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Multi-component solid solution hardening

Part 1 *Proposed model*

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A relation for multi-component solid solution hardening has been derived: if the binary athermal or thermal solid solution hardening of ν dilute and random distributions of solute atoms i in the base metal is given by $\Delta\tau_i = R_i C_i^q$, and if these ν distributions are present together in the base metal without interacting with each other, the multi-component solid solution hardening is given by:

$$\Delta\tau = \left[\sum_i \Delta\tau_i^{1/q}\right]^q \quad \text{with} \quad i = 1 \ldots \nu.$$

A more general relation is also derived for the case where the solute atoms influence both the thermal and athermal component of the yield stress. The model can be extended for when different solute atoms interact with each other. A relation is also proposed for the case where each solute has a different concentration exponent q_i. The agreement of the model with experimental results is considered in Part 2.

1. Introduction

Although binary solid solution hardening (SSH) has been the subject of many theoretical studies, only a few investigators have explored the problem of multi-component SSH. The purpose of the present article is to predict the multi-component SSH when the binary SSH caused separately by each of the solutes is known.

Before considering the model in detail it is necessary to take into account the fact that the flow stress τ should be divided into two components: the athermal component or internal stress τ_μ and the thermal component or effective stress τ^*, the latter depending on temperature T and deformation velocity $\dot{\gamma}$ [1]:

$$\tau = \tau^*(T, \dot{\gamma}) + \tau_\mu. \tag{1}$$

If only the concentration dependence of the strengthening effect is taken into account, several binary SSH theories and experiments (e.g. [2–4]) result in one of the following three equations:

$$\Delta\tau_i = R_i C_i^q \tag{2}$$

$$\Delta\tau_i = K_i C_i^n + P_i(T, \dot{\gamma}) C_i^m \tag{3}$$

$$\Delta\tau_i = R_i C_i^{q_i} \tag{4}$$

where $\Delta\tau_i$ is the increase of the flow stress due to the solute element i with concentration C_i; q, n and m are constant concentration exponents independent of the solute; q_i is a concentration exponent with a different value for each solute i; the coefficients R_i, K_i and P_i are independent of the concentration C_i.

The ternary SSH $\Delta\tau$, when two atom distributions with different obstacle strengths are added to a pure metal, has been calculated by a few investigators [2, 5–8]. Their results are given in Table I, in which Equation 13 can be derived as the asymptotic solution* of the set of multi-

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* At small concentrations,strong interactions and relatively small interaction widths, $Gf_{0\nu}/w_\nu$ is much greater than unity (asymptotic behaviour) and ρ_ν is approximated either by $\rho_\nu \approx C_\nu G f_{0\nu} \dot{\Phi}_\nu(\xi)/w_\nu$ or by $\rho_\nu = 0$ substitution of these expressions for ρ_ν in the set of multi-component equations derived from Labusch [2] yields Equation 13. (ρ_ν is the distribution function for the spacings of the obstacles ν from the unit length of dislocation. These obstacles are characterized by their individual densities C_ν, their interaction forces $f_{0\nu}\, \dot{\Phi}_\nu(\xi)$, and interaction widths $w_\nu \cdot g$ is the solution of the appropriate Green's function.)

