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SOLUTE DEPENDENCE OF COLD WORK STRENGTHENING IN ALUMINUM ALLOYS

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Abstract

Work hardening behavior of aluminum alloys at room temperature is analyzed using previously reported data. The samples include solution treated alloys which show GP zone strengthening, alloys which are fully solutionized and some O-temper commercial alloys. The strengthening increment due to coherent second phases appears to be independent of strain. Using the solutionized data, model parameters from the Ludwig strain hardening model are fit to a model for solute dependence, which is an extension of a standard expression to multiple solutes and work hardening parameter. The solute exponent for the undeformed strength is 2/3 for binary alloys. In strengthening effect, the four solutes studied rank on a wt% basis as Cu≈Mg≈Mn>Si for the undeformed strength and Si>Cu>Mg>Mn for the work hardening K. In addition to elemental effects, magnesium and silicon were found to have a positive, synergistic effect on strength. No other pairwise interaction was found to be consistently significant. The final model provides yield strength as a function of prior rolling strain and the solute levels of copper, magnesium, manganese and silicon. The strengths predicted by the final model are considerably smaller than those found for non-heat treatable, commercial alloys, the difference being apparently due to incoherent, second phase particles. The effect of these particles on work hardening is obtained by subtracting the predicted solute effect from the observed response for a selected group of commercial alloys. This second phase strength component is also analyzed with a Ludwig expression, and the strain exponent is considerably lower in general than that due to solute.

Introduction

The objective of this work is an equation or set of equations that predict the contribution of solute to strength in strain hardened aluminum alloys. This is of potential use in the design of new alloys, as well as control of manufacturing consistency for current alloys. The focus is on the alloying elements Cu, Mg, Mn and Si, which are known to contribute as solute to the strength of commercial alloys. The strength measured and predicted is the yield strength in a tension test, as a function of prior rolling strain and the solute content. However, in order for such a model of solute contribution to be useful, some means must be derived by which these effects can be combined with other sources of strength, such as dispersoids and coherent precipitates.

The strengthening effect of solute on the initial (O-temper) yield strength of metal alloys is well recognized and the individual strengthening effects are at least partially understood.[1] Dorn, et al.[2] showed, for a range of binary aluminum alloys, that solute increased the strain hardening response essentially in proportion to the effect on the initial yield stress. Within Alcoa there has been a great deal of investigation of the effect of alloy additions on strain

hardening, giving a rich background of information.[3,4,5,6,7] Some of this information is used in this report.

Experimental Data

In order to obtain the strain and solute dependence of work hardening at room temperature for aluminum alloys, data was used from previous Alcoa reports.[3,4,7] In all cases, the datum considered is the tensile yield strength at .002 offset for different rolling strains. With a few exceptions, all of the samples were treated and rolled at laboratory scale. Generally, such laboratory rolling involves a number of relatively small reductions of thin material, resulting in reasonably homogeneous reduction and negligible temperature increase.

The analysis was restricted to samples containing solute elements from the group Cu, Mg, Mn and Si. Samples were classified into three groups, depending on whether solute was the only source of strength (Group S), or whether coherent (Group Z) or incoherent second phases (Group A) were present as well. Samples containing both types of precipitate were not included. Summary information on these groups is given in Table I. In some cases, the choice between groups S and Z was a matter of judgement, based on the alloy levels and the undeformed yield strength. In other cases, the strength after low temperature anneal, i.e. 400 $^{\circ}$F for 20 minutes, was used to detect the presence of age hardening. Substantially reduced yield strengths after annealing were found for a number of undeformed samples. These "reverted" strengths were used as estimates for the undeformed yield strength in the absence of aging, and samples so found are given the additional designation S*, so that they belong to both of groups Z and S*.

Table I. Alloy grouping summary. Note that group S* is a subset of group Z.

Group	N_{alloys}	N_{data}
Solute Only (S)	32	182
Solute + Coherent 2nd Phase (Z)	11	48
Solute + Coherent 2nd Phase, adjustable (S*)	4	16
Solute + Incoherent 2nd Phase (A)	37	237

Strain Dependence of Strength

The strain dependence of cold work hardening in aluminum alloys has been modelled in a number of ways. Five different expressions were fit to the three data groupings described above. These were the Holloman, Ludwig, a Pythagorean variant of Ludwig, Swift and Voce expressions. The clear result of fitting alloys locally or globally with common parameters was that the Voce expression fit the worst, but otherwise there were no striking differences in the fitting ability of the different expressions. The form used here is the Ludwig equation:

$$\sigma = \sigma_a + K \cdot \varepsilon^n \tag{1}$$

where σ_a is the strength in the absence of work hardening or at O-temper for annealed samples. This formulation was chosen for it's simple separation of the work hardening from the undeformed strength.

