The influence of temperature and storage time at RT on nucleation of the $\beta''$ phase in a 6082 Al–Mg–Si alloy

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Abstract

The age hardening process of a 6082 Al–Mg–Si alloy by isothermal ageing at 100, 125 and 150 °C for 0 to 40 days has been investigated by both conventional and high-resolution transmission electron microscopy. Changes in sizes and densities of the pre-$\beta$ and $\beta''$ phases during ageing can explain the evolution of hardness, in particular a plateau in the curve of the hardness versus ageing time. Fully coherent pre-$\beta''$ particles (GP-I zones) are formed from atomic clusters that were created upon annealing or at natural ageing. Room temperature (RT) storage reduces the number of pre-$\beta''$ particles by a factor of 5. Ageing at 125 and 150 °C causes the phase pre-$\beta''$ to transform to the phase $\beta''$. An ageing temperature of 100 °C was found to be too low to initiate the transformation of pre-$\beta''$ to $\beta''$.

Keywords: Precipitation; Annealing; Transmission electron microscopy (TEM); Aluminium; Hardness

1. Introduction

Al–Mg–Si alloys have been studied extensively because of their technological importance and their exceptional increase in strength obtained by precipitation hardening. The Al–Mg–Si alloys are mostly used in extruded Al products in Western Europe, as well as for construction and automotive purposes. The ease with which these alloys can be shaped, their low density, their very good corrosion- and surface-properties and good weldability are factors that together with a low price make them commercially very attractive. The alloy in the present study, with the designation AA6082, is optimised to be the strongest alloy in the group, with only minor setbacks in its other properties. The contents of Si and Mg are in the range of 0.5–1 wt%, usually with a Si/Mg ratio larger than one. Mn, typically 0.7 wt%, is also an important addition, while Fe is a natural impurity (~0.2 wt%). Historically, such alloys are said to have excess silicon relative to Mg$_2$Si, due to the presumption that the hardening phase $\beta''$ also has this composition. In this concept the remaining Si is proposed to be present in other phases, such as Al–Fe–Si and Al–Si–Fe–Mn particles. In recent years, however,
it has become evident that the composition of the β" phase contains Mg and Si in a ratio close to 1 rather than 2 [1–3]. The structure of this phase was finally resolved in the mid-90s, by our group, using high-resolution electron microscopy and quantitative electron diffraction [2,3]. In this work it was proven that the ideal composition of the β" phase is Mg5Si6, a phase with just the right ratio of Mg/Si to explain the excess amount of Si that optimises the strength in 6082. Other recent studies [4–6] also confirm that the most effective hardening phase for these type of materials is β".

The precipitation sequence that is generally accepted [7,8], is the following: SSSS→atomic clusters→GP-zones→β"→β/B′ phase→β (stable), where, SSSS is super saturated solid solution. Some authors consider the GP zones as GP-1 zones while the β" particles are called GP-2 zones [8]. Recently [9], we have been able to determine the structure of the GP-zone, the precursor of the β" phase. We shall call this phase pre-β", since it has a unit cell, which is only slightly different from that of the β" phase. Pre-β" is fully coherent with the matrix and has atomic positions very close to that of the Al-matrix. The pre-β" phase also contains Al-atoms and is an intermediate between very small clusters and the β" phase.

Little quantitative data has been published to explain the details of changes in hardness versus annealing time, and the dependence of hardness and microstructure on the storage time at room temperature (RT) is still poorly understood. Using conventional and high-resolution TEM, we have investigated the occurrence (sizes and densities) of the pre-β" and β" precipitates in relation to the hardness in detail. This was done in the temperature interval in which the β" phase is stable [1,4,10,11].

2. Experimental procedures

Slices of 2 cm thick homogenised billets of an AA6082 alloy (Al 98.0, Mg 0.6, Si 0.9, Mn 0.5, Fe 0.2, all in wt%), were received from Hydro Al. The slices were cut into 1 × 1 × 1 cm³ pieces, which were given a heat treatment in salt bath at 540 °C for 55 min. Subsequent quenching was done in water at RT. One series of samples was immediately heat-treated in an oil bath at the respective temperatures 100, 125 and 150 °C, while a second series was first stored at RT for 7 days and then heat-treated in the same way as for the first series. The estimated time at RT for the first series was in the order of 10 s. For both sample series the annealing times at each annealing temperature varied from 1 h to more than 40 days. In the case of annealing or ageing at 100 °C, only specimens without RT storage were investigated.

All samples are labelled with three numbers: x/xxx °C/x h (or x d). The first number refers to the storage time at RT: 0 for no storage or 7 for 7 days. The second number indicates the annealing temperature and the third number is the time during which the specimen was isothermally annealed at the specified temperature. The symbol ‘h’ stands for hours and ‘d’ for days. All the samples annealed for different times at the same temperature and under the same storage condition will be referred as being part of a series. In total five such sample series were investigated: the 0/125 °C series, the 7/125 °C series, etc.

