PRECIPITATION SEQUENCE DURING AGEING OF AN Al-4.2wt.%Mg-0.6wt.%Cu ALLOY

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ABSTRACT The present work is a study of the precipitation sequence during ageing at 180°C of an Al-4.2wt.%Mg-0.6wt.%Cu alloy by means of TEM, SAD and tensile testing. The precipitation sequence has been related to the changes in the yield strength during ageing. A two-fold precipitation sequence has been found. On one side S"- and further on S'-phase (precursors of the Al_2MgCu phase) precipitate heterogeneously on dislocation loops and helices, on the other hand a homogeneous precipitation sequence in the matrix of the type: Cu/Mg clusters (GPB zones)→ S"→ S' has been also observed. The contribution of different phases to the materials yield strength has been evaluated.

Keywords: *Al-Mg-Cu alloy, TEM, precipitation sequence, precipitation hardening*

1. INTRODUCTION

Aluminium sheets are considered as an alternative of steel for car-body panels and therefore they require a good cold formability. Additionally they must retain or preferably increase their strength when the part is painted and baked. Recently, some efforts have been devoted to the development of precipitation hardening effect in Al-Mg alloys of the 5xxx series by introducing small additions of Cu [1-7]. This would add to their excellent formability an improved mechanical strength since precipitation hardening during the paint-baking cycle is expected.

Several studies on ageing of commercial Al-Mg-Cu alloys (Cu:Mg ratio of 0.11-0.29 in wt.) show that precipitation follows the sequence reported for Al-Cu-Mg alloys: GPB zones and S' (Al_2MgCu) phase have been observed to precipitate and to dissolve during heating of annealed and water quenched samples [2-3, 6-7]. The precipitation hardening in Al-Cu-Mg alloys has been extensively studied [8-15]. According to Silcock [8] and Bagaryatsky [9] the precipitation sequence in an Al-3wt%Cu-1.5wt.%Mg can be represented as follows:

$$\alpha \text{ (supersaturated solid solution)} \rightarrow \text{GPB zones} \rightarrow S'' \rightarrow S' \rightarrow S.$$

Cu/Mg clusters, called Guinier-Preston-Bagaryatsky (GPB) zones, first precipitate out from an oversaturated α solid solution [8, 9]. However all the attempts to observe them at this stage by means of strain field contrast in conventional Transmission Electron Microscopy (TEM), Selected Area Diffraction (SAD) and high resolution TEM (HRTEM) failed. Differential Scanning Calorimetry (DSC) exothermal (50-150°C) and endothermal (150-280°C) peaks have been assigned to the GPB zones formation and dissolution [10, 11]. Ringer et al. reported recently that Cu/Mg sub-nanometer clusters have been observed after a short ageing time by means of atom probe field ion microscopy (APFIM) and a "cluster hardening" mechanism has been proposed to precede the GPB zones formation [12, 13]. Bagaryatsky proposed two intermediate structures (S" and S') both with slightly distorted S structure and with different matrix-precipitate coherence [9]. Large stresses are considered to be associated with the coherence of S". The existence of the S" phase has not been clearly confirmed. Many authors did not observe it [8, 10,15]. Zahra et al. [11] and Cuisiat et al. [14] reported evidence of the existence of S" phase. The S' phase has a face centred orthorombic structure with lattice parameters a=4.04, b=9.25 and c=7.18 Å. On the other hand, Wilson et al. [15]

suggest that S' is not preceeded by S" and it nucleates heterogeneously on dislocations and dislocation loops, which can release partially the misfit between the precipitates and the matrix. It follows certain orientation relationships with the α matrix, i.e. $[100]_{S'}\|[100]_{\alpha}$, $[010]_{S'}\|[021]_{\alpha}$, $[001]_{S'}\|[012]_{\alpha}$, and it grows as laths in the <100> directions of $\{210\}_{\alpha}$ habit planes [15]. The stable Al_2CuMg phase, referred to as S phase, differs in structure and lattice parameters very little with the metastable S'phase and some authors suggest that they should be considered as one phase and the different notation schould be dropped [13]. Age hardening in Al-Cu-Mg alloys has been related to the homogeneous precipitation of Guinier-Preston-Bagaryatsky (GPB) zones in the matrix. Ringer et al. recently proposed a "cluster hardening" mechanism [12], which was found to be responsible for the sharp initial increase in the hardness and in their vision this clustering precedes the GPB zones formation.

