THE EFFECT OF ALLOY CHEMISTRY ON THE STRENGTH AND RECOVERY CHARACTERISTICS OF Al-Mn-Mg-Cu ALLOYS.

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Abstract

Al-Mn-Mg-Cu based alloys are widely used for packaging materials in particular for beverage containers. The alloys are used in the "H19" or "H19 + stabilized" condition and gain the majority of their strength from work hardening during cold rolling. Softening of the alloys occurs during elevated temperature operations such as the curing of lacquers. The final strength of the material is a combination of these two processes and strongly influences the product performance. In this work the influence of manganese, magnesium and copper additions on the work hardening characteristics of the alloys was evaluated using the Holloman expression ($\sigma_2 = k\epsilon^n$). The value of 'n' was found to be relatively independent of alloy chemistry within the ranges studied. The value of 'k' varied with alloying additions in a systematic manner. The effect of each alloying element has been compared with published data and conclusions drawn. The recovery characteristics of material in the "H19" temper were determined as a function of alloy chemistry in the temperature range 175°C to 275°C. It will be shown that recovery follows a logarithmic process and that, on a normalized basis, it is comparatively independent of alloy chemistry.

Introduction

Quaternary Al-Mn-Mg-Cu are widely used throughout the world as the base alloy for beverage containers; the alloy is usually within the 3104 specification. The alloys are used in the "H19" or "H19 + stabilized" conditions and gain the majority of their strength from dislocation sub-structures built-up during cold rolling. Softening of the alloys occurs by recovery during elevated temperature operations such as curing of lacquers which take place after can making. The final strength of the can body is a combination of these two processes and thus strongly influences the product performance for example dome reversal pressure. In this work the influence of manganese, magnesium and copper additions on the work hardening characteristics of this alloy system was evaluated by application of the Holloman expression ($\sigma_2 = k\epsilon^n$). The recovery characteristics of material in the H19 temper was also determined as a function of alloy chemistry in the temperature range 175°C to 275°C and modelled as if a single recovery process (cross-slip) was occurring.

Experimental details

Table 1 details the alloy chemistries evaluated in the programme. The alloy's compositions were designed to examine a number of factors:-

Influence of Magnesium	Ingots 37, 38, 39 and 40
Influence of Copper	Ingots 37, 38, 41, and 42
Influence of Manganese	Ingots 37, 38, 43 and 36
Influence of Fe/Si	Ingots 44, 45, 46 and 51

In this paper the results of ingots 44, 45 ,46, and 51 are included with regard to their applicability in analysing the effect of Mg, Cu and Mn content.

10 kg ingots were cast into water cooled steel moulds which reproduces the solidification rate found in D.C. cast commercial ingots. The ingots were homogenized at 610°C for 8 hours and cooled to 500°C (2 hour hold) followed by hot rolling to 2.5 mm on a laboratory rolling mill. The hot rolled material was recrystallized at 400°C for 1 hour and then cold rolled to final gauge (0.250 mm) without interanneals. Samples were taken at intermediate gauges for evaluation.

Samples of the sheet at final gauge were recovered in a oil bath at temperatures between 175°C to 250°C. Tensile tests in duplicate were carried out on the as-rolled and recovered material.

Results and discussion
Work Hardening

Table 2 details some of the tensile properties (σ_2) obtained on as-rolled sheet. Table 2 also shows the computer calculated values for 'n' and 'k' in the Holloman equation ($\sigma_2 = k\epsilon^n$) where 'ϵ' is the logarithmic strain in cold rolling taken from the experimental data. Two calculations were carried out. Firstly 'n' and 'k' were allowed to vary independently and in the second case the value of 'n' was arbitrarily fixed at 0.225. Figures 1a-c show these 'n' and 'k' values plotted against the alloy's magnesium, manganese and copper content respectively. The data is shown for alloys in which the other chemical compositions were approximately constant (see above). In all cases the value of 'n' appears independent of alloy chemistry whereas the value of 'k' increases linearly with the atomic fraction of the alloy element to the power 2/3. The slopes for the three major alloying additions can be calculated with the following results:-

$$k_{Mg} = 158 + 1729 * (Mg)^{2/3}$$
$$k_{Mn} = 178 + 2579 * (Mn)^{2/3}$$
$$k_{Cu} = 229 + 2704 * (Cu)^{2/3}$$

"(Mg)" etc refers to the atomic fraction of the alloying element ie. (at%/100).

