Simultaneous Calculation of Mechanical Properties and Phase Equilibria

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Many formulas have been developed to describe the mechanical properties of various microstructures, but there have been relatively few attempts to combine such formulations directly with multicomponent phase diagram calculations obtained by the CALPHAD technique. This paper describes some of the techniques used in developing such a combined approach as part of a more comprehensive materials property program (MPP). The basic requirement is to describe the mechanical properties of the overall alloy by determining the effect of each solute, and the grain size, on the mechanical properties of the various phases in a multicomponent system. As some of the coefficients are not readily available, methods have to be evolved that echo problems already faced by the CALPHAD community with respect to characterizing the thermodynamics of metastable phases. It will be shown how the inter-relation of various mechanical properties, such as yield strength and hardness, can also be used to produce self-consistent data. The promising results obtained for dual-phase materials can be considered a firm foundation for future work on more complex systems.

Introduction

Over the years, one of the central themes of physical metallurgy has been the relation of properties to microstructure. In the absence of detailed information about the properties of individual phases, this has taken several forms, such as using model microstructures, calculating strength parameters from atomic properties, and, most frequently, by using regression analysis to provide numerical input to general algorithms [1979Pic, 1994Tom]. The resulting parameters are then usually combined with experimental data for the volume fractions of the relevant phases, and possibly with other parameters that describe the distribution and dimensions of those phases. A typical example drawn from [1979Pic] gives the proof stress (PS) of austenite in the following terms:

$$\begin{aligned}0.2\%\,\text{PS (MPa)} = 15.4\{&4.4 + 23(\text{C}) + 1.3(\text{Si}) \\ &+ 0.24(\text{Cr}) + 0.94(\text{Mo}) + 1.2(\text{V}) + 0.29(\text{W}) \\ &+ 2.6(\text{Nb}) + 1.7(\text{Ti}) + 0.82(\text{Al}) + 32(\text{N}) \\ &+ 0.16(\delta\text{-ferrite}) + 0.46d^{-1/2}\} \qquad \text{(Eq 1)}\end{aligned}$$

where the terms in brackets refer to the weight percent of the alloying additions, δ-ferrite is the volume fraction of delta ferrite, and d is the austenite grain diameter in millimeters.

With Eq 1, and similar equations, it is possible to conduct thought experiments about the likely result of making potential microstructural changes through heat treatment or arbitrary changes in composition. However, if such a process leads to an interesting combination of properties, it is still necessary to find a combination of alloy composition and heat treatment that will produce the desired microstructure, volume fractions of phases, and partitioning of alloying elements.

This can be a time-consuming and expensive procedure with no guarantee that the desired combination of compositions and phases is even realizable. It is therefore worth considering alternative ways of obtaining the desired result. One way is to start with phase equilibrium data and manually transfer such results to another program, which then calculates the desired properties. Such a method was used in an earlier paper relating to the elastic modulus [1993Mio]. However, the alternative discussed in the present paper is to start with the prediction of the volume fraction and composition of the phases that result from a particular alloy composition and heat treatment, and to simultaneously calculate the selected mechanical properties in the same software package. This can be viewed as a natural extension of the CALPHAD method, whose current capability allows the accurate prediction of the mole fractions and compositions of all the phases present in complex multicomponent alloys [1998Sau].

This route removes any uncertainty as to whether it is possible to achieve a particular combination of volume fractions and phase compositions and gives maximum flexibility when considering the effect of particular variables. The key development is therefore to devise a method of combining the results of CALPHAD predictions with a calculation of the mechanical properties. To offer significant advantages, such a program must also be robust, user-friendly, and readily integrated with other properties. Further details of the associated materials properties program (MPP) are given in [2000Sau1]. The present paper is therefore part of a continuous spectrum of development in the last decade, as depicted in "The dream of a microstructure and property

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prediction system" suggested by Tomota *et al.* [1994Tom]. Work on simulating quenching *via* the DANTE system (Distortion Analysis for Thermal Engineering) [2000Fer] is another example of the direction in which software is currently moving.

