transformation, for example), it takes a finite amount of time for the SRO of point defects to 'conform' to the new symmetry (point defects re-arrange in the lattice through thermally induced defects). These relaxation phenomena lead to aging-induced time-dependent two-way shape memory effect or to the stabilization of martensite [59]. At the same time, the onset of the so-called "strain glass" transformation has been associated with the existence of point defects that induce structural disorder in the austenite, suppressing the formation of long-range martensite domains [60].

Defects thus may play a very important role in the behavior of SMAs and, as shown in Fig. 5b, one outcome of the CALPHAD sublattice model used to describe the austenite B2 phase in the Ni-Ti system is the prediction of point defect thermodynamics, including their concentration as a function of composition and temperature. Further understanding of the effect of point defects on the response of SMAs will certainly require the prediction of defect structures, which can be realized through the use of appropriate CALPHAD models. The effect of point defects on behavior of HTSMAs has not been investigated extensively, although there are a few works that suggest their importance. In Ti-Pd and Ti-Pd-Ni HTSMAs, martensite aging effect has been shown to be highly dependent on composition [61] as substitution of Pd by Ni increases the total concentration of anti-site defects (ASD). Similar martensite aging has been observed in Co-Ni-Ga [62] and Ni-Ti-Hf alloys [63]. Point defects have also been shown to stabilize martensite in Ni-Mn-Ga SMAs [64].

Precipitate Engineering

The CALPHAD approach allows for the development of self-consistent thermodynamically rigorous descriptions of an alloy system, including metastable phases that may be observed as part of the evolution of a material system toward equilibrium [65, 66] under thermodynamic [67] or kinetic constraints [68]. In SMAs—as in a wider range of alloy systems—metastable phases may play a fundamental role at controlling their transformation behavior and overall performance. A classical example is that of Ni-rich Ni–Ti SMAs, where the precipitation of metastable precipitates with the Ni_4Ti_3 stoichiometry changes the transformation temperature [69]—due to Ni depletion from the matrix; affects the nature and sequence of the martensitic phase formation [70]; and improves the cyclic stability through minimization of irreversible plastic deformation [71].

Engineering of precipitate structure requires understanding of the phase stability of the metastable phases relative to the matrix. Recently, Povoden-Karadeniz et al. [46] developed a thermodynamically consistent CALPHAD model of the NiTi system that takes into account the metastable Ni_4Ti_3 and Ni_3Ti_2 precipitate phases. The thermodynamic models for the metastable phases were developed by combining metastable solvus lines with first-principles calculations of their enthalpies of formation. The metastable phase diagram for NiTi considering metastable equilibrium between the B2 matrix and the Ni_4Ti_3 precipitate is shown in Fig. 6.

Optimal Microstructural Design

Prediction of phase stability in multicomponent multiphase SMAs through CALPHAD models can also be used to design optimal microstructures without sacrificing functional response. SMAs based on the Co–Ni–Ga system have shown relatively high transformation temperatures [62] comparable to those of NiTi–Hf and NiTi–Zr HTSMAs and have shown good cyclic stability. Unfortunately, polycrystalline Co–Ni–Ga HTSMAs are rather brittle due to grain boundary incompatibilities arising from the limited number of martensite variants owing to the relatively high symmetry of the martensite crystal structure (tetragonal- L1_0).

The ductility of brittle single-phase Co–Ni–Ga polycrystals can be improved through the precipitation—preferentially at grain boundaries as shown in Fig. 7—of a ductile Co-rich γ (fcc) secondary phase [72]. Nano-dispersed L_{12} precipitates have also been shown to contribute to the cyclic stability of Co–Ni–Ga alloys [73]. Design of Co–Ni–Ga alloys would thus entail careful selection of initial composition and heat-treatment schedule to attain optimal phase constitutions. While alloy design is highly

Fig. 6 Metastable phase diagram of the Ti–Ni system considering equilibrium between Ni_4Ti_3 and B2 matrix. Symbols denote conditions of experimentally observed TiNi–B2 + Ti_3Ni_4 metastable equilibrium. References listed in the figure correspond to those listed in [61]. Figure reproduced with permission from [61]

Fig. 7 Optical micrograph of Co–2 at.% Ni–30 at.% Ga alloy annealed at 1200 °C (top) and 900 °C (bottom). Reproduced with permission from [62]

complex, phase-stability predictions derived from CALPHAD models can contribute significantly. In Fig. 8, we show the predicted isothermal section (at 1200 °C) in the Co–Ni–Ga system derived from the thermodynamic assessment by some of the present authors [74]. From the

Fig. 8 Calculated ternary phase diagram of Co–Ni–Ga system at 1200 °C [64] in comparison with experiments taken from [62, 66, 67]

isothermal section, it can be seen that there is a wide range of compositions in which the β (austenite) phase is in equilibrium with the ductile γ phase. The composition of the austenite, though, is fixed by the tie-lines corresponding to each β – γ equilibrium state, although one could explore different sequences of heat-treatment temperatures in order to allow for more flexible design of composite microstructures. The simultaneous design of β – γ – γ' complex microstructures is even more challenging due to further constraints arising from the fact that, in three-phase equilibrium states in ternary systems, the compositions of all the phases are fixed, and what changes is just the phase fractions. Sophisticated tools [75] for the efficient exploration of multicomponent thermodynamic spaces could be used to identify promising composition–temperature combinations that are likely to satisfy alloy design criteria.

So far, we have seen how CALPHAD models can be used to understand the thermodynamics of the martensitic transformation in SMAs, the thermodynamics of point defects, the determination of metastable phase diagrams, as well as the design of complex microstructures. With regard to the application of CALPHAD methods to the understanding of phase stability in HTSMAs, there are a limited number of works [53, 76–80] that were not included in this section but that, in addition to the assessment of the Co–Ni–Ga HTSMA system by two of the present authors [74], constitute the bulk of the works on CALPHAD assessments of HTSMAs. When one considers that the phase stability in some of the most promising HTSMAs, such as those based on the NiTiHf and NiTiZr systems [1, 7], remain unexplored within the CALPHAD framework, it is clear that there remains significant effort to be done.

Ab Initio-Based Thermodynamics of HTSMAs

To calculate the electronic structure of crystalline materials, a solution to the many-ion + many-electron Schrödinger equation has to be found [81]. The problem, intractable in practice, has been resolved through the development of DFT [82–84], which essentially reduces the original problem to the solution of an equivalent one-electron system [82]. Practical application of DFT to computational materials science has been greatly simplified by the recent development of efficient ab initio codes [85–88], based on either a full-electron or a pseudopotential description of the electron wave functions. Within DFT, the electronic structure and the total energy of a given crystal is determined by only specifying the electric charge of each nucleus in the structure as well as their arrangement in space (lattice type). All ground-state properties (mechanical, thermodynamic, and structural) can then be determined from the resulting electronic charge.

Over the last decade, DFT calculations have been used to elucidate the intrinsic thermodynamic properties of several (HT)SMA systems as well as to assist in the development of CALPHAD methods (see Fig. 4) as the use of DFT-derived thermodynamic properties can be used to supplement the (usually) scarce experimental data on thermochemistry and phase stability of material systems [89]. While there are hundreds of papers employing DFT to understand different aspects of the behavior of SMAs, here we focus on examples that are directly related to their thermodynamics and phase stability.

Perhaps one of the first applications of first-principles-based methods to the investigation of SMAs is the application of the BFS method [90] adopted by Bozzolo et al. to investigate the site occupancy and thermodynamic properties of the austenite B2 phase in several SMA systems [91–94]. The BFS approach assumes that the formation energy of a particular atomic configuration can be quantified in terms of individual contributions that account for the lattice strain energy as well as chemical effects. The strain's contribution to alloy energetics is obtained from cohesive, structural, and mechanical properties of the pure constituent elements, while the chemical contribution accounts for bonding behavior. The BFS method provides a very efficient way to investigate the energetics associated with alloying in lattice systems. However, the method is only directly related to first-principles calculations, and the subtle effects that cannot be simply separated into mechanical and chemical contributions are not taken into account.

