Multi-component solid solution hardening

Part 2 Agreement with experimental results

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The model for multi-component solid solution hardening proposed in Part 1, is compared with experimental results. The observed ternary solid solution hardening in some fcc Cu- and Pb-base alloys and some bccV-, Nb- and Ta-base alloys is shown to agree well with the predictions of the model.

1. Introduction

In part I [1], a formal treatment of multicomponent solid solution hardening has been presented which can be summarized as follows: if the binary athermal or thermal solid solution hardening (SSH) of ν dilute and random distributions of solute atoms *i* in a base metal is given by:

$$\Delta \tau_i = R_i C_i^q \qquad i = 1 \dots \nu, \qquad (1)$$

and if these ν distributions are present together in the base metal without interacting with each other, then the total SSH is given by:

$$\Delta \tau = \left[\sum_{i} \Delta \tau_{i}^{1/q} \right]^{q}.$$
 (2)

This relation has been shown to be also valid under certain conditions [1] in the case where the solute atoms influence both the thermal and athermal components of the flow stress.

The agreement of this model with experimental results on ternary SSH in both fcc and bcc alloys is now discussed.

2. Fcc solid solutions

Systematic research on SSH of binary and ternary Pb-In-Tl alloys has been performed in our laboratory and partly published [2-7]. Lead-base single crystals with 0 to 20 at.% In and/or 0 to 50 at.% Tl have been tested in tension at 78 K. Details of the experimental procedure are given by Van der planken and Deruyttere [2]. The nominal composition, which did not differ systematically from the chemical analysis, and the critical resolved shear stress (CRSS) τ_0 of 49 samples with 20

different compositions are given in Table I.

The CRSS of the Pb–In alloys increases linearly with increasing indium content, except for the highest concentration [2]. If the CRSS of the binary Pb–Tl alloys is plotted against the square root of the thallium concentration, a linear relationship is obtained except for the low concentrations where anomalies are observed [2]. For both binary systems a good fit [4] covering the whole range can be obtained using the $C^{2/3}$ dependency proposed by Labusch *et al.* [8].

To find an analytical expression for the ternary

TABLE I CRSS of Pb-In-Tl alloys at 78 K [3, 4]

In	Tl	τ_0	Number of specimens		
(at.%)	(at.%)	(g mm ⁻²)			
0.2	_	59.7	4		
0.4		68.8	4		
0.8	-	78.8	6		
5.0		209	3		
10.0	-	372	4		
20.0	-	575	4		
_	2.0	53.4	3		
_	6.0	86.2	2		
_	15	183	2		
_	30	231	2		
-	50	304	2		
1.0	1.0	103	3		
2.0	4.0	157	2		
5.0	1.0	208	1		
5.0	5.0	243	1		
9.0	2.0	371	1		
5.0	10.0	304	1		
10.0	5.0	383	2		
8.0	17	401	1		
12	23	479	1		

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SSH, Van der planken and Linnekens [4, 6] made two different approximations in which the difference between observed and calculated CRSS was important. Therefore, the fitting of the experimental results to the present model [1] is now examined.

According to data of Weinberg [9], the athermal strengthening effect at 78 K due to small alloying additions, such as 1% Sn, to Pb is small compared with the thermal hardening. The same conclusion can be drawn from the data of Van der planken et al. [7] for highly concentrated alloys such as Pb-40% Tl and Pb-60% Tl. Therefore, it is believed that in the whole concentration range investigated, the major part of the hardening is thermal. This assumption justifies the use of Equations 1 and 2, as discussed in Part 1 [1], to fit the data of Table I. Adapted to the present case, they become:

 $\Delta \tau_{01} = R_1 C_{\text{In}}^q$

and

$$\Delta \tau_{02} = R_2 C_{\rm Tl}^q$$

$$\tau_0 = \tau_{00} + (\alpha C_{\rm In} + \beta C_{\rm TI})^q \qquad (4)$$

(3)

$$R_1 = \alpha^q \text{ and } R_2 = \beta^q \tag{5}$$

where τ_{00} is the CRSS of pure lead, τ_0 and τ_{00} are in gmm^{-2} , C in atomic fractions.

The parameters α , β , q and τ_{00} of Equation 4 have been computed using the non-lineair regression program BMDP3R [10]. The smallest residual sum of squares

$$\left(\text{RSS} = \sum_{l=1}^{49} \left(\tau_{0 \text{ obs}_{1}} - \tau_{0 \text{ calc}_{1}}\right)^{2}\right) \text{was obtained}$$

with the parameter values q = 0.730, $\alpha = 2.81 \times$ 10^4 , $\beta = 4.64 \times 10^3$ and $\tau_{00} = 33.1$. The same programme has been used to estimate the values of α , β and τ_{00} with the equality constraints $q = \frac{2}{3}$ (e.g. Labusch [8]), $q = \frac{1}{2}$ (e.g. Fleischer [11]) and q = 1 (e.g. Mott and Nabarro [12]). The results of these computations are summarized in Table II. A scatter plot of the experimental and calculated values of τ_0 for the four different values of q is given in Fig. 1a to d.

