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New trends in metallic alloys / Alliages métalliques : nouvelles tendances

Combinatorial approaches for the design of metallic alloys

Approches combinatoires pour la conception d'alliages métalliques

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ABSTRACT

The design of new metallic alloys is faced with the challenge of an increasing complexity of the alloys composition, processing and resulting microstructures necessary to answer to multiple property targets, together with a requirement that the design stage be faster and less expensive. This paper shows that combinatorial methods, combining numerical and experimental approaches, can be applied to the specific requirements of alloy design and lead to improved understanding of fundamental processes of physical metallurgy, such as precipitation, together with improved alloy compositions and processing.

RÉSUMÉ

La conception de nouveaux alliages métalliques est confrontée au défi d'une complexité croissante de leur composition, du traitement et des microstructures résultantes nécessaires pour répondre à de multiples objectifs quant à leurs propriétés, ainsi qu'à l'exigence d'une étape de conception plus rapide et moins coûteuse. Cet article montre que les méthodes combinatoires, associant des approches numériques et expérimentales, peuvent être appliquées aux exigences spécifiques de la conception des alliages et conduire à une meilleure compréhension des processus fondamentaux de la métallurgie physique, tels que la précipitation, ainsi qu'à des compositions et des traitements d'alliages améliorés.

1. Introduction

Engineering alloys have evolved towards an increasing complexity as they are used in more demanding conditions to, e.g., reduce the carbon footprint of transportation, energy production or industrial processes. Specific alloys are required for every part of an engineering structure with an optimized combination of (often antagonistic) characteristics such as

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strength, toughness, corrosion resistance, density, processability or cost. The traditional way of "designing" alloys by making a discrete set of ingots of varied compositions is a despairingly slow and costly procedure, even more so as industrial alloys commonly contain more than ten elements, interacting in intricate ways during processing steps comprising an equally large number of parameters.

Developing the methodology for accelerated alloy design has become a strong driver for research in material science and specifically in metallurgy [1–4], especially since the launch in the USA of the Materials Genome Initiative (MGI) in 2011. However, what makes accelerated alloy design particularly challenging for structural materials is that their properties are not directly controlled by their composition, but instead by their microstructure (phase fraction, size, shape, chemistry), among others at the nanoscale, which depends both on composition and processing parameters through phase transformations and their kinetics. Schematically, one could define the strategy for accelerated alloy design as following a sequence of complementary objectives:

(1) develop a knowledge-based capacity to predict the structure, microstructure and properties of alloys so as to minimize the number of experimental trials for alloy development;
(2) develop high-throughput experimental and numerical methods allowing one to explore increasingly large parts of the alloy design space (chemical composition and processing parameters);
(3) develop methods that allow finding an optimal alloy from the design space.

These objectives are obviously coupled with each other, since the development of predictive models is the key building block of optimization procedures and, in turn, requires large datasets for assessing the model quality.

On the modeling side, large databases are being developed throughout the world to assess from atomistic calculations the structure and physical properties of multi-constituent phases [5–8]. While this data is of great interest to feed larger-scale models, it is quite far from being able, from first principles, to describe the full multi-scale microstructure development in an alloy, even of a simple chemical composition. Therefore, the modeling effort needs to be carried out using a variety of scales and techniques, bridging them as much as possible to make it possible to reach the goal of numerically-driven alloy design.

On the experimental side, high-throughput methods can be classified into two broad categories. In the first, the traditional way of elaborating discrete sets of alloys is maintained, but procedures are developed to drastically increase the productivity of these methods. A compromise needs then to be found between the small size of the samples and the possibility to process them representatively and test their mechanical properties. In the second category, one finds the fabrication of compositionally graded alloys, and/or alloys with gradients of processing parameters. These materials enable to study continuously the material design space and, when associated with spatially resolved automated characterization techniques (such as X-ray diffraction), make it possible to acquire very large datasets coupling the chemical composition with the alloy's characteristics.

The knowledge gained through the accumulation of data, may it come from first principles calculations, from thermodynamics or kinetics – both experimental and theoretical –, from a classical data collection using a conventional route – discrete alloy fabrication and characterization – or from high-throughput experiments, may then be used as a basis for predictive model development and hence for alloy design *a priori*. Nevertheless, the design space of engineering alloys is so huge that it prohibits a complete naive exploration. Indeed, if, for instance, we consider that nickel-based alloys may incorporate up to twenty elements, whose concentrations can take fifty values each, this makes a total of $50^{20} \sim 10^{34}$ possible different alloys. Assuming that a fast model takes only one millisecond to compute the properties of each alloy – which is very optimistic –, the total calculation time would reach 300 000 trillion years, i.e. thirteen orders of magnitude longer than the age of the Universe! This fully justifies the recourse to automatic optimization methods, in particular stochastic-based algorithms called metaheuristics.

This paper will present a few examples of numerical and experimental high-throughput methods for a more efficient exploration of the parameter space that we have used in the past few years.

In the first part, a methodology for optimizing alloy design in a multi-dimensional variable space will be presented, based on the combination of computational thermodynamics using the CALculation of PHAse Diagrams (CALPHAD) method, physical metallurgy models, data mining (e.g., neural networks or Gaussian processes), and optimization using multi-objective genetic algorithms.

In a second part, an experimental methodology capable of providing the necessary data for such optimization methods will be presented. This methodology involves the fabrication of materials with gradients of composition and/or processing parameters, the time- and space-resolved characterization using X-ray methods of the phase transformation path occurring in this alloy compositional space, and the confrontation of these results with models.

Application examples of this methodology and perspectives for future research will be discussed.

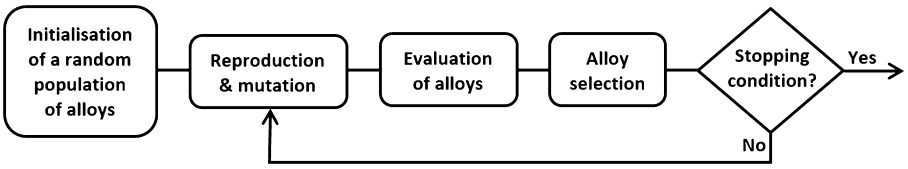

Fig. 1. Simplified flow chart of genetic algorithm optimization.

2. Examples of computational alloy design strategies

2.1. Genetic algorithm optimization

As stated in the introduction, the immensity of the input design space is such that it is not possible, even using fast predictive tools, to explore systematically all possible alloys within a given system. To circumvent this problem, the use of mathematical optimization tools has been proposed. Metallurgical problems being by nature rather non-linear, strongly coupled, sometimes non-continuous (e.g., formation or not of a phase) and often non-derivable because only discrete predictions can be made, the main strategies have been to employ stochastic-based algorithms called metaheuristics, like "simulated annealing" [9], "particle swarm" [10], "cuckoo search" [11], or "genetic algorithms" (GA) [12], the latter being the most popular and those that we have implemented. The principle behind GAs is to mimic the processes involved in the theory of biological evolution, by simulating reproduction, mutation and selection of a population of alloys whose compositions – and sometimes processing parameters – constitute the genes: each gene represents the concentration of a given alloying element – and sometimes a processing parameter. A typical GA can be illustrated by the flow chart of Fig. 1: a population of "individuals", made of tens, hundreds or thousands of different alloys is first generated randomly. Then, couples of alloys are chosen at random to become "parents" by reproducing, i.e. their genes are randomly mixed to produce "children", and some alloys are also randomly selected for mutation, e.g., some of their genes are randomly changed to produce "mutants". The "performance" of all children and mutants is then evaluated by calculating a "fitness function/criterion", taking into account the predicted characteristic(s) to be optimized and a possible set of constraints also called "go/no-go criteria". The kinds of models that can be used to achieve this will be described later. At this stage, only (some of) the best individuals are selected to survive in the population at the next generation and (some of) the less performing ones are discarded/killed. The process then loops back to the reproduction/mutation stage, and it is let to evolve until a stopping or convergence criterion is reached, when a pre-set number of generations is reached or when the maximum acceptable computation time is attained.