The BFS method has been used to predict the site preference of ternary alloying additions (Fe, Pt, Pd, Au, Al, Cu, Zr, and Hf) to NiTi [91] and the formation energies of (Ni,X)Ti alloys—with X = Fe, Pd, Pt, Au, Al, Cu, Zr, and

Hf [93]. Overall, the BFS method yields results in qualitative agreement with the available experimental data. More importantly, the efficiency of the BFS method enables the rapid exploration of a wide region in the composition space.

One of the most common applications of DFT to SMAs, is the investigation of point defect thermodynamics. Lu et al. [95] calculated the energetics of point defects (including vacancies and anti-site defects) in NiTi. The predicted thermal equilibrium concentration of point defects at 923 K is shown in Fig. 9. Notably, the results compare extremely well (qualitatively) to the predictions made using the CALPHAD thermodynamic assessment by Tang and Sundman [44] shown in Fig. 5b as both approaches predict large concentrations of vacancies in the Ti-rich region of the stoichiometry, while Ni anti-site defects dominate the defect structure in Ni-rich compositions.

Other works [96] have used similar approaches to investigate defect structures in ternary SMA systems. In addition to the thermodynamics of intrinsic point defects, DFT can be used to investigate the behavior of extrinsic impurities. For example, Moitra et al. [97] have investigated the equilibrium configuration of hydrogen impurities. Such calculations are important given the susceptibility of NiTi-based SMAs to hydrogen embrittlement [98]. Very recently, the present authors and collaborators [99] have used DFT methods to predict the site preference for different ternary additions to NiTi-based SMAs as shown in Fig. 10. The site preference agrees very well with the work by Bozzolo et al. using the BFS method [91–94] and with the available experimental data.

As mentioned earlier, DFT calculations can be used to provide insights into the alloy thermodynamics in SMA systems, including the competition between austenite and

martensite, which ultimately determines the martensitic transformation temperature ranges. Frenzel et al. [100] used DFT calculations in combination with calorimetry measurements to identify the dominant factors controlling the transformation temperature in NiTi-based SMAs. Their calculations showed that local atomic relaxations had a strong effect on the energy difference between B1 and B19'. Notably, they found that in the Ni-poor region, the energy difference between austenite and martensite was invariant with respect to compositional changes in agreement with experiments. In contrast, large atomic relaxations in Ni-rich compositions due to anti-site led to a steep decrease in energy difference between B2 and B19', resulting in a dramatic decrease in transformation temperatures, again in agreement with experiments [69]. One of the authors of the present paper used DFT methods to investigate the phase competition between austenite and martensite in the Co–Ni–Ga system [9] and found that an increase in the valence electron-to-atom ratio (e/a) was associated with an increase in the energy difference between austenite (L_{21}) and martensite (L_{10}) in this system as shown in Fig. 11, in qualitative agreement with experiments. One must note, however, that in this case, magnetism was found to play an equally important role in determining the energy difference between austenite and martensite, resulting in the transformation temperature (M_S) being a function of both e/a ratio and the effective magnetic valence of the alloy [9].

While DFT has been used to elucidate the factors that control the phase competition between austenite and martensite, we should emphasize that quantitative predictions of transformation temperatures from the first principles remains a challenging problem as one must consider all the possible thermally excited degrees of freedom (electrons, phonons, and even magnons) and their couplings. This has only been done in a limited number of systems, notably in the work by Neugebauer and his collaborators [101, 102] on the prediction of the phase diagram of Ni_2Mn -based ferromagnetic SMAs. Such predictions required extremely computationally intensive calculations as the calculation of vibrational (including anharmonicity) and magnetic contributions to the free energy of lattices is still highly nontrivial, particularly when one considers that the accuracy of such methods yields inaccuracies in predicted transformation temperatures in the order of tens (and even hundreds) of degrees K.

Perhaps one of the most demonstrably useful application of DFT calculations within the context of phase stability in SMAs is the use of DFT-derived thermodynamic data (e.g., enthalpies of formation) within CALPHAD thermodynamic assessments (see Fig. 4). As mentioned earlier, Povoden-Karadeniz et al. used DFT calculations to supplement their CALPHAD assessment with the enthalpies of

Fig. 9 Thermal equilibrium point defect concentrations of B2–TiNi at 923 K, as a function of atomic fraction of Ni. Reproduced with permission from [84]

Fig. 10 Site preference of X element in Ni–Ti–X. The upper row (TiR) indicates site preference for Ti-rich compositions and the lower row (NiR) for Ni-rich compositions, respectively

	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Mg												Al	Si	
Ti												Ni	Ni	
Ti												Ti	Ti	
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge		
	Ti		Ni	Ni	Ni	Ni	Ni		Ni	Ni	Ni	Ni		
	Ti		Ti	Ni	Ni	Ni	Ni		Ni	Ti	Ni	Ni		
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	
	Ti	Ti	Ni	Ni	Ni	Ni	Ni	Ni	Ti	Ti	Ti	Ti	Ni	
	Ti	Ni	Ti	Ni	Ni	Ni	Ni	Ti	Ti	Ti	Ti	Ti	Ti	
		Hf	Ta	W	Re	Os	Ir	Pt	Au					
		Ti	Ni	Ni	Ni	Ni	Ni	Ni	Ni					
		Ti	Ti	Ni	Ni	Ni	Ni	Ni	Ti

Fig. 11 Effect of valence electron-to-atom ratio (e/a) on the energy difference between austenite and martensite in close to stoichiometric Co–Ni–Ga alloys derived from DFT calculations. Reproduced with permission from [9]

formation of metastable phases in the Ni–Ti binary system. Moreover, DFT calculations can be used to estimate the lattice stability of end members of sublattice models (chemical configurations with full occupation of one constituent per site within the CEM [52]). As such end members are seldom observed experimentally (they may be unstable or metastable at best), DFT calculations are the only means to obtain consistent thermodynamic descriptions. In recent years, DFT calculations and experiments

have been used to obtain CALPHAD models of HTSMAs, including those belonging to the Co–Ni–Ga [74] and Fe–Ni–Ti [47, 76] systems. Despite its promising potential, the combination of DFT and CALPHAD approaches to develop thermodynamically consistent descriptions of the phase stability in HTSMAs remains wide open.

Computational Kinetics of (HT)SMAs

Understanding of the phase stability and thermodynamic behavior is a necessary, although not sufficient, step toward establishing the connection between chemistry/processing and microstructure. This connection in turn is but one of the many steps necessary to realize an ICME framework for the more efficient (and accelerated) development of HTSMAs, as shown in Fig. 2. The connection between thermodynamics and microstructure, understood in the context of this work in terms of the phase constitution as well as the spatial distribution of microstructural constituents (excluding non-thermodynamic defects such as interfaces, grain boundaries, and dislocations) in SMAs as the result of the evolution of the material system toward equilibrium as part of the synthesis process or as a consequence of the operating conditions of the material. Having a thermodynamic description of a given SMA

material system, computational kinetics can be used to address these issues.

Since a pre-condition to a full computational treatment of the kinetics of microstructural evolution in materials is the availability of reliable thermodynamic description of the systems, it is not surprising that there are only a very limited number of works that have used computational techniques to address the kinetic behavior of SMAs, even more so in the case of HTSMAs. In this section, we will discuss some examples in which computational kinetics has been used to describe some aspects of microstructural evolution in SMAs, particularly those alloy systems in which a multiphase microstructure is either desired or is the result of the operating conditions of the materials.