Weinberg [9] found that the treatment prior to testing of pure Pb crystals, which are extremely ductile, has a great influence on the CRSS. He found three different values depending on the treatment of the lead single crystals between growth and testing. This factor and the influence of impurities may explain why τ_{00} calculated $(33.1 \,\mathrm{gmm^{-2}})$ is lower than the τ_{00} observed in centration in the binary systems Nb-O [16],

TABLE II Computation results for Pb-In-Tl alloys at 78 K

q	τ_{00}	$R_1 = \alpha^q$	$R_2 = \beta^q$	RSS
0.730	33.1	1760	474	17600
2 3	20.9	1600	470	18700
$\frac{1}{2}$	-26.6	1280	480	33200
1	68.6	2690	514	34700

our laboratory $(50^{+17}_{-6} \text{ g mm}^{-2})$.

Fig. 1a shows that the proposed model agrees well with the experimental results for Pb-In-Tl binary and ternary alloys.

The multi-component Labusch equation [13, 14]

$$\Delta \tau = (\Delta \tau_1^{2/3} + \Delta \tau_2^{2/3})^{3/2} \tag{6}$$

also gives a good fit, as may be seen from Fig. 1b. However, the difference between the observed and calculated CRSS of pure lead is much greater, and the value of the residual sum of squares is 6% higher than in the case that q = 0.73. It may be noted that the numerical values of both exponents are close to each other. The residual sum of squares is much greater for $q = \frac{1}{2}$ and q = 1, and systematic deviations from a straight line occur in Fig. 1c and d. Moreover, when $q = \frac{1}{2}$ is used, an unrealistic negative value of τ_{00} is obtained.

The $C^{2/3}$ dependence of the strengthening effect in the binary Pb-In and Pb-Tl alloys at 78 K is in agreement with a recent SSH theory, proposed by Labusch et al. [8] for fcc and hcp substitutional alloys.

Ternary SSH in Cu-Si-Ge in the plateau range [14] is also in agreement with Equation 6 and with the present model. The concentration dependence of the binary Cu-Si and Cu-Ge alloys $(q = \frac{2}{3})$ is again in agreement with the theory of Labusch et al. [8].

3. Bcc alloys

The model is also in agreement with experimental results on V-, Nb- and Ta-base ternary alloys. Both substitutional and interstitial athermal SSH are generally found to be linear in these VA alloys [15]. The influence of the alloying elements on the thermal component is more complex. Both alloy hardening and softening are possible and impurities, even when present in small quantities, can markedly change the hardening behaviour [16].

The athermal SSH increases linearly with con-



Figure 1 Comparison between observed and calculated critical resolved shear stress of Pb-In-Tl alloys at 78 K for (a) q = 0.730, (b) $q = \frac{1}{2}$, (c) $q = \frac{1}{2}$, and (d) q = 1.

Nb-Mo [17] and Nb-W [18]. Thus, the ternary SSH for dilute Nb-O-W and Nb-W-Mo alloys is expected to be the sum of the binary SSH if no interactions between the solutes occur. This is in agreement with experiments of Gibala *et al.* [16] for the system Nb-O-W and Mizia and Koss [19] for the system Nb-Mo-W.

At 77 K, the yield stress of niobium is still strongly temperature dependent. However, the SSH of 1.7 at. % Re is additive to the linear SSH of Mo in Nb, if these alloys are purified by ultra-high vacuum degassing at elevated temperatures [16], in agreement with the predictions of the present model. Some solid solution softening in these ternary alloys at low Mo concentrations has to be taken into account as a result of the interaction between Mo and Re atoms.

The observed additivity [20] of the strengthening effects caused by interstitially dissolved O and N in the VA metals (V, Nb and Ta) at room temperature and for those concentration ranges in which the binary SSH increases linearly with concentration, also confirms the predictions of the present model.

A nearly linear thermal SSH is observed in high purity and ultra-high vacuum degassed niobium solid solutions [16]. Stephens and Witzke [21], investigating binary and ternary SSH at 77 and



Figure 2 Comparison between observed and calculated VHN for Nb-Hf-Mo solid solutions at (a) 77 K and (b) 300 K.

300 K in less pure niobium and in an extended concentration range, proposed a concentration exponent of $\frac{1}{2}$ to fit their binary hardness data. However, the hardness data for the ternary Nb-Hf-Mo alloys were correlated in a different way, i.e. by means of a linear relationship between the observed hardness value and the sum of the Mo and Hf concentrations present in these alloys. When the data of pure Nb and those of the binary alloys are plotted on this figure, significant scatter appears. A much better fit is obtained by means of Equations 1 and 2. The optimized parameter values q, HV_0 , R_1 and R_2 , obtained by a nonlinear regression technique, analogous to that described for the Pb-In-Tl alloys, are given in Table III. Scatter plots of observed versus calculated hardness values are given in Fig. 2a (77 K) and b (300 K). The difference between observed and calculated hardness value is less than 13% for all the binary and ternary Nb-Hf-Mo alloys, at both temperatures.

TABLE III Computation results for Nb-Hf-Mo alloys

HV _o	$R_1 = \alpha^q$	$R_2 = \beta^q$	T(K)
153	382	546	77
59.3	405	528	300
	<i>HV</i> _o 153 59.3	$ \begin{array}{ccc} HV_{0} & R_{1} = \alpha^{q} \\ 153 & 382 \\ 59.3 & 405 \end{array} $	$\begin{array}{c ccc} HV_0 & R_1 = \alpha^{q} & R_2 = \beta^{q} \\ \hline 153 & 382 & 546 \\ 59.3 & 405 & 528 \end{array}$

4. Conclusion

It can be concluded that the previously reported model [1] for multi-component solid solution hardening agrees well with experimental results concerning substitutional and interstitial ternary

solid solution hardening in some fcc and bcc alloys, both in the plateau region and at lower temperatures.

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