REVIEW

Mathematical models in materials science

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Modelling has now become a routine part of materials science. It is appropriate therefore to assess some of the successes and failures of the method and to understand how and if modelling differs from ordinary quantitative science. The subject is now sufficiently mature to bear some constructive self-criticism and to temper exaggerated claims. The discussion here of modelling methods and outcomes is intended to be generic, although the examples used come from the author's experience of work on metals.

Keywords: Modelling, Validation, Reviews, Mechanical properties, Phase diagrams, Microstructure development

Introduction

There is much to be gained by creating theory appropriate for materials science, in particular that which is experimentally verifiable and which does not compromise with the complexity of technology. Modelling as a subject has become as much a part of materials science as experimental characterisation for two reasons. First, to compete, industry must achieve solutions using minimal resources. Second, scientists are excited by the quantitative expression of multivariate problems.

One approach in explaining the subject is to categorise it into distinct fields connected according to length scales (Fig. 1*a*). There is the physics associated with the bonding between atoms, the chemistry of atomic arrangements followed by the microstructure of aggregated crystals and their defects, where the thermodynamic approach triumphs. The ultimate is the engineering continuum where parameters such as modulus and strength are macroscopically averaged.

While in Fig. 1*a* there is a two way flow of information between the different subjects, the emphasis on linking the length scales makes the task of creating a sufficiently complex model impossible in practice (*sufficient complexity* will be defined later, but it refers to the solution of real life technologies without simplification). Furthermore, diagrams such as those in Fig. 1*a* imply a lesser significance to the flow between distant subjects, whether this is intentional or not.

Figure 1*b* in contrast emphasises clusters of models as tools to be exploited by individuals with the ability to recognise limitations, to make approximations and to communicate between disciplines. The ambition is to deal with the problem as posed, and hence to create new methods and connections as required. These *materials modellers*, a rather recent breed, are located mostly in materials science departments. The purpose of this paper is to present a description of modelling and to highlight the performance of the subject over the last two decades. While the discussion is intended to be generic, the examples used come from the author's own experience in metals.

Purpose of models

The role of models in materials science is often overstated. It is important to appreciate that scientific progress can happen from simple observations as well as from numerical computations. Anderson[1] expressed this nicely in his 1977 Nobel lecture:

'One of my strongest stylistic prejudices in science is that many of the facts nature confronts us with are so implausible …, that the mere demonstration of a reasonable mechanism leaves no doubt of the correct explanation. This is so especially if it also correctly predicts unexpected facts…. Very often such, a simplified model throws more light on the real workings of nature than any number of 'ab initio' calculations of individual situations, which even where correct often contain so much detail as to conceal rather than reveal reality. It can be a disadvantage rather than an advantage to be able to compute or to measure too accurately, since often what one measures or computes is irrelevant in terms of mechanism. After all, the perfect computation simply reproduces Nature, does not explain her.'

It is rare that mathematical models alone influence an outcome. It is more often the case that they are a part of a process which includes insight and experimental observations. Models might be classified as follows:

(i) those which lead to an unexpected outcome that can be verified
(ii) those which are created or used in hindsight to explain diverse observations
(iii) existing models which are adapted or grouped to design materials or processes
(iv) models used to express data, reveal patterns, or for implementation in control algorithms.

While these categories are not exclusive, they serve to highlight the applications of models, with the emphasis being on quantitative expression, whether that is fuzzy or discrete. How then does this differ from ordinary science, which also yearns for the mathematical formulation of Nature?

