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Modelling solid solution hardening in high entropy alloys

Isaac Toda-Caraballo and Pedro E.J. Rivera-Díaz-del-Castillo*

Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Rd, Cambridge CB3 0FS, UK

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Abstract—Solid solution hardening (SSH) is one of the major contributions to the excellent mechanical properties displayed by high entropy alloys (HEAs). SSH is first analysed for binary systems in face-centred cubic and body-centred cubic alloys with different elemental additions in the temperature range 5–623 K. The prediction of the SSH has been possible by using Labush's approach for SSH modelling, where the necessary parameters have been incorporated without fitting to experimental data. Among these parameters, elastic misfit is shown to be prominent; experimental evidence suggests it has a dominant effect with respect to other misfit forms. Nevertheless, Labush's approach cannot be directly applied to model SSH in HEAs, since it is based on the misfit produced in the lattice of a solvent/reference atom, which does not exist in HEAs. Its extension to HEAs has been performed by using Mooren's approach for the computation of interatomic spacing in multicomponent alloys, allowing the creation of a model for elastic misfit in HEAs. This has led to a methodology for computing SSH effect in HEAs, where the results have successfully been compared with a collection of experimental data from the literature. The explanation of how different atoms can modify the yield strength can be formulated in terms of this approach.

Keywords: High entropy alloys; Solid solution hardening; Critical resolved shear stress; Multicomponent alloys; Yield strength

1. Introduction

High entropy alloys (HEAs) are multicomponent systems composed of elements displaying a nearly equiatomic configuration with contents ranging between 5 and 35 at.%. [1]. The high entropy of such mix benefits the formation of face-centred cubic (fcc) or body-centred cubic (bcc) solid solutions [2]. They display an excellent mechanical response and good wear resistance at low and high temperatures [3–5], as well as good plastic behaviour [6–8]. Due to their recent discovery, the development of new HEAs represents a challenge in materials science. A model that can predict which elemental additions and compositions produce an HEA has still not been produced, but a set of parameters and rules to aid such a process has been proposed. A parameter accounting for the difference in atomic sizes, the enthalpy of mixing and the entropy of the system [2,9] can be combined with valence electron concentration and Pauling electronegativity [10,11] to suggest alloys that could display a solid solution and high entropy.

There are very few publications focused on predicting other properties of HEAs; they are usually an adaptation of existing models in conventional alloys, thus missing the complexity of HEAs. It is generally accepted that solid solution hardening (SSH) is the main cause of the exceptional mechanical properties of HEAs. The high yield strength or hardness that some HEAs display is mainly related to the SSH, order strengthening effects and grain boundary strengthening. In Ref. [12], an estimation of the contributions to yield strength showed that half of its value is due to SSH and order strengthening, while the rest relates to grain size strengthening. This emphasizes the need for a description of the mechanisms influencing these effects. The goal of this paper is to propose a model for computing the effect of SSH in HEAs. This has been done by analysing SSH in binary systems via Labush's [13] classical approach, and by extending it to multicomponent alloys. Results collected from the literature have been compared with the model, which is able to explain the hardening effects of different elements in complex alloys reported in the literature.

2. Solid solution hardening in binary systems

Fleisher carried out one of the first studies on the effect of solute atoms in solid solution [14]. In his work, he assumed a low solute content; thus, the effect of a solute atom in the crystal structure of the solvent can be described in isolation from the other solutes. Dislocations are then blocked by the isolated atoms. Under these assumptions, he concluded that the SSH effect $\Delta\sigma_{ss}$ is:

$$\Delta\sigma_{ss} = B_i X_i^{1/2} \tag{1}$$

where X_i is the i solute content and B_i is a constant dependent on the shear modulus μ of the alloy, the mismatch parameter ϵ_i and a fitting constant Z:

* Corresponding author.

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$$B_i = 3\mu\epsilon_i^{3/2}Z; \quad \epsilon_i = |\eta_i'| + \alpha|\delta_i| \tag{2}$$

Here, ϵ_i accounts for the elastic misfit η_i' and, for the atomic size misfit δ_i,

$$\eta_i' = \frac{\eta_i}{1+0.5|\eta_i|}; \quad \eta_i = \frac{d\mu}{dX_i}\frac{1}{\mu}; \quad \delta_i = \frac{da}{dX_i}\frac{1}{a} \tag{3}$$

a being the cell parameter of the alloy and α being a parameter that accounts for the difference in the interaction forces between screw and edge dislocations and the solute atom. It is accepted that $3 < \alpha < 16$ for screw dislocations and $\alpha > 16$ for edge dislocations [15].

Taking a step forward, Labush [16] considered a higher concentration of solute atoms, where the dislocation is subjected to a frictional effect, due to the constant interaction with solute atoms, rather than a blocking effect from isolated atoms. The expression derived is similar to Fleisher's approach and takes the form:

$$\Delta\sigma_{ss} = B_i X_i^{2/3} \tag{4}$$

where the parameters B_i and ϵ_i are:

$$B_i = 3\mu\epsilon_i^{4/3}Z; \quad \epsilon_i = \left(\eta_i'^2 + \alpha^2\delta_i^2\right)^{1/2} \tag{5}$$

There are obvious similarities between the two approaches, and some works in the literature show good agreement by fitting $\Delta\sigma_{ss}$ experimental data to both $X_i^{1/2}$ and to $X_i^{2/3}$ [17,18]. Nevertheless, a larger number of works report better agreement of experimental results with Labush's approach [15,19–21]. We will therefore consider Labush's approach for SSH.