Expressions for Solute Dependence of Strength

Haasen[1] reports that the solute dependence of the O-temper strength in binary alloys is:

$$\sigma_a = \sigma_{a0} + p \cdot C^m \tag{2}$$

where C is the composition of the alloying element in arbitrary units and p is a constant for that element. Theoretically, the m parameter is given by Haasen[1] to be either 1/2 or 2/3. The former value, m=1/2 is referred to as the Fleischer-Friedel case and applies when obstacles to dislocation movement are dilute, so that interactions are highly localized. The latter case, m=2/3 is referred to as the Mott-Labusch case and pertains when obstacles are concentrated, so that dislocations interact with a diffuse network of obstacles. Empirically, Haasen[1] reports values of m=2/3 or 3/4 for binary FCC alloys in general.

For the case of multiple solutes, the equation used here is:

$$\sigma_a = \sigma_{a0} + \left\{ \sum_{i=1}^{M} \left[p_i^{1/m} \cdot C_i + \sum_{j=1}^{i-1} \left(p_{ij}^{1/m} \cdot C_i \cdot C_j \right) \right] \right\}^m \tag{3}$$

The limiting case of this form for no interactions, i.e. all $p_{ij} = 0$, can be deduced by an extension of the "Mott statistics" theory for the value m=2/3. Derivations such as presented, for example, by Labusch[8] or Kocks, et al.[9] can be readily extended to multiple species of solutes by supposing that the internal stress fields associated with each species differ in magnitude but have the same range. The interaction terms, p_{ij} are included to test for possible synergism between solutes. Doherty and McBride[10] have reported the synergistic effects of certain combinations of solutes, such that the strength obtained is greater than the sum of the independent contributions of each solute element. Such synergism would correspond microphysically to a structural correlation between solute atoms, but not to the extent that they constitute a coherent precipitate or GP zone.

The physical phenomena underlying the Ludwig K term are different from those underlying the Ludwig σ_a. Whereas σ_a is the stress needed to free a dislocation from a "cloud" of solute, $K\epsilon^n$ is proportional to the linear density of a "forest" of dislocations left by prior deformation. The role of the solute is to retard the recovery process by which dislocations in this "forest" mutually annihilate. Neither the Labusch theory nor the data reviewed by Haasen give any guidance as to how Ludwig K should depend on solute content. Lacking an alternative description, the solute dependence assumed for K is the same as that used for σ_a in Equation 3:

$$K = K_0 + \left\{ \sum_{i=1}^{M} \left[k_i^{1/m} \cdot C_i + \sum_{j=1}^{i-1} \left(k_{ij}^{1/m} \cdot C_i \cdot C_j \right) \right] \right\}^m \tag{4}$$

If it were further supposed that solute inhibited movement in the field of other dislocations in the same way solute inhibits motion in an external stress field, then the exponent m would be equal for Equations 3 and 4 and values for k_i would be proportional to values for p_i. This possibility will be tested by fitting the postulated expressions to the present data.

Experimental Results for Solute Dependence of Strength

In considering the compositional dependencies of the Ludwig parameters, the strain hardening exponent, n is fixed at a global value of .33, since multiple regressions yielded no consistent compositional dependencies. Using this global n value, the compositional dependencies for Ludwig K and σ_a were first tested for the binary alloys. Examples are given in Figures 1 and 2, where the Ludwig K and σ_a values are plotted against solute content for Al-

