

## PAINT-BAKING PROPERTIES OF Al-Mg ALLOYS WITH ADDITION OF Cu

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**ABSTRACT** Traditional Al-Mg alloys have been alloyed with small amounts of Cu in order to make them age hardenable. The influence of Mg and Cu content, pre-deformation and cooling speed after annealing have been investigated. The hardening mechanism during ageing has been studied and the contributions of GPB zones, S'' and S' precipitates have been estimated. The differences in ageing response between water quenched and compressed air cooled, or undeformed and pre-deformed samples have been related to different contributions of GPB zones, S''- and S' precipitates.

**Keywords:** *Aluminium, automotive, precipitation hardening.*

### 1. INTRODUCTION

When Aluminium alloys are considered for the replacement of steel in car body applications, a choice must be made mainly between Al-Mg alloys of the AA5xxx series or Al-Mg-Si alloys of the AA6xxx series. The first have in general a better formability, but have the disadvantage that some softening occurs during the paint-baking cycle. Therefore Al-Mg-Si alloys are often preferred, because their strength will increase during baking, due to the precipitation of coherent  $\beta''$  precursors of  $Mg_2Si$ . In the recent past some efforts have been devoted to the development of precipitation hardenable Al-Mg alloys by adding small amounts of Cu [1-8]. It has been shown [6,7] that Cu decreases the hot formability, although the ductility can be improved by a modified pre-heat treatment. Cold rolled samples have been annealed under lab scale conditions and have been reported [4,5,8] to have an excellent hardening response during a simulated paint-baking treatment, providing that they can be cooled fast enough after annealing. In the mean time a better understanding of the precipitation hardening mechanism in these alloys has also been acquired [9,10]. The present paper will describe the ageing (paint-baking) response of some experimental Al-Mg-Cu alloys, and discuss the influence of cooling rate after annealing and pre-deformation on this ageing response.

### 2. EXPERIMENTAL CONDITIONS

During this study four Al-Mg based alloys with chemical composition mentioned in table 1, have been used. The alloys have been cast and hot and cold rolled using a classical industrial installation. Annealing treatments have been carried out in a salt bath (10s at 550°C). Two cooling rates from the annealing temperature have been used: water quench (~500°/s) and compressed air cooling (~30°/s) Tensile tests have been carried out on samples with a gauge width of 20 mm and an initial gauge length of 80 mm (DIN 50114). The tensile speed was 10MPa/s until  $R_{p0.2}$  and 24 mm/min further on (DIN 50145). The tensile samples were taken parallel to the rolling direction. The r-values are determined at 10, 12 and 14% and the n-values between 10-12, 12-14 and 14-16% of deformation and then averaged. TEM samples were prepared by double jet electro-polishing in a perchloric acid - methanol solution (volume ratio 1/9) at a temperature of 249K and a voltage of 15V. The TEM analysis were performed with a Philips CM200FEG at 200kV.

### 3. EXPERIMENTAL RESULTS

#### 3.1 As annealed properties

Table 1 shows some mechanical properties of the alloys annealed during 10s at 550°C and water quenched. During this treatment the cold rolled samples fully recrystallise and the Cu atoms are brought in solid solution. The alloys Y and Z have a lower yield stress (YS) because of the lower Mg content. Alloy X has a lower YS than A because of the higher grain size due to the lower Mn content (mean intercept of 42µm vs. 16µm).

The influence of Cu on the room temperature formability is somewhat unclear: comparing alloy X with alloy A shows a higher uniaxial elongation and a better n value, but a lower r value.

Table 1. Alloy compositions and some mechanical properties in recrystallised condition (samples parallel to rolling direction).