TABLE I Ternary solid solution hardening theories

Reference	Binary SSH	Ternary SSH	Comments
–	–	$\Delta\tau = \Delta\tau_1 + \Delta\tau_2$	
Koppenaal and Kuhlmann Wilsdorf [5]	$\Delta\tau_i \sim C_i^{1/2}$	$\Delta\tau = (\Delta\tau_1^2 + \Delta\tau_2^2)^{1/2}$	
Foreman and Makin [6]	$\Delta\tau_i \sim C_i^{1/2}$	$\Delta\tau = \Delta\tau(1)\frac{C_1}{C_1 + C_2} + \Delta\tau(2)\frac{C_2}{C_1 + C_2}$	(*a*)
Foreman and Makin [6]	$\Delta\tau_i \sim C_1^{1/2}$	$\Delta\tau \approx \Delta\tau_1 + \Delta\tau_2$	(*b*)
		$\Delta\tau \approx (\Delta\tau_1^2 + \Delta\tau_2^2)^{1/2}$	(*c*)
		$(\Delta\tau_1^2 + \Delta\tau_2^2)^{1/2} < \Delta\tau < \Delta\tau_1 + \Delta\tau_2$	(*d*)
Ruf and Koss [7]	$\Delta\tau_i = R_iC_i^{1\cdot 0}$	$\Delta\tau = [R_1^2C_1^2 + (R_1^2 + R_2^2)C_1C_2 + R_2^2C_2^2]^{1/2}$	(*e*)
Labusch [2], Friedrichs and Haasen [8]	$\Delta\tau_i = \frac{Cf_{0i}^{4/3}w_i^{1/3}C_i^{2/3}}{b(4T)^{1/3}}$	$\Delta\tau^{3/2} = \Delta\tau_1^{3/2} + \Delta\tau_2^{3/2}$	(*f, g*)
derived from Labusch [2]	$\Delta\tau_i = \frac{Cf_{0i}^{4/3}w_i^{1/3}C_i^{2/3}}{b(4T)^{11\ 3}}$	$\Delta\tau = \frac{C(f_{01}^2C_1 + f_{02}^2C_2)}{b(4T)^{1/3}\frac{f_{01}^2C_1}{w_1} + \frac{f_{02}^2C_2}{w_2}}{}^{1/3}$	(*f, h*)
Fredrichs and Heasen [8]	$\Delta\tau_i = \frac{f_{0i}^{3/2}C_i^{1/2}}{2b\sqrt{T}}$	$\Delta\tau = \frac{C_1f_{01}^2 + C_2f_{02}^2}{2b\sqrt{T}(C_1f_{01} + C_2f_{02})^{1/2}}$	(*f*)

Comments

(a) Law of mixtures: $\Delta\tau_i$ is the strengthening effect when all solute atoms are of type i;
(b) when a few strong obstacles are introduced among many weak ones;
(c) for two fairly weak obstacles;
(d) for two strong obstacles;
(e) for a mixture of medium and weak obstacles;
(f) w_i = interaction width, f_{0i} = maximum interaction force, T = line tension, b = Burgers vector;
(g) $w_1 = w_2 = w$ is assumed;
(h) $w_1 = w_2 = w$ is not assumed.

component equations given by Labusch [2]. If $w_1 = w_2$, Equation 13 reduces to Equation 12.

The relations for multi-component SSH, derived in the present paper, are restricted to the common case in which the binary SSH is given by Equation 2, 3 or 4.

2. Proposed model

The quite different SSH equations shown in Table I result from different physical assumptions and mathematical approximations. Therefore, in the present multi-component model only a minimum of physical assumptions are made in order to not restrict the general applicability of the derived equations. The proposed model first assumes the distributions of solute atoms in the solvent to be (1) dilute, (2) statistical, and (3) without interactions. The case where interactions are present is considered in Section 4.

Consider ν distributions of solute atoms i, of which the athermal strengthening effect, when each solute is separately present in the solvent, is given by:

$$\Delta\tau_{\mu i} = K_iC_i^n \qquad i = 1 \ldots \nu. \qquad (15)$$

For SSH, the distributions can be characterized by three parameters: the concentration of solute atoms C_i, the strenghtening coefficient K_i, and the concentration exponent n, the latter being assumed the same for all solutes.

To find the hardening when different solutes are present simultaneously, a fictitious solute j with strengthening coefficient K_j, concentration exponent n and the following athermal strengthening equation is considered:

$$\Delta\tau_{\mu j} = K_j C_j^n. \tag{16}$$

The following equivalent concentrations of solute atoms j are defined:

$$C_{eqji} = \left(\frac{K_i}{K_j}\right)^{1/n} C_i \qquad i = 1 \ldots \nu. \tag{17}$$

From Equations 15 and 17 it follows that:

$$\Delta\tau_{\mu i} = K_i C_i^n = K_j C_{eqji}^n \quad i = 1 \ldots \nu. \tag{18}$$

This means that the athermal stress caused by C_i solute atoms i with strengthening coefficient K_i can be thought to be produced by C_{eqji} solute atoms j with strengthening coefficient K_j.