Vickers hardness measurements (1 kg loads) were performed for each sample using a Matsuzawa DVK-1 S unit. TEM and HREM specimens were prepared by conventional electropolishing with a Tenupol-3 machine using an electrolyte consisting of 1/3 HNO₃ in methanol. The TEM analysis was carried out with a Philips CM30T operating at 150 kV and a high resolution Philips CM30UT/FEG operating at 300 kV. The CM30T was used at 150 kV as at this acceleration voltage no beam-induced defects are created which could hamper the analysis of the number of precipitates. A Gatan parallel electron energy loss spectrometer (PEELS) attached to the CM30T was used to measure the specimen thicknesses, which data are required for the determination of the precipitate densities in various specimens of three series. The particles are visually counted from TEM images. To reduce the effect of the non-uniform particle distribution four to five bright field images, at similar magnifications (150000x) from different areas have been analysed for each of the specimens.

The CM30UT/FEG microscope is equipped with a Photometrix 1024 × 1024 slow scan CCD cam-
era (12 bits dynamical range) enabling a linear recording of HREM images. Computer control of the CCD camera and the microscope was performed with a Tietz software package. Series of 16 HREM images with 3.2 nm focus increment were recorded for the exit wave reconstructions. The reconstructions were done using a software package based on algorithms developed by Van Dyck and Coene [12]. The reconstructed exit wave functions contain both amplitude and phase information since they are complex. In this paper only the amplitude images are presented. The phase images were, however, quite similar.

3. Results

3.1. Hardness measurements

Hardness curves of the specimens obtained under various heat treatments are presented in Fig. 1(a)–(e).

The hardness curves of the samples isothermally annealed at 125 and 150 °C without storage exhibiting similar characteristics. During the initial stages the hardness increases drastically from a value of 50–55 HV given by the SSSS to 110–115 HV. This is followed by a plateau during which there is little or no increase, and finally by a second increase to a maximum of 125–130 HV.

The specimens stored first at RT for 7 days and then followed by the same annealing treatments at 125 and 150 °C exhibit a different behaviour from the ones without room temperature storage. For the 7-days stored series the hardness increases monotonously until a maximum is obtained (115 HV), in contrast with the non-RT aged specimens, which show a plateau with little or no increase in hardness.

The hardness evolution of the 0/100 °C series is similar to that of the 7/ series, but in this case the maximum value achieved is 120 HV.

3.2. TEM analysis

In order to find a correlation between the hardness evolution and the microstructure and the types of precipitates formed, representative specimens from each series were examined by TEM analysis. The specimens selected for the TEM examinations and their corresponding microstructures are summarised in Table 1. An exact number for the particle density is very difficult to determine due to many sources of error like non-linear thickness variation of the sample, non-uniformity in the distribution of precipitates, difference in the image contrast resulting in counting errors, etc. However, the observed densities differ significantly between the series or within different specimens of the same series. A comparison between these samples in the discussions below is, therefore, reliable.

In addition to the β” phase, another phase that is more coherent with the Al-matrix is present in some specimens. This new phase, noted as GP-I zone or pre-β” phase, is the precursor of the β” phase [9,13]. The β” and pre-β” phases show similar TEM images and diffraction patterns, but may be distinguished using the projected interatomic distances in the reconstructed exit waves. Taken along the needle direction ([010] direction), some interatomic distances between the projected atoms are different for pre-β” and β” because one Mg atom in the unit cell of pre-β” differs from β” in height along [010].

All β” and pre-β” particles are small needles oriented parallel to the (100) directions in the Al matrix. For this reason the conventional TEM analysis has been performed with the specimens in (100) orientation, which is the best orientation for visualising the β” phase [1–3].

During the early stages of annealing of the 0/150 °C series, a high volume fraction of very small pre-β” precipitates has been formed (see Table 1 and Fig. 2). The pre-β” phase can be found in the specimens annealed for 4 and 11 h, but in the 2 d specimen the precipitates have already transformed to the β” type. The reconstructed exit waves of β” as well as pre-β” precipitates from the samples in the series 0/150 °C are given in Ref. [9].

TEM analysis of the specimens of the 0/100 °C series show that a large amount of very fine and coherent pre-β” phase is forming from the beginning of annealing. This is in agreement with the nucleation process found in the 0/150 °C series, in the first stage of annealing (before the transformation pre-β”→β” occurs). In contrast with the latter
Fig. 1. Hardness curves for the series: (a) 0/125 °C; (b) 0/150 °C; (c) 7/125 °C; (d) 7/150 °C; (e) 0/100 °C. For each series the annealing times for representative positions in the curves (i.e. inflexion points) is also indicated.