Phase-Field Modeling of Microstructural Evolution in SMAs

Phase-field modeling (PFM) has been successfully employed to model complex mesoscopic phenomena, such as solidification [103], solid-state transformations [104], and electrochemical processes [105]. This approach relies on the description of evolving microstructures in terms of time-dependent continuous fields or order parameters, which can be conserved (e.g., charge, mass) [106] or non-conserved (e.g., crystal orientation, degree of crystallinity) [107].

The free energy of a microstructure (see Fig. 12) is defined in terms of local, non-local, as well as long-range contributions. Local contributions are a function of the values of the order parameters at a given location in space

and time (i.e., chemical free energy). Non-local contributions, on the other hand, depend not only on the values of the order parameters but also on their gradients. These contributions account for the energy costs associated with the formation of heterogeneities (i.e., interfaces) in the microstructure. Finally, long-range contributions arise from generalized fields and their conjugate displacements, such as those arising from the elastic and electrostatic interactions in a heterogeneous material system [108–115].

The free energy of the entire microstructure is then expressed in terms of properties spatial variation of which is given in relation to the order parameters, and the microstructure is then evolved by finding—through variational principles—the fastest path for the relaxation of the degrees of freedom (order parameters) that describe the microstructure, as shown in Fig. 12. The field description of microstructures eliminates the problem of tracking the motion of internal surfaces during numerical simulations, permitting the investigation of arbitrarily complex microstructures with intricate phase boundaries, and without having to make a priori assumptions regarding the path taken by the microstructure as it relaxes toward an equilibrium state [103].

Over the last decade, there have been a large number of works on the use of phase field models to describe the microstructural evolution in shape memory alloys. The works have ranged from microstructural evolution simulations in polycrystalline SMAs [115, 116]; domain evolution in ferromagnetic SMAs where magneto-thermo-elastic coupling is explicitly considered [117, 118]; to simulations of complex microstructural evolution in which

Fig. 12 Schematic depicting the main formalisms associated with Phase Field Modeling. Y. M. Jin is acknowledged for providing some of the graphics used to generate this figure

Fig. 13 3D views of the equilibrium shape of an isolated Ni_4Ti_3 precipitate obtained by Zhou et al. [114]. Reproduced with permission

precipitation of secondary phases takes place [14, 119–122]. In this work, we will focus on the latter examples as the use of PFM to investigate martensite domain structure in SMAs is outside the scope of the work and has been covered extensively elsewhere [123].

Perhaps one of the earliest applications of PFM to simulate the microstructural evolution of multiphase (precipitate-strengthened) SMAs is the work by Zhou et al. [124], where they studied the effect of the precipitation of Ni_4Ti_3 on the transformation behavior in Ni-rich Ni–Ti binary SMAs. In that work, a fully consistent thermodynamic treatment for the (metastable) equilibrium between B2 and Ni_4Ti_3 precipitates was used through the development of a CALPHAD description for the B2 and Ni_4Ti_3 phases—the description of the latter was not available until the assessment work by Povoden-Karadeniz [46]. The thermodynamic description was then incorporated into a phase field model that accounted for elastic interactions between the matrix and the precipitates, assuming coherent interfaces between them. Using the model, Zhou et al. were able to simulate the evolution of the shape and size of the precipitate taking into account the orientation relationships resulting from interfacial conditions and elastic interactions, as shown in Fig. 13. Moreover, using the matrix + precipitate microstructure they proceeded to study the effect of heterogeneities in compositions and strain fields on the stability of martensite structures (including B19' and the R-phase).

A more recent and related work [14] examined the precipitation of the so-called P-phase in (Ni,Pt)Ti HTSMAs. Experimental observations of the orientation relationship between the B2 matrix and the P-phase, free energy data (CALPHAD models), interfacial interactions and elastic properties of the matrix and the precipitate were used to build a PFM capable of describing the shape and spatial distribution of the precipitates, as well as the resulting composition and stress/strain heterogeneities. To account for the evolution of precipitate distributions, the authors simulated the nucleation process through Langevin noise. One of the most important results from this work was the estimate of the increase in the M_S temperature as a function of aging time. By accounting for the elastic

interactions between the martensite nucleus and the strain field associated with P-phase precipitates it was possible to estimate changes in the driving force for the martensite transformation and as a result changes in M_S .

In the rather small number of simulation works in which PFM has been used to investigate microstructural evolution in multiphase SMAs, several salient facts become apparent. A necessary condition for the development of quantitative PFM simulations of precipitation behavior requires a thermodynamic description of the phases taking part in (metastable) equilibrium. These descriptions are typically assessed within the CALPHAD method described earlier in this work. However, chemical thermodynamics alone are not sufficient to develop quantitative microstructural evolution models and one must rely on experimental information as well as other simulation techniques, including DFT methods [119] to parameterize model inputs such as elastic constants, interfacial energies and orientation relationships between matrix and secondary phases.

Finally, while useful at predicting the shape and distribution evolution of precipitate phases, PFM are limited by the computational costs associated with high fidelity models and sometimes it may be useful to use other, more efficient, mean-field approaches to investigate the effect of aging time and temperature on microstructures of heterophasic SMAs. Such an approach may be necessary for the development of ICME frameworks for the accelerated design of SMAs.

Mean Field Precipitation Kinetics Modeling in SMAs

As mentioned in this work and elsewhere, aging is usually used to control the precipitation of secondary phases as they can be used to tune the transformation behavior and improve the functional stability of SMAs. CALPHAD models accounting for possible metastable phases as well as phase field models to predict the shape and size evolution of precipitate phases can be used to develop a quantitative understanding not only of the nature of the kinetics of precipitation but can be used to investigate the effect of the resulting microstructures on the martensitic

transformation. PFM are however limited by their large computational cost, which make it impractical when attempting to simulate the overall evolution of precipitate structures under arbitrary time–temperature schedules.

More efficient, although less detailed, approaches to investigate the evolution of precipitate populations are based on mean-field treatments of nucleation and growth. A particularly powerful approach is the so-called Kampmann–Wagner (KW) [125] model for precipitation [126–128].

In recent implementations (e.g., the MatCalc code) based on this framework [64], the thermal history of the system is broken into isothermal segments. Precipitates of equal size and composition and grouped into classes, and the evolution of each class is determined according to the so-called thermodynamic extremum principle [127].

Nucleation of new precipitates is taken into account at each time step based on a multicomponent extension of classical nucleation theory [129]. The nucleation rate is calculated from the thermodynamic driving force (Fig. 14) for precipitate nucleation taking into account the mean-field composition of the matrix at a given time; the rate of atomic transfer across the precipitate/matrix interfaces; as well as barriers to nucleation arising from finite matrix/precipitate interfacial energy, $\gamma^{m/p}$, and volumetric

strain energy barriers arising from elastic/volume mismatch between the precipitates and the matrix.

After nucleation of each precipitate class, they evolve in composition and size under the assumption of maximum rate of dissipation of the total (including interfacial energies) Gibbs energy of the matrix + precipitate system [128] where the main dissipative mechanisms are interface motion and diffusion within precipitate and matrix phases. The aspect ratio of precipitates, h ,—in principle this could be simulated using PFM [124]—modifies the geometry of the diffusion fields around the precipitates and this can also be accounted for the most complete precipitation models [130] based on the Kampmann–Wagner formalism.

The major advantage of this approach is the fact that the evolution of the *radius and composition* of each precipitate (group) can be described through a linear system of equations, improving the numerical efficiency of the algorithms. On the other hand, a major disadvantage is that the gain in efficiency of a mean-field approach comes at the expense of lack of details regarding the interactions between chemistry and elastic interactions that arise naturally in PFM and that are particularly important considering the early stages of the nucleation and growth process, well before the regime where bulk thermodynamics and kinetics dominates.