There has been some literature on the influence of alloy chemistry on the values of 'n' and 'k' (eg. 1,2). The recent analysis of Doherty et al.(3) confirmed the work of Stumpf at Alcoa that the value of 'k' is a function of the atomic fraction of the addition element to the power 2/3 multiplied by a parameter H. The values of H were determined for a number of binary systems (for magnesium $H_{Mg} = 1470 \pm 150$; for copper $H_{Cu} = 3600 \pm 150$ and for manganese $H_{Mn} = 1060 \pm 80$). The values of the slope in the preceding equations can be compared to the values of H from the binary systems. The result for magnesium and copper are in reasonable agreement considering the comparison is

between a binary and a quaternary alloy. However, the experimental value for manganese in this work is two and a half times greater than expected.

Doherty et al.(3) also examined a number of ternary and complex alloy systems and indicated that in some systems the strengthening contributions from the various elements could be added linearly. Both Al-Mg-Mn and Al-Mn-Cu were identified as systems showing no synergistic effects. Therefore it was decided to linearly add the various contributions to 'k' using the actual alloy chemistries and the values of H noted above. A simple additive equation was used (equation 1) and a more complex expression from Doherty et al (3) (equation 2) which is the more correct mathematical expression:-

Equation 1.
$$k = 90 + 3600*(Cu)^{2/3} + 1470*(Mg)^{2/3} + 1060*(Mn)^{2/3}$$

Equation 2.
$$\begin{aligned}
k = 90 + 1/6*\{&3600*(Cu)^{2/3} + 1470*(Mg)^{2/3} + 1060*(Mn)^{2/3}\\
+ &3600*[(Cu+Mg)^{2/3} + Cu + Mn)^{2/3}-(Mg)^{2/3}-(Mn)^{2/3}]\\
+ &1470*[(Cu+Mg)^{2/3} + (Mg+Mn)^{2/3}-(Cu)^{2/3}-(Mn)^{2/3}]\\
+ &1060*[(Cu+Mn)^{2/3} + (Mg+Mn)^{2/3}-(Mg)^{2/3}-(Cu)^{2/3}]\\
+ &2*3600[Cu+Mg+Mn)^{2/3}-(Mg+Mn)^{2/3}] + 2*1470[Cu+Mg+Mn)^{2/3}\\
&(Cu+Mn)^{2/3}] + 2*1060[Cu+Mg+Mn)^{2/3} - (Mg+Cu)^{2/3}]\}
\end{aligned}$$

90 being the value of 'k' for pure aluminium.

Figure 2a compares the calculated values of 'k' with those experimentally determined using $n = 0.225$. There is an approximately linear fit for both calculated values of 'k' with equation 1 (a 'r' value of 0.76) giving calculated values closer to the measured values when compared with equation 2 (r value of 0.80). The results show a significant deviation from that expected if there were no synergistic effects. The intercept of the line does not pass through zero but more significantly the slope of the line is 0.66 not 1 as would be predicted. A synergism parameter (S) defined as:

$$S = (K_{meas} - K_{calc}) / (K_{calc} - K_{Al})$$

gave values of 0.36 ± 0.05. Figure 2b plots this parameter S as a function of manganese content. The curve suggests that Mn is the main contributor to this synergism effect as might be expected from the measured value of H (see above). However this conclusion can only be tentative since most of the data points are clustered at a Mn content of ~0.95%.

One of the main sources of error in the analysis will be that in the experimental alloys the Mn will be principally in the form of small (~200 nm) dispersoids of Al_6Mn and not in solid solution as a consequence of the homogenization cycle prior to hot rolling. The amount of Mn in solid solution is expected to be ~0.4% and relatively independent of alloy chemistry. Therefore if the dispersoids were having a significant strengthening effect in themselves it should be found in the strength prior to rolling. Inspection of the data given in tables 1 and 2 suggests this not to be the case.