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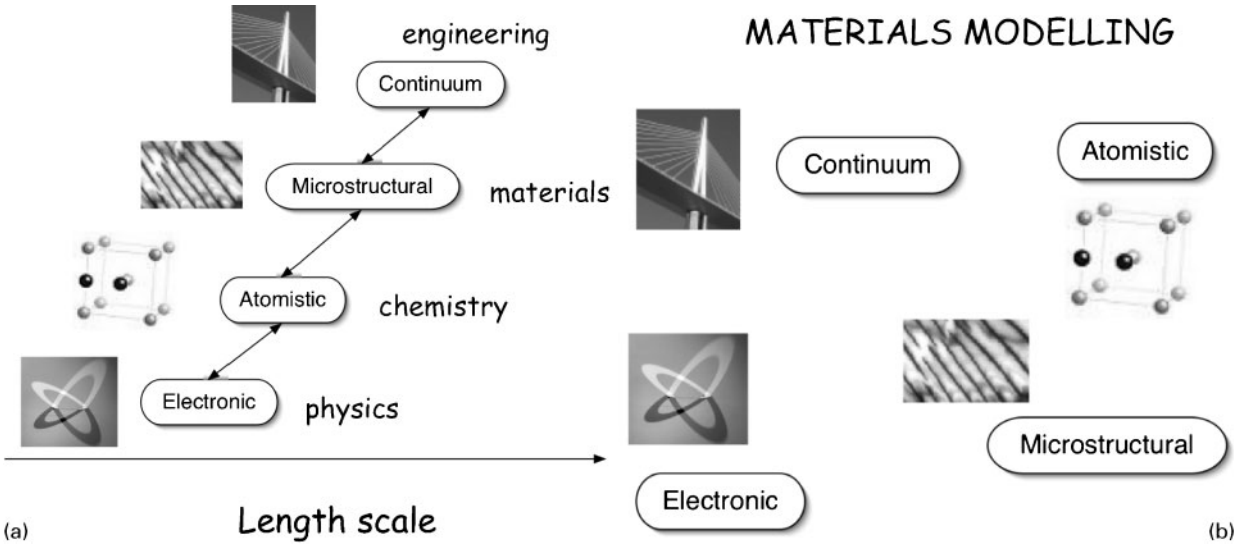
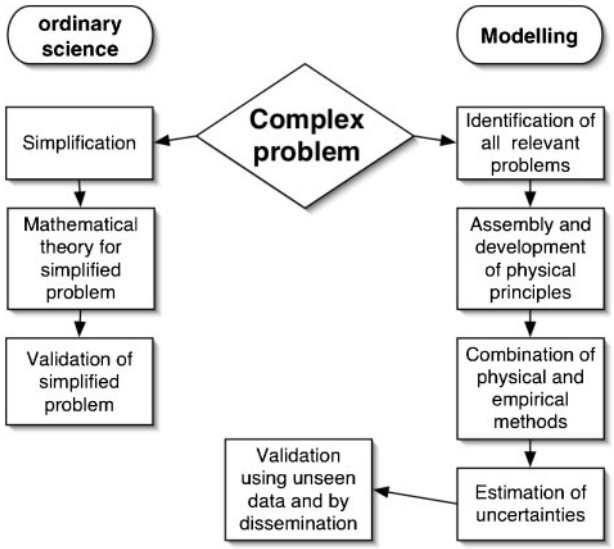


1 ***a*** **sequential process of mathematical modelling and** ***b*** **interdisciplinary and disconnected approach**

The difference becomes obvious when faced with a complex problem (Fig. 2). The technique of conventional science is then to reduce the problem until it can be expressed using rigourous mathematical theory and then to do simplified experiments to validate the theory. This procedure often loses the technology relevant in the original problem, although the work adds to the pool of knowledge.

Modelling, in contrast, faces the problem at the level of complexity posed. It begins with wide consultation to identify all the relevant issues. Methods are then assembled and developed, and if necessary combined with empirical techniques to create an overall procedure, taking considerable care to estimate uncertainties. Validation of the model is by testing against unseen data, by creating tangible components and by exposing the software to other scenarios. In this way, the technological goal is hopefully achieved, and problems are identified which in the longer term need to be resolved using the scientific approach. Like ordinary science, the proper use of models also leads to insight, but by tackling complexity at the level that is posed, it can reveal issues which are lost during the simplification characteristic of ordinary science. For example, it is unlikely that the existence of a detrimental phase in high strength steel weld deposits would have been revealed without the creation of a model which uncompromisingly accounts for the full range of variables that influence the Charpy toughness.[2–6]



2 The defining qualities of a model compared with the conventional scientific method[7]

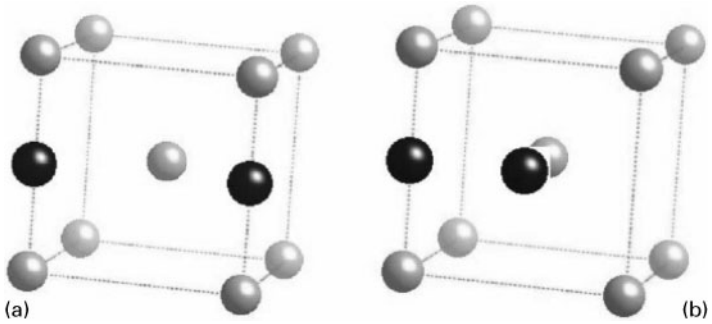
Excess information and information loss

Modern instruments such as the atom probe,[8,9] the orientation imaging microscope[10–12] or the four-dimensional X-ray microscope[13,14] generate huge and often overwhelming quantities of data.