Fig. 14 Precipitate modeling based on classical nucleation theory and mean-field description of precipitate growth [120]

Fig. 15 Predicted bimodal precipitate distribution in slow cooled Ni₅₂Ti₄₈ SMAs

The assessment of the CALPHAD model for the Ni–Ti binary system by Povoden-Karadeniz et al. [46] accounted for the metastable Ni₄Ti₃ and Ni₃Ti₂ phases thanks to the use of KW models. When compared with experimentally determined metastable solvus, the models enabled the adjustment of the entropy-like terms in the expressions for the Gibbs energies of the metastable phases, having estimated the enthalpy-like terms from DFT calculations of formation enthalpies.

In a more recent work, some of the present authors [131] tested the thermodynamic, kinetic, and precipitation model parameters (e.g., matrix/precipitate interfacial energies) assessed by Povoden-Karadeniz et al. against experiments by Zel'dovich et al. [132] on the effects of slow cooling of Ni-rich NiTi SMAs (Ni₅₁Ti₄₉ and Ni₅₂Ti₄₈) from temperatures well above the metastable solvus with Ni₄Ti₃ (typically above 870 °C). In that work, Ni₅₂Ti₄₈ alloys were observed to form a bimodal distribution of precipitates, with large particles forming as a result of favorable kinetics (i.e., large diffusion rates) at the high temperatures where the alloys crossed the metastable NiTi + Ni₄Ti₃ solvus during cooling. At these high temperatures, the thermodynamic driving force for nucleation is rather low so the precipitation kinetics is dominated by growth. At intermediate temperatures, both thermodynamics and kinetics are unfavorable and the growth of the initial population of precipitates is somewhat arrested, while nucleation is inhibited due to small driving forces for precipitation. Upon further cooling, the precipitation kinetics is dominated by copious nucleation. The end-result is a bimodal distribution, where there is a two orders of magnitude difference between precipitate populations. Figure 15 shows results from precipitation simulations with good

qualitative agreement with the experimental observations by Zel'dovich et al.. Provided reliable thermodynamic and kinetic models are available, similar approaches can be carried out in precipitate-strengthened HTSMAs.

Integrating Computational Thermodynamics and Kinetics Within an ICME Framework for HTSMAs

Accelerated material design through an ICME framework requires, as minimal and necessary albeit non-sufficient conditions, knowledge about the thermodynamics and kinetics of materials in order to establish chemistry + processing – structure relationships. Quantifiable microstructure metrics can in turn be used in combination with other physical models to establish the connections between microstructures and performance of the materials being developed. An example of some aspects of such an ICME framework applied to the accelerated development of HTSMAs is shown in Fig. 16.

In the case of HTSMAs for actuation applications, the need to control not only transformation behavior but also the cyclic stability of such material systems has led to the development of complex multiphase alloys in which nano-dispersed precipitates are used to tune transformation temperatures and to reduce the accumulation of slip-induced damage [1, 6, 10, 14]. Despite the lack in thermodynamics and kinetic models necessary for the implementation of ICME framework much progress has been made toward bridging this gap in the past few years and as more experimental work becomes available, the development of computational thermodynamics and kinetics models for HTSMAs will certainly accelerate.

Fig. 16 A prototype ICME framework for the development of precipitate-strengthened HTSMAs

Moreover, there is already a mature body of work in which the connection between microstructure and shape memory response has been made to the point where predictions are in quantitative and qualitative agreement with experiment [13, 133]. Making the chemistry-processing-structure-performance connection is thus possible.

In fact, very recent work by Frankel and Olson [18] has demonstrated the feasibility of using computational models and experiments to accelerate the development of HTSMAs. Specifically, those authors proposed a framework based on a Hierarchical Materials Design approach [26] to develop precipitate-strengthened NiTi- and PdTi-based HTSMAs in which Ni₂TiAl-type Heusler nano-dispersed precipitates were used to control transformation temperatures and cyclic stability of the alloys. The design parameters for that exercise were based on well-defined operating temperature ranges as well as superior cyclic stability, in addition to high strength and other performance metrics relevant to specific potential applications in the automotive and biomedical fields. Controllable design variables were the initial composition of the material as well as processing parameters such as aging temperature and time. One of the major design goals was to engineer alloys in such a way that the misfit between the precipitates and the matrix was minimized in order to enhance the driving force for nucleation of precipitates (hence achieving small, nanodispersed particles) and to minimize interfacial work and hysteresis associated with the martensitic transformation.

The connection between chemistry and processing and precipitate microstructure was achieved through the use of relatively simple Lifshitz–Slyozov–Wagner (LSW)-type coarsening models in which coarsening is assumed to be dominated by bulk diffusion, resulting in a time exponent of the growth rate of 1/3. Frankel and Olson also used strengthening models to account for precipitate looping and shearing mechanisms. Models accounting for the interfacial misfit as a function of composition of both matrix and precipitates. Moreover, they used a CALPHAD-like approach to predict the influence of composition on the austenite finish temperature, A_f . Parameterization of the models was carried out through calibration against extensive experimental work.

The work resulted in a number of alloy systems and processing schedules that demonstrate adequate performance for some specific applications. Despite their success, the authors recognized the need for the development of more quantitative and predictive models that can be used to extrapolate chemistry + processing – structure relations beyond the compositional ranges explored. This can only be achieved through CALPHAD assessments of the thermodynamics (i.e., phase stability) and kinetics (i.e., atomic mobilities) of these alloy systems.

Challenges Specific to HTSMAs Potentially Addressable Through Computational Thermodynamics and Kinetics

Up until this section, the discussions in this paper have focused mostly on the use of ICME approaches to investigate the design of the austenite matrix in order to improve the functional behavior of SMAs. Given the scarcity of research in this regard, most of the discussions have focused on SMAs rather than their high-temperature counterparts. Provided adequate thermodynamic and kinetic models were available, however, there is nothing in the discussions previously made that cannot be used for the development of HTSMAs. We have yet to discuss, however, the challenges specifically relevant to HTSMAs already discussed in “Unique Challenges of High Temperature Shape Memory Alloys” section. Before continuing we would like to note that to the best of the authors’ knowledge none of the alloy design strategies outlined below have been formally addressed within an ICME framework and they constitute at best a possible roadmap for further research.

Improving Stability of Precipitate-Strengthened HTSMAs microstructures

Earlier in this paper, it was mentioned that one of the major challenges for precipitate-strengthened HTSMAs is the destabilization of precipitate phases as operating temperatures

increase. This de-stabilization is mainly due to three factors: (1) the coarsening of precipitates at prolonged aging time; (2) the dissolution of precipitate phases as the operating temperatures approach the (metastable) solvus corresponding to the matrix + precipitate equilibrium; (3) the precipitation of secondary-undesirable phases that change matrix compositional and transformation behaviors.

In most precipitate-strengthening systems, a major obstacle is the stabilization of the precipitate structure at elevated temperature. Given the fact that there will always be a distribution of particle sizes Ostwald's ripening is always expected to occur. In this case, the only suitable approach to decrease the rate at which the precipitate structure coarsens would be to engineer the alloy in order to either reduce the mobility of the matrix/precipitate interface or decrease the effective bulk diffusion rates. In Al–Sc–Li alloys, precipitate stabilization at elevated temperatures has been achieved through the selection proper chemistry and heat treatment conditions that result in the formation of precipitates with core/shell structures in which the outer region of the precipitate phases function as a diffusion barrier that prevents further precipitate growth [134].

Increasing the thermal stability of precipitates in HTSMAs is a challenge that must be overcome as operating temperatures increases. Usually, this is accomplished through minor alloying additions that improve the stability of the precipitates against dissolution in the matrix. Such an approach was followed in the case of Co-based super alloys in which W was found to be the key addition to stabilize coherent $L1_2$ $Co_3(Al,W)$ precipitates. In a related problem, the formation of detrimental phases upon thermal aging can potentially be prevented through careful selection of alloying additions that decrease the stability of such phases. As mentioned earlier, the formation of detrimental phases upon thermal aging can be prevented through proper alloying additions. In Ti–Ta HTSMAs this has already been demonstrated as Al additions have been shown to decrease the stability of the ω phase [11].