Doing so, alloys with compositions that are favorable to the target characteristic(s) will progressively transmit their "good genes", and the population will converge towards an overall better performance and will finally contain optimized alloys. In their simplest form, GAs operate as exposed above and in Fig. 1, but their efficiency can be enhanced by implementing a set of techniques. For instance, "immortality" can be given to the best alloys, so that they will be carried over through generations unless they are replaced by better ones. In a similar way, the best individuals obtained from the beginning can be stored in a separate archive, which can increase the number of good alloys beyond that of the population; this is notably useful in the case of multi-objective optimization, which will be described later. A drawback of evolutionary computation is that the selection procedure tends to reproduce elites, leading after a while to a loss in genetic diversity and/or to the presence of duplicates, which sometimes degrades the global search efficiency. Efforts have thus been put into maintaining a high diversity in the population to keep a potential source of new good gene values: to do so, duplicate removal can be enforced, and mutation of a limited number of genes can be partly replaced by a complete mutation of all genes, i.e. by some sort of "spontaneous generation" of individuals. The selection stage may also include, in addition to the choice of best individuals, diversity criteria favoring alloys that differ as much as possible from each other.

The basic implementation of a GA consists in optimizing a single objective, e.g., a mechanical property, while possibly satisfying a set of constraints. The result is thus a final population of alloys, ranked by order of the target property, in which only one candidate material possesses the best characteristic. However, the use of a material almost never involves the exploitation of a single property, and sets of requirements are usually to be fulfilled, i.e. combinations of characteristics, e.g., strength, ductility, cost… of course, one may imagine creating a composite fitness function incorporating in a single variable all the relevant characteristics, e.g., one may want to maximize the quantity "strength $\times$ ductility/cost". Still, the algorithm will produce only a single best alloy, the one with the optimal value of the fitness function. Nevertheless, for a given application, the best material may not be this one, and for each envisioned application the acceptable trade-off between characteristics may not be identical. It is usually preferable that the end-user, or the decision-maker, can choose from a set of alloys, all having different combinations of characteristics, provided that all the proposed solutions represent the best possible compromises between characteristics. This is addressed within the frame of multi-objective optimization (MOO). The concepts behind MOO are those of domination, non-domination and Pareto-optimality, as illustrated in Fig. 2 in the case one wanted to maximize the strength and minimize the cost of alloys.

For instance, Alloy A dominates Alloy B since the former has at the same time a higher strength and a lower cost than the latter. Alloy A is, as all alloys represented by closed symbols, non-dominated, i.e. no alloy possesses at the same time a higher strength and a lower cost, which is explicitly represented in the case of Alloy C. All non-dominated alloys constitute

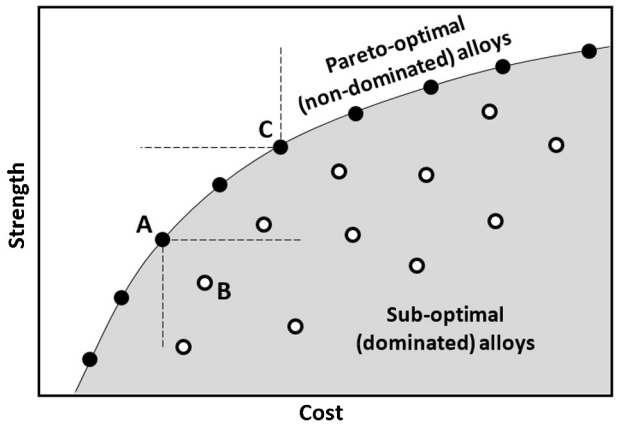

Fig. 2. Concepts used in MOO if one wants to maximize the strength and minimize the cost of alloys: Alloy A dominates Alloy B, Alloy C is non-dominated as are all alloys in the Pareto-optimal set (closed symbols), whereas all alloys below the optimal curve in the gray area (open symbols) are dominated and hence sub-optimal.

the Pareto set, lie on the Pareto curve and are said to be Pareto-optimal. They represent the best possible trade-offs between strength and cost. On the contrary, all alloys in the gray area (open symbols) are dominated by alloys of the Pareto set and are therefore sub-optimal. These concepts can be extended to any number of characteristics. However, finding the Pareto set, or even members of the set, is not trivial. GAs were found to be able to tackle efficiently this problem, which is then called genetic algorithm multi-objective optimization (GAMOO). In the case depicted in Fig. 2, the algorithm would try to make the population evolve towards both the top and the left of the graph. To accomplish this, instead of ranking alloys according to a single calculated characteristic or composite criterion, a non-domination sorting can be implemented, i.e. non-dominated alloys are selected or favored to survive from a generation to the next one. One of the most popular algorithms deriving from this concept is the so-called "Non-dominated Sorting Genetic Algorithm, version II" (NSGA-II) [13], which we have modified and adapted, for alloy design, to deal with the highly constrained nature, the high dimensionality and the specific combinatorial features of metallurgical problems; examples will be presented later.

It must be noted at this point that, being stochastic optimization processes, metaheuristics like genetic algorithms never guarantee to find the complete and true Pareto set, nor even members of the true Pareto set. And there is no way to assess it unless the true set is known in advance; of course, this may happen in benchmark problems specifically designed to test the efficiency of algorithms, but it never happens in real situations where GAs are precisely used to discover unknown optimal solutions! Nevertheless, the used algorithms have themselves been benchmarked in complex situations and successfully tested. Besides and with a more pragmatic perspective, they have been used to design alloys that surpass previously existing ones (examples will be presented later), which gives confidence in their abilities.

2.2. The need for fast predictive models

Alloy design by optimization needs criteria to be optimized. For instance, in GAs, the fitness function, the constraints and the ranking of individuals must involve estimates of alloys characteristics as a function of composition. Models are therefore necessary, which can give at least trends in view of property optimization, or at best reliable predictions. Many modeling approaches exist to predict the properties of alloys as a function of composition and/or processing parameters. They range from ab initio simulation using first principles at atomic scale – solving quantum mechanics Schrödinger equation, for instance using the density functional theory, DFT – to purely empirical regression using data mining tools, and including Monte Carlo simulation, molecular dynamics, computational thermodynamics, computational kinetics, finite elements, phase field simulation, etc. It is neither the aim here to list them all exhaustively nor to give their respective advantages or drawbacks in terms of accuracy. Nevertheless, to be exploitable by a metaheuristic to design new alloys, they need not only to present a good predictive efficiency, but they must also be fast. Indeed, during the running of a GA optimization, the characteristics of several thousands, tens of thousands, or more often hundreds of thousands or even millions of different alloys must be predicted. Being very far from the unattainable gigantic numbers of possible materials exemplified in the introduction, these numbers are still quite large. If one allows an optimization to run for one month, a time during which one million predictions must be made, this leaves, for each alloy, less than three seconds to predict all the properties relevant to the design problem. Even if massive parallel computing would reduce the overall calculation time, such a consideration clearly excludes time-demanding modeling approaches, like ab initio simulation, Monte Carlo simulation, molecular dynamics, phase field simulation, or the calculation of thermomechanical processes by finite elements. For this reason, the community of computational alloy design by combinatorial optimization has mainly adopted three categories of predictive tools:

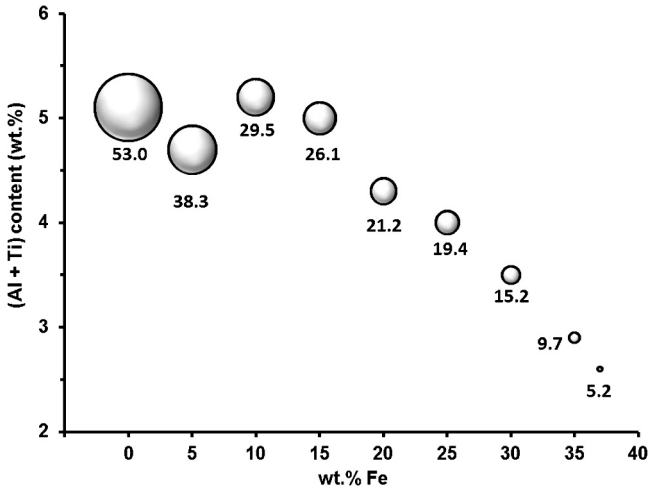

Fig. 3. (Al + Ti) content of optimized superalloys as a function of iron concentration. The maximized volume fraction of γ' is represented by the size of bubbles; the corresponding percentage of γ' is written below or next to each symbol.

- those that can be calculated by simple equations, by solving elementary matrices or equation systems or by running through limited loops; this can include physical models – examples will be given later – but also, for instance, the cost of alloying elements;
- thermodynamics using Calphad software;
- data mining/machine learning tools, which will be presented later.

All usually run in times limited to fractions of a second, or a few seconds maximum for Calphad if properly configured. Such approaches will be described below. There is no intention to be exhaustive, but to give a focus on a few examples in the domain of computational alloy design by combinatorial optimization.