Alloy	Mg (wt%)	Si (wt%)	Fe (wt%)	Mn (wt%)	Cu (wt%)	YS (MPa)	UTS (MPa)	A <sub>80</sub> (%)	r	n
A*	4.05	0.16	0.28	0.37	0.014	119	264	26.1	0.78	0.30
X	4.22	0.15	0.31	0.14	0.58	107	272	29.6	0.64	0.35
Y	2.93	0.12	0.23	0.09	0.55	80	230	27.1	0.68	0.32
Z	2.99	0.14	0.16	0.11	0.88	88	245	26.0	0.67	0.33

\* A is a commercial AA5182 alloy

#### 3.2 Ageing response

Figure 1 illustrates the ageing response of the Cu alloyed samples. Obviously the YS of alloy A in the as annealed condition does not change during the ageing treatment at 180°C. The Cu alloyed variants however show an increase in YS of 32MPa (Y), 35MPa (X) and 49MPa (Z), or respectively 40, 33 and 57%. This clearly shows that in principle a considerable age hardening can be obtained under normal paint baking conditions (180°C; 30'), provided that the Cu atoms are kept in solid solution after the annealing treatment. A pre-deformation of 2% increases the YS due to work hardening. Ageing after pre-deformation leads to softening in the AA5182 alloy, but additional strengthening due to precipitation is observed in the Cu alloyed variants. The results also show that the precipitation hardening during a simulated paint baking cycle increases with increasing Cu content (X vs. A and Z vs. Y) and, although to a lesser extent, with constant Cu content and increasing Mg (X vs. Y). Especially after pre-deformation, the difference between Cu containing and traditional alloys is remarkable.

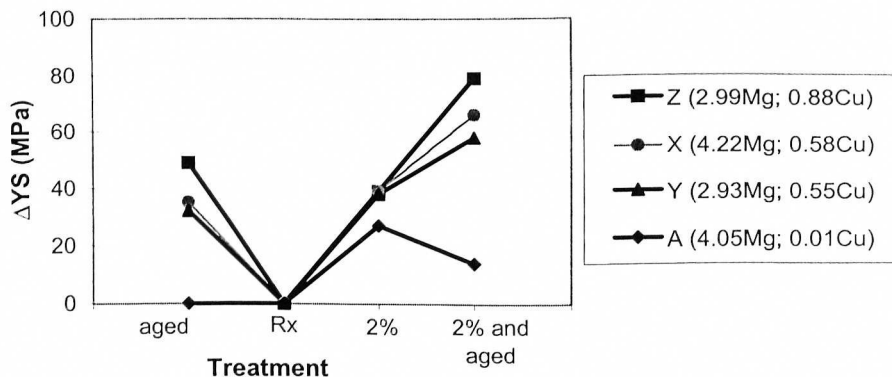


Figure 1. Increase in YS of salt bath annealed and water quenched alloys respectively after ageing at 180°C during 30', after uniaxial deformation of 2% and after a combination of both.

The combined influence of ageing and pre-deformation is more systematically shown in figure 2. The figure shows the increase in YS due to ageing after different pre-deformations. During ageing of alloy A, softening due to recovery mechanisms is taking place; this softening increases with increasing pre-strain. In the Cu alloyed variants this softening is counterbalanced by precipitation hardening. Figure 2 illustrates how the YS after a simulated press and paint-baking cycle (cold deformation + ageing) is shifted to higher values due to the addition of Cu. The absolute value of the YS after deformation and ageing is shown in figure 3. Alloy Y, although with lower Mg than alloy A, reaches the same YS as alloy A due to the precipitation strengthening effect of Cu. Alloy X with nearly the same Mg content as alloy A, is 20 to 40% stronger than A.