With the exception with the last example, it is unclear whether the alloy design strategies mentioned above to improve the functional stability of precipitate-strengthened HTSMAs are feasible at all. Since the available compositional design space has barely been explored, this cannot be ruled out entirely. However, the alloy design strategy would need to consider *simultaneously* the connection between chemistry, processing and transformation temperatures and precipitate structure.

Enhancing Oxidation Resistance of HTSMAs

High operating temperatures of HTSMAs, combined with the relatively high susceptibility for oxidation of constituent elements make the development of oxidation resistance of

HTSMAs an even more difficult challenge to address. Until now, very few studies on the oxidation behavior of HTSMAs have been carried out. Even though there are almost no experimental results, the constituents of the most promising HTSMA systems are unlikely to be stable against oxidation conditions at elevated temperatures. This is particularly true when considering that the likely oxidation products will not result in a passivating layer. While the TiO_2 layer formed when NiTi–X HTSMAs are subject to oxidation exhibits parabolic growth [24], it is unlikely that such a layer would result in adequate protection, particularly because the oxygen transport rate in TiO_2 is relatively high.

Oxidation resistance of any significant quality can only be achieved in alloys capable of inducing the formation of SiO_2 , Cr_2O_3 , or Al_2O_3 passivating layers. In these three cases, the parabolic growth rates are sufficiently low to enable the formation of a protective layer with minimal metal loss [135]. If none of Si, Cr, and Al constitutes major elements in an HTSMA composition, their addition into conventional HTSMAs would have to be considered, in order to have any hope of providing any resistance to oxidation at temperatures above 400 °C.

Beyond the presence of oxide-forming elements, however, the following conditions must be met in order to ensure the formation of a passivating layer: (i) the oxide-forming element must have a high chemical activity in the host lattice; (ii) the diffusivity of the oxide former in the alloy should be sufficiently high and the diffusivity of oxygen in the alloy should be sufficiently low to prevent internal oxidation and promote the formation of a stable passivating layer at the metal surface. These conditions have been used in the recent development, for example, of alumina-forming stainless steels [25]. Similar approaches, grounded firmly on computational thermodynamics and kinetics have been proposed by Sato et al. for the improvement of oxidation resistance in Ni-based super alloys [136].

Unfortunately, a major difference quickly arises between oxidation-resisting structural alloys versus their HTSMAs counterparts: the transformation itself. While even preliminary work still needs to be carried out, it is not clear if a passivating layer would retain its integrity upon multiple actuation cycles considering that the metal/oxide interface would change its character as the alloy transforms from austenite to martensite and back. A thin enough passivating layer may be sufficiently compliant to accommodate such change although it is far from clear whether this is possible in the first place.

Conclusions and Recommendations

In this work, we have reviewed some of the most important challenges and opportunities related to the integration of computational thermodynamics and kinetics as an integral

ingredient for the development of ICME frameworks for SMAs in general and HTSMAs in particular. As our understanding of HTSMAs progresses, tailoring material properties around specific engineering performance metrics, rather than designing actuators and devices around the properties of the materials, will become increasingly feasible. Tailoring of HTSMA response will make necessary the exploration of a wide space in the composition + processing material design space. This is only made more complex as it has become evident that optimal alloy systems will necessarily be multicomponent and multiphase, with some of the phases potentially being metastable.

Computational thermodynamics can assist in this very challenging material design exercise by (1) providing an understanding of the phase stability and competition between the matrix and secondary (precipitate) phases; (2) quantifying driving forces for precipitation of precipitate phases; and (3) developing an understanding of defect structure in non-stoichiometric austenites. Phase field models in turn can incorporate CALPHAD descriptions of thermodynamic and other physical properties to develop quantitative simulations not only of the time evolution of the size and shape of precipitates but also the effect of such precipitate's structure on the transformation behavior of the HTSMAs. Mean-field approaches to precipitation kinetics can in turn be used to establish the connection between (potentially complex) processing schemes and microstructure, which in turn can be used to predict the functional response of the alloys.

Unfortunately, there are no reliable thermodynamic and kinetic models for most of the HTSMAs of interest. This deficiency, however, can be addressed by bringing CALPHAD expertise within the HTSMA community. Interest in collaboration can be brought about by dedicated efforts toward the implementation of full ICME approaches to design relatively well-understood systems (such as NiTi-based SMAs with small ternary additions) as there is already a significant and relevant body of literature. Once this has been demonstrated, the implementation of such methods to develop more complex alloy systems will certainly become a reality.

A more challenging problem is the fact that many of the problems associated exclusively to HTSMAs (such as thermal stability of microstructure and/or oxidation resistance) have barely been explored. In any case, full ICME deployment would necessitate accurate computational thermodynamic and kinetic models.

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References

1. Ma J, Karaman I, Noebe R (2010) High temperature shape memory alloys. *Int Mater Rev* 55:257
2. Firstov GS, Van Humbeeck J, Koval YN (2006) High temperature shape memory alloys problems and prospects. *J Intel Mat Syst Str* 17:1041
3. Kumar PK, Desai U, Monroe JA, Lagoudas DC, Karaman I, Bigelow G, Noebe RD (2011) Experimental investigation of simultaneous creep, plasticity and transformation of Ti50.5Pd30Ni19.5 high temperature shape memory alloy during cyclic actuation. *Mater Sci Eng A* 530:117
4. Kumar PK, Lagoudas DC (2010) Experimental and microstructural characterization of simultaneous creep, plasticity and phase transformation in Ti50Pd40Ni10 high-temperature shape memory alloy. *Acta Mater* 58:1618
5. Sehitoglu H (2015) A new journal helping to shape the future of materials. *Shape Mem Superelasticity* 1:3
6. Evirgen A, Karaman I, Noebe RD, Santamarta R, Pons J (2013) Effect of precipitation on the microstructure and the shape memory response of the Ni50.3Ti29.7Zr20 high temperature shape memory alloy. *Scr Mater* 69:354
7. Santamarta R, Arróyave R, Pons J, Evirgen A, Karaman I, Karaca H, Noebe R (2013) TEM study of structural and microstructural characteristics of a precipitate phase in Ni-rich Ni–Ti–Hf and Ni–Ti–Zr shape memory alloys. *Acta Mater* 61:6191
8. Niendorf T, Krooß P, Somsen C, Eggeler G, Chumlyakov YI, Maier HJ (2015) Martensite aging—avenue to new high temperature shape memory alloys. *Acta Mater* 89:298
9. Dogan E, Karaman I, Singh N, Chivukula A, Thawabi HS, Arroyave R (2012) The effect of electronic and magnetic valences on the martensitic transformation of CoNiGa shape memory alloys. *Acta Mater* 60:3545
10. Benafan O, Garg A, Noebe R, Bigelow G, Padula S, Gaydos D, Vaidyanathan R, Clausen B, Vogel S (2015) Thermomechanical behavior and microstructural evolution of a Ni (Pd)-rich Ni24.3Ti49.7Pd26 high temperature shape memory alloy. *J Alloys Compd* 643:275
11. Buenconsejo PJS, Kim HY, Miyazaki S (2011) Novel β -TiTaAl alloys with excellent cold workability and a stable high-temperature shape memory effect. *Scr Mater* 64:1114
12. Arróyave R, Junkaew A, Chivukula A, Bajaj S, Yao C-Y, Garay A (2010) Investigation of the structural stability of Co₂ NiGa shape memory alloys via ab initio methods. *Acta Mater* 58:5220
13. Cox A, Baxevanis T, Lagoudas DC (2014) Finite element analysis of precipitation effects on Ni-rich NiTi shape memory alloy response. *Mater Sci Forum* 792:65
14. Gao Y, Zhou N, Yang F, Cui Y, Kovarik L, Hatcher N, Noebe R, Mills M, Wang Y (2012) P-phase precipitation and its effect on martensitic transformation in (Ni, Pt) Ti shape memory alloys. *Acta Mater* 60:1514
15. Allison J (2011) Integrated computational materials engineering: a perspective on progress and future steps. *JOM* 63:15
16. Spanos G, Allison J, Cowles B, Deloach J, Pollock T (2013) Integrated computational materials engineering (ICME): implementing ICME in the aerospace, automotive, and maritime industries. *Miner Met Mater Soc (TMS)*
17. Meng XL, Cai W, Fu YD, Li QF, Zhang JX, Zhao LC (2008) Shape-memory behaviors in an aged Ni-rich TiNiHf high temperature shape-memory alloy. *Intermetallics* 16:698