Mg and Al-Cu binaries respectively. Also given are regression results for the composition exponent, m in Equation 2. There appears to be a significant difference in the m exponent between σ_a and K. Interestingly, the m values for σ_a are within error of the Mott-Labusch value of 2/3 and are consistent with the general results for FCC alloys as reviewed by Haasen.[1] The m values for K are barely within error of 1, but it is not clear whether m = 1 has any special physical significance.
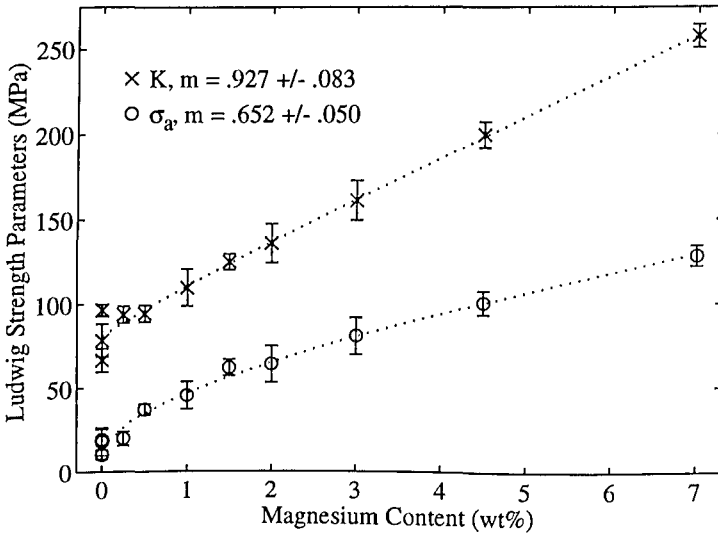

Figure 1. Effect of magnesium content on Ludwig K and σ_a parameters (obtained for global n=.33) for Al-Mg binary alloys. Also included are regression results for optimal solute content exponent, m in Equation 2 (standard errors are approximate).

In Figure 2, there is a discontinuous step in the response of σ_a to copper content at ~2 wt% Cu. This is almost certainly the effect of natural aging in two of the higher copper alloys. The adjusted values of σ_a are obtained for the 2 and 4 wt% Cu points by applying the difference between the reverted yield strength and the age hardened yield strength to the Ludwig σ_a values. These adjusted values appear to fit on the same curve as the lower copper, non-age hardened binary alloys. In addition, there is little to no step discernable in the plot of Ludwig K against copper content. This suggests that natural aging affects only the undeformed yield strength and not the work hardening rate. Support for this comes from global regressions on the three data groupings, where Ludwig n values were similar for groups Z and S, those with and without the effects of natural aging. Further support that aging affects the undeformed strength and not the subsequent hardening can be obtained from tests done by Waller and Anderson,[3] as well as by Doherty,[7] on alloy 2024 in the W and T4 conditions. The W condition involves no intentional aging, while the T4 condition is the stable, naturally aged condition and should result in larger yield strengths. The strain responses in both of these

reports appear to be a fixed distance apart, consistent with the supposition that aging from W to T4 condition affects the undeformed strength, but not the subsequent strain hardening.
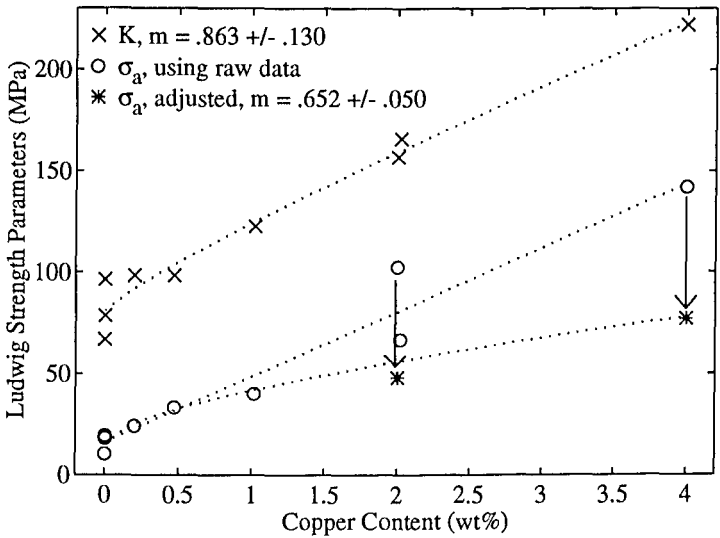

Figure 2. Effect of copper content on Ludwig K and σ_a parameters for Al-Cu binary alloys. Two values of σ_a are adjusted based on remeasurement of the undeformed yield strength.

Best Global Model for Cold Work and Solute Strengthening

In order to predict the effect of solute on strength for real alloys, a best fit model was obtained for the effect of solute content on Ludwig parameters K and σ_a, using Equations 3 and 4, for alloy grouping S+S*. The strength data for the S* alloys were first adjusted by the difference between the age hardened strength and the reverted yield strength. This adjustment is justified by the results shown above in Figure 2.