2.3. Calphad

It is not the aim of this paper to present a full description of the theory behind the CALculation of PHAse Diagram (Calphad) method [14], but its main features may be useful in order to understand its use in alloy design. The main principle is the minimization of the total Gibbs free energy, G, of an alloy system in given conditions of pressure, P, and temperature, T. The molar Gibbs free energy, G_i, of each potential phase i, is described as a function of its composition, P and T through mathematical expressions resulting from more or less complex theoretical and/or empirical thermodynamic calculations. Their parameters are adjusted to numerous measurements made on simple systems (mostly unaries, binaries, and ternaries) and/or with respect to ab initio simulations. The total free energy of an alloy is then the sum, over all possible phases, of the products $n_i G_i$, with n_i the number of moles of phase i. Complex numerical approaches, which are specific to each software, are then implemented to find the repartition of all elements in the alloy that gives the lowest possible value of G, i.e. the thermodynamic equilibrium. Possible outputs of computational thermodynamics are therefore the nature, fraction, and composition of phases, but also thermodynamic quantities like activity, enthalpy, entropy, free energy… Commercial and open-source software suites now exist, along with thermodynamic databases for most categories of engineering alloys.

Many examples can be found of alloys designed using Calphad, and the method is now routinely used in the metallurgical industry, but we will here focus only on the use of combinatorial optimization relying on computational thermodynamics predictions. One of the first uses of Calphad predictions to guide the evolution of a genetic algorithm to design new alloys was published by Xu et al. [15]. They questioned the Calphad software to obtain, for each composition, at the same time constraints on phase formation and equilibria as well as the driving force for nucleation of different types of secondary phases in the solid state. By maximizing the driving force, the authors intended to favor the formation of numerous nano-sized strengthening precipitates by heat treatment, which was assessed by a simple nucleation rate model. Similarly, Calphad was coupled with a GA to design affordable superalloys in the system Ni–Fe–Cr–W–Al–Ti–Si–C–B [16]. Iron was added to reduce cost but, observing that increasing the iron content in nickel-based superalloys would usually reduce the volume fraction of the γ' reinforcing intermetallic phase Ni_3(Al, Ti), it was tried to maximize both using a GA, while satisfying a set of constraints on microstructural stability. Nevertheless, since the iron content can be fixed as an input, the strategy did not involve a multi-objective optimization; instead, only the volume fraction of γ' at heat treatment temperature was maximized for each iron content. Results are summarized in Fig. 3, where the sum of Al and Ti contents of optimized alloys is plotted as a function of iron concentration, the size of bubbles representing the maximized volume fraction of γ'.

The simultaneous optimization of several objectives was also reported using Calphad, for instance by performing, from a mathematical point of view, the single objective GA optimization of a criterion aggregating several characteristics. For instance, by employing the ratio of the strengthening contribution – based on the calculation of the driving force for nucleation of precipitates – over alloying cost as a criterion to be maximized, alloys with a lowered cost were designed without sacrificing strength [17].

2.4. When physical models fail: data mining/machine learning

In many cases, the mechanisms involved in what makes a material property are so complex that it is not possible, at present, to make reliable predictions on physical grounds only. This is the case, for instance, of the thermomechanical properties of alloys. The phenomena involved that are linked to the presence of each element, and the interactions between elements and phenomena, are usually not fully and quantitatively described over the whole possible range of composition, even for a given category of alloys. At the opposite, since the early ages of modern metallurgy, where proper chemical analysis, microstructural characterization and mechanical property testing exist, large amounts of data have been collected over hundreds, and sometimes thousands, of different alloys in a given family. So, when a rational physical model is not available, raw data analysis may provide good regressions that are, in the end, able to produce reliable predictions. This can be attempted using conventional regression, i.e. by fitting pre-defined mathematical equations to data. Besides, the branch of computer science called data mining proposes tools to perform non-linear multi-variate regressions that are fully flexible, i.e. the user does not need any a priori knowledge on the shape of the interpolant, the latter being automatically determined from data through machine learning. Thanks to the implementation of Bayesian statistical features, this can be made while avoiding overfitting and being able to identify trends within noisy data. It is not the aim here to explain the mathematical bases of such tools, nor to give a complete list of their use in alloy design, but the main used ones will be listed, along with a few illustrative examples. The most famous and popular tools for data mining in metallurgy are artificial neural networks (ANN), for which a review on their use to model some properties of materials was published as early as in 1999 [18]. Other methods exist and have been applied to metallurgy, like support vector regression [19], genetic programming [20] or Gaussian processes [21]. The performance of the latter to predict the mechanical properties of alloys has notably been compared to that of ANN [22].

Such data mining tools have been associated with optimization algorithms to design new alloys. For instance, a single objective GA optimization of either the tensile strength or ductility of steels has been performed, based on the predictions of ANNs [23]. An optimization can also be performed on a single objective aggregating several predicted characteristics; this was made to design steels through the GA maximization of a “desirability function” incorporating several mechanical properties (yield stress, tensile strength and elongation) predicted by ANNs [24]. True multi-objective optimization based on data mining models were also undertaken, for instance to design steels by GAs using ANN predictions of the tensile strength, the reduction of area and the tensile elongation [25]. A similar approach was used to optimize, by GAs, both the tensile strength and the creep resistance of nickel-based superalloys, including predictions made by neural networks models and genetic programming [20]. Single-crystal superalloys were also designed using multi-objective optimization relying on a set of alloy characteristics predicted by Gaussian processes (also called “Kriging models”), including mechanical properties and Calphad results, for which features of the main phases were fitted as “surrogate models” [26].

2.5. Integrated computational alloy design by combinatorial optimization

The examples in both sub-sections above show that coupling optimization algorithms to either Calphad or data mining can be used to propose new alloy compositions. Nevertheless, in the former case, only microstructural features are optimized, e.g., either the driving force for nucleation of precipitates [17] or their volume fraction [16], but these features, even if involved in the obtainment of good mechanical properties, do not guarantee the optimality of the properties themselves. In this respect, it becomes interesting to exploit both Calphad predictions to ensure phase formation and data mining models to predict final properties. In a similar manner, designing alloy compositions while maximizing only mechanical properties predicted by data mining is rather risky, in that detrimental phases may actually form in some areas of the design space not covered by data and degrade mechanical properties with respect to expectations. This could be easily remarked when the design of superalloys by GAs relying on pure data mining models led to compositions which, when later checked by Calphad, showed highly unrealistic phase constitutions, principally made of detrimental and usually undesirable intermetallic compounds [20]. This was noticed, to a less dramatic extent, when designing single-crystal superalloys using a similar approach, in which only the fractions of the major phases were described by data mining: minor detrimental phases actually formed in the most promising alloy, hence degrading its creep resistance [26], although Calphad would have been able to predict it.

To avoid such drawbacks, it is necessary to couple both data mining predictions with direct Calphad simulation as early as the alloy optimization stage. This was made, for instance, to design superalloys by GA minimization of a single aggregated objective, defined as the ratio of the cost of alloying elements over the creep strength (for a given temperature and expected lifetime) [27]. Creep resistance was predicted using Gaussian processes, whereas a set of constraints on phase formation was enforced, using direct Calphad simulation during optimization, to ensure processability and microstructural stability. Results are illustrated in Fig. 4, where the predicted creep rupture stress (for 1000 h at 750 °C) is plotted for the designed alloy in

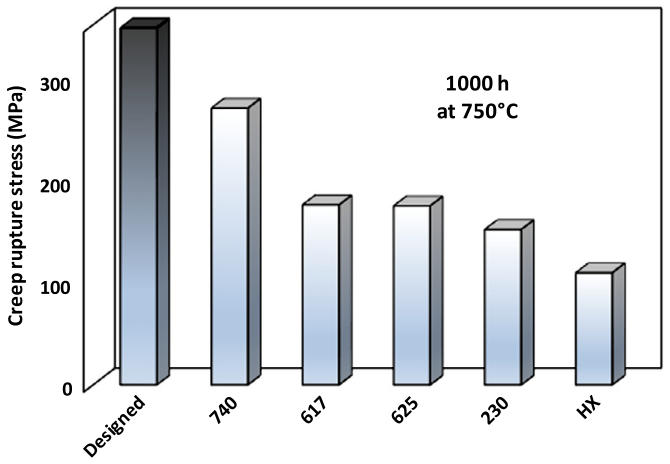

Fig. 4. Predicted creep rupture stress (for a lifetime of 1000 h at 750 °C) of the designed alloy (left) compared to concurrent commercial alloys.