In order to have efficient hardening during the artificial ageing treatment, which for car-body applications is typically 30 min at 160-180°C, a deeper knowledge of the precipitation hardening in Al-Mg-Cu alloys has been recently developed [7]. The aim of the present work is to report the precipitation sequence during ageing at 180°C of an Al-4.2wt.%Mg-0.6wt.%Cu alloy and to relate this to the changes in the yield strength of this material.

2. EXPERIMENTAL

An experimental Al-Mg-Cu alloy was supplied by Hoogovens Aluminium N.V., Belgium and has a composition of Al-4.22%Mg-0.58%Cu-0.15%Si-0.31%Fe-0.14%Mn (in wt.%). It was industrially hot and cold rolled to a final thickness of 1.05 mm. Annealing has been performed in laboratory conditions by means of salt bath at 550°C for 10 s. and water quench. The yield strength was evaluated by means of tensile testing of samples taken in the rolling direction. The aging treatment was given in an oil bath for different times at 180°C. Thin foils for TEM observations were prepared by double jet electropolishing of 3 mm disks, cut by sparking from foils ground and polished to 0.2 mm. A 20% perchloric acid in methanol electrolyte was used at -35°C and a voltage of 15 V. The TEM observations were done at 200 kV with a Philips CM 200FEG. All the observations are performed in the <100> matrix orientations along the exact zone axis, or in two beam conditions with **g**=200, which are the most suitable conditions for the GPB zones, S" and S' phase visualisation.

3. RESULTS AND DISCUSSION

The strengthening curve of the annealed alloy as function of the ageing time at 180°C is shown in fig. 1 in relation to the different precipitation events (this relations will be discussed further on). It can be seen that the low strength of the as-annealed alloy increases drastically in the first minutes at 180°C, similar to the sharp increase in hardening observed in Al-Cu-Mg alloys [8, 12-13]. Then there is a continuous but relatively small increase up to 16000 minutes (about 11 days) when a modest peak of hardness forms.

In order to understand the cause for the strengthening, TEM observations at different times of ageing at 180°C were performed. The corresponding microstructures are shown in fig. 2. The microstructure of the as-annealed sample (fig. 2(a)), which shows the lowest yield stress, is characterised by dislocations and dislocation loops. No precipitation is observed neither on the dislocations nor in the matrix. After 1024 min at 180°C (fig. 2(c)) and at all later stages heterogeneous precipitation on dislocation loops and helices is observed. Elongated in the <100> direction of the matrix, these precipitates decorate the dislocation loops and grow with the ageing time in order to form assembles of "corrugated sheets" with a {210} type of habit plane. These precipitates were identified by means of HRTEM and SAD as S' phase, see [7]. However, very fine precipitates decorating the dislocation loops and helices were noticed at much earlier ageing times.