In the case of the three-dimensional atom probe, collections of many millions of data in which individual atoms are chemically and spatially resolved are frequently reduced to images with a dramatic reduction in information content. While these pictorial representations are useful, the totality of data could, for example, be exploited to reveal the nature of solid solutions.[15]

The orientation imaging microscope has been a boon in the study of the microscopic aspects of crystallographic texture. The instrument measures individual crystal orientations relative to a frame of reference. Each such orientation is characterised by three pieces of information, the axis and angle of rotation. The accompanying image reveals also the boundaries between adjacent crystals, another two degrees of freedom. However, the wealth of information is lost in many publications which present just coloured orientation maps or plot only the distribution of rotation angles.

These examples highlight the fact that researchers often have the capability to collect fine detail but perhaps not the patience or skill to exploit that information fully. Precisely the same issues arise in materials modelling where data can often be generated at resolutions not possible using experiments (for example, heat and fluid flow during welding[16]). The outputs of such methods are 'coarse grained' before publication. Similarly, atomistic calculations require huge computing resources, and yet the answers they produce are quite simple, for example, the cohesive energy of postulated crystal structures or the elastic



a carbon atoms located a lattice parameter apart; *b* carbon atoms in near neighbour interstitial sites

3 A pair of carbon atoms (dark) in octahedral interstices within the ferrite unit cell

moduli. One could query whether the stages involved in reaching the required accuracy of the final answer contain information about intermediate states. Otherwise there is little insight to be gained, as pointed out by Anderson[1] and more recently by Cottrell.[17]

To summarise, the danger with computationally intensive methods is that the focus shifts on the final outcome rather than on the steps leading to that solution. It is of course difficult to assess the utility of large quantities of data when scientific expertise tends to be highly specialised. For this reason, a good practice would be to make the data freely available so that others can look at the information with a fresh perspective. The World Wide Web makes this an easy task to implement. Thus, after publication, Brun *et al.*[66] made some 2700 sets of creep data, each with 32 variables available on MAP.[18] These were then used by Meyer and Gutte[19] to create a hybrid creep model which includes the thermodynamics of such steels.

Phase diagrams

Kaufman,[20,21] Hillert,[22,23] Kubaschewski and Evans[24] and others[25,26] pioneered the method in which a combination of solution models and carefully assessed experimental data is used to estimate phase diagrams. This has been remarkably successful in enabling the routine estimation of multicomponent, multiphase diagrams, so much so that many industries have embraced the method (for recent reviews see Refs. 27 and 28).

The method relies on thermodynamic data so calculations are only possible for known phases. Thus, the Z phase ([Cr,VNb]N) which became prominent in research on ferritic power plant steels[29] could not be implemented in alloy design procedures. The phase can cause a dramatic decline in the long term creep properties. It was not until the necessary data were measured and assessed that equilibrium calculations could be attempted.[30]

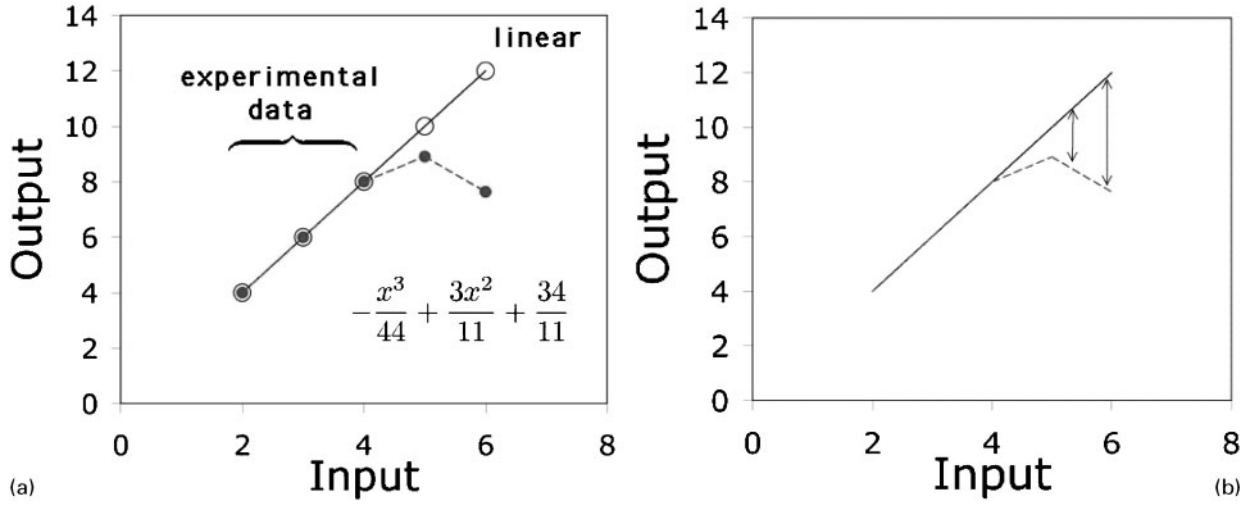
In some cases, the necessary experiments may be impossible to conduct. For example, the equilibrium solubility of silicon in cementite is incredibly small but it is necessary to understand the thermodynamic properties of relatively large concentrations trapped in cementite during its paraequilibrium precipitation.[31–33]