Other authors have theorized over SSH [22,23], although the main features in their analysis were introduced in Fleisher's and Labush's approaches. Neither of the two models, however, considers the effect of temperature on SSH. Butt [24–30] and other authors [31,21,32–37] have considered the variation of the critical resolved shear stress (CRSS), τ, with temperature (in the low temperature regime) and composition. Based on their work, the CRSS is described as [24]:

$$\tau = \tau_0 e^{-mk_bT/W_0} \tag{6}$$

where τ_0 is the CRSS at 0 K, k_b is the Boltzmann constant, $m = 25 \pm 2.3$ is a constant and W_0 is a constant dependent on the material, which describes the binding energy of an edge-dislocation segment with the solute atoms in its proximity [38]. It has been reported that Eq. (6) describes the low-temperature regime of yield strength up to 1/3 of the absolute melting temperature [25]. For higher temperatures, a plateau in the yield strength is observed and Eq. (6) is not valid anymore. A possible explanation for the plateau was proposed by Labush [13]: dislocation segments jump mostly forward when crossing obstacles at low temperature, while at higher temperatures the thermal activation allows a larger number of backward jumps. The probabilities of forward and backward jumps are similar, explaining the plateau during this thermally activated mechanism. Nevertheless, a more elaborate explanation is required to understand this phenomenon.

By combining Eqs. (4) and (6), the SSH effect in the low-temperature regime is assumed to be

$$\tau = \left(B_{i,0}X_i^{2/3}\right)e^{-mk_bT/W_0} \tag{7}$$

where $B_{i,0}$ is the hardening parameter at 0 K. Therefore, an exponential dependence of B_i with composition is postulated, and Eq. (5) can be rewritten as:

$$B_i = 3\mu\epsilon_i^{4/3}Z_0 e^{-mk_bT/W_0} \tag{8}$$

with Z_0 now redefined as a constant that is dependent on the solvent but independent of temperature.

Fig. 1a displays a collection of 334 experimental results on SSH effect from the literature [21,24–37]. They contain fcc, bcc and hexagonal close-packed (hcp) solid solutions, with a maximum solute content of 0.5 atomic fraction and temperatures ranging from 5 to 623 K. The corresponding B_i fitted values are displayed in Fig. 1b as a function of temperature. When data for different temperatures are reported in the literature for a binary system, a line with slope $-mk_b/W_0$ can be produced in logarithmic scale. All binary systems with data at different temperatures, except for Ni–Cr, are below 1/3 of their respective melting temperature. Thus, a constant value W_0 is assumed. In the case of Ni–Cr, as can be observed in Fig. 1b, experimental data suggest that W_0 changes at $T = 523$ K; this is very close to 576 K, which corresponds to 1/3 of the melting temperature of Ni. In the case of Ta, the maximum temperature available in the literature is 623 K, but this is well below

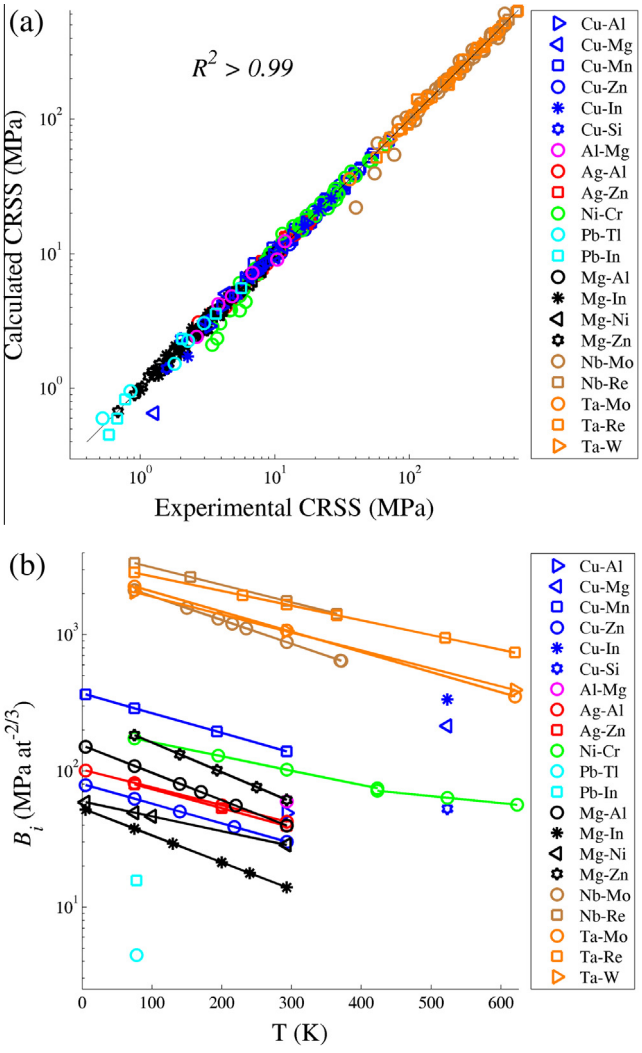

Fig. 1. (a) Experimental vs. calculated CRSS with composition for the systems and temperatures plotted, with a $R^2 > 0.99$. (b) Fitted values of B_i for different solvent–solute systems at temperatures ranging from 5 to 623 K. Data obtained from Refs. [21,24–37].