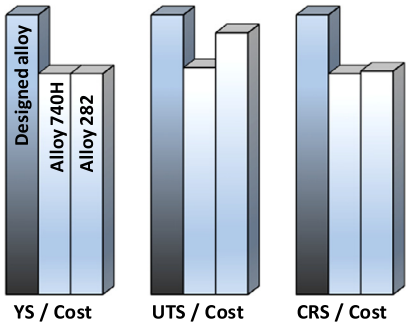

Fig. 5. Predicted relative ratios (arbitrary units) of mechanical properties at 750 °C (YS = yield stress, UTS = ultimate tensile stress, CRS = creep rupture stress for 1000 h lifetime) over cost, for the designed alloy compared to concurrent commercial alloys.

comparison with the main concurrent commercial alloys available at that time for similar uses (power plant applications). The predicted creep resistance of the designed alloy exceeds that of commercial alloys, for a reduced cost (for instance, the cost of elements of the designed alloy is roughly half of that of Alloy 740).

A true multi-objective optimization was performed in a similar case, to design the composition of superalloys by optimizing six objectives while satisfying constraints on constitution using Calphad, to ensure microstructural stability and oxidation resistance [28]. The objectives were the maximization of three mechanical properties (yield stress, tensile strength, and creep strength for a lifetime of 1000 h) predicted at 750 °C using Gaussian processes, the minimization of the cost of alloying elements, the minimization of the so-called "brittle temperature range" (it is linked to the out-of-equilibrium solidification temperature range, which is obtained by Calphad; it serves as a criterion to improve castability and weldability by avoiding hot tearing), and the minimization of the γ/γ' lattice misfit (obtained by a combination of Calphad simulation and Gaussian processes; its minimization is expected to be beneficial to creep resistance). The GA optimization led to several thousands of Pareto-optimal alloys. Some results are presented in Fig. 5 for one of the designed materials, selected as a potential replacement for Inconel 740H and Haynes 282 in future power plant applications. Relative ratios of the three predicted mechanical properties over cost are higher than those of concurrent alloys, while microstructural stability and processability of the new alloy are equivalent or superior. It must be noted that the Gaussian processes prediction of mechanical properties, relying on a Bayesian statistical approach, also provides a predictive error estimate, allowing one to perform a sort of "robust design", i.e. the predicted mechanical properties themselves are not optimized, but their mean value reduced by one standard deviation of their predicted distribution. This maximizes the chances that the actual alloys will match expectations. With a similar purpose, phase formation obtained by Calphad to ensure microstructural stability, e.g., to avoid the formation of undesirable phases, is not computed only at the expected heat treatment or service temperatures, but over a range of temperatures, also to ensure a kind of "robustness".

A similar case study was performed within the compositional domain covered by the patent of a last-generation polycrystalline superalloy, with the aim of finding Pareto-optimal compositions; several thousands of them were found [29]. An alloy was then selected, fabricated and characterized. It develops the expected microstructure and possesses better mechanical properties, in particular, creep resistance, than the alloy having the nominal composition, while being 12% less expensive thanks to the incorporation of less costly alloying elements (see Fig. 6) [30]. Measured properties are in agreement with

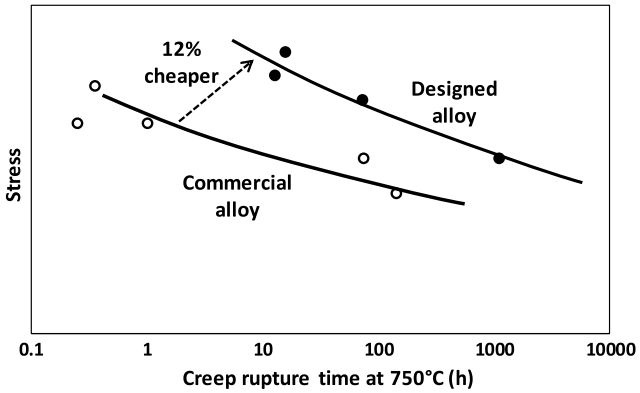

Fig. 6. Measured creep resistance of the optimized alloy compared to its nominal composition counterpart.

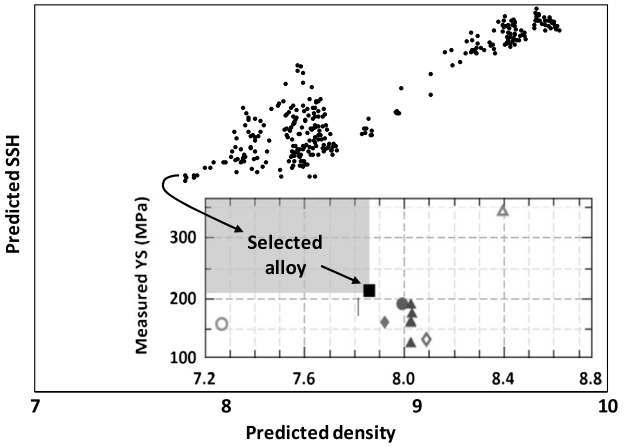

Fig. 7. Predicted SSH of ∼300 designed alloys as a function of predicted density. The insert shows the measured yield stress (YS) of the selected alloy as a function of predicted density, compared to other large grain and annealed HEAs.

predicted ranges. This shows that, even within the compositional ranges of existing alloy grades, optimal solutions may still exist.

A final example is given in the case of the GA multi-objective design of so-called "high-entropy alloys" (HEA). The latter are a new class of materials, constituted of multi-concentrated single phase solid solutions, i.e. they are usually defined as being made of at least five different elements whose molar concentrations are all between 5% and 35% [31]. They were originally supposed to gain their single-phase stability from their high configurational entropy, although the actual situation is in fact a bit more complex [32]. Being concentrated single solid solutions, they were originally expected to display unusual combinations of properties, like strength, ductility, corrosion resistance, etc. GAMOO was performed to design new HEAs with optimal combinations of solid solution hardening (SSH) and density, by exploiting two recent models providing predictions for these properties in HEAs [33,34]. Nevertheless, achieving a single solid solution in a multiconcentrated alloy is particularly difficult, and a new model to predict it was used, combining data mining (Gaussian processes), a set of physicochemical criteria (like the enthalpy of mixing, the electronegativity mismatch between atoms or the size distribution among them, etc.) as well as Calphad [35]. During genetic algorithm optimization over a panel of sixteen elements, the predicted stability of a single solid solution was maximized along with SSH, while density was minimized [36]. Fig. 7 presents the results of the most stable ∼ 300 alloys in a plot of SSH vs. density. One alloy ($Al_{10}Co_{17}Fe_{34}Mo_5Ni_{34}$) was selected among them, fabricated (cast, homogenized at 1300 °C, cold rolled to 90% thickness reduction and annealed at 1100 °C to recrystallize it) and characterized. X-ray diffraction and scanning electron microscopy confirmed its single-phase nature. Its tensile elongation is close to 50%. The insert in Fig. 7 displays the measured yield stress of the new alloy as a function of the predicted density,[1] compared to other reported HEAs in a similar heat treatment state, i.e. fully annealed

[1] It must be noted that the horizontal axis of Fig. 7 is predicted density, even for the insert, due to the fact that the actual density was not reported for some of the plotted alloys. Nevertheless, the measured density of the new designed alloy is in very good agreement with the predicted value, giving confidence in the predicted densities displayed here.

with large grains, so as to evidence mostly the solid solution strengthening. As can be seen, no other HEA lies in the gray area at the top left of the new material, meaning that the designed alloy is actually optimal in terms of SSH for its density.

3. Examples of experimental approaches to combinatorial metallurgy

From the above-mentioned examples, it becomes clear that the quality of alloy optimization relies on the availability of models with a predictive capability and/or large amounts of experimental data covering substantial amounts of the alloy design space. This requirement is well suited to the optimization of alloys within a well-chartered category of existing alloys, but not to the design of out-of-the-box alloys that precisely venture in areas of chemical composition and processing parameters not covered by much existing data! Example of such new concept alloys could be new generations of Ti alloys relying on transformation-induced plasticity effects or alloys processed by non-conventional ways such as additive manufacturing or severe plastic deformation. This is where experimental approaches become particularly useful, to achieve two complementary objectives: (1) to generate large sets of experimental data that can be used directly by the above-mentioned optimization algorithms, in a "big-data driven science" perspective [37], and (2) in a more conventional way, to assess and to improve the robustness of predictive models, these models being then used in optimization procedures. In the following, we will show examples of strategies for high-throughput experimentation in metallurgy.