Silicon is important in the design of TRIP assisted steels[34–38] or other stronger steels which exploit transformation plasticity.[39–45] However, silicon also forms an adherent oxide resulting in poor surface finish. In the absence of thermodynamic data it is not possible to calculate the optimum concentration needed to suppress cementite and at the same time avoid the surface oxide. One possibility is to calculate the necessary data using electron theory.

In atomistic calculations using *ab initio* methods, the computing requirements increase dramatically with the number of atoms. Initial (unpublished) work by Jae Hoon Jang and In Gee Kim at POSTECH suggests that the difference in energy between a unit cell of cementite ($Fe_{12}C_4$ + one isolated Si atom) and ($Fe_{11}SiC_4$ + one isolated iron atom) would amount to a few kJ/mol. This huge increase in enthalpy on substituting one iron atom with a Si atom occurs because of the large concentration of silicon in $Fe_{11}SiC_4$. More realistic concentrations in the context of TRIP steels should be smaller but will require very large computing times. This may become possible in the near future.

Another interesting problem where *ab initio* methods are most useful is in the quasi-chemical theory for the solution of carbon in ferrite.[46–51] Large concentrations of carbon are routinely trapped in the ferrite during martensitic or bainitic transformations. It is important therefore to be able to calculate the phase boundaries at low temperatures and for concentrations of carbon well in excess of equilibrium. One of the parameters needed to do this properly is the carbon–carbon interaction energy ω.[46] For ferrite there have over the years been considerable discussions as to whether the interaction between adjacent carbon atoms is attractive or repulsive[49,51–54] but it turns out that it is not possible to reach a firm conclusion based on experimental data alone.[50] The solubility of carbon in ferrite is too small at temperatures close to ambient, to experimentally determine its thermodynamic behaviour.

Ab initio calculations are ideal for this purpose.[55] Calculations were made for the two scenarios as illustrated in Fig. 3. An attractive interaction is expected when the carbon atoms are located a distance a_α (lattice parameter of ferrite) apart because tetragonal martensite would otherwise never form, which serves as a test for the calculation method. The results did indeed indicate attraction with a carbon–carbon interaction energy of $-0{\cdot}169$ eV whereas because of the closer distance of approach, the interaction between carbon atoms located $\frac{1}{2}a_\alpha$ is strongly repulsive at 2·166 eV. This means that interstitial sites close to a carbon atom are blocked from occupation by another carbon atom. This information can be substituted directly into the quasi-chemical thermodynamic models.



4 Two functions which exactly match the experimental data[2,4,6] and extrapolate differently

Mechanical properties

A great deal is understood about the mechanical behaviour of metals. It is possible for example to calculate elastic moduli using first principles methods and to estimate the yield strength taking into account the size and distribution of defects and the overall microstructure. However, there is no facility for estimating more sophisticated properties where the number of variables involved is very large and their effects are ill understood. It is not surprising therefore that numerous attempts have been made to use neural network modelling to deal with complex properties such as fatigue,[56–59] toughness,[60–63] corrosion resistance[64] and creep rupture life.[19,65–68]

A neural network is a general method of regression analysis.[69–72] A few of the advantages of the network over conventional regression can be listed as follows:

(i) there is no need to specify a function to which the data are to be fitted. The function is an outcome of the process of creating a network
(ii) the network is able to capture almost arbitrarily non-linear relationships
(iii) with Bayesian methods, or methods based on committees of models, it is possible to estimate the uncertainty of extrapolation.

The subject has been reviewed extensively in the context of materials science[71,72] but it is worth commenting on the treatment of uncertainties. *Noise* is easy to understand – when an experiment is repeated, the outcome is different because some unknown variable has not been controlled. *Modelling uncertainty* arises when many functions are able to accurately represent known data but extrapolate differently. In Fig. 4, the input values 2, 3 and 4 represent experimental data. Both the linear and non-linear functions exactly represent the experimental data, but make different predictions when it comes to input values 5 and 6, i.e. when the functions are used to extrapolate beyond the experimental data. It is impossible, without physical understanding, to choose between these two.