Basic Approach

Several stages are required to achieve the stated objectives:

- describing the effect of individual solutes on the mechanical properties of solid solutions;
- combining the effect of various solutes to obtain the properties of multicomponent single phases of different crystal structures;
- correlating the different mechanical properties;
- combining the properties of individual phases to obtain the properties of the aggregate alloy; and
- validating the predicted results against experimental values.

1. Description of the Mechanical Properties of Solid Solutions for Individual Solutes

Standard algorithms for the effect of various solutes on the mechanical properties of a particular solvent are generally restricted to a particular range of composition. Following the CALPHAD approach for the description of thermochemical properties, there is a need to describe the relevant properties across the entire system. This is easily achieved for the stable phases, where there is extensive solubility, but that still leaves a need for reliable end-member properties for the properties of solutions with other (metastable) crystal structures.

It should be noted that grain size is normally ignored when constructing databases for phase diagram calculations, but this variable plays a much greater role when dealing with mechanical properties. Provision has therefore been made to include a Hall-Petch coefficient (k_H) [1970Hal, 1993Fan1] for each solute, so that the strength parameter can be expressed as a flow stress (σ_o) together with a grain-size dependence on $d^{-1/2}$, as shown in Eq 2:

$$\sigma = \sigma_o + k_H d^{-1/2} \qquad \text{(Eq 2)}$$

Examples for the variation of σ_o in fcc Fe-Ni and bcc Fe-Cr solutions, which both show extensive solid solubility, are shown in Fig. 1 and 2, respectively. As with thermochemical properties, some judgment has to be exercised in weighting the experimental data. For example, some data of [1965Tie] in Fig. 2 have been omitted in deriving the polynomial that describes the value of σ_o for Fe-Cr in our assessment, because it is felt that these data are associated with either segregation or the sigma phase.

As there is a need to estimate the properties of metastable end members for each solute in each relevant crystal structure, analogous information is also required for bcc Fe-Ni and fcc Fe-Cr solid solutions. Almost by definition, this involves low solubilities, at least at one end of the system, and reliable extrapolation then becomes much more difficult. Because it is possible to generate many alternative algorithms to reproduce properties over a limited range of compositions, it has to be accepted that end-member properties at the other end of the system will be more uncertain.

The experience of early work in the CALPHAD community, however, has shown that such end-member properties can still be acceptable, because their inherent deficiencies can be compensated by suitable interaction coefficients and, in most cases, only a very simple polynomial is required. It is however mandatory that the selected effective end-member properties are kept constant; otherwise, the method cannot be extended to other alloys containing the same components.