18. Frankel DJ, Olson GB (2015) Design of heusler precipitation strengthened NiTi- and PdTi-base SMAs for cyclic performance. *Shape Mem Superelasticity* 1:162–179
19. Prasher M, Sen D (2014) Influence of aging on phase transformation and microstructure of Ni 50.3 Ti 29.7 Hf 20 high temperature shape memory alloy. *J Alloys Compd* 615:469
20. Ramaiah K, Saikrishna C, Bhagyaraj J, Bhaumik S (2013) Influence of Sc addition on microstructure and transformation behaviour of Ni_{24.7}Ti_{50.3}Pd_{25.0} high temperature shape memory alloy. *Intermetallics* 40:10
21. Atli K, Karaman I, Noebe R, Garg A, Chumlyakov Y, Kireeva I (2010) Improvement in the shape memory response of Ti_{50.5}Ni_{24.5}Pd₂₅ high-temperature shape memory alloy with scandium microalloying. *Metall Mater Trans A* 41:2485
22. Buenconsejo PJS, Kim HY, Hosoda H, Miyazaki S (2009) Shape memory behavior of Ti–Ta and its potential as a high-temperature shape memory alloy. *Acta Mater* 57:1068
23. Otsuka K, Ren X (2001) Mechanism of martensite aging effects and new aspects. *Mater Sci Eng A* 312:207
24. Smialek JL, Humphrey DL, Noebe RD (2010) Comparative oxidation kinetics of a NiPtTi high temperature shape memory alloy. *Oxid Met* 74:125
25. Brady MP, Yamamoto Y, Santella ML, Maziasz PJ, Pint BA, Liu C, Lu Z, Bei H (2008) The development of alumina-forming austenitic stainless steels for high-temperature structural use. *JOM* 60:12
26. Olson GB (1997) Computational design of hierarchically structured materials. *Science* 277:1237
27. Office of Science and Technology, White House (2011) Materials genome initiative for global competitiveness. Office of Science and Technology, White House, Washington, DC
28. McCluskey PJ, Xiao K, Gregoire JM, Dale D, Vlassak JJ (2015) Application of in situ nano-scanning calorimetry and X-ray diffraction to characterize Ni–Ti–Hf high-temperature shape memory alloys. *Thermochim Acta* 603:53
29. Cao S, Zhao J-C (2015) Application of dual-anneal diffusion multiples to the effective study of phase diagrams and phase transformations in the Fe–Cr–Ni system. *Acta Mater* 88:196
30. Saunders N (1998) CALPHAD: calculation of phase diagrams: a comprehensive. Pergamon, Oxford
31. Kaufman L, Bernstein H (1970) Computer calculation of phase diagrams. With special reference to refractory metals. Academic Press, New York
32. Kaufman L, Nesor H (1973) Theoretical approaches to the determination of phase diagrams. *Annu Rev Mater Sci* 3:1
33. Olson G, Kuehmann C (2014) Materials genomics: from CALPHAD to flight. *Scr Mater* 70:25
34. Lukas HL, Fries SG, Sundman B (2007) Computational thermodynamics: the Calphad method. Cambridge University Press, Cambridge
35. Arróyave R, Liu ZK (2006) Intermetallics in the Mg–Ca–Sn ternary system: structural, vibrational, and thermodynamic properties from first principles. *Phys Rev B* 74:174118
36. Zhou S, Arroyave R, Randall CA, Liu Z-K (2005) Thermodynamic modeling of the binary barium-oxygen system. *J Am Ceram Soc* 88:1943
37. Arróyave R, Liu Z (2006) Thermodynamic modelling of the Zn–Zr system. *Calphad* 30:1
38. Venimadhav A, Soukiasian A, Tenne D, Li Q, Xi X, Schlom D, Arróyave R, Liu Z, Sun H, Pan X et al (2005) Structural and transport properties of epitaxial Na_xCoO₂ thin films. *Appl Phys Lett* 87:172104
39. Arróyave R, Van De Walle A, Liu ZK (2006) First-principles calculations of the Zn–Zr system. *Acta Mater* 54:473
40. Perevoshchikova N, Appolaire B, Teixeira J, Aeby-Gautier E, Denis S (2012) A convex hull algorithm for a grid minimization of Gibbs energy as initial step in equilibrium calculations in two-phase multicomponent alloys. *Comput Mater Sci* 61:54
41. Lu X-G, Selleby M, Sundman B (2005) Assessments of molar volume and thermal expansion for selected bcc, fcc and hcp metallic elements. *Calphad* 29:68
42. Hallstedt B, Dupin N, Hillert M, Höglund L, Lukas HL, Schuster JC, Solak N (2007) Thermodynamic models for crystalline phases. Composition dependent models for volume, bulk modulus and thermal expansion. *Calphad* 31:28
43. Saunders N, Miodownik AP (1998) CALPHAD (calculation of phase diagrams): a comprehensive guide. Pergamon, Oxford
44. Tang W, Sundman B, Sandström R, Qiu C (1999) New modelling of the B2 phase and its associated martensitic transformation in the Ti–Ni system. *Acta Mater* 47:3457
45. Tang W (1997) Thermodynamic study of the low-temperature phase B19' and the martensitic transformation in near-equiatomic Ti–Ni shape memory alloys. *Metall Mater Trans A* 28:537
46. Povoden-Karadeniz E, Cirstea D, Lang P, Wojcik T, Kozeschnik E (2013) Thermodynamics of Ti–Ni shape memory alloys. *Calphad* 41:128
47. Cacciamani G, De Keyser J, Ferro R, Klotz UE, Lacaze J, Wollants P (2006) Critical evaluation of the Fe–Ni, Fe–Ti and Fe–Ni–Ti alloy systems. *Intermetallics* 14:1312
48. Tang W, Sandström R, Miyazaki S (2000) Phase equilibria in the pseudobinary Ti_{0.5}Ni_{0.5}–Ti_{0.5}Cu_{0.5} system. *J Phase Equilib* 21:227
49. Sitepu H, Schmahl WW, Allafi JK, Eggeler G, Dlouhy A, Toebbens D, Tovar M (2002) Neutron diffraction phase analysis during thermal cycling of a Ni-rich NiTi shape memory alloy using the Rietveld method. *Scr Mater* 46:543
50. Ren XB, Otsuka K (2000) Why does the martensitic transformation temperature strongly depend on composition? *Mater Sci Forum* 327:429
51. Hillert M, Jarl M (1978) A model for alloying in ferromagnetic metals. *Calphad* 2:227
52. Hillert M (2001) The compound energy formalism. *J Alloys Compd* 320:161
53. Santhy K, Kumar KH (2015) Thermodynamic reassessment of Nb–Ni–Ti system with order–disorder model. *J Alloys Compd* 619:733
54. Palumbo M (2008) Thermodynamics of martensitic transformations in the framework of the CALPHAD approach. *Calphad* 32:693
55. Cotes S, Baruj A, Sade M, Guillermet AF (1995) Thermodynamics of the g/e martensitic transformation in Fe–Mn alloys: modelling of the driving force, and calculation of the M_s and A_s. *J Phys IV* 5:83
56. Ghosh G, Olson G (1994) Kinetics of FCC → BCC heterogeneous martensitic nucleation—I. The critical driving force for athermal nucleation. *Acta Metall Mater* 42:3361
57. Borgenstam A, Hillert M (2000) Nucleation of isothermal martensite. *Acta Mater* 48:2777
58. Ren X, Otsuka K (2000) Universal symmetry property of point defects in crystals. *Phys Rev Lett* 85:1016
59. Ren X, Otsuka K (1997) Origin of rubber-like behaviour in metal alloys. *Nature* 389:579
60. Sarkar S, Ren X, Otsuka K (2005) Evidence for strain glass in the ferroelastic-martensitic system Ti₅₀ – xNi₅₀ + x. *Phys Rev Lett* 95:205702
61. Cai W, Otsuka K, Asai M (1999) Martensite aging effect in Ti–Pd and Ti–Pd–Ni high temperature shape memory alloys. *Mater Trans JIM* 40:895
62. Dogan E, Karaman I, Chumlyakov Y, Luo Z (2011) Microstructure and martensitic transformation characteristics of CoNiGa high temperature shape memory alloys. *Acta Mater* 59:1168