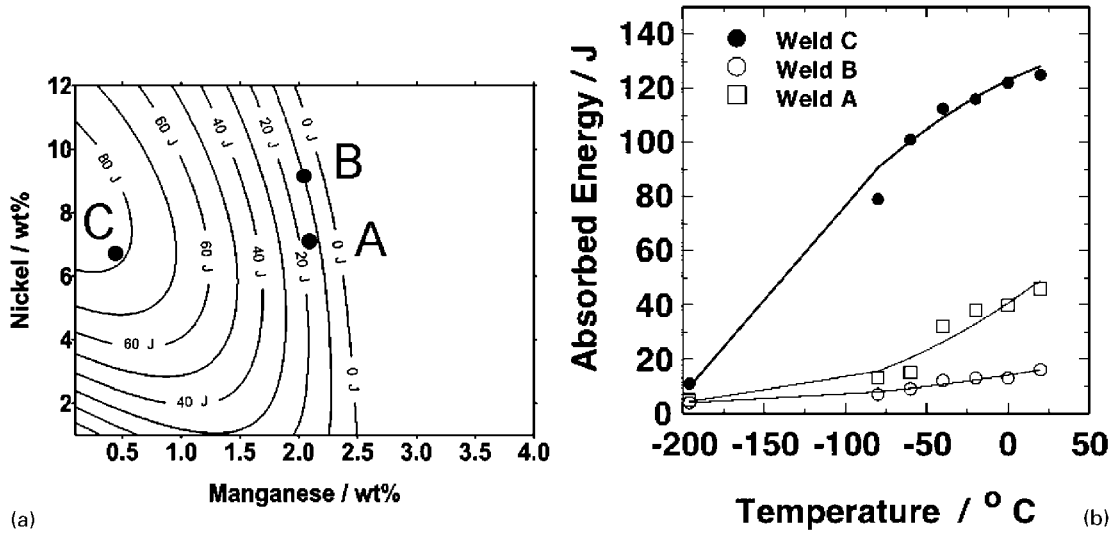
This could be interpreted as a crisis, but instead, the difference in the predicted values from the two functions can be taken as an indication of the uncertainty of extrapolation. This uncertainty arises because the functions representing the data extrapolate differently. It is extremely useful to have this indication of uncertainty when dealing with non-linear functions which are not physically based. MacKay's work has been seminal in expressing neural networks in a Bayesian framework so that the modelling uncertainties become transparent.[69]

There are now examples where neural networks in combination with microstructural calculations and experience have short circuited the development of welding alloys. Murugananth and co-workers[2–6] compiled a neural network model which led to the discovery that in strong weld metals, nickel is only effective in increasing toughness when the manganese concentration is small. This is illustrated in Fig. 5, where the contour plot shows the impact energy at -60°C for welds A (7Ni–2Mn), B (9Ni–2Mn) and C (7Ni–0·5Mn); the details are described elsewhere.[2,3,73] Experiments validated the neural network predictions so fundamental work was commenced to understand the Ni–Mn phenomenon.

The mechanism by which a combination of high manganese and nickel concentrations leads to a deterioration in strength has been studied in detail by Keehan and co-workers.[4–6] It appears that when the transformation temperatures are sufficiently suppressed, such that there is only a narrow gap between the bainite and martensite start temperatures, a coarse phase labelled *coalesced bainite* forms.

Coalesced bainite occurs when adjacent small platelets of bainite ('subunits') merge to form a single larger plate.[74] This striking change in form occurs at large undercoolings. Since adjacent subunits of bainite have an identical crystallographic orientation, they may merge given sufficient driving force to sustain the greater strain energy associated with the coarser plate, and if there is nothing to stifle the lengthening of the subunits.[74] The first condition is satisfied by the large undercooling. The second implies that coalescence is only possible at the early stages in the transformation of austenite, when growth cannot be hindered by hard impingement with other regions of bainite.

Experiments have now confirmed that the coarse, coalesced bainite appears in weld metals containing large concentrations of both manganese and nickel, such that the bainite forms at temperatures close to the



5 ***a*** **contours showing the combined effect of manganese and nickel on the calculated toughness for −60°C of weld metal produced using arc welding with a heat input of 1 kJ mm^{-1}, a base composition (wt-%) of 0·034C–0·25Si–0·008S–0·01P–0·5Cr–0·62Mo–0·011V–0·04Cu–0·038O–0·008Ti–0·025N and an interpass temperature of 250°C and** ***b*** **full results for welds A–C**

martensite start temperature (Fig. 6).[4–6] It leads to a deterioration in toughness and can be avoided by careful modifications of composition, for example, by reducing the manganese concentration when the nickel concentration is high.