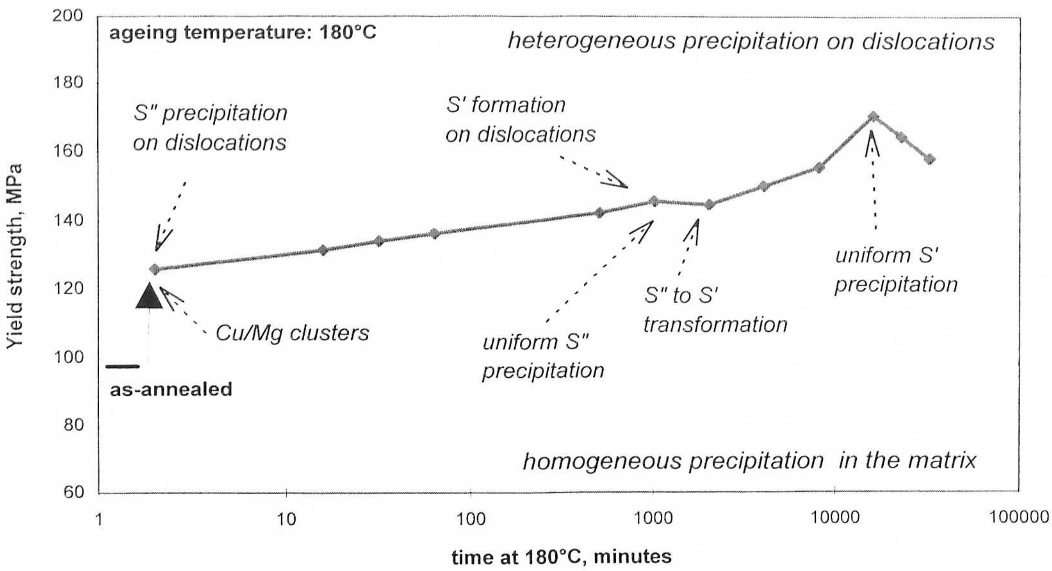

Fig. 1: Yield strength vs. ageing time, in minutes, at 180°C for the investigated Al-4.2wt.%Mg-0.6wt.%Cu alloy. All important hardening mechanisms are shown.

16 minutes at 180°C, see fig. 2(b). They are visualised due to the strain field contrast in two beam conditions with **g**=[200] in matrix orientation close to <100>. Some of these precipitates show weak but clearly resolvable spots on the SAD pattern, which following Cuisiat [14], might be interpreted as the intermediate S" phase. More details on the identification of the S" phase can be found in [7]. At higher ageing times (from 2048 min at 180°C) uniform precipitation in the matrix is also observed. Elongated precipitates are visualised in fig. 2(d) by means of coffee-bean contrast in two-beam conditions, which have been identified by means of SAD and HRTEM as S" precipitates, see [7]. It has been observed also that these precipitates can transform directly into S' phase. The peak of ageing can clearly be related with a homogeneous precipitation of S' phase, as shown in fig. 2(e). It has to be noted that these precipitates follow the orientation relationships S'-α matrix, as observed by Wilson et al. [15], although that they have been derived for S'phase, heterogeneously precipitating on dislocations. This fact supports a conclusion that this orientation relationships are general. The overageing, fig 2(f), has been attributed to S' precipitates growth. A comparison between the last two microstructures shows that the change is found mainly in the thickness of the platelike S' precipitates. This is probably related to a coherency loss in directions perpendicular to the platelets surface and accordingly to release of stresses around the precipitates, since the coherency of S' precipitate with the α matrix is different in different matrix orientations [15]. Some decrease of the precipitates density with overaging has been also observed.

In agreement with the reports of other authors [12-13], GPB zones precipitation (or better in the terminology of Ringer "Cu/Mg clusters") could not be observed by means of TEM and SAD in the present work. In order to prove the Cu/Mg clusters formation and to evaluate the respective contribution of clusters and S" to the precipitation hardening at the early stages of ageing, a reversing experiment was performed. As shown by DSC results [6-7, 10-11], four peaks (2 exothermal and 2 endothermal) might be detected during reheating of a salth bath annealed and water quenched sample: Cu/Mg clusters precipitation (125-140°C), Cu/Mg clusters dissolution (200-270°C), S' peaks precipitation (280-350°C), S' dissolution (360-430°C). Additionally to them,