It is now assumed that the ν distributions produce the same strengthening effect as one statisitical distribution of solute atoms of type j with a concentration C_{eqj} equal to the sum of the equivalent concentrations C_{eqji}. The total hardening is then given by:

$$\Delta\tau_\mu = K_j\left(\sum_i C_{eqji}\right)^n. \tag{19}$$

The graphical interpretation of the model is shown in Fig. 1 for the case of a ternary solid solution ($v = 2$). Combining Equations 17, 18 and 19:

$$\Delta\tau_\mu = \left(\sum_i K_i^{1/n} C_i\right)^n \tag{20}$$

$$\Delta\tau_\mu = \left(\sum_i \Delta\tau_{\mu i}^{1/n}\right)^n. \tag{21}$$

It should be noted that the strengthening factor K_j does not appear in Equations 20 and 21. The final result is independent of the choice of the reference distribution. A similar equation can be derived for the thermal hardening. It is presented together with Equation 21 as Equation 22 in Table II.

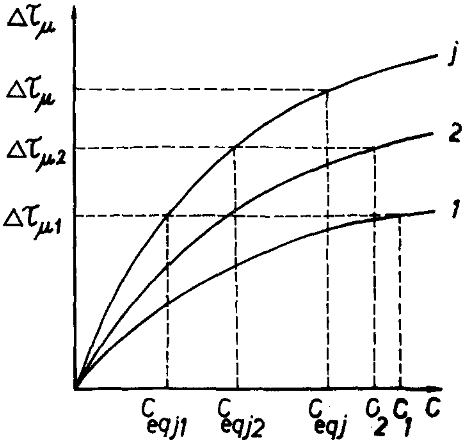

Figure 1 Athermal strengthening effect versus concentration for the proposed model for athermal ternary solid solution hardening when the solutes have a common concentration exponent and no interactions.

$$C_{eqj} = C_{eqj1} + C_{eqj2}$$

The athermal and thermal strengthening effects, given by Equations 21 and 22 respectively, are additive according to Equation 1. Consequently, the total SSH is given by Equation 23 (see Table II). Equations 21 and 22 are of the same mathematical form. If the hardening is only either thermal or athermal and given by Equation 2, the strengthening effect in a multi-component solution is given by:

$$\Delta\tau = \left[\sum_i \Delta\tau_i^{1/q}\right]^q. \tag{24}$$

For ternary SSH, Equation 24 becomes Equation 5 if $q = 1$, Equation 6 if $q = \frac{1}{2}$ and Equation 12 if $q = \frac{2}{3}$. Equations 5, 6 and 12 have also been derived by Mizia and Koss [9] for the special case where the strengthening coefficients are identical. Both types of solute atoms then behave identically:

$$\Delta\tau_1 = RC_1^q$$

$$\Delta\tau_2 = RC_2^q$$

and

$$\Delta\tau = R(C_1 + C_2)^q = [\Delta\tau_1^{1/q} + \Delta\tau_2^{1/q}]^q. \tag{25}$$

TABLE II Equations derived for multi-component solid solution hardening

Binary SSH	Multi-component SSH	
$\Delta\tau_{\mu i} = K_i C_i^n$	$\Delta\tau_\mu = \left(\sum_i \Delta\tau_{\mu i}^{1/n}\right)^n$	(21)
$\Delta\tau_i^* = P_i(T, \dot{\gamma}) C_i^m$	$\Delta\tau^* = \left(\sum_i \Delta\tau_i^{*1/m}\right)^m$	(22)
$\Delta\tau_i = K_i C_i^n + P_i(T, \dot{\gamma}) C_i^m$	$\Delta\tau = \left(\sum_i \Delta\tau_{\mu i}^{1/n}\right)^n + \left(\sum_i \Delta\tau_i^{*1/m}\right)^m$	(23)

3. Extension to different concentration exponents

Different concentration exponents (Equation 4) are in many cases a consequence of different types of solute–dislocation interactions. If one component causes a long-range, e.g. Snoek interaction, and the other component causes a short-range, e.g. Fleischer interaction, then the total ternary SSH is additive according to Equation 1 [10]. However, when the different components cause interactions of the same nature, as is assumed in the computer simulation model by Ono [4], the following treatment is proposed.