63. Manca A, Shelyakov AV, Airoldi G (2003) Ageing in parent phase and Martensite stabilization in a Ni50Ti30Hf20 alloy. *Mater Trans* 44:1219
64. Khovaylo V, Kainuma R, Ishida K, Omori T, Miki H, Takagi T, Datesman A (2008) New aspects of martensite stabilization in Ni–Mn–Ga high-temperature shape memory alloy. *Philos Mag* 88:865
65. Najafabadi R, Srolovitz D, Ma E, Atzmon M (1993) Thermodynamic properties of metastable Ag–Cu alloys. *J Appl Phys* 74:3144
66. Aliravci CA, Pekköleryüz MÖ (1998) Calculation of phase diagrams for the metastable Al–Fe phases forming in direct-chill (DC)-cast aluminum alloy ingots. *Calphad* 22:147
67. Bajaj S, Haverty MG, Arróyave R, Shankar S (2015) Phase stability in nanoscale material systems: extension from bulk phase diagrams. *Nanoscale* 7:9868
68. Khvan AV, Cheverikin VV, Dinsdale AT, Watson A, Levchenko VV, Zolotarevskiy VS (2015) Formation of metastable phases during solidification of Al–3.2 wt% Mn. *J Alloys Compd* 622:223
69. Frenzel J, George EP, Dlouhy A, Somsen C, Wagner M-X, Eggeler G (2010) Influence of Ni on martensitic phase transformations in NiTi shape memory alloys. *Acta Mater* 58:3444
70. Eggeler G, Khalil-Allafi J, Gollerthan S, Somsen C, Schmahl W, Sheptyakov D (2005) On the effect of aging on martensitic transformations in Ni-rich NiTi shape memory alloys. *Smart Mater Struct* 14:S186
71. Weighardt S, Maier H, Chumlyakov Y (2013) Dependence of functional degradation on crystallographic orientation in NiTi shape memory alloys aged under stress. *J Alloys Compd* 577:S219
72. Oikawa K, Ota T, Imano Y, Omori T, Kainuma R, Ishida K (2006) Phase equilibria and phase transformation of Co–Ni–Ga ferromagnetic shape memory alloy system. *J Phase Equilib Diffus* 27:75
73. Dadda J, Maier H, Karaman I, Chumlyakov YI (2009) Cyclic deformation and austenite stabilization in Co35Ni35Al30 single crystalline high-temperature shape memory alloys. *Acta Mater* 57:6123
74. Chari A, Dogan E, Talapatra A, Chivukula AR, Garay A, Karaman I, Arróyave R (2014) Computational thermodynamics of the CoNiGa high temperature shape memory alloy system. *Calphad* 45:167
75. Galvan E, Malak Jr RJ, Gibbons S, Arroyave R (2014) Constraint satisfaction approach to the design of multi-component, multi-phase alloys. In: ASME 2014 international design engineering technical conferences and computers and information in engineering conference. American Society of Mechanical Engineers, New York, p V02BT03A010
76. De Keyser J, Cacciamani G, Dupin N, Wollants P (2009) Thermodynamic modeling and optimization of the Fe–Ni–Ti system. *Calphad* 33:109
77. Zhu W, Duarte L, Leinenbach C (2014) Experimental study and thermodynamic assessment of the Cu–Ni–Ti system. *Calphad* 47:9
78. Qiu A-T, Liu L-J, Wei P, Lu X-G, Li C-H (2011) Calculation of phase diagram of Ti–Ni–O system and application to deoxidation of TiNi alloy. *Trans Nonferrous Met Soc China* 21:1808
79. Matsumoto S, Tokunaga T, Ohtani H, Hasebe M (2005) Thermodynamic analysis of the phase equilibria of the Nb–Ni–Ti system. *Mater Trans* 46:2920
80. Wang C, Guo Y, Lu Y, Liu X (2014) Thermodynamic assessment of the Ti–Ir system. *J Phase Equilib Diffus* 35:269
81. Hafner J (2000) Atomic-scale Computational materials science. *Acta Mater* 48:71
82. Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects. *Phys Rev* 140:A1133
83. Hohenberg P, Kohn W (1964) Inhomogeneous electron gas. *Phys Rev* 136:B864
84. Kohn W, Becke AD, Parr RG (1996) Density functional theory of electronic structure. *J Phys Chem* 100:974
85. Soler JM, Artacho E, Gale JD, García A, Junquera J, Ordejón P, Sánchez-Portal D (2002) The SIESTA method for ab initio order-N materials simulation. *J Phys Condens Matter* 14:2745
86. Kresse G (2009) VASP, Vienna ab-initio package simulation, vol 2007. Vienna University, Vienna
87. Hafner J (2007) Materials simulations using VASP—a quantum perspective to materials science. *Comput Phys Commun* 177:6
88. Gonze X, Beuken JM, Caracas R, Detraux F, Fuchs M, Rignanese GM, Sindic L, Verstraete M, Zerah G, Jollet F (2002) First-principles computation of material properties: the ABINIT software project. *Comput Mater Sci* 25:478
89. Turchi PE, Abrikosov IA, Burton B, Fries SG, Grimvall G, Kaufman L, Korzhavyi P, Manga VR, Ohno M, Pisch A (2007) Interface between quantum-mechanical-based approaches, experiments, and CALPHAD methodology. *Calphad* 31:4
90. Bozzolo G, Ferrante J, Smith JR (1992) Method for calculating alloy energetics. *Phys Rev B* 45:493
91. Bozzolo G, Noebe RD, Mosca HO (2005) Site preference of ternary alloying additions to NiTi: Fe, Pt, Pd, Au, Al, Cu, Zr and Hf. *J Alloys Compd* 389:80
92. Bozzolo G, Mosca HO, Noebe RD (2007) Phase structure and site preference behavior of ternary alloying additions to PdTi and PtTi shape-memory alloys. *Intermetallics* 15:901
93. Bozzolo G, Mosca HO, del Grosso MF (2008) Energy of formation, lattice parameter and bulk modulus of (Ni, X) Ti alloys with X = Fe, Pd, Pt, Au, Al, Cu, Zr, Hf. *Intermetallics* 16:668
94. Mosca H, Bozzolo G, del Grosso M (2012) Atomistic modeling of ternary additions to NiTi and quaternary additions to Ni–Ti–Pd, Ni–Ti–Pt and Ni–Ti–Hf shape memory alloys. *Phys B* 407:3244
95. Lu J, Hu Q, Wang L, Li Y, Xu D, Yang R (2007) Point defects and their interaction in TiNi from first-principles calculations. *Phys Rev B* 75:094108
96. Shi H, Frenzel J, Martinez G, Van Rompaey S, Bakulin A, Kulkova S, Van Aert S, Schryvers D (2014) Site occupation of Nb atoms in ternary Ni–Ti–Nb shape memory alloys. *Acta Mater* 74:85
97. Moitra A, Solanki KN, Horstemeyer M (2011) The location of atomic hydrogen in NiTi alloy: a first principles study. *Comput Mater Sci* 50:820
98. Ki Yokoyama (2004) Eguchi T, Asaoka K, Nagumo M. Effect of constituent phase of Ni–Ti shape memory alloy on susceptibility to hydrogen embrittlement. *Mater Sci Eng A* 374:177
99. Singh N, Talapatra A, Junkaew A, Duong T, Gibbons S, Li S, Thawabi HS, Olivos E, Arroyave R (2015) Effect of ternary additions to structural properties of NiTi alloys. *Comput Mater Sci* (accepted)
100. Frenzel J, Wiczorek A, Opahle I, Maaß B, Drautz R, Eggeler G (2015) On the effect of alloy composition on martensite start temperatures and latent heats in Ni–Ti-based shape memory alloys. *Acta Mater* 90:213
101. Hickel T, Uijttewaal M, Al-Zubi A, Dutta B, Grabowski B, Neugebauer J (2012) Ab initio-based prediction of phase diagrams: application to magnetic shape memory alloys. *Adv Eng Mater* 14:547
102. Siewert M, Gruner M, Dannenberg A, Chakrabarti A, Herper H, Wuttig M, Barman S, Singh S, Al-Zubi A, Hickel T (2011) Designing shape-memory Heusler alloys from first-principles. *Appl Phys Lett* 99:191904
103. Boettinger WJ, Warren JA, Beckermann C, Karma A (2002) Phase-field simulations of solidification. *Annu Rev Mater Res* 32:163