Genetic algorithms

Design problems usually begin with a specification of the required properties. It is useful therefore to discover, using a model, the domain of inputs that lead to the desired properties. This is frequently done by a trial and error process beginning with inputs and seeing whether the output is achieved.

Genetic algorithms do this more efficiently.[75] Consider a model with n input variables and one output. The desired value of the output is y_0. The algorithm begins with a set of N randomly selected sets of inputs $(x_1,x_2,\ldots x_n)_{i=1,N}$. When the calculations are completed there will be N corresponding values of the output y_i. A fitness function is defined to express the deviation of y_i from y_0.

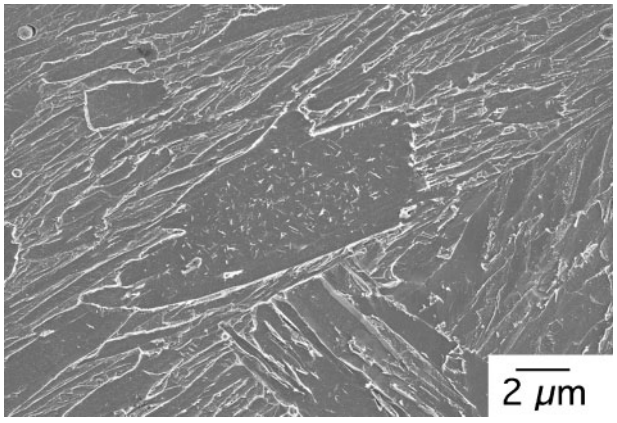
Some of the original sets of inputs which show strong deviations from y_0 are disposed and replaced with others. The new sets can again be chosen randomly by perturbing the more successful sets or by combining inputs from different sets, e.g. $(x_1,x_2,\ldots x_n)_1 = (x_1,x_2)_2 \cup (x_3,\ldots x_n)_5$ etc. The new sets of input then generate new outputs and the process is repeated until the domain of inputs which leads to values close to y_0 is identified.

A combination of neural networks and genetic algorithms has in this way been used to design a novel low silicon TRIP assisted steel with a microstructure consisting of δ-ferrite dendrites and a mixture of bainitic ferrite and carbon enriched retained austenite. The steel has been manufactured and tested to reveal a tensile strength of about 1 GPa and a uniform elongation of 23% (Fig. 7).[76]

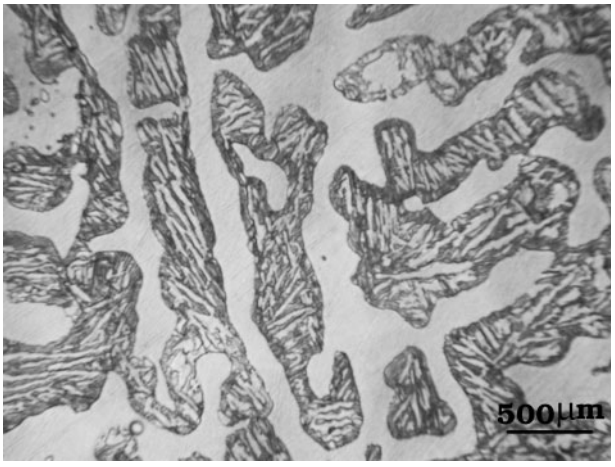
Strong steels

Steels which are strong and yet have sensible levels of toughness, cost or other properties are difficult to achieve. This is an area where materials modelling has led the steel industry with the creation of new products which are now commercialised.

One example is the invention of *Blastalloy 160*, which has a yield strength of 1110 MPa and a Charpy



6 Coalesced bainite in a 7Ni–2Mn (wt-%) weld metal[4–6]



7 The microstructure of δ–TRIP steel[76]

toughness of ~176 J at room temperature.[77,78] The alloy is designed as a blast resistant material for the hulls of fighting ships and meets processability requirements. It therefore has to be weldable so the carbon concentration is kept to a minimum. Its chemical composition derived using thermodynamic and kinetic modelling is Fe–0·04C–3·64Cu–6·61Ni–1·78Cr–0·58Mo–0·11V (wt-%).

The alloy relies on a mixed microstructure of bainite and martensite, but is secondary hardened using 3 nm sized body-centred cubic copper and M_2C precipitates. Multistep heat treatments are used to introduce a dispersal of nickel rich austenite which enhances toughness by transformation plasticity.