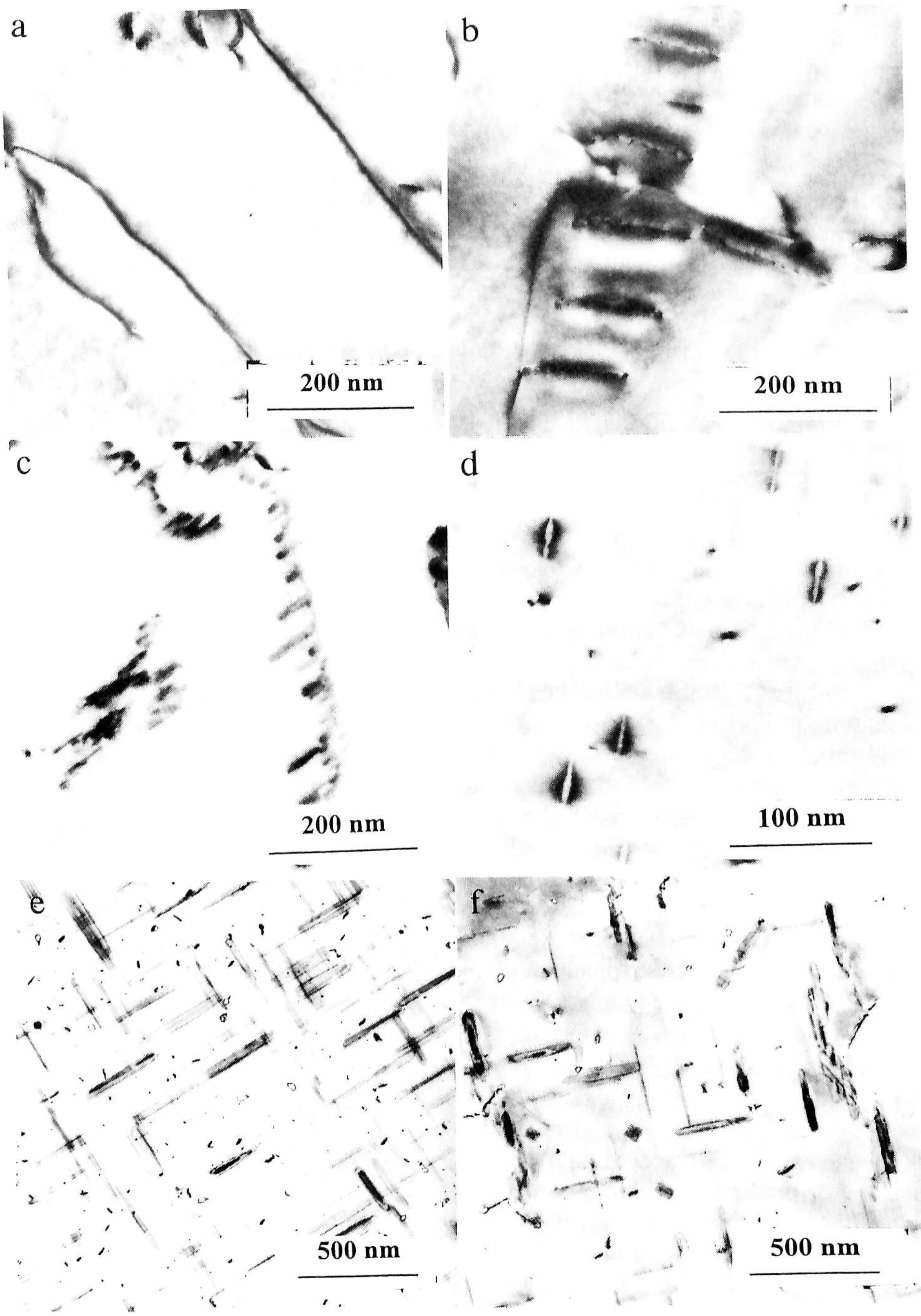

Fig. 2: Microstructure after different ageing times at 180°C: a) as-quenched: precipitation is not observed; b) 16 min: heterogeneous precipitation of S" phase on dislocations; c) 1024 min: precipitation of S' phase on dislocations; d) 2048 min: homogeneous S" phase precipitation in the matrix; e) 11 days (peak of strength): uniform S' phase precipitation in the matrix; f) 22 days (overaging): S' precipitates growth in thickness and decrease of density.