Again a statistical distribution j is taken as fictitious reference distribution:

$$\Delta\tau_j = R_j C_j^{q_j}. \tag{26}$$

The following equivalent concentrations of solute atoms j are defined:

$$C_{eqji} = \left(\frac{R_i}{R_j}\right)^{1/q_j} C_i^{q_i/q_j} \qquad i = 1 \ldots \nu. \tag{27}$$

From Equations 4 and 27 it follows that:

$$\Delta\tau_i = R_j C_{eqji}^{q_j} \qquad i = 1 \ldots \nu. \tag{28}$$

If it is assumed that the total strengthening is caused by $(C_{eqj1} + \ldots C_{eqj\nu})$ atoms j, it follows that:

$$\Delta\tau = R_j \left(\sum_i C_{eqji}\right)^{q_j}. \tag{29}$$

Combining Equations 4, 27 and 29:

$$\Delta\tau = \left[\sum_i R_i^{1/q_j} C_i^{q_i/q_j}\right]^{q_j} \tag{30}$$

$$\Delta\tau = \left[\sum_i \Delta\tau_i^{1/q_j}\right]^{q_j}. \tag{31}$$

Equation 31 shows that in the case of different concentration exponents, the equivalency principle does not lead to a univocal expression. Indeed, the total strengthening effect is not dependent on the strengthening coefficient R_j, but it does depend on the concentration exponent q_j of the reference distribution. It is therefore proposed to define q_j as a weighted average:

$$q_j = \frac{\sum\limits_i q_i \Delta\tau_i}{\sum\limits_i \Delta\tau_i}. \tag{32}$$

The set of h Equations 31 and 32 is in agreement with boundary conditions such as are discussed in Section 5. No boundary conditions have been found for which these relations do not hold.

In the more general case where the total binary SSH of the ν distributions is given by Equation 33, we propose that the total multi-component SSH is given by Equations 34 and 35:

$$\Delta\tau_i = K_i C_i^{n_i} + P_i(T, \dot{\gamma}) C_i^{m_i} \qquad i = 1 \ldots \nu \tag{33}$$

$$\Delta\tau = \left[\sum_i \Delta\tau_{\mu i}^{1/n_j}\right]^{n_j} + \left[\sum_i \Delta\tau_i^{*\,1/m_l}\right]^{m_l} \tag{34}$$

with

$$n_j = \frac{\sum\limits_i n_i \Delta\tau_{\mu i}}{\sum\limits_i \tau_{\mu i}}$$

and

$$m_1 = \frac{\sum\limits_i m_i \Delta\tau_i^*}{\sum\limits_i \Delta\tau_i^*}. \tag{35}$$

4. Interactions between solutes

In many solid solutions, the assumption of statistical distributions breaks down, mainly at low temperatures. For example, Sagues and Gibala [11], when studying O and N anelasticity in Ta–Re–N and Ta–Re–O alloys, identified single N atoms, ReN pairs, Re_2N triplets, single O atoms and Re_xO clusters, with $x = 1$ to 3.

Consider a solid solution with ν statistical distributions i. Suppose the elements v and w form pairs vw. C_i is the total atomic fraction of element i present in the alloy. C_i' is the concentration of single atoms i and C_{vw}' is the concentration of pairs vw. The athermal or thermal binary SSH is assumed to be given by Equation 2. The SSH due to C_i' solute atoms i will then be:

$$\Delta\tau_i' = R_i C_i'^{q} \qquad i = 1 \ldots v, w \ldots \nu. \tag{36}$$

The SSH due to the vw pairs is here assumed to be given by:

$$\Delta\tau_{vw}' = R_{vw} C_{vw}'^{q} \tag{37}$$

The following relations can be stated:

$$C_i' = C_i \qquad i = 1 \ldots \nu \tag{38}$$

except v and w

$$C_v' = C_v - C_{vw}' \tag{39}$$

$$C_w' = C_w - C_{vw}'. \tag{40}$$

According to Hasson and Arsenault [12], the concentration of vw pairs is related to the concentration of single atoms v and w by:

$$C'_{vw} = \frac{m_{vw}}{m_v m_w} C'_v C'_w \exp(\Delta G_{vw}/RT). \quad (41)$$

where m is the multiplicity of orientations of a component and ΔG_{vw} is the molar free energy of the binding of the vw pair. ΔG_{vw} can be determined by internal friction studies. For a given temperature Equation 41 is simplified to:

$$C'_{vw} = SC'_v C'_w \quad \text{and} \quad S \quad \text{constant.} \quad (42)$$

Equations 39, 40 and 42 form a set of three independent equations from which C'_v, C'_w and C'_{vw} can be calculated.