104. Chen LQ (2002) *Annu Rev Mater Res* 32:113
105. Guyer JE, Boettinger WJ, Warren JA, McFadden GB (2004) Phase field modeling of electrochemistry. I. Equilibrium. *Phys Rev E* 69:021603/1
106. Cahn JW, Hilliard JE (1958) Free energy of a nonuniform system I. Interfacial free energy. *J Chem Phys* 28:258
107. Allen SM, Cahn JW (1979) A microscope theory of antiphase boundary and its application to antiphase domain coarsening. *Acta Metall* 27:1085
108. Jin YM (2013) Phase field modeling of current density distribution and effective electrical conductivity in complex microstructures. *Appl Phys Lett* 103:021906
109. Jin YM (2012) Phase-field microelastic modeling of microstructure evolutions in free-standing thin films. *Acta Mater* 60:6547–6554
110. Jin YM (2011) Competitive roles of elastic and magnetic interactions in twin boundary behaviors of magnetic shape memory alloys. *Appl Phys Lett* 99:062507
111. Jin YM (2009) Effects of twin boundary mobility on domain microstructure evolution in magnetic shape memory alloys: phase field simulation. *Appl Phys Lett* 94:062508
112. Wang J, Leinenbach C, Liu H, Liu L, Roth M, Jin Z (2009) Re-assessment of diffusion mobilities in the face-centered cubic Cu–Sn alloys. *Calphad* 33:704
113. Jin Y, Wang Y, Khachaturyan A (2001) Three-dimensional phase field microelasticity theory and modeling of multiple cracks and voids. *Appl Phys Lett* 79:3071
114. Jin Y, Khachaturyan A (2001) Phase field microelasticity theory of dislocation dynamics in a polycrystal: model and three-dimensional simulations. *Philos Mag Lett* 81:607
115. Jin Y, Artemev A, Khachaturyan A (2001) Three-dimensional phase field model of low-symmetry martensitic transformation in polycrystal: simulation of Xsi martensite in Au–Cd alloys. *Acta Mater* 49:2309
116. Artemev A, Jin Y, Khachaturyan A (2002) Three-dimensional phase field model and simulation of cubic $\rightarrow$ tetragonal martensitic transformation in polycrystals. *Philos Mag A* 82:1249
117. Zhang J, Chen L (2005) Phase-field model for ferromagnetic shape-memory alloys. *Philos Mag Lett* 85:533
118. Li L, Li J, Shu Y, Chen H, Yen J (2008) Magnetoelastic domains and magnetic field-induced strains in ferromagnetic shape memory alloys by phase-field simulation. *Appl Phys Lett* 92:172504
119. Kamachali RD, Borukhovich E, Hatcher N, Steinbach I (2014) DFT-supported phase-field study on the effect of mechanically driven fluxes in Ni₄Ti₃ precipitation. *Modell Simul Mater Sci Eng* 22:034003
120. Ke C, Cao S, Zhang X (2014) Three-dimensional phase field simulation of the morphology and growth kinetics of Ni₄Ti₃ precipitates in a NiTi alloy. *Modell Simul Mater Sci Eng* 22:055018
121. Guo W, Steinbach I, Somsen C, Eggeler G (2011) On the effect of superimposed external stresses on the nucleation and growth of Ni₄Ti₃ particles: a parametric phase field study. *Acta Mater* 59:3287
122. Ke C, Cao S, Zhang X (2015) Phase field modeling of Ni-concentration distribution behavior around Ni₄Ti₃ precipitates in NiTi alloys. *Comput Mater Sci* 105:55
123. Mamivand M, Zaeem MA, El Kadiri H (2013) A review on phase field modeling of martensitic phase transformation. *Comput Mater Sci* 77:304
124. Zhou N, Shen C, Wagner M-X, Eggeler G, Mills M, Wang Y (2010) Effect of Ni₄Ti₃ precipitation on martensitic transformation in Ti–Ni. *Acta Mater* 58:6685
125. Kampmann R, Wagner R, Haasen P, Gerold V, Wagner R, Ashby M (1984) Decomposition of alloys: the early stages. In: Haasen P, Gerold V, Wagner R, Ashby MF (eds) 2nd *Acta Scripta Metallurgica* conference. Pergamon Press, Oxford, p 91
126. Kozeschnik E, Svoboda J, Fischer F (2004) Modified evolution equations for the precipitation kinetics of complex phases in multi-component systems. *Calphad* 28:379
127. Kozeschnik E, Svoboda J, Fratzl P, Fischer F (2004) Modelling of kinetics in multi-component multi-phase systems with spherical precipitates: II: numerical solution and application. *Mater Sci Eng A* 385:157
128. Svoboda J, Fischer F, Fratzl P, Kozeschnik E (2004) Modelling of kinetics in multi-component multi-phase systems with spherical precipitates: I: Theory. *Mater Sci Eng A* 385:166
129. Russell KC (1980) Nucleation in solids: the induction and steady state effects. *Adv Colloid Interface Sci* 13:205
130. Kozeschnik E, Janssens K, Bataille C (2012) Modeling solid-state precipitation. Momentum Press, New York
131. Johnson L, Arróyave R (2015) Coupling precipitation simulations and mesh adaptive direct search for the prescription of heat treatments in precipitation-engineered shape memory alloys (in preparation)
132. Zel'dovich V, Sobyana G, Pushin V (1997) Bimodal size distribution of Ti₃Ni₄ particles and martensitic transformations in slowly cooled nickel-rich Ti–Ni alloys. *Scr Mater* 37:79
133. Baxevanis T, Cox A, Lagoudas D (2014) Micromechanics of precipitated near-equiatom Ni-rich NiTi shape memory alloys. *Acta Mech* 225:1167
134. Radmilovic V, Ophus C, Marquis E, Rossell M, Tolley A, Gautam A, Asta M, Dahmen U (2011) Highly monodisperse core–shell particles created by solid-state reactions. *Nat Mater* 10:710
135. Pint BA, Distefano JR, Wright IG (2006) Oxidation resistance: one barrier to moving beyond Ni-base superalloys. *Mater Sci Eng A* 415:255
136. Sato A, Chiu Y-L, Reed R (2011) Oxidation of nickel-based single-crystal superalloys for industrial gas turbine applications. *Acta Mater* 59:225