Nonetheless, there should always be an attempt to select

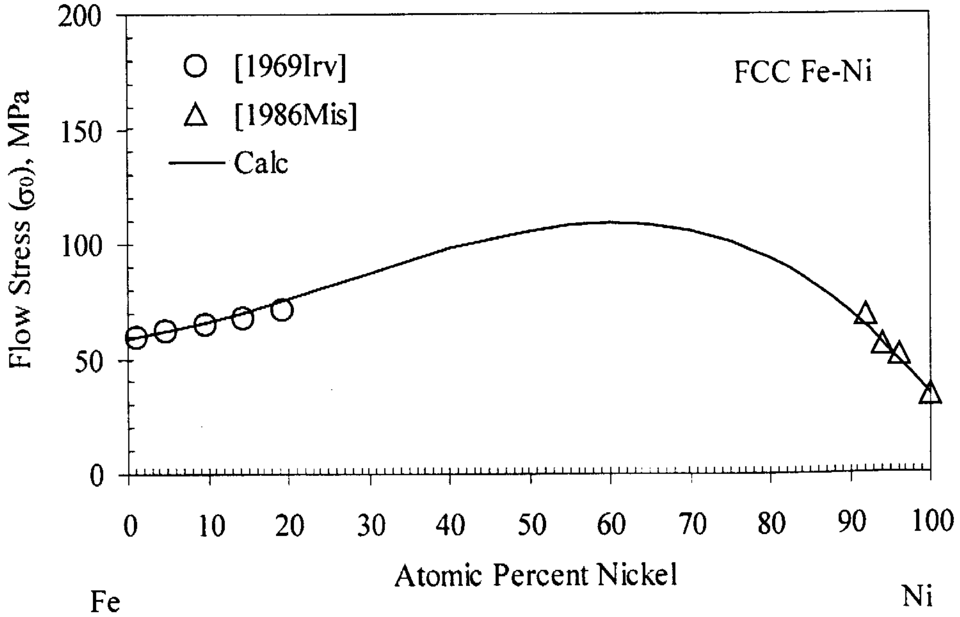

Fig. 1 Variation of flow Stress (σ_0) for the FCC solid solution in Iron-Nickel alloys at 25 °C

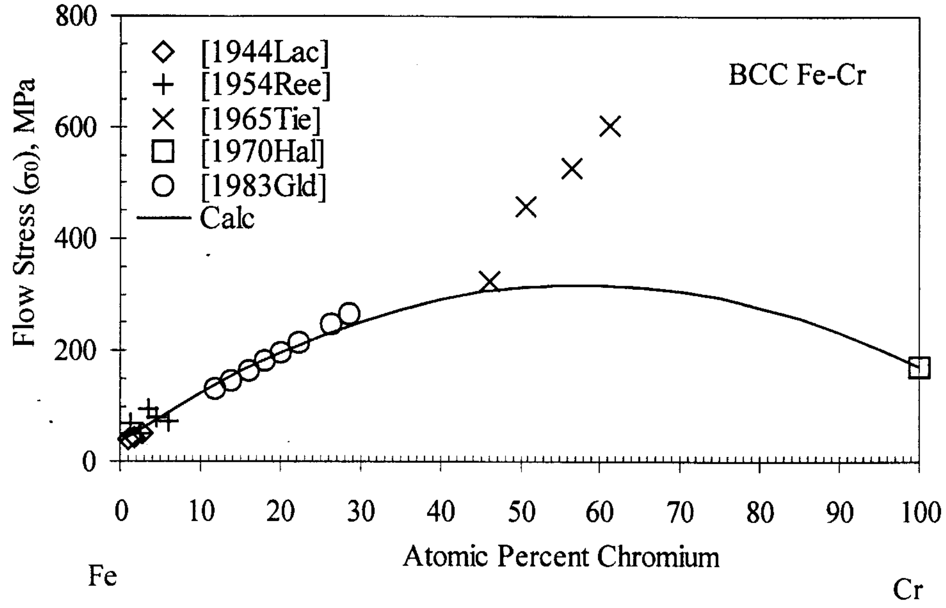

Fig. 2 Variation of flow Stress (σ_0) for the BCC solid solution in Iron-Chromium alloys at 25 °C