Table 1
The particle density, size and type of the precipitates as a function of storage time, annealing time and temperature

<table>
<thead>
<tr>
<th>Samples investigated</th>
<th>Particle density (particles/µm³)</th>
<th>Needle length (nm)</th>
<th>Needle cross section (nm²)</th>
<th>Precipitate type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/150 °C/4 h</td>
<td>350,000 to 450,000</td>
<td>7.5+/−0.6</td>
<td>3−5.2</td>
<td>Pre-β⁺</td>
</tr>
<tr>
<td>0/150 °C/11 h</td>
<td>350,000 to 450,000</td>
<td>9.5+/−0.6</td>
<td>3−5.2</td>
<td>Pre-β⁺</td>
</tr>
<tr>
<td>0/150 °C/2 d</td>
<td>100,000 to 200,000</td>
<td>10.1+/−0.6</td>
<td>3−5.2</td>
<td>β⁺</td>
</tr>
<tr>
<td>0/150 °C/9 d</td>
<td>100,000 to 200,000</td>
<td>16.3+/−0.6</td>
<td>3−5.2</td>
<td>β⁺</td>
</tr>
<tr>
<td>7/150 °C/4 h</td>
<td>No precipitates</td>
<td>No precipitates</td>
<td>No precipitates</td>
<td>No precipitates</td>
</tr>
<tr>
<td>7/150 °C/11 h</td>
<td>Very low</td>
<td>8.5+/−0.6</td>
<td>1−2</td>
<td>Pre-β⁺</td>
</tr>
<tr>
<td>7/150 °C/2 d</td>
<td>40,000−60,000</td>
<td>24.0+/−0.6</td>
<td>7.5+/−0.7</td>
<td>Pre-β⁺β⁺</td>
</tr>
<tr>
<td>7/150 °C/9 d</td>
<td>40,000−60,000</td>
<td>35.2+/−0.6</td>
<td>11.0+/−0.7</td>
<td>Pre-β⁺β⁺</td>
</tr>
<tr>
<td>0/100 °C/8 d</td>
<td>&gt;500,000</td>
<td>4−6</td>
<td>1−5</td>
<td>Pre-β⁺</td>
</tr>
<tr>
<td>0/100 °C/17 d</td>
<td>&gt;500,000</td>
<td>4−6</td>
<td>1−5</td>
<td>Pre-β⁺</td>
</tr>
</tbody>
</table>
case, no β" precipitates have been formed in the 0/100 °C series, even for annealing times up to 17 d. Fig. 3 presents bright field and HREM images of the sample 0/100 °C/17 d. Exit wave reconstructions for the 0/100 °C samples showed only a small deviation from the pure Al lattice: the atom columns look only a bit blurred in the precipitates. This indicates that some of the atoms are not well aligned along the atom columns in the viewing direction. Thus, no clear images of the atomic arrangements could be obtained, which is also logically given the facts that the specimen is considerably thicker than the clusters themselves and that the atomic arrangements in these clusters are still close to that of the Al-matrix.

Compared to that of the 0/150 °C series, the microstructure of the 7/150 °C series (Fig. 2) shows a very different evolution with annealing time (Table 1). In the 4 h annealed specimen no precipitates could be observed. In the 7/150 °C/11 h specimen a very low density of pre-β" particles was observed, while a mixture of pre-β" precipitates together with a coarse β" structure was present in the samples 7/150 °C/2 d and 7/150 °C/9 d (see Table 1 and Fig. 4). In contrast with the more homogeneous distribution in 0/150 °C/2 d...
Fig. 4. Reconstructed exit waves of particles of the 7/150 °C series: (a) β' from the specimen 7/150 °C/9 d; (b) pre-β' from 7/150 °C/9 d. The viewing direction is (100)Al.

and 0/150 °C/9 d samples, the 7/150 °C/2 d and 7/150 °C/9 d samples contain pre-β” and β” particles covering a whole range in sizes and cross-sections: from 8 nm/1 to 2 nm² to 25–35 nm/7–11 nm². The microstructure of the 7/150 °C/9 d sample is similar to that of 7/150 °C/2 d.

4. Discussion

The hardness curves of the investigated series and the dependence of the hardness evolution on the storage time at RT can be explained in terms of microstructure and phase transformations. Only three out of the five series were investigated in TEM (Table 1), but the same physical processes should take place in the 0/125 °C as in the 0/150 °C series, and in the 7/125 °C as in the 7/150 °C series. This assumption is based on the fact that the respective hardness curves show similar profiles (Fig. 1).