3.1. Fabrication of compositionally and processing parameter gradient materials

The design space of metallic alloys comprises dimensions of chemical composition and of processing parameters, such as temperature, time, stress, or strain. Each set of these parameters results in a given microstructure, which then translates in a specific set of properties. Although it is obviously impossible to explore the complete design space of a multi-constituent alloy, it is possible to obtain large datasets of microstructure by fabricating materials with continuous gradients of chemical composition and/or processing parameters. Other strategies for mapping the alloy design space involve the fabrication of many samples of different chemical composition using rapid alloy prototyping techniques; however, we will not describe them in details here and the reader is invited to read elsewhere the corresponding descriptions [38,39].

Fabricating compositionally graded materials has been mostly achieved in the recent literature using thin film deposition techniques [40], especially physical vapor deposition (PVD). Using multi-target devices, it is possible to obtain a complete coverage of a ternary alloy system, and it has been applied to determine the phase diagram of different systems, as well as to characterize some functional properties, such as thermoelectric efficiency [41], glass forming ability for amorphous metals [42] or ability for shape memory effect [43].

However, when considering the design of structural metallic materials whose properties are defined by the microstructure resulting of multiple steps of thermo-mechanical treatments, these techniques are limited by the ability to process the compositional gradients subsequently to the deposition stage. Therefore, successful attempts for mapping the compositional space of metallic alloys should involve the fabrication of bulk alloys with gradients of composition. Different experimental techniques have been used in the past to achieve this purpose [44–47]. If we concentrate on the techniques in the solid state, thus maintaining a microstructure free of solidification defects, the principle is to join two alloys of different composition with the best possible interface quality and then to subject the bi-material joint to thermo-mechanical treatments leading to an enlarged diffusion gradient. The requirements for the compositionally gradient material can be summarized as follows:

- the initial interface between the two joined materials should be planar so that the end composition gradient has a well-defined geometry;
- for the range of compositions defined by the gradient, some conditions should exist where they exist in a single-phase field so as to avoid composition discontinuities;
- the diffusion treatment whose role is to produce the composition gradient should not alter the overall composition of the material (e.g., selective oxidation, loss of solute elements...);
- the end scale of the gradient should be much larger (at least two orders of magnitude) than the characteristic distance for the microstructure features of interest, so that one can neglect the long-range diffusion in the gradient when studying the microstructure development;
- The end-scale of the gradient should be much larger than the probe used for microstructure characterization so that a sufficient number of different alloy compositions can be probed and that the composition variation within the probed volume can be neglected. Besides, a sufficient length of material with uniform composition should be left on each side so that it can be checked that the microstructure is uniform under conditions of constant composition;
- following these two last requirements, the span of the gradient obtained by diffusion only is often not practical and must be enlarged by plastic deformation (e.g., rolling), whose role is, in addition, to homogenize the grain microstructure throughout the gradient material. Consequently, the interface between the two joined materials should be strong enough to withstand this operation without cracking.

A first example of such a process will now be given on steel. In this case, the aim is to fabricate compositionally graded alloys with varying compositions of several substitutional elements, in the presence of carbon, in order to determine the

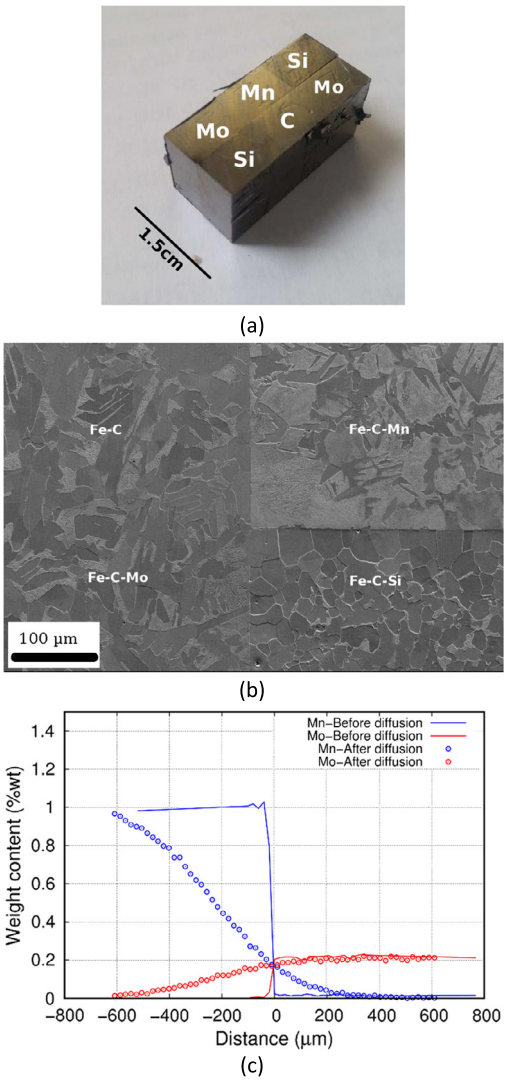

Fig. 8. a) Photograph of a diffusion multiple as assembled, made from three ternary Fe–X–C alloys (X = Si, Mn, Mo) and a binary Fe–C alloy. Some flakes of tantalum foil protecting the multiple during hot compression are visible at its surface. b) Secondary electron micrograph of a junction between the four alloys. The interfaces are free of pores and secondary phases. In the case of the Fe–C/Fe–Mo–C interface, the austenite grains have grown across the interface, which is no longer visible using secondary electrons. c) Composition profile in substitutional alloying element across Fe–C/Fe–Mn–C and Fe–C/Fe–Mo–C interfaces, as assembled (line) and after the diffusion treatment (circles).

interactions of solutes within the austenite-to-ferrite transformation interface. The main target in this case is to record the transformation kinetics as a function of composition using in situ synchrotron X-ray diffraction. In consequence, the size of the composition gradients must be compatible with the size of a typical synchrotron X-ray probe (about 100 × 100 μm^2).

The first step in making the diffusion multiple is to join blocks of base alloys together while meeting the requirements listed above. It was chosen here to join them using hot compression in a controlled atmosphere to obtain high quality solid-state joints. Fig. 8a shows an example of a diffusion multiple made from six samples: a binary alloy Fe–0.3%C and five ternary alloys (1 × Fe–0.3%C–1%Mn, 2 × Fe–0.3%C–0.2%Mo, and 2 × Fe–0.3%C–1.5%Si). Such a diffusion multiple yields several interdiffusion zones containing up to three substitutional alloying elements (quinary systems). Observation of the interfaces of the multiple as assembled shows that they are free of pores or secondary phases such as oxides or nitrides, as shown in Fig. 8b. In certain cases, grains grow across the interface to the point that it can no longer be distinguished in the microstructure. These elements are indicative of interfaces able to withstand mechanical processing without failing.

The second step consists of a diffusion treatment at high temperature for several days. Controlling the atmosphere is once again of prime importance to prevent oxidation or decarburization of the sample. The diffusion treatment is thus conducted in a furnace under vacuum with getter metal (Ti, Zr) shavings and micro-leakage of high purity Ar to ensure ultra-low oxygen activity. The diffusion gradients developed after this step are in the order of a few hundreds of micrometers, as

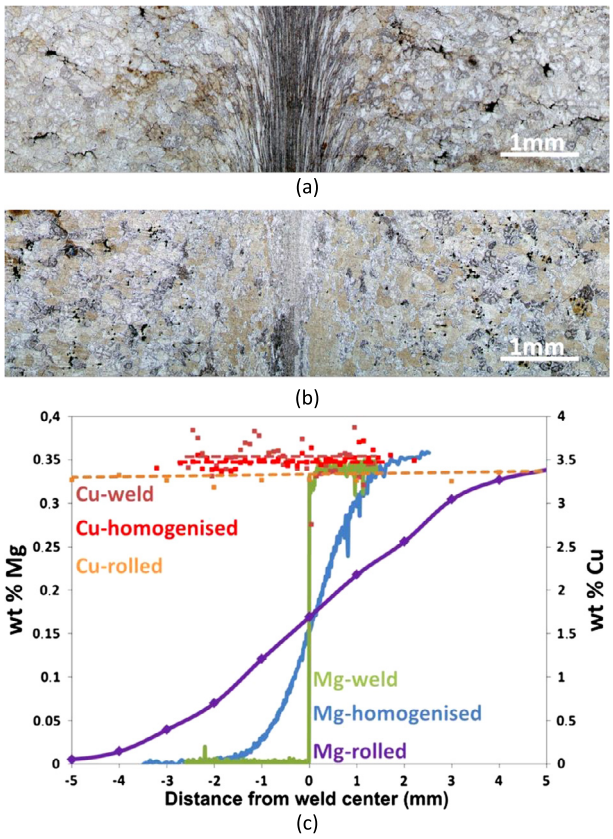

Fig. 9. Optical micrographs of a linear friction weld (interface plane is vertical in the center of the micrograph) between an Al–Cu–Li alloy and an Al–Cu–Li–Mg alloy in the as-welded state (a) and after the inter-diffusion heat treatment (b). (c) Concentration profiles in Cu and Mg across the weld interface measured in the as-welded state, after inter-diffusion and after rolling. (Reproduced from [49].)

illustrated by Fig. 8c. At the end of this step, the diffusion multiple is furnace cooled to produce a coarse and ductile microstructure.