No account has yet been taken of the iron and silicon contents of the alloys. The Si (up to 0.17%) will largely be incorporated into intermetallic particles and there will be little free Si in the alloy. The iron will generally be in the form of coarse (> 5μm) particles which have little significant contribution to the alloy's strength or work hardening behaviour. It thus appears likely that these two elements do not contribute to the S parameter in themselves. Clearly more work is necessary to resolve this issue and to examine the alloy's microstructure and to repeat the experiments without the

homogenization cycle to retain the Mn in solution.

Recovery

Figure 3 shows recovery data obtained on two different alloy chemistries at extreme ends of the 3104 range in the H19 temper (ϵ = 2.3). The data is plotted as a function of $\ln(t+1)$ where t is the exposure time in seconds. This plot enables a true zero to be shown. It should be noted that at 250°C and 275°C and long exposure times some recrystallization was detected in the samples and these data points have been ignored. The data has been normalized with respect to the material's as-rolled strength. No significant difference is observed between the two alloy chemistries shown or between all the alloys investigated. The recovery data follows a linear response on the graph ie a logarithmic decay in strength. This is expected from integration of simple models of recovery in which dislocation annihilation is governed by cross slip (4):-

$$d\sigma/dt = K \exp(-Q/RT)$$

where K and Q are complex variables dependent on alloy chemistry and the driving force for recovery.

The slope of the curves in figure 3 can be calculated as a function of the recovery temperature. The resultant graph of $\ln(d\sigma/dt)$ v. $1/T(K^{-1})$ is shown in figure 4. The graph shows that a linear relationship exists between 423K (150°C) and 548K (275°C) with little significant difference between the alloys. This is expected provided a single mechanism is occurring during the process. From the data shown in figure 4 the activation energy for recovery can be determined to be $\sim 34.9 \pm 1.6$ kJ/mole.

This data enables the percentage loss in strength to be estimated for all soak times within the range investigated provided that recovery is the sole process occurring. The driving force for recovery (stored energy ie dislocations generated during rolling) has also been investigated but is outside the scope of this paper.

In summary it may be stated that the work hardening behaviour follows the expected trend when each individual alloying element (Mg, Mn or Cu) is considered. However, attempts to apply the trend for each element by using estimates from binary alloys to model the work hardening behaviour show a consistent underestimation of the value of "k" in the Holloman equation. The reason is unclear but appear attributable to the alloys Mn content. In contrast the recovery of the alloys follows a logarithmic decay in strength which can be effectively modelled using a simple recovery mechanism. The recovery process appears independent of alloy chemistry on a normalised basis within the range studied.

Conclusions

1. An approximately linear increase in the work hardening coefficient "k" is found when single elements are increased using the atomic fraction addition to the power of 2/3.
2. The value of "k" is underestimated when the effect of alloy chemistry is considered as a sum of three binary alloys.
3. The deviation in the value of "k" is ~ 0.35 and appear mainly attributable to the Mn addition.
4. The recovery of material in the H19 temper is logarithmic in the temperature range 150°C to 275°C.
5. Recovery is independent of alloy chemistry in the range studies when the data is normalised to H19 strengths.

<div align="center">References</div>

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2. RA Sanders, SF Bauman and HC Stumpf in "Aluminium Alloys - Contemporary Research and Application" V31 Academic Press p66 (1989).
3. RD Doherty and J McBride in "Aluminium Alloys for Packaging" TMS p 347 1992.
4. C Barioz, Y Brechet, JM Legresy, MC Cheynet, J Courbon, P Guyot and GM Raynaud. 3rd. Int Conf on Aluminium Alloys Trondheim v2 p347 1992.