In the case of no storage at RT, after homogenisation at 540 °C a huge amount of non-equilibrium quenched-in vacancies are present in the material. These vacancies enhance the creation of a very large number of coherent pre-β” precipitates at the beginning of annealing. The initial pre-β” precipitates is likely to contain a substantial amount of Al [9]. There are two continuous processes: diffusion of Mg and Si from the solid solution to the pre-β” precipitates and replacement of Al by Mg and Si in these precipitates. The overall result is an increase in precipitate length and a gradual reduction of the full coherency with the Al matrix, while the number density remains almost constant up to 11 h of annealing time [9]. The interfacial area of the precipitates and the distortion induced in the matrix increase during this time, and consequently, the hardness increases as well. Due to the large coherency (lattice match) the hardness increase induced by initial pre-β” precipitates is less than that of β” precipitates (about 110 HV versus a maximum of 125 HV).

The structural phase transition toward the β” structure (probably triggered by the Al replacement) starts to take place after 11 and 14 h of annealing for the 0/150 and 0/125 °C, respectively. For the 0/150 °C series, the hardness does not increase significantly in the time window of the transformation from pre-β” to β” particles (from 11 h to 2 d), resulting in a plateau (Fig. 1b)). A maximum is reached only when β” precipitates are present. The particle density of β” is lower than that of pre-β” (Table 1), but the hardness generated by the β” precipitates is higher because these precipitates generate more strain due to the fact that they are less coherent with the matrix than the pre-β” particles. At longer annealing times the β” precipitates grow further in size, which leads to a decrease in both number density and hardness.

The hardness curve for the 0/125 °C series has a very similar profile to the one for 0/150 °C series. The only difference is that the change in hardness behaviour starts after 14 h (11 h for 0/150 °C) and
and surroundings. This reduced diffusion delays the formation of pre-
\( \beta^n \) particles. As a consequence the pre-
\( \beta^n \) phase will form from the pre-
\( \beta^n \) precipitates. In this latter case the process: clusters\( \rightarrow \)pre-
\( \beta^n \)\( \rightarrow \)\( \beta^n \) is continuous and the hardness increases at a constant rate.

5. Conclusions

A 6082 Al-alloy has been subjected to iso-
thermal heat treatments at temperatures that favour
the formation of \( \beta^n \), the main hardening phase in
this type of material. The following conclusions
have been drawn:

1. Atomic clusters are created during storage at
RT.
2. GP-I zones (or pre-\( \beta^n \) particles) are the first pre-
icipitate to form in this type of alloy. If the
annealing temperature is higher than 125 °C, the
\( \beta^n \) phase will form from the pre-\( \beta^n \) precipitates.
3. Storage at RT was found to have an important
effect on the precipitation of pre-\( \beta^n \) and \( \beta^n \) phases, and the overall microstructure development. The atomic clusters, which formed during storage at RT and the low concentration of the quenched-in vacancies in the stored samples have a delaying effect upon the nucleation of pre-\( \beta^n \) in the 7/125 and 7/150 °C series. Consequently, the final \( \beta^n \) structure developed in these samples is coarse. In contrast, the large number of pre-\( \beta^n \) precipitates formed in the samples annealed immediately after homogenisation transform into a dense structure of small \( \beta^n \) particles. The number density of \( \beta^n \) precipitates in this case is almost five times higher compared to the samples stored 7 d at RT.
4. Storage at RT has a negative effect upon the
hardness and lower annealing temperatures pro-
duce stronger materials. The highest hardness
(130 HV) is achieved in 0/125 °C series.
5. Although the initial stages of nucleation when
annealing at 100 °C are similar to those in the
0/125 and 0/150 °C series, no \( \beta^n \) phase is for-
lates up to 9 d of annealing time (compared to 2
d for 0/150 °C). A maximum hardness of 130 HV
is reached after 15 d (9 d for 0/150 °C). The speed
of transformations is slower than at 150 °C as a
result of the temperature dependence of the dif-
fusion coefficients.

During the annealing at 100 °C with no storage
at RT only one type of precipitates is formed,
namely pre-\( \beta^n \) phase. No pre-\( \beta^n \)\( \rightarrow \)\( \beta^n \) phase trans-
formation occurs, indicating that the temperature is
too low to nucleate \( \beta^n \) particles. The growth of the
pre-\( \beta^n \) precipitates leads to a hardness increase for
which \( \frac{d(H)}{d(\log(t))} \) is constant, where \( H \) is the
hardness and \( t \) is the time.

Storage at RT results in a hardness increase from
a value of 50–55 HV immediately after homogen-
isation to a value of 80 HV after 7 days. This indi-
cates that atomic clusters are formed during the
storage [1,13]. During the first hour of the
annealing treatment at 125 or 150 °C, the hardness
decreases from 80 to 60–65 HV, indicating that
many atomic clusters have been dissolved. How-
ever, the hardness is higher than that of the SSSS
(50–55 HV) and some of the co-clusters formed
during RT storage are likely to survive.

These clusters are potential nucleation sites for
the pre-\( \beta^n \) phase. The amount of quenched-in vac-
cancies