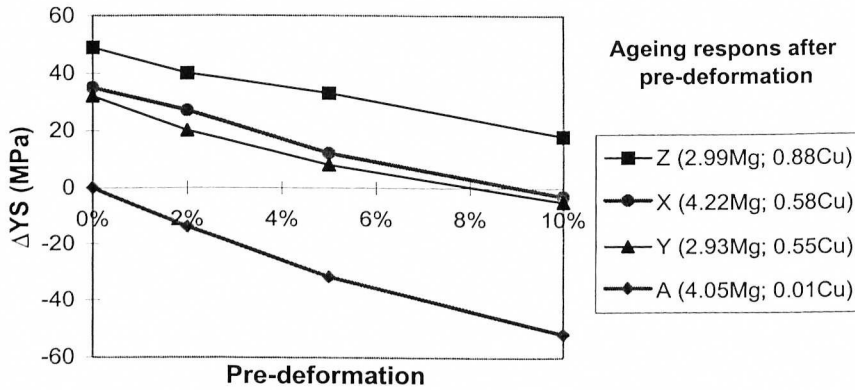


Figure 2. Change in YS (with the YS of the pre-deformed samples as reference) after ageing during 30' at 180°C, as function of the deformation applied before ageing.

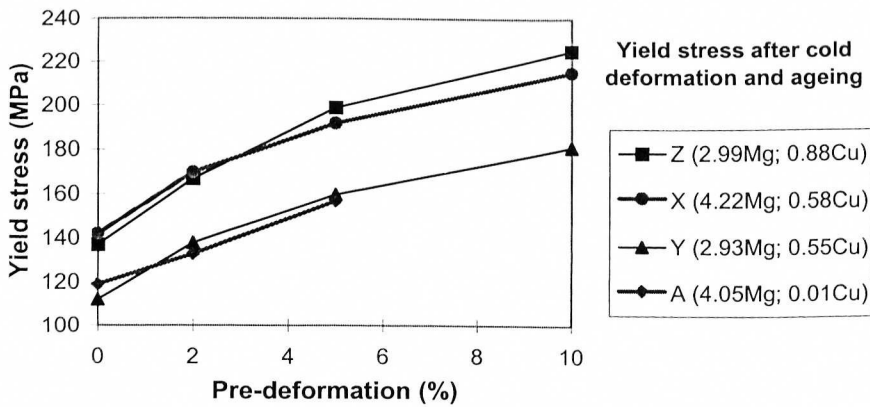


Figure 3. YS of four alloys after a simulated press and paint-baking cycle (cold deformation + ageing) as function of different deformation levels.

### 3.3 Effect of cooling rate

The previous results were obtained for samples that have been water quenched in order to retain a maximum of Cu atoms in solid solution. It can be expected that a slower cooling rate will reduce the ageing response because of premature precipitation of Cu during cooling. This effect is shown in figure 4. Samples of alloy X have been cooled from 550°C with four different cooling rates. The Thermo-Electrical Power (TEP) measurements clearly show that Cu is more and more lost with slower cooling rates.

Table 2. Yield Stress of alloy X in as annealed (550°C, 10'') and annealed and aged condition for two cooling rates after annealing [water quenching (WQ) and compressed air cooling (CAC)].

YS (MPa)	X (WQ)	X (CAC)
annealed	107	147
aged	142	161

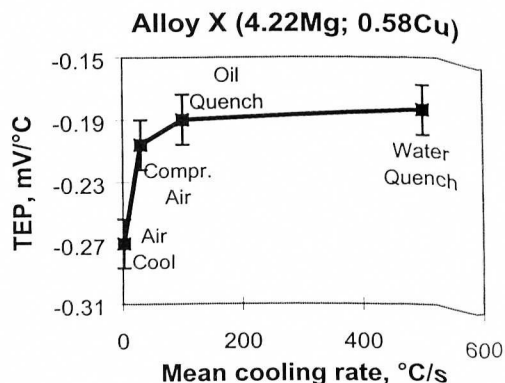


Figure 4. Thermo-Electrical Power as function of the mean cooling rate for alloy X.