The third step consists in mounting the sample in a block of low-carbon steel, which is then cold rolled in a succession of numerous small passes so as to avoid high-strain-rate related damage and promote homogeneous plastic deformation. In order to enlarge all the gradients, the successive passes are applied at a right angle to evenly distribute the deformation in the plane of the sample. Large reductions in excess of 85% can be thus applied, although it can prove necessary to trim edge cracks forming in the steel holder between passes. The gradients obtained at this stage are several millimeters long.

The diffusion multiple is then finalized, with a short high temperature heat treatment. The purpose of this last step is to recrystallize the sample and eliminate the small-scale inhomogeneity possibly introduced in the gradients by the plastic deformation. This procedure leads to a diffusion multiple with extended composition gradients, so that the composition variation within the X-ray probe is negligible, and fine grains, so that the diffraction patterns obtained consist of easy-to-interpret Debye–Scherrer rings.

A second example will now be given in the case of aluminium alloys, where the aim was to determine the role of solute elements on the phase transformation kinetics (and more generally on the precipitation pathway). Therefore, we endeavored to fabricate a compositionally graded material with varying Mg content within a constant Al–Cu–Li base.

Although diffusion bonding by hot pressing has been used before to join two aluminium alloys and subsequently obtain a diffusion couple by interdiffusion [48], the presence of an alumina layer at the interface makes it impossible to process the diffusion couple by plastic deformation. This hinders the microstructure control provided by the combination of rolling and recrystallization/solution treatment, and prevents a sufficient enlargement of the diffusion gradient. In order to make a planar interface between two materials and yet get rid of the interface layer, we have used Linear Friction Welding (LFW) [49]. During LFW, the two material blocks are linearly displaced with an alternating motion parallel to the interface plane together with a force normal to this plane. The friction results in heat, and eventually large plastic deformation and expulsion of the interface layer outside the joint. The resulting interface between the two materials is planar, defect- and oxide-free, and has a microstructure characteristic of large strain deformation, as shown in Fig. 9a. Following this process, the distribution of solute elements is discontinuous, as no significant inter-diffusion occurs during the LFW process, as shown in Fig. 9c. After LFW, the joint was subjected to an inter-diffusion heat treatment, allowing the redistribution of Mg. Fig. 9c shows that this treatment results in an extension of the composition gradient to ∼3 mm and a large grain

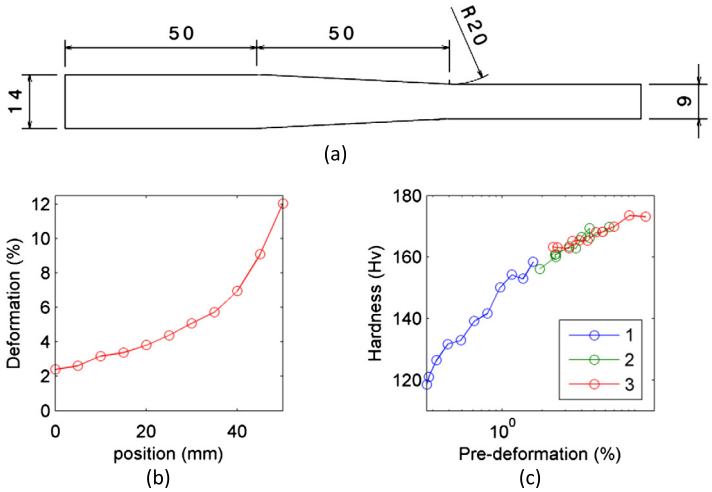

Fig. 10. (a) Uniaxial tensile sample of an Al–Cu–Li alloy with a section gradient, (b) mean deformation as a function of position along one gradient sample and (c) hardness measurements plotted as a function of pre-deformation for the three pre-deformed samples covering the complete pre-deformation range and heat treated 18 h at 155 °C. (Reproduced from [50].)

microstructure due to the recrystallization of the highly-deformed region (Fig. 9b). Finally, the material is subjected to a rolling step, which extends the dimension of the gradient to more than 10 mm and provides a homogeneously deformed microstructure, after a solutionizing heat treatment that finalizes the processing of the gradient sample.

As mentioned above, the alloy design space also comprises dimensions of processing parameters. In the past, Sinclair et al. [45] have for example combined gradients of chemical composition with gradients of temperature to study the temperature dependence of the effect of Nb on recrystallization in Fe. Other processing parameters often include plastic deformation, which has major impacts on microstructure development via phase transformations. An easy way to vary continuously plastic deformation is to deform in tension a sample of varying cross-section and characterize the resulting strain gradient by, e.g., digital image correlation (DIC).

In a first instance, we have used this process to determine the effect of the level of pre-deformation on precipitation strengthening in an Al–Cu–Li-based alloy after artificial ageing [50], as shown in Fig. 10. Using the combination of three tensile samples of varying cross-sections, strain levels between 0 and 12% were continuously generated, and the corresponding strengthening has been characterized.

In a second instance, a comparable process has been used to evaluate dynamic precipitation during plastic deformation of an Al–Zn–Mg–Cu alloy (7000 series) [51]. Although dynamic precipitation can be studied in-situ during a tensile test, providing all necessary data about the strain-dependent precipitation kinetics without the use of strain gradient material, such experiments are limited to relatively slow strain rates in order to measure the signal arising from the precipitates in a reasonable time frame. As shown in Fig. 11, the use of tapered samples made it possible to study for the first time dynamic precipitation at high strain rates ($\sim 2\ s^{-1}$), representative of a metal forming operation.

3.2. Quantitative characterization of microstructure evolution with space and time resolution

Once materials with suitable gradients of composition and/or processing parameters have been fabricated, the next step is to devise characterization techniques capable of obtaining quantitative data taking full advantage of the diversity of the material conditions present in the sample. In the literature, many different strategies have been devised depending on the microstructure feature or related property to be characterized.

If we concentrate only on microstructure characterization, a first obvious choice can be a direct observation by microscopy techniques. When dealing with recrystallization or allotropic transformations, for instance, the scale of the microstructure to be characterized can be comparable to that of the composition gradient, allowing in one single image to evidence the microstructure distribution [44,45]. However, one must remember that in this case one of the requirements stated above is not fulfilled, namely the microstructure development may be biased by the presence of a gradient of composition/temperature at a comparable scale.

When the features of interest are much smaller than the scale of the gradient, one needs to make sequential characterizations at discrete points of the gradient sample [46]. Characterizing, e.g., precipitates with transmission electron microscopy along a systematic set of samples representative of many alloying characteristics can rapidly become too time-consuming to be practical.

X-ray techniques are generally well suited for a space-resolved microstructure characterization. High-throughput X-ray diffraction (XRD) is now being widely used to map the presence of phases in compositionally graded thin films in order to

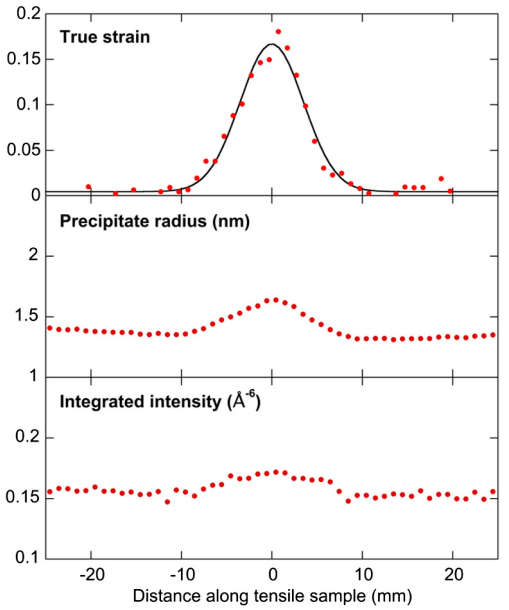

Fig. 11. Distribution of strain and resulting characteristics of the precipitate microstructure (precipitate size and integrated volume fraction, representative of the precipitate volume fraction) after straining at 20 mm/s a sample of 7000 series aluminum with a variable section. (Reproduced from [51].)

establish phase diagrams [52–54]. The automated analysis of large numbers of multi-phase diffraction diagrams requires the development of advanced numerical tools such as machine learning.