Another case in a higher category of strength is the steel containing fine bainite, produced by transformation at low temperatures.[42,45,79] The theory used in its design relies on the atomic mechanisms of solid state transformations, particularly the mechanisms of nucleation and growth of bainite and martensite. Transformation at low temperatures leads to finer plates of bainite.[80–82] The key criterion to achieve fine bainite then becomes one of keeping the bainite start (B_S) and martensite start (M_S) temperatures separate. Bainite nucleation involves the partitioning of carbon which gives it a thermodynamic advantage over the diffusionless nucleation of martensite. In a high carbon steel it is possible therefore to suppress both B_S and M_S while keeping $B_S - M_S$ significantly positive. In this way, transformation to bainite can be achieved at temperatures as low as 125°C. Of course, the time required for transformation increases dramatically as the temperature is reduced, but fine bainite can be generated by transforming at 200°C for a reasonable amount of time. The result is a cheap steel which can be large in all its dimensions and yet plates of bainite which are only 20–40 nm in thickness, corresponding to a high strength, ductility and toughness. The typical composition is Fe–1C–1·5Si–2Mn–1·3Cr–0·25Mo–0·1V (wt-%).

This seems to be the first nanostructured metal to be manufactured on a large scale.

Creep resistant steels

A huge amount of effort, both experimental and the development of theory, has been devoted to the design of ferritic steels capable of resisting creep and oxidation at 600–650°C over 100 000 h and 100 MPa.[83–87] The actual stress applied during service is <100 MPa so the expected life is 250 000 h. It is fair to say that the work has been singularly unsuccessful in achieving a ferritic steel capable of sustaining 650°C. Early theoretical predictions failed to perform[66] and experimental programmes throughout the world failed to do much better than the established *NF616*[83] and *HCM12A*[88] steels designed for lower operating temperatures.

It is not relevant here to comment on why the experimental programmes did not succeed, but the reasons for the failure of theory might in hindsight be summarised as follows:

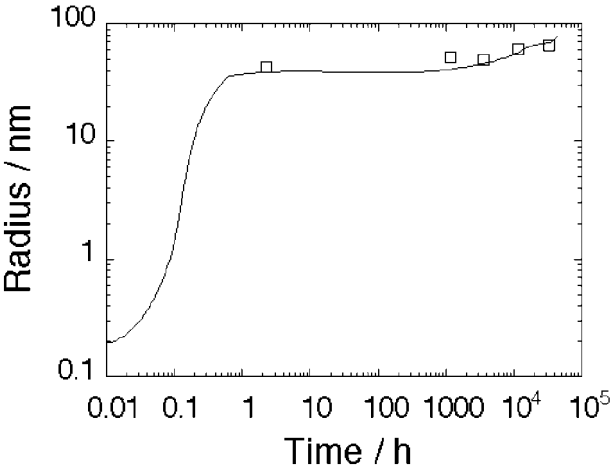
(i) for the kind of steels considered, there are at least 50 variables which determine the creep rupture life. The dislocation theory available for the estimation of creep rupture life is too simplistic to be applied in alloy design

(ii) empirical models for creep, such as those based on neural networks[66] had large associated modelling uncertainties.[72] These uncertainties might have been smaller if quantities of existing data in industrial archives and other development programmes would have been made available

(iii) the microstructure models, which can be used for intuitive design, suffered from a lack of thermodynamic data. The Z phase, which some identify with the long term deterioration of properties,[29] is such a case where data have only recently become available

(iv) there are no models for oxidation resistance as a function of many parameters implicit in alloy design

(v) finally, it is possible that it may not in principle be possible to achieve the required properties. It is not clear how such a proof might be formulated given the number of parameters that determine creep and oxidation properties.