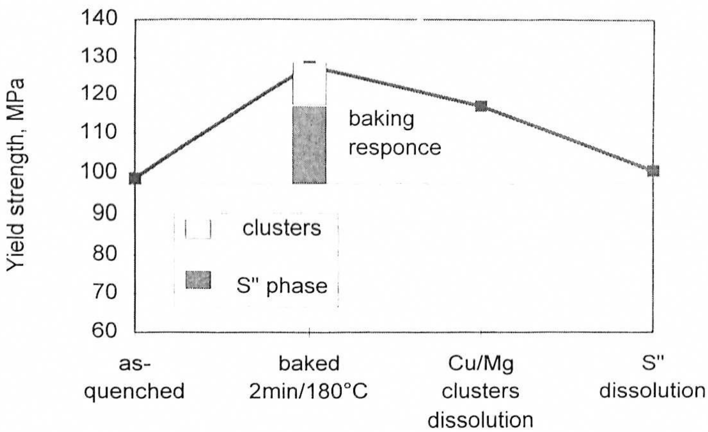

Fig. 3: Yield strength of as-quenched, aged (for 2 min. at 180°C), aged and GPB zones dissolution treated samples and aged and S" dissolution treated samples.

an exothermal peak in the range 150-210°C has been observed [7, 11], which was related to precipitation of the S" phase. Two groups of salt bath annealed and water quenched samples have been aged for 2 minutes at 180°C. Subsequently, one part of them received an Cu/Mg clusters dissolution treatment (60 sec. at 250°C followed by water quench) and the other part a S' dissolution treatment, which also has to dissolve the S" phase (60 sec. at 375°C followed by water quench). The yield strength of those samples was measured. The results are shown in fig. 3. In the very beginning of the ageing at 180°C (just 2min) both Cu/Mg clusters and S" phase form and the yield strength increases from 98 to 126 MPa. Fig. 3 shows that the contribution of the S" precipitates to the hardening at this stage is bigger than the one of the Cu/Mg clusters (about 60:40%). This is a new point in the understanding of the precipitation sequence in Al-Mg-Cu alloys, since up to now it was considered that the precipitation hardening in these alloys is mainly due to Cu/Mg clusters formation.

Summarising, a two-fold precipitation sequence was observed in the present Al-4.2wt.%Mg-0.6wt.%Cu alloy. Immediately after the start of ageing at 180°C, S" phase precipitates heterogeneously on dislocations. It develops further in S' phase, which decorates the dislocations and the dislocation helices. Parallel to it, an uniform precipitation in the matrix also takes place. Cu/Mg clusters (GPB zones) precipitate very fast in the beginning of the ageing process. On a later stage homogeneous S" phase precipitation in the matrix is observed. Since Cu/Mg clusters were not observable by TEM and SAD their link with the S" phase is just hypotetical. Further on S" phase transforms to S', as it has been well shown in [7]. Since no difference between the S' and S phase has been detected, the last stage (S' $\rightarrow$ S) of the sequence has been dropped. The whole precipitation sequence is schematically illustrated in fig. 1 in relation to the changes of the yield strength of the material. The precipitation hardening mechanism can be related partially to S" and S' phases, but also a contribution of the Cu/Mg clusters has been found. The observed peak of strength was associated with uniform S' precipitation in the matrix and the initial stages of hardening were linked to heterogeneous S" precipitation on dislocations and to uniform Cu/Mg clusters precipitation in the matrix.

The suggested mechanism explains the material strengthening when ageing is combined with pre-deformation, especially the fact that with introducing predeformation, although the clusters

(GPB zones) precipitation is inhibited due to the annihilation of the quenched-in vacancies, a precipitation hardening effect is observed with baking, see [4, 16]. This can be clearly related to hardening due to S" phase precipitating on dislocations. Heterogeneous precipitation of the S" phase on dislocations has a complex effect: first, it does not permit considerable softening because part of the dislocations are "locked" by the nucleous of the precipitating phase, so some work hardening is retained and second, it causes considerable precipitation hardening. This compensates to a large extent the loss of hardening due to the inhibition of clusters formation because of the pre-deformation.