X-ray techniques are also particularly well suited to perform in-situ experiments, thus giving access to the kinetics of microstructure development. This is particularly obvious for phase transformations, using either X-ray diffraction for phase fractions [55], or small-angle scattering (SAXS) for nano-scale precipitate characterization (size and volume fraction) [56]. However, other microstructure development processes can also be quantified such as dislocation density evolution and the occurrence of recrystallization [57].

When applying in-situ experiments on a material with a composition gradient, it becomes possible to map, e.g., phase transformation kinetics in compositional space by scanning continuously the gradient sample with the X-ray beam during a heat treatment. Before we show examples of such experiments, it is interesting to list a few requirements that need to be fulfilled for a successful characterization:

- as stated above, the scale of the gradient should be compatible with the scale of the X-ray probe so that a sufficient number of compositions can be mapped. Typically, a factor of at least 10 should be aimed for between the gradient size and the probe size (typically 100 μm for a synchrotron beam and 1 mm for a laboratory beam);
- the kinetics of the studied phase transformation should be compatible with the measurement time across all compositions within the gradient, including the sample displacement time. For example, with a measurement time of 10 s (including sample displacement) and 20 measured positions, a given alloy composition will be characterized only every 200 s, which should give a sufficient time resolution with respect to the studied phase transformation kinetics;
- specific furnaces must be available, which are compatible with the measurement technique (e.g., in transmission for SAXS) and provide a uniform temperature distribution across the full gradient sample dimension.

We have performed such time- and space-resolved in-situ experiments for the characterization of the decomposition of the solid solution of Al–Cu–Li-based alloys with varying Mg additions [58]. Fig. 12 shows the Mg-dependent kinetics of clustering at room temperature (left column, clustering kinetics for different Mg contents; right column clustering as a function of Mg content for different ageing times). Analyzing such extensive SAXS data obviously requires the availability of a robust interpretation model to extract the relevant microstructural data. In the case of clustering, we have devised such a model based on the characterization of composition fluctuations within the cluster-comprising solid solution, in terms of amplitude (represented by a number of square excess solutes in the clusters per unit volume) and in terms of spatial extension. In addition, some larger features, that we interpret as nanometer-scale precipitates forming at structural defects such as dislocations are detected and also dependent on the alloy composition. Clusters and precipitates were distinguished by their size, the former being of a characteristic size well below 1 nm and the latter of a radius of about 2 nm.

This extensive dataset obtained in one single experiment provides a very rich understanding of the effect of Mg on the clustering of Cu in this alloy system. Namely, it makes it possible to show that the effect of Mg on Cu clustering is monotonously increasing with Mg concentration, starting at the first measurable Mg content. The experimental dataset makes it possible to determine that above ∼0.2%Mg, this effect saturates. Moreover, the influence of Mg concentration on

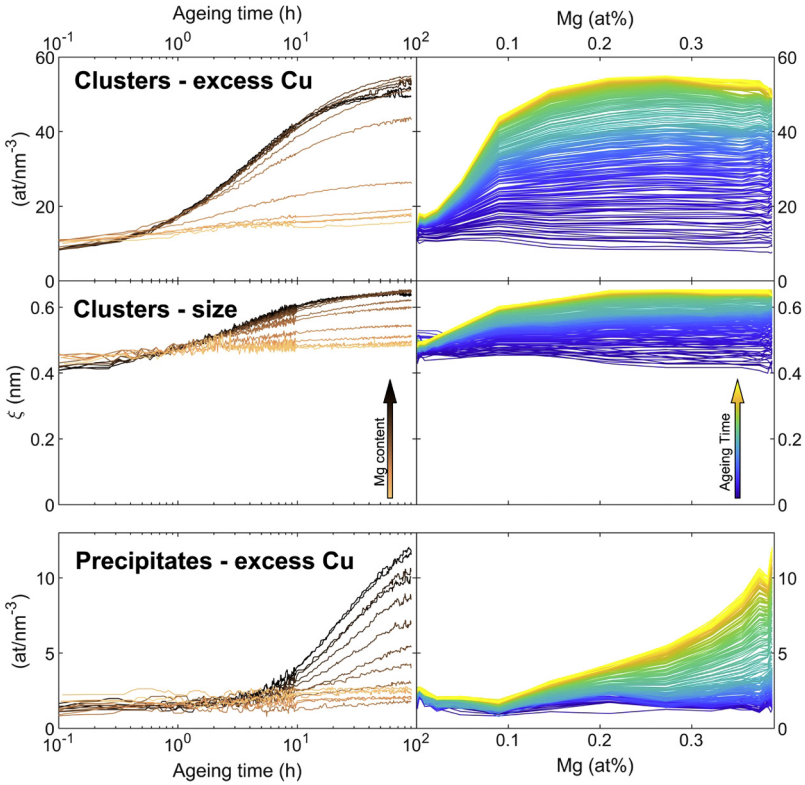

Fig. 12. Evolution of the cluster and precipitate characteristics during natural ageing across the diffusion couple between an Al–Cu–Li alloy and an Al–Cu–Li–Mg alloy corresponding to that of Fig. 9. Top figures, excess Cu atoms involved in clusters; middle figures, cluster size; bottom figures, excess Cu atoms involved in precipitates. Left column: curves for increasing Mg content as a function of natural ageing time; right column: curves for increasing aging time as a function of Mg content. (Reproduced from [58].)

the larger scale objects, despite being also monotonous, is shown to be quite different, since it is measurable only for Mg contents above ∼0.1%Mg. Clearly, all this information would have been very difficult to obtain from a discrete set of alloy compositions.

Following the microstructure development during natural ageing, we have performed a similar evaluation during artificial ageing at 155 °C [49]. In this alloy system, the most desirable phase formed during artificial ageing is the T_1 phase (Al_2CuLi) that forms elongated platelets, which nucleate preferentially on matrix dislocations. The same compositionally graded material as presented above (Al–Cu–Li with varying Mg) was used, except that it was uniformly pre-deformed in tension by 4% to introduce precipitate nucleation sites. In-situ SAXS monitoring during heat treatment at 155 °C provided the Mg-dependent precipitation kinetics in this system, as shown in Fig. 13. When normalized to the maximum volume fraction reached at the end of the heat treatment, there are two apparent precipitation kinetics groups, one for Mg contents lower than ∼0.1% and the other above this value, with a sharp transition between the two, illustrating a bifurcation of phase transformation kinetics in the compositional space. Combining this dataset with electron microscopy carried out on the two end compositions of the gradient, it was concluded that the two kinetics were representative of a different phase transformation path: T_1 phase for large Mg contents, and θ' phase for low Mg contents, this transition being related to the solvus for the formation of a precursor phase on the dislocations that helps the T_1 phase to nucleate. Again, it would have been extremely difficult to characterize this sharp transition using discrete sets of alloy compositions.

3.3. *Use of compositionally-resolved kinetics data for modeling*

As described above, characterizing continuously in compositional space the kinetics of microstructure evolution can improve our understanding of the effect of specific chemical elements on phase transformations and evidence bifurcations in kinetic paths followed during heat treatments. One other useful application of such databases, in more simple cases, where a single mechanism for microstructure evolution is active for a range of chemical compositions, is the use of the generated data for challenging the capability of the models describing this microstructure evolution. Indeed, microstructure models, e.g., for precipitation kinetics, are usually compared to relatively scarce experimental data, generally on one alloy composition and a few heat treatment conditions. When the alloy composition changes, so does the supersaturation, in a way different from that of temperature, which changes also the mobility of the solute species. Thus, being able to evaluate

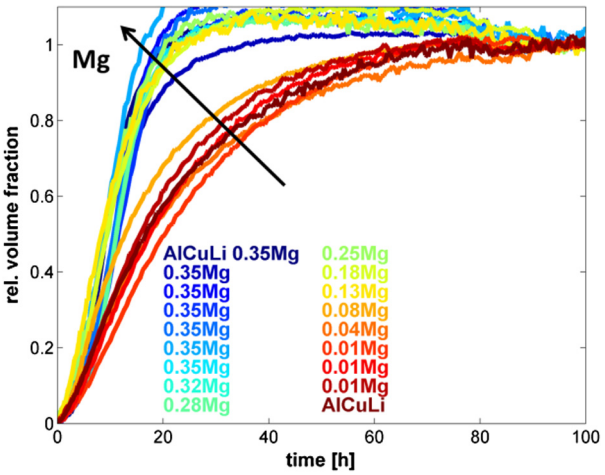

Fig. 13. Evolution of relative precipitate volume fraction measured from the SAXS data as a function of ageing time at 155 °C for a series of Mg concentrations within the diffusion couple between an Al–Cu–Li alloy and an Al–Cu–Li–Mg alloy corresponding to Fig. 9. (Reproduced from [49].)

the predictive capability of models on a wide range of alloy composition and heat treatment conditions is certainly a severe test for existing models, which should point to where further developments are necessary.