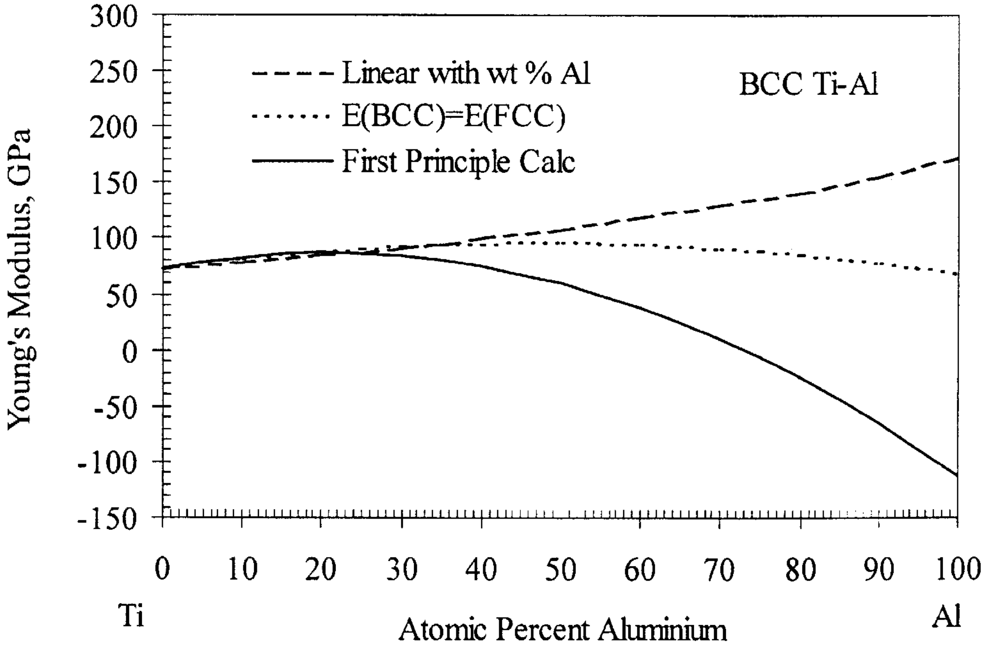

Fig. 3 Alternate ways of depicting the variation of Young's Modulus (E) versus concentration in BCC Ti-Al alloys [1985Elf, 2000Mio]

the most realistic values for the end-member properties. In this respect, it is interesting to refer to the analogous treatment of elastic properties. Here, there is the advantage that data are also available from first principle calculations and, more importantly, that such calculations can be made for metastable structures [1997Cra, 1998Gri]. Such information can then be used as a guide to estimations of elastic moduli for metastable end members, even in those cases where such materials are mechanically unstable. Figure 3 shows the effect of making three different assumptions for the Young's modulus of bcc Al [2000Mio].

Case (a): Assume that the Young's modulus of bcc Ti-Al varies linearly with composition.

Case (b): Assume that the Young's modulus of bcc Al has the same value as for fcc Al.

Case (c): Use a calculated negative value for E (bcc Al) consistent with first principle calculations and extrapolation of elastic constants from Fe-Al.

By contrast, there is very little dispute about the terminal value for bcc Ti as the data, which are available for the extensive solid solutions of Ti-V, Ti-Cr, and Ti-Mo, converge onto a single point (Fig. 4). It is unfortunate that first principle calculations cannot as yet be used to aid the equivalent prediction of plastic properties, because the latter depend so strongly on lattice defects and dislocation geometry.

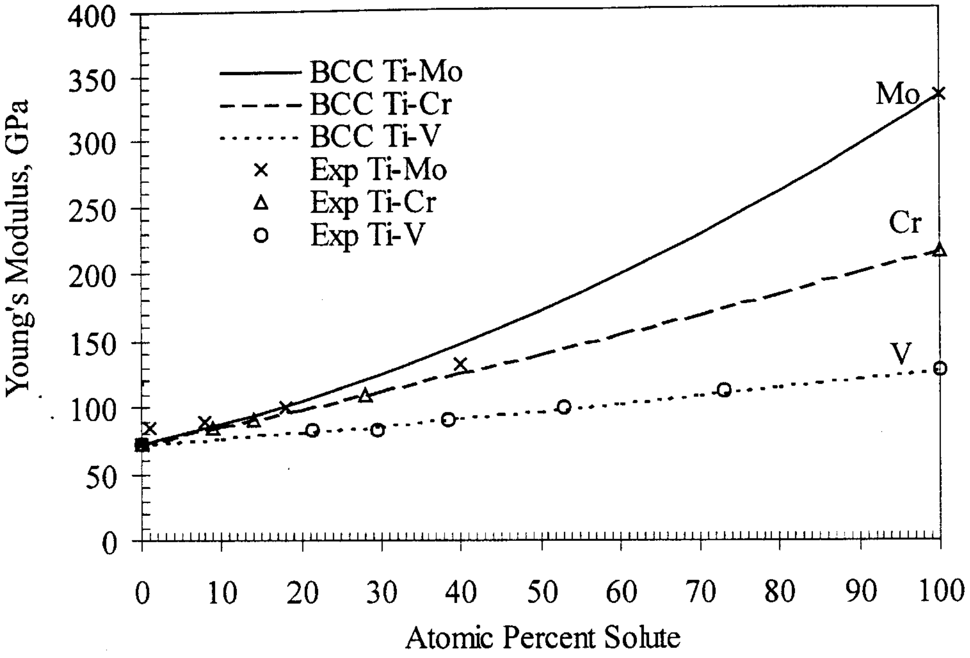

Fig. 4 Variation of Young's Modulus (E) versus concentration in BCC Ti-Mo, Ti-Cr and Ti-V alloys [1957Gra, 1975Fis, 1984Col, 2000Mio]