In obtaining the best fit model, Ludwig n was again taken to be .33. Based on stepwise multiple regressions, a single value of m=3/4 was chosen for the concentration exponent, instead of maintaining different values for K and σ_a. This value is considerably different from those obtained earlier for Al-Mg and Al-Cu binary alloys, i.e. ~2/3 for Ludwig σ_a and ~.9 for Ludwig K. The results shown in Figures 1 and 2 for magnesium and copper binaries were confirmed by joint analysis of all the binary alloys together, without interaction terms. It must be concluded that the way interactions are included in Equations 3 and 4 is "wrong" because it overwhelms the otherwise well established concentration exponent for binary alloys. However, no theoretical alternative suggests itself, and the total current data are fit well by the one concentration exponent, m=3/4. Of the interaction terms, only Mg·Si was consistently significant in stepwise regressions on Ludwig σ_a and K values.

The final model parameters, obtained by regressing on the strength data directly, are given in Table II. For Ludwig K, i.e. the solute enhanced hardening, silicon has the largest impact and manganese the weakest, on a wt% basis. Upon conversion to an atomic basis, copper has by far the strongest effect and magnesium the weakest. For Ludwig σ_a, copper has the strongest effect and silicon the weakest, on either a wt% or atomic fraction basis. Most remarkable of these systematics is that silicon is so strong a contributor to K while so negligible a contributor to σ_a. This argues strongly against basing a microphysical theory for K on the same solute-dislocation interaction potentials as postulated in the Labusch theory of σ_a.

Table II. Results for Ludwig K and σ_a dependence on solute content, obtained from regression on strength data in group S+S* directly, using n=.33, m=3/4 and considering only the Mg·Si interaction. Value given as 0 reflects constraint that coefficients be positive. The RMS error for the fit is 14.2 MPa and the adjusted R^2 value is .9799.

Result	σ_a (MPa)		K (MPa)	
σ_{a0} or K_0	18.8 +/- 3.2		75.3 +/- 3.8	
	(wt %)	(Atomic %)	(wt %)	(Atomic %)
p_{Cu} or k_{Cu}	22.2 +/- 3.4	52.4 +/- 8.1	50.9 +/- 3.7	120.0 +/- 8.8
p_{Mg} or k_{Mg}	26.6 +/- 2.2	24.0 +/- 3.1	40.4 +/- 2.5	36.4 +/- 2.2
p_{Mn} or k_{Mn}	29.4 +/- 8.1	59.9 +/- 16.5	16.3 +/- 9.9	33.1 +/- 20.2
p_{Si} or k_{Si}	0.00	0.00	62.4 +/- 4.3	65.0 +/- 4.4
$p_{Mg·Si}$ or $k_{Mg·Si}$	137.7 +/- 9.4	129.1 +/- 8.8	120.0 +/- 11.6	112.6 +/- 10.9

Table II shows an overall RMS error of 14.2 MPa, but there are 11 replications in composition-strain space over the S+S* grouping, comprising 24 data points. From an analysis of variance, the RMS replication, or pure error is calculated as ~8.1 MPa, while the RMS fitting error is ~14.6 MPa. The F statistic is 3.2, for degrees of freedom equal to 174 and 13. This is significant at 99% confidence, indicating that the error in fitting is large compared to the error in replication. A similar analysis of variance for local fitting of the Ludwig expression to individual alloys in group S results in an analogous F statistic of 1.2 for degrees of freedom equal to 73 and 13, which is not significant. Thus, for the global model, the excess of misfit beyond replication error is primarily due to the assumption of common values for solute exponent m and strain exponent n, and is not due to the adequacy of the Ludwig expression for strain dependence.

The Effect of Incoherent Second Phase Particles on Cold Work Strengthening

The effect of incoherent second phases on work hardening can be estimated by comparison between groups A and S. It was found in the global Ludwig n regressions that the presence of incoherent second phases lowers the Ludwig n value, i.e. the work hardening curve is flattened. This determination can be sharpened by estimating the solute content of a commercial alloy for which there is cold work data. The solute portion of work hardening can be calculated using Equation 1 for hardening, with n=.33, and Equations 3 and 4 for parameters K and σ_a, with m=3/4 and the coefficient values given in Table II. The solute component of hardening response can then be subtracted from the alloy response, leaving the second phase component of hardening, assuming that the two components are additive. It might be hypothesized that these components should add as their squares, analogous to the Pythagorean Ludwig expression referred to earlier. This was the explicit conclusion of Nembach and Martin[11] for the system of coherent cobalt precipitates and solute gold in a copper matrix. In

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the present situation, the numbers argue against this. The solute portion of H19 3004 can be estimated as ~230 MPa and the total H19 strength is known to be ~310 MPa. This linear difference of ~80 MPa is consistent with that found in direct experiments by Stumpf.[12] Taking the second phase strengthening to add with the solute portion according to their squares would require the second phase portion to be ~210 MPa, which seems unlikely.