We will now present an example of such an evaluation [59]. The case study was precipitation of Co in Cu, which was chosen because it is a rather simple model system, making the comparison with modeling easier: precipitates are considered as almost pure Co, they are spherical in the conditions of relatively low temperature and early ageing times considered for this study, and their volume fraction is relatively low (not more than 2%). A diffusion couple between pure Cu and a Cu–2%Co alloy has been fabricated, with an extension of the diffusion zone of ∼2 mm, and then heat-treated in-situ while scanning continuously with an X-ray beam and measuring the SAXS signal to characterize the precipitation kinetics. The extension of the diffusion zone being rather small, one challenge was to characterize precisely the alloy composition probed by the X-ray beam at each measuring point. This was achieved by performing measurements at X-ray energy both below and above the K-edge of Co. Measurements below the K-edge (avoiding Co fluorescence) were used for precipitate characterization and measurements above the K-edge (where the amount of fluorescence is directly related to the composition in Co) served to determine the local Co composition. Three experiments were performed at three different temperatures, and for each of them the precipitation kinetics was determined for 20 alloy compositions, thus generating a very large database for precipitation kinetics (actually the largest available at the present time to our knowledge).

The choice of model to compare with this microstructure database was guided by the requirement that it should be sufficiently precise to capture effects of varying supersaturation and temperature changes on the different stages of precipitation, to describe the relevant parameters for comparison with the experimental data (average precipitate size, volume fraction and number density) and sufficiently fast so that it can be applied to the full experimental database. A natural choice was to use a Kampmann–Wagner class model describing the evolution of the precipitate size distribution discretized in size classes [60]. This type of model being a mean field model, it describes the interaction of each size class with the average solid solution and is therefore well suited to the description of dilute precipitation as considered for our Cu–Co case. Fig. 14 shows the experimental database for precipitation kinetics, where the different alloy compositions are identified by the color intensity, and the model output. At each temperature, only three parameters were adjusted to describe the full range of alloy compositions: Co solubility in the Cu matrix, diffusion constant, and interfacial energy. The comparison between experimental data and modeling is overall rather satisfactory, except for the description of the nucleation stage, which points out that the classical nucleation theory is ill-adapted to describe this stage of precipitation in comparison with experimental data. Actually, a systematic bias exists at this stage between the model output and the experiments, which arises from the fact that the model considers only the stable precipitates (those having grown beyond the nucleation radius), whereas the SAXS experiment characterizes the complete distribution of particles, including stable precipitates and unstable clusters. The difference between these two populations is, of course, maximum during the nucleation stage.

4. Concluding remarks

The numerical and experimental approaches presented in this paper are still somewhat disconnected. On the numerical side, current fast models available for alloy optimization rely on relatively simple criteria such as maximizing the volume fraction of precipitates or the driving force for their formation. It is beyond the reach of currently available models to describe predictively the microstructure and related properties for a random set of alloy compositions and choice of processing parameters. We have shown how this lack of predictive models can be supplemented by data mining tools, capable of extracting from large scattered datasets enough relevant information for improving currently used alloys. However, if this strategy is now able to push alloy optimization towards its limits by finding the best possible trade-offs between

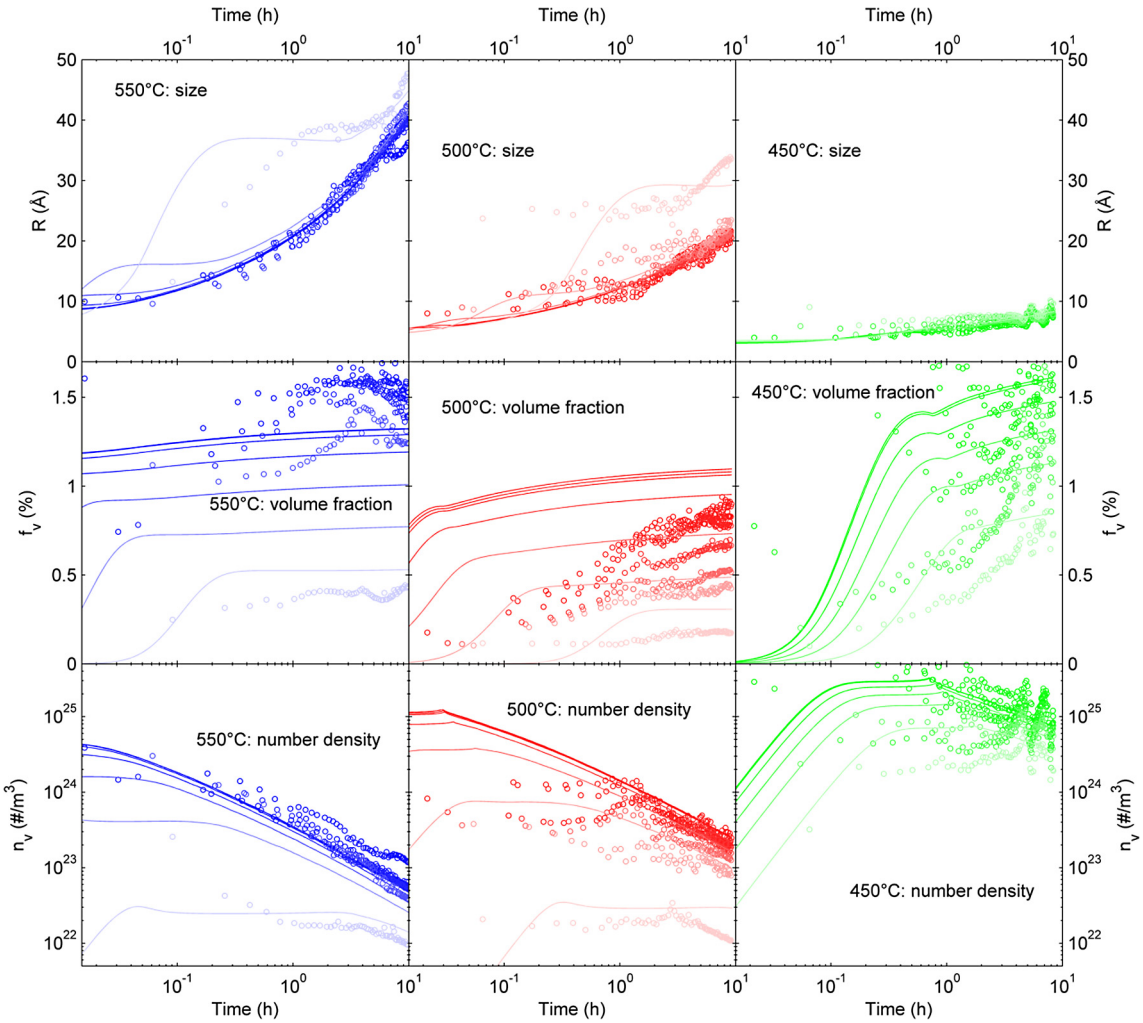

Fig. 14. Time- and concentration-resolved precipitation kinetics of a Cu–(Cu2%Co) diffusion couples obtained for three temperatures, 550 °C (blue), 500 °C (red), and 450 °C (green). The circles are the SAXS experimental results, the lines are the results of the precipitation model. The color shades are related to the local Co content (darker = more Co). (Reproduced from [59].)

characteristics, the approach is obviously limited to well chartered areas of alloy design space where a large amount of data is available, and will by construction not be able to design completely new alloy families, especially where undocumented mechanisms operate. On the experimental side, high-throughput methods are reaching a maturity where they can provide large microstructure databases, which can precisely serve both the objective of improving the predictive power of fast physically-based models, and provide databases on which data mining tools and machine learning approaches can be applied to provide guidance for alloy design in areas of design space too complex to be tackled by modeling alone. Now it becomes necessary to combine these numerical and experimental approaches in collaborative case studies. Such an endeavor requires a multi-disciplinary team of experimentalists, modeling and optimization experts and could be applied in many alloy systems that are currently the stake of fast development such as new generation Ti alloys, multiple solutes-containing Al alloys, advanced steels, or high-entropy alloys.

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