2. Deriving the Overall Properties of Each Phase

Once data are available for each solute, these have to be combined to obtain the overall mechanical properties of each phase (*e.g.*, α) in a particular alloy system. The simplest approach (Eq 3) is to make the further assumption that the effect of each solute (i, j, k) is a function of both its intrinsic value in the pure elements and the value modified by various solute interactions:

$$\sigma_\alpha = \sum_i x_i\sigma_i + \sum_i\sum_j x_ix_jf(\sigma^0_{i,j}) + \sum_i\sum_j\sum_k x_ix_jx_kf(\sigma^0_{i,j,k}) + \dots \qquad \text{(Eq 3)}$$

Here, σ_α is the resultant property of the phase in question, σ^o_i is the property of element i, $x_{i,j,k}$ are the various atomic fractions of elements i, j, and k in the phase and $f(\sigma^0_{i,j})$ represent functions associated with the various solute interactions.

In essence, the use of such mixing terms is similar to that used for thermodynamic models and allows properties to be determined for a full continuum of compositions for each relevant phase. This means, for example, that the same equation can be used for the fcc phase in both steels and Ni-based superalloys. This has a clear advantage over earlier polynomial expressions, *e.g.*, Eq 1, which are restricted to limited composition ranges. The approach has been validated by plotting predicted tensile property values versus experimental data for multicomponent solid solutions in Fig. 5.

3. Inter-Relationship between Various Mechanical Properties

As tensile data are not always available, it is useful to extend the range of input data through the inter-relationship between hardness and tensile properties. Quantitative relationships between these properties were developed by Tabor [1951Tab] based on the assumption that the stress σ is related to the (true) strain ε by Ludwig's law (Eq 4) *via* the work-hardening coefficient n and a constant A:

$$\sigma = A\varepsilon^n \qquad \text{(Eq 4)}$$

By determining the average pressure under a hardness indentor of a given geometry, it is then possible to derive equations for the relation between the hardness and the proof stress (σ_{PS}) (Eq 5) and the ultimate tensile strength (UTS) (Eq 6).

$$H_V = C\sigma_{PS}(\varepsilon_1/\varepsilon_2)^n \qquad \text{(Eq 5)}$$

$$\text{UTS}/H_V = (1 - n)C^{-1}(12.5n/(1 - n))^n \qquad \text{(Eq 6)}$$

The value of C, which in practice lies between 2.9 and 3.3, is in good agreement with a theoretical value of 3; ε_1 is the average strain under the indentor; and ε_2 is the strain chosen for the PS.

The database therefore has to contain values for n, but this is advantageous as this is a parameter that is frequently used in process modeling. For Eq 4 to be valid, it is also necessary to assume that no structural changes are induced by deformation. Modifications must therefore be introduced for alloys where deformation martensite is produced, unless the extent of phase transformation is identical in the two modes of testing. Different forms of fracture under tension and compression can also cause deviations in this relationship [2000Shen].

Nonetheless, Eq 4 to 6 can be used with confidence, as shown in Fig. 6. This figure shows the correlation between