4. CONCLUSIONS

The following conclusions can be drawn:

- A two-fold precipitation sequence during ageing at 180°C has been found in an Al-4.2wt.%Mg-0.6wt.%Cu alloy:

$\alpha \rightarrow S" \rightarrow S'(S)$ (heterogeneously on dislocations)

$\alpha \rightarrow$ Cu/Mg clusters (GPB zones) $(\rightarrow)$ $S" \rightarrow S'(S)$ (homogeneously in the matrix)

- The precipitation hardening mechanism was related mainly to S" and S' phases appearance.
- The observed peak of strength was associated to uniform S' precipitation in the matrix.
- The initial stages of hardening, which are important for industrial application, were linked mainly to heterogeneous S" precipitation on dislocations, but uniform precipitation of Cu/Mg clusters in the matrix gives also an important contribution.

ACKNOWLEDGEMENTS

This work was performed with the financial aid of the "Vlaams Instituut voor de Bevordering van het Wetenschapelijk-Technologish Onderzoek in de Industrie", under contract nr. 95/0280.

REFERENCES

[1]. T. Fujita, K. Hasegawa, M. Suga: European Patent no. 0616044 A2, (1994).
[2]. Y. Suzuki, M. Matsuo, M. Saga, M. Kikuchi, Proc. 5th Int. Conf. on Al Alloys, Grenoble, 1996, Material Science Forum Vols. 217-222, (1997), 1789.
[3]. T. Fujita, K. Hasegawa, S. Mitao, N. Niikura, T. Koike, M. Funakawa, N. Yoshihara, K. Ohori, SAE paper No.950719, Society of Automotive Engineers, Inc.,Warendale, PA, (1995), 41.
[4]. B. Verlinden, P. Ratchev, P. De Smet and P. Van Houtte, Proc. of the Conference Thermo-Mechanical Processing, Theory, Modeling, Practice, 4-6 September, 1996, Stockholm, Sweden, ed. B. Hutchinson, ASM, Metals Park, Ohaio (1997), 323.
[5]. P. Ratchev, B. Verlinden, P. Van Houtte and P. De Smet, Mat. Sci and Eng., A222 (1997), 189.
[6]. P. Ratchev, B. Verlinden, P. Van Houtte, Scripta Metall. et Mater., 30 (1994), 599.
[7]. P. Ratchev, B. Verlinden, P. De Smet and P. Van Houtte, Acta Materialia, accepted.
[8]. J.M. Silcock, J. Inst. Met., 89 (1960-61), 203.
[9]. Y. A. Bagaryatsky, Dokl. Akad. S.S.S.R., 87 (1952), 397.
[10]. A.K. Jena, A.K. Gupta and M.C. Chaturvedi, Acta Metall., 37 (1989), 885.
[11]. A. M. Zahra, C. Y. Zahra, W. Lacom, K. Spiradek, Proc. Int. Conf. on Light Metals, Amsterdam, 20-22 June, 1990, ed. T. Khan and G. Effenberg (1990), 633.
[12]. S. Ringer, K. Hono, T. Sakurai and I.J. Polmear, Scripta Materialia, 36, 5 (1997), 517.
[13]. S. Ringer, T. Sakurai and I.J. Polmear, Acta Materialia, 45, 9 (1997), 3731.
[14]. F. Cuisiat, P. Duval, R. Graf, Scr. Metall., 18, (1984), 1051.
[15]. R. Wilson and P. G. Partridge, Acta Metall., 13 (1965), 1321.
[16]. P. Ratchev, B. Verlinden, P. De Smet and P. Van Houtte, Scripta Materialia, accepted.