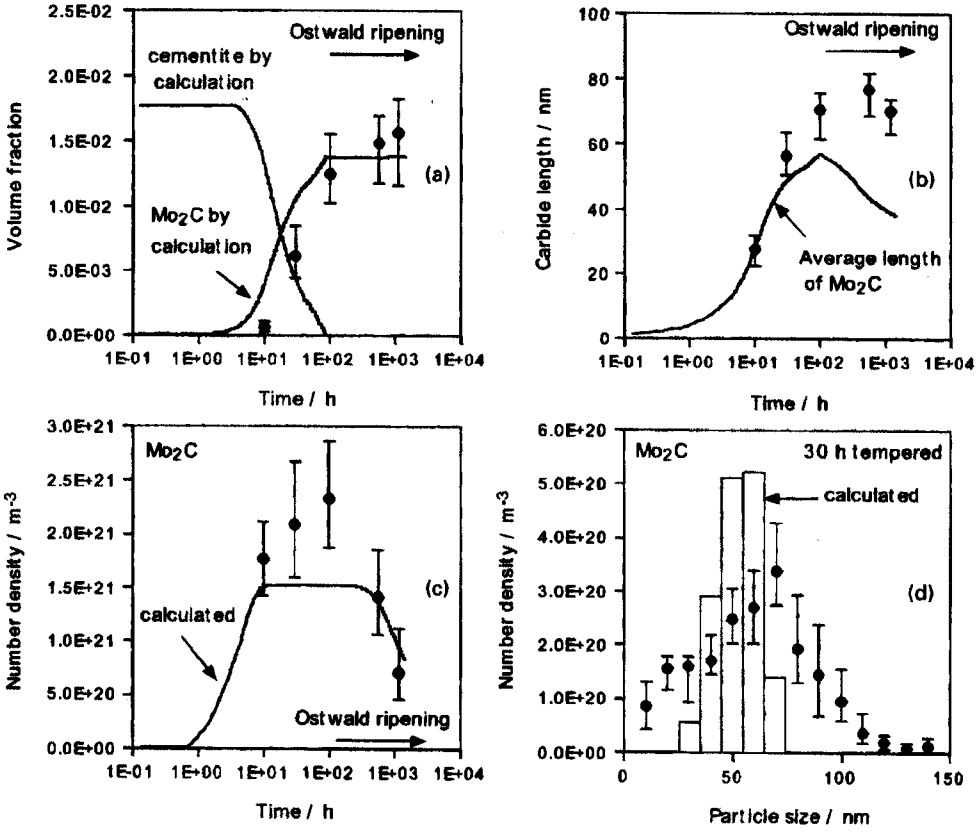
8 'Equivalent circle radius' of $M_{23}C_6$ particles plotted as a function of time at 650°C[91]

It is worth pointing out that models have nevertheless contributed to reductions in experimental programmes, for example in limiting the addition of solutes to avoid the formation of δ-ferrite.

Expense of modelling

Modelling is often presented in research proposals as a method which leads to lower costs by minimising experiments. One example used to illustrate this is the calculation of phase diagrams across the periodic table. To do this experimentally for 100 elements would require much more than 100! experiments. However, there is no evidence to suggest that calculations might be a cheaper way to proceed. Furthermore, many of the calculation methods are not sufficiently accurate to be used in alloy design.[89]

The friction stir welding process[90] has led to a plethora of highly sophisticated models which include coupled thermal, high strain rate plasticity and transport subroutines together with complex tool and workpiece geometries. The output then consists of vector and scalar fields giving a comprehensive description of the process. The calculations have been validated in a limited way but in many cases not by exposure to users of the process. A user needs process maps which highlight the domain of input parameters (tool rotation



9 Comparison between theory and experiment for molybdenum carbide precipitation in an Fe–Mo–C system[92]

speed, tool shape, penetration, etc.) which is associated with successful welds. However, the computations are so time consuming that it is not practical to use the methods for producing process maps. This seems to be a case where the generation of experimental maps may be a lot cheaper and faster than using models.

Validation of models

There is a weakness in the experimental validation of models. This is well illustrated by the fact that there are two fitting parameters in almost all of kinetic theory, the interfacial energy and the number density of nucleation sites. There is no satisfactory method of calculating these values in a generalised manner. Nucleation processes occur on a scale which is not easy to monitor. For this reason, many published kinetic models make comparisons at a point where the particles are coarse and hence most of the information about the nucleation stage is lost.

Figure 8 is a case where classical nucleation and growth theory was used to simulate the precipitation of $M_{23}C_6$ in a particular power plant steel.[91] The fitting parameters included the number density of nucleation sites and the carbide–ferrite interfacial energy per unit area. The experimental data plotted are however for a stage where coarsening rather than precipitation dominates. This is not a good test of the kinetic assumptions since it is the early part of the precipitation curve that is sensitive to nucleation and growth phenomena.

Figure 9 shows a variety of comparisons for molybdenum carbide in ferrite in a simple Fe–Mo–C system.[92] The only fitting parameters used are the interfacial energy per unit area and the number density of nucleation sites, but the treatment is otherwise multicomponent and in a simultaneous transformations framework[93,94] which avoids assumptions about the dissolution of cementite during the precipitation of the alloy carbide. The comparison with experimental data covers the early stages of precipitation and the closure with theory is not all that impressive. Much more work is needed to achieve a performance which is useful in industry.

Summary

It is true to say that major advances have been made in the mathematical modelling of all aspects of materials science. And indeed, novel technologies and materials have resulted from these efforts, a very few examples of which have been presented in this paper. However, it is also truly important to recognise the shortfalls of the technique, of which there are many, so that progress can be better defined.

The biggest gains seem to occur when emphasis is on treating the problem at the level of complexity appropriate to technology. This not only serves to help industry, but more importantly, provides challenging problems which do not surface in ordinary science.

Finally, there is a need when comparing experimental data against models to be transparent on what is actually being validated.

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