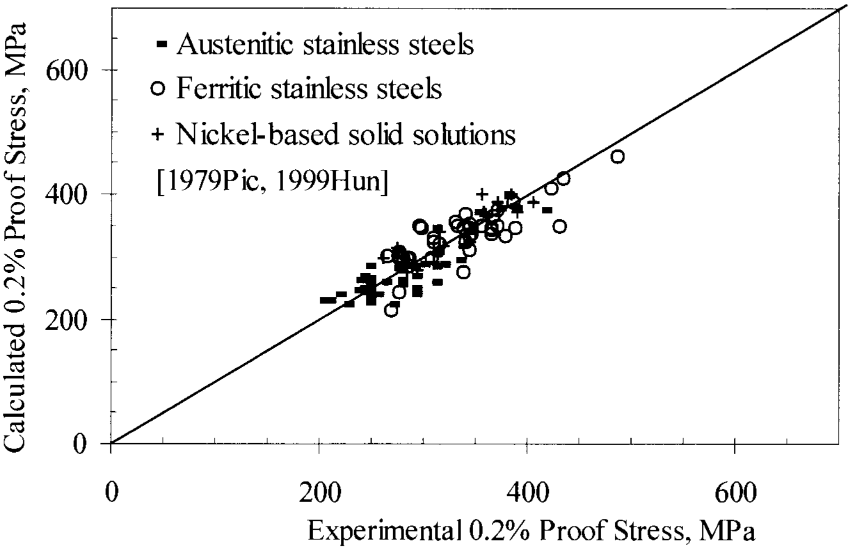

Fig. 5 Predicted versus experimental 0.2% proof stress of various multi-component solid solutions

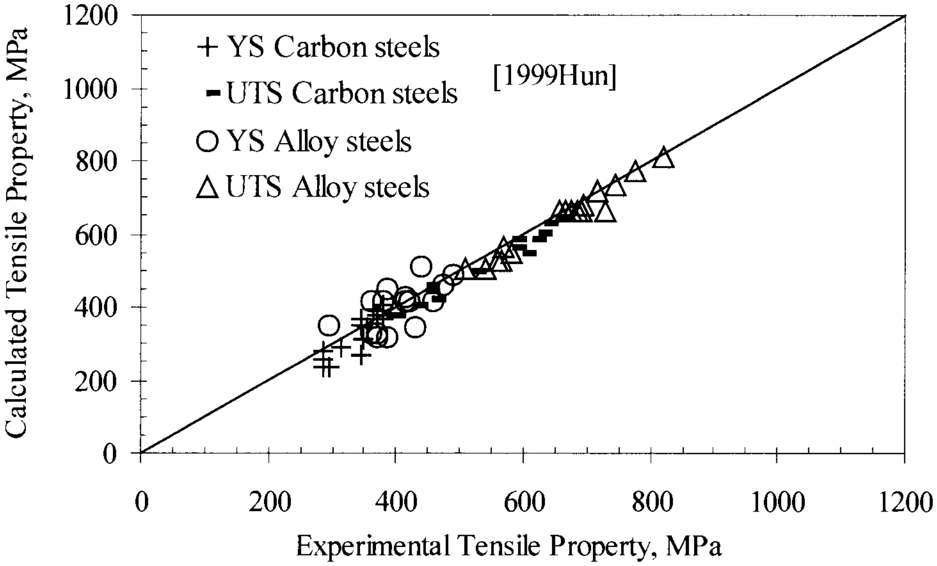

Fig. 6 Correlation of experimental tensile properties with values calculated from VPN via equations [4–6]

tensile data calculated from experimental hardness values and experimental tensile data for a large number of alloys studied in this paper.

Augmenting the range of input data by hardness testing is particularly useful when small specimens have been quenched to retain extended solid solutions and it is difficult to produce tensile specimens. Intermetallic compounds are another example where hardness information far exceeds that for other mechanical properties. The possibility of interconverting hardness and tensile strength parameters is also useful from the end-user point of view. For example, wear has traditionally been related to hardness rather than PS or UTS. In this case, it also of interest to have the relative hardness values of the various constituents. In other situations such as weld cracking, it is more conventional to make correlations with the UTS.

4. Combining the Properties of Two (or More) Phases

The next step is to combine the data for individual multicomponent phases with the calculated volume fractions of each phase and evaluate the properties of the overall alloy. As shown by Fan, the simple law of mixtures is only a special case of a more generalized approach [1994Fan], but any differences are small provided the properties of the constituent phases do not differ by a factor greater than ×2. As this is the case in the systems discussed in this paper, the simple law of mixtures has been adopted here, although there is provision in the program for the generalized case.