Table 1. Alloy chemistries of as-cast ingots (weight percent)

ALLOY	Mg	Mn	Cu	Fe	Si
36	1.110	0.832	0.174	0.309	0.174
37	1.218	0.944	0.247	0.340	0.185
38	1.090	0.965	0.169	0.305	0.168
39	1.280	0.962	0.173	0.308	0.168
40	1.488	0.955	0.169	0.301	0.172
41	1.102	0.951	0.236	0.305	0.174
42	1.120	0.953	0.300	0.304	0.177
43	1.072	1.163	0.167	0.298	0.166
44	0.928	0.926	0.278	0.306	0.123
45	1.152	0.958	0.182	0.501	0.182
46	1.238	0.922	0.156	0.318	0.103
51	1.229	0.915	0.159	0.621	0.138

Table 2. Experimental tensile data with measured and calculated values of n and k

CODE	$\sigma_{.2}$ $\epsilon = 0$	$\sigma_{.2}$ $\epsilon = \sim 0.2$	$\sigma_{.2}$ $\epsilon = \sim 1.0$	$\sigma_{.2}$ $\epsilon = \sim 2.5$	n	k	k n =.225	k Eq.1	k Eq 2
36	59	166	245	300	.2295	247.1	245	225.5	207.4
37	69	178	267	292	.2086	256.5	265	240.7	218.0