In table 2 the YS of alloy X is shown after respectively annealing (550°C, 10'') and water quenching (WQ) or annealing and compressed air cooling (CAC). After CAC the YS is 40MPa higher than after WQ, apparently as a result of precipitation hardening during cooling. Surprisingly the strengthening in the WQ alloy after ageing at 180°C for 30' is still a bit lower than the strengthening during CAC from 550°C to RT, which only takes about 20s. When the CAC alloy is aged at 180°C, some additional strengthening is observed, which indicates that not all the Cu has precipitated during cooling. Figure 5 illustrates that the same is true for the alloys Y and Z. When the YS is measured as a function of time during ageing, a clear difference in behaviour between the WQ and CAC alloys is observed. In the WQ alloys the YS jumps from 107 to 135MPa in the first minute of ageing, and then gradually increases, reaching 142MPa after 30' and a peak of 180MPa after about 11 days. The YS of the CAC alloy starts at 147MPa and gradually increases (without sudden jump) reaching a peak in about 2.5 days. This behaviour will be discussed in the next section.

From this experimental results it can be concluded that the Cu alloyed variants of the AA5xxxx alloys show an increased YS after CAC, compared with WQ, which for some applications can be considered as a negative point. On the other hand the final YS of these CAC (YS after a simulated press and paint baking operation) is also higher, which is of course positive.

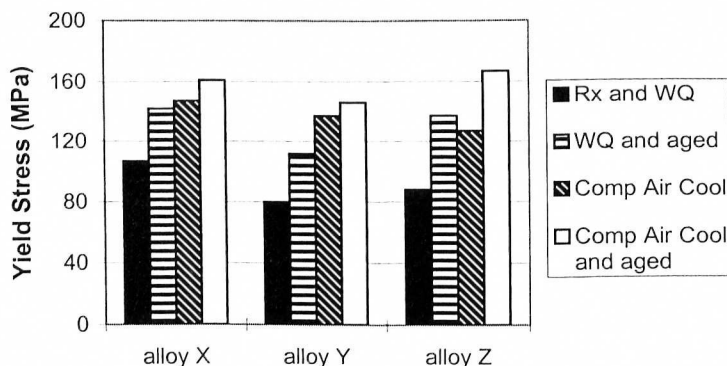
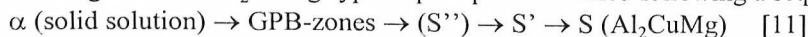


Figure 5. Yield Stress of four alloys in as annealed (550°C, 10'') and annealed and aged condition for two cooling rates after annealing [water quenching (WQ) and compressed air cooling (CAC)].

#### 4. DISCUSSION

Previous results clearly show that classical Al-Mg alloys can be made age hardenable with the addition of small amounts of Cu. This ageing response is most effective when Cu atoms are as much as possible retained in solid solution after annealing. An increase in YS and a corresponding reduction in ageing response after slower cooling from the annealing temperature, seems logical due to the premature precipitation of Cu during cooling. The general idea is that precipitation hardening is due to  $\text{Al}_2\text{CuMg}$ -type of precipitates formed following a sequence:



In this view the GPB zones play an important role in the hardening. In this respect it is surprising that our pre-deformed samples still have an excellent ageing response, since it was confirmed by DSC measurements [9] that in this case the GPB precipitation peak was completely suppressed. Another remaining question concerns the different hardening behaviour between WQ and CAC samples, more particular why the WQ samples show a sudden increase in YS during the first minutes of ageing. To answer these questions, the precipitation sequence in alloy X was carefully analysed [9, 10]. The results can be summarised as follow.

During ageing of the WQ samples a two-fold precipitation mechanism has been revealed. In the first minutes of ageing  $\text{S}''$  precipitates are formed heterogeneously on dislocation lines and helices. At the same time GPB zones (or Cu/Mg clusters as found by Ringer et al [12]) are formed homogeneously in the matrix. Reversion experiments (since GPB and  $\text{S}''$  go into solution at different temperatures they can selectively be removed) have shown that after some minutes of ageing,  $\text{S}''$  has a somewhat higher contribution to the strength than the GPB zones. At later stages  $\text{S}''$  also forms uniformly in the matrix and this is related to the further hardening. After long ageing times (some days)  $\text{S}''$  (both on dislocations and in the matrix) can transform into  $\text{S}'$  although this reaction is very slow (the peak of hardness is found after only 11 days).