5. Final Validation

The final step is to test the calculated results against available experimental data for the alloy as a whole. Figure 7

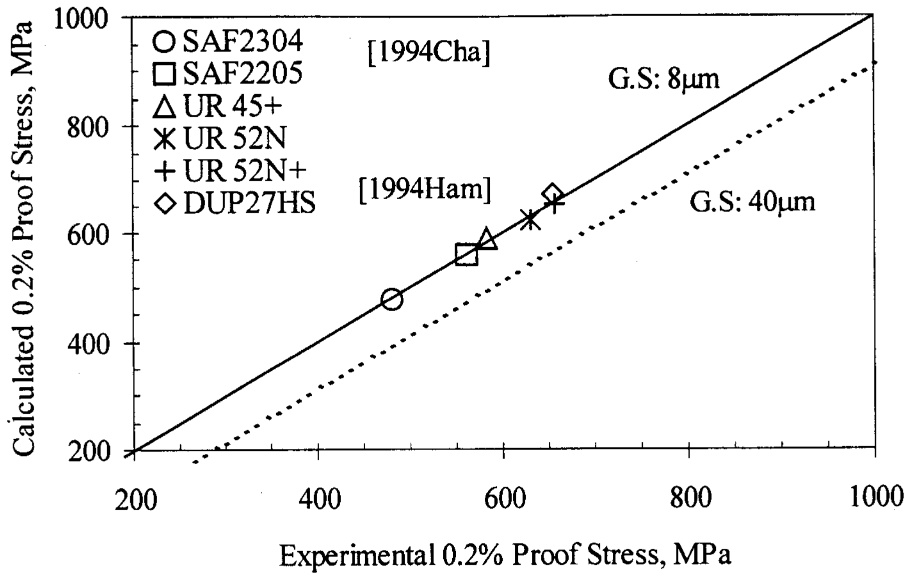

Fig. 7 Predicted versus experimental results for duplex stainless steels with different grain sizes (G.S.)

Table 1 The composition and grain size of duplex stainless steels in Fig. 7

Alloy	Grain size (μm)	Composition (wt.%) [94Cha, 94Ham]							
		C	Cr	Cu	Mn	Mo	N	Ni	Si
UR35N	8	<0.03	23	...	1	...	0.1	4	0.4
UR45N	8	<0.03	22	...	1	3	0.15	5.3	0.4
UR45+	8	0.015	23	...	1	3.3	0.18	6	0.4
UR52N	8	<0.03	25	1.5	1	3	0.22	6.5	0.4
UR52+	8	0.015	25	1.5	1.41	3.5	0.25	7	0.4
DUP 27HS	8	<0.03	27	2.4	0.65	4	0.3	7.6	0.45

shows the degree of validation that has been achieved for the room-temperature properties of dual-phase stainless steels whose structures have been retained by quenching from the annealing temperature. Further details for the alloys used in Fig. 7 are given in Table 1. The relevant volume fractions at the annealing temperature have been derived by applying density data to the mole fractions calculated at that temperature, using the current Thermotech Steel Database [2000Sau2]. This figure also shows the effect of making calculations for a larger grain size (40 μm), which demonstrates the large effect of grain size versus solution strengthening.

Provision is also being made for the possibility that one of the high-temperature phases undergoes a phase transformation on quenching. This possibility was explored in earlier work on the variation of the modulus in Ti-6Al-4V quenched from various temperatures [1993Fan2]; at that time, the data for volume fractions and the composition of the phases were derived from the literature and inserted manually into the equations describing the overall properties.

Conclusions

It has been shown that the aim of simultaneously calculating phase equilibria and the associated mechanical properties can be realized by following a route that is similar to that used in the development of the CALPHAD technique. The extent to which a variety of input data can be related on a sound physical basis has also been explored and used to build up a coherent database. The examples presented here are mostly concerned with dual-phase stainless steels, but it is clear that a sound foundation has been provided for future work on more complex systems.

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