38	59	167	259	301	.2289	250.3	248	226.9	206.6
39	63	176	267	309	.2228	258.3	260	236.0	217.4
40	66	183	270	334	.2227	270.5	273	244.6	228.7
41	62	173	263	305	.2267	258.1	257	234.3	210.9
42	62	171	265	314	.2306	260.3	257	241.4	215.4
43	63	179	273	309	.2252	263.2	263	229.9	206.3
44	57	170	261	307	.2375	256.0	250	229.4	202.8
45	60	170	265	300	.2297	256.1	254	231.0	210.8
46	63	175	264	303	.2240	259.0	257	240.7	218.0
51	60	171	258	306	.2282	253.8	250	231.0	213.7
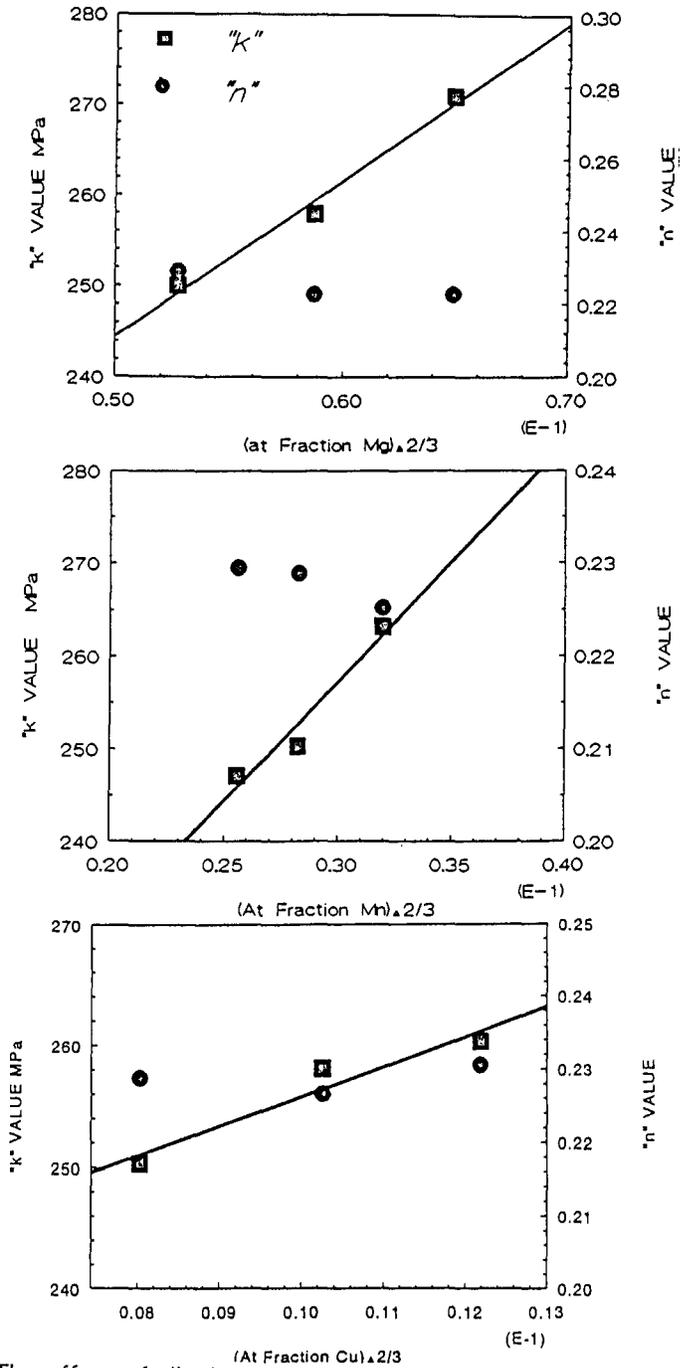
Figure 1. The effect of alloying addition on the value of "k" a. Mg, b. Mn, c. Cu
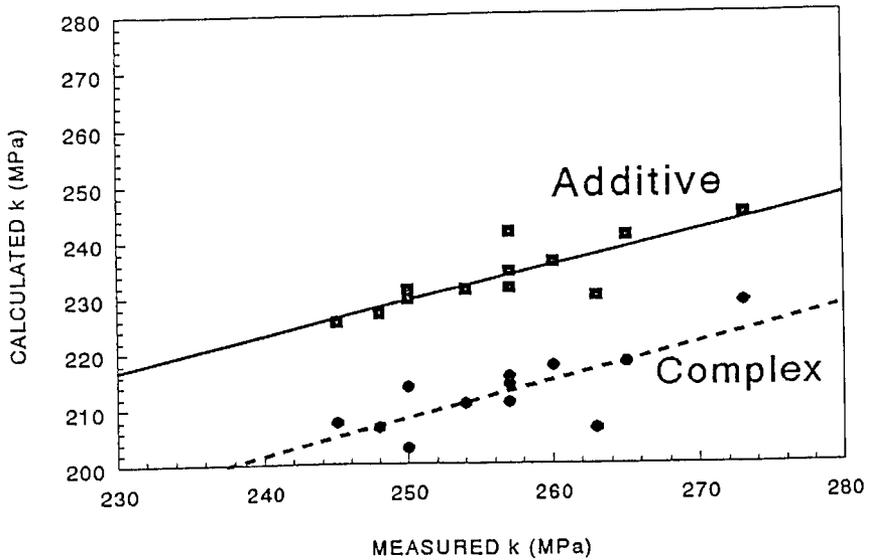
Figure 2a. The difference between measured and calculated value of "K".
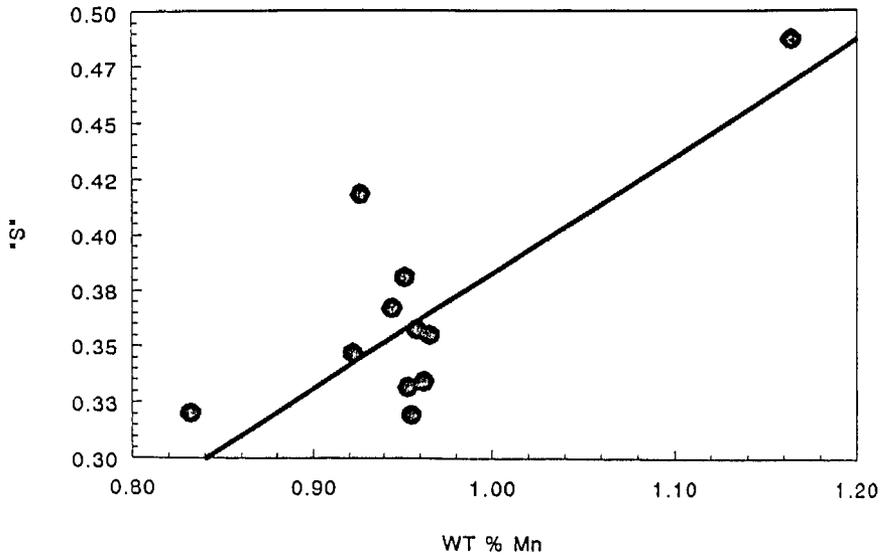
Figure 2b The variation of the synergism factor S with the alloy's manganese content