The result of assuming that solute and second phase portions of strengthening are additive is given in Figure 3 for experimental data from Waller and Anderson[3] for alloy 3004. The response of second phase hardening shown in Figure 3 is well behaved and is quite well fit by a Ludwig hardening expression. The Ludwig n value for the second phase hardening component is .183, for an alloy n of .275 and a solute component n of .33. Many of the second phase component n values calculated for 3xxx and 5xxx type alloys are in the neighborhood of .15 for alloy n values around .28. As for the second phase morphology, it is likely that both dispersoids and constituent particles affect this strengthening component. It can be said that the second phase σ_a strength component is more sensitive to dispersoids than constituent particles (since calculated σ_a values were close to zero for alloys with no dispersoids), while the second phase K strength component is sensitive to both dispersoids and particles. More definitive description of second phase strengthening would require analysis of a more suitable data set, including second phase characterization. The present data set gives only a rough idea of how second phase strengthening depends on strain and how it combines with solute strengthening.
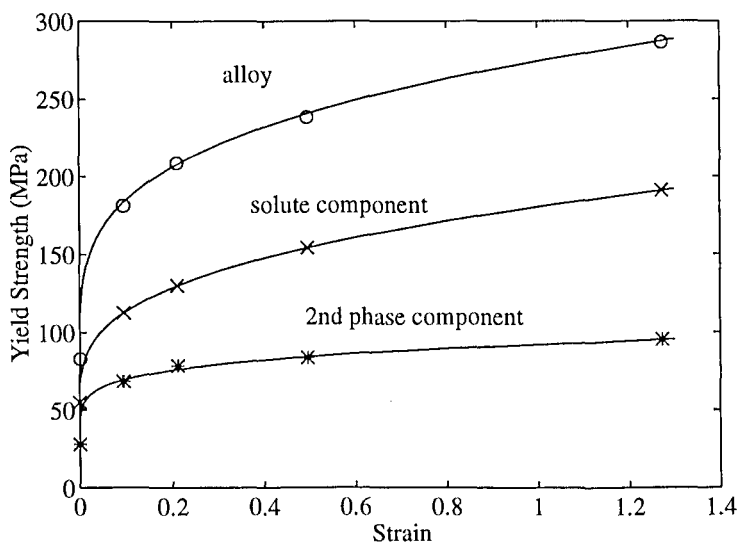

Figure 3. Subtraction of modelled solute strengthening from observed[3] 3004 alloy work hardening response. Solute dependence parameters are taken from Table II.

Summary

The principal results of strain and solute dependence analysis for the cold work hardening of aluminum alloys, in terms of yield strength versus prior rolling strain are as follows:

Fitting of Ludwig parameters K and σ_a, for global Ludwig n=.33, to solute content for binary alloys showed σ_a increasing with solute to the exponent ~.66 and K increasing with solute to the exponent ~.9. Fitting over all alloys and including interaction terms resulted in a global exponent of ~.75.

Fitting of Ludwig parameters K and σ_a, for global Ludwig n=.33, over all alloys resulted in the relative solute strengthening on a weight percent basis as Cu≈Mg≈Mn>Si for Ludwig σ_a and Si>Cu>Mg>Mn for Ludwig K. Similar rankings on an atomic percent basis were Mn>Cu>Mg>Si for Ludwig σ_a and Cu>Si>Mg≈Mn for Ludwig K.

The Mg·Si interaction term consistently passed significance tests for both Ludwig K and σ_a. This term is positive in both cases, suggesting that magnesium and silicon act together to provide greater strength than the sum of their respective binary effects.

The modelled effect of solute on work hardening was subtracted out from 3004 alloy response, in order to obtain an estimate of the portion of work hardening due to second phases. The resulting strength-strain curve is well fit by the Ludwig equation and the best fitting n value, .183 is substantially smaller than the Ludwig n value fitting the solute hardening portion.

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