In the pre-deformed samples, quenched-in vacancies are swallowed by dislocations and formation of GPB zones is inhibited to a large extend; in DSC measurements the GPB peak almost disappeared. The new dislocations on the other hand create additional nucleation sites for  $\text{S}''$  precipitates. It is difficult to visualise  $\text{S}''$  precipitates in such a way as to estimate their number density. However, during a treatment at  $275^\circ\text{C}$  ( $\text{S}'$  precipitation peak on the DSC curve) on WQ and 5% stretched samples,  $\text{S}'$  precipitates are formed and it was observed that their number density is larger, and their size is one order of magnitude smaller than the one of  $\text{S}'$  in unstretched samples. It is assumed that the same is true for  $\text{S}''$ . These  $\text{S}''$  precipitates hinder the movement of the dislocations and prevent to a certain extent the recovery of the sample during ageing. Hardening during ageing of pre-deformed samples can thus be attributed mainly to  $\text{S}''$  precipitates.

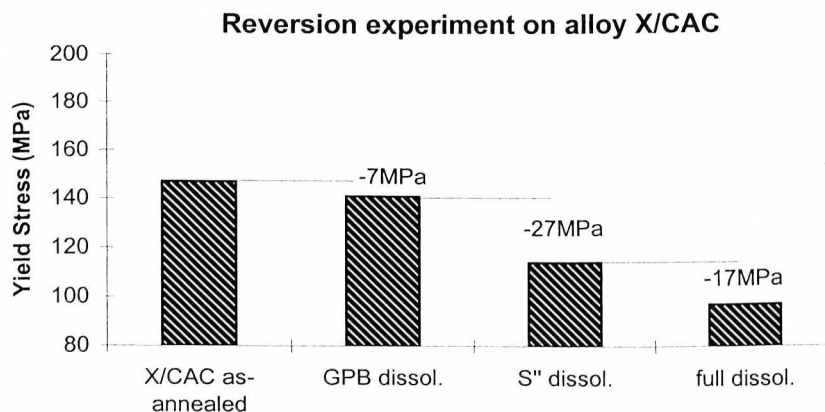


Figure 6. Yield stress of alloy X (annealed and CAC) after selective dissolution of GPB zones and GPB and  $\text{S}''$  respectively.

In samples with less drastic cooling after annealing (e.g. compressed air cooling) the initial hardening (increase in YS compared with the WQ samples) was found to be related mainly to S'' precipitates formed on dislocations during cooling. Figure 6 shows some results of reversion experiments carried out on alloy X (annealed and CAC). The results show that the YS decreases with only 7 MPa after a selective dissolution of the GPB zones (clusters). A selective dissolution of GPB and S'' lowers the YS with 34 MPa (27 MPa more). This indicates that the strengthening during CAC can be attributed mainly to the precipitation of S'' (in contrast with the WQ samples where about 50% of the strengthening during the first minutes of ageing was attributed to GPB zones). During ageing of as annealed and CAC alloys, further hardening appeared to be related with additional precipitation of S''.

## 5. CONCLUSIONS

Al-Mg alloys (AA5xxx) can be made age hardenable by adding relatively small amounts of Cu, without impairing the ductility in as annealed condition. Under normal paint-baking conditions, an excellent hardening can be obtained, providing that the Cu atoms are adequately kept in solid solution after annealing.

If Cu atoms can precipitate during cooling after annealing (e.g. compressed air cooling), an increase in as annealed YS (compared with water quenched samples) and a decrease in ageing response is observed. This is related to a different contribution of S'' and GPB zones to the hardening. In water quenched samples, hardening can initially be attributed for about 50% to GPB zones and 50% to S'' on dislocations. During further ageing, S'' is formed in the matrix. In compressed air cooled samples, S'' and S' formed during cooling, are responsible for the increase in YS. Further hardening during ageing is due to additional S'' precipitation.

After water quench and pre-deformation the main contribution to hardening is coming from S'' precipitates.

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