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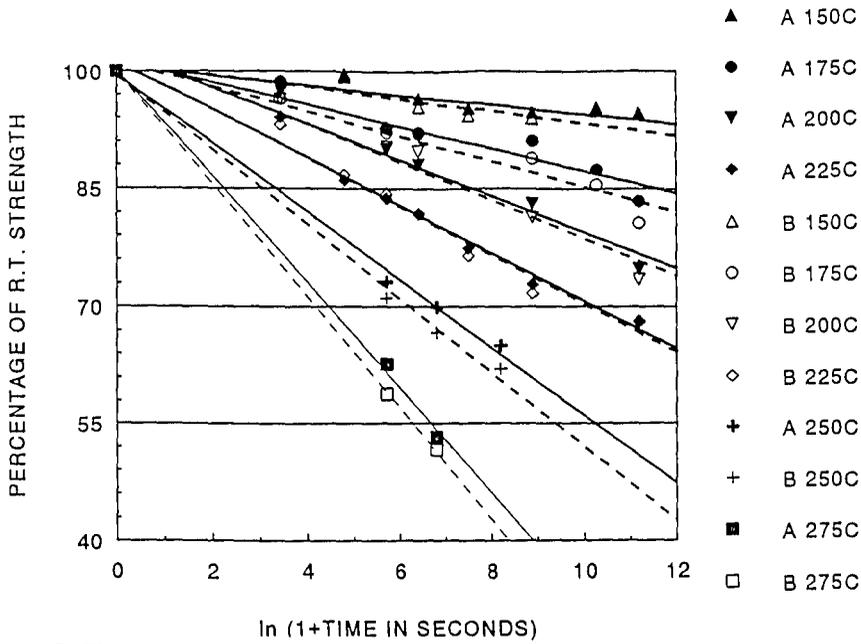
Figure 3. The retention of normalised 0.2%proof stress with time and temperature.
A = Al-0.93%Mg-1.03%Mg-0.17%Cu-0.17%Si-0.34%Fe
B = Al-1.11%Mn-1.32%Mg-0.32%Cu-0.17%Si-0.36%Fe
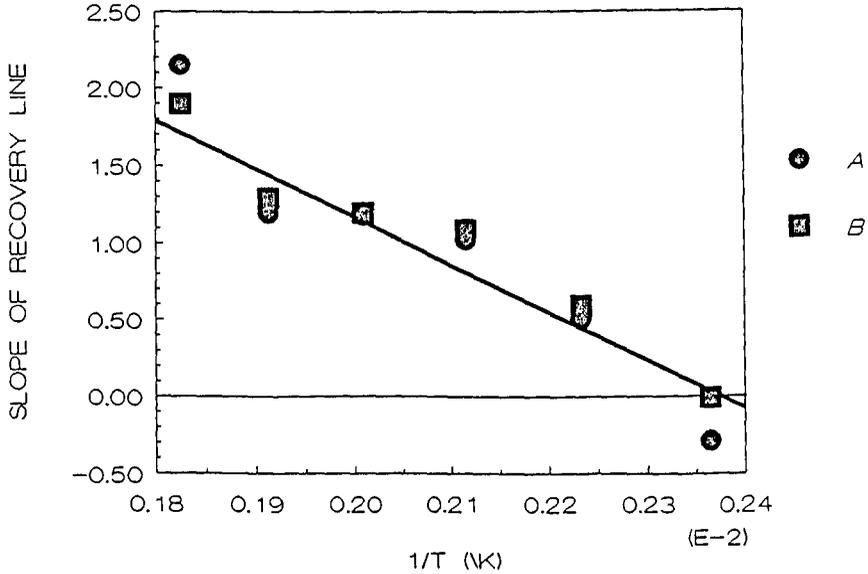
Figure 4. The slope of the recovery curves in figure 3 as a function of 1/T.

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