The total strengthening effect can now be thought to be due to $(\nu + 1)$ statistical distributions and according to Equation 24 is given by:

$$\Delta\tau = (\Delta\tau_1^{1/q} + \ldots \Delta\tau_v'^{1/q} + \Delta\tau_{vw}'^{1/q} + \Delta\tau_w'^{1/q} + \ldots \Delta\tau_\nu^{1/q})^q. \quad (43)$$

In the special case of a ternary alloy with $C'_{vw} \ll C_v$ and $C'_{vw} \ll C_w$, Equation 43 is reduced to:

$$\Delta\tau = (\alpha C_1 + \beta C_1 C_2 + \gamma C_2)^q. \quad (44)$$

with α, β and γ independent of C_1 and C_2.

Analogous equations can be derived for the cases where (1) the strengthening effects are both thermal and athermal, (2) more than one or more complex clusters are present, (3) the concentration exponents for the different elements and for the clusters are different.

5. Discussion

The agreement of the proposed model with previously reported calculations of the multi-component SSH (Table I) is considered first. The model is in contradiction with Equations 8 and 10 of Foreman and Mankin. However, their computer simulation model (1) is only valid for point obstacles [2], and (2) assumes a crossing mechanism which is only valid for a linear array of obstacles [13].

The model is also in contradiction with the multi-component SSH Equations 7, 11, 13 and 14. However, these equations can only be valid in special cases and break down in other conditions, e.g. ($\Delta\tau_i = R_i C_i^q$ is assumed).

Equation 7: if $q = \frac{1}{2}$ and $C_1 = C_2$ and $R_1 > 2.4\, R_2$, then $\Delta\tau < \Delta\tau_1$ (45)

Equation 11: if $C_1 = C_2$ and $R_2/R_1 \approx 0$, then, $\Delta\tau \approx \sqrt{2}\Delta\tau_1 > \Delta\tau_1$ (46)

Equation 13: if $q = \frac{2}{3}$ and $C_1 = C_2$ and $f_{01} = f_{02}$ and $w_1 > 7w_2$, then $\Delta\tau < \Delta\tau_1$ (47)

Equation 14: if $q = \frac{1}{2}$ and $f_{01} = Nf_{02}$ and $C_1 = C_2/N^2$ and $N > 3$, then $\Delta\tau < \Delta\tau_1$ (48)

On the other hand, the model is in agreement with the other equations of Table I, i.e. Equation 5 (only if $q = 1$), Equation 6 of Koppenaal and Kuhlmann-Wilsdorf [5], Equation 9 of Foreman and Makin [6], Equation 12 derived using the Labusch method [2], and also with Equation 25 of Mizia and Koss [9].

Equations describing the multi-component SSH when interactions between solutes occur, or when solutes have different concentration exponents, have not been found in the literature. The equations of Section 3, unlike those of Sections 2 and 4, have not been completely derived from the model, as an assumption had to be made concerning the concentration exponent of the reference distribution. However, no boundary conditions similar to those just discussed for Equations 7, 11, 13 and 14 have been found where these equations break down.

Equation 23 is a rather complex expression with $2(\nu + 1)$ parameters. However, this equation reduces to Equation 24 with only half the number of parameters when (1) $n = m = 1$, (2) $n = m$ and P_i/K_i constant, (3) $\Delta\tau_\mu \gg \Delta\tau^*$ or $\Delta\tau_\mu \ll \Delta\tau^*$.

From Equation 24 it can be concluded that for a mixture of distributions of solute atoms without interactions but with a common concentration exponent q, the total strengthening effect can be smaller than, equal to or greater than the sum of the separate strengthening effects.

$$\Delta\tau = \left[\sum_i \Delta\tau_i^{1/q}\right]^9 \lesseqgtr \quad \Delta\tau_i \quad \text{if} \quad \begin{matrix} q < 1 \\ q = 1 \\ q > 1 \end{matrix}$$

According to Equation 43, either a supplementary hardening or a softening can be caused by interactions between different solute atoms. Such interactions are responsible for extrinsic alloy softening in group VA metals [14]. Attempts to make quantitative calculations of this type of solid solution softening can be made by using the formulae of Section 4, whereas relations, describing intrinsic multi-component solid solution softening, will be given elsewhere [15].

The present model is in agreement with experimental results for Pb-, Cu-, V-, Nb- and Ta-base ternary alloys, as shown in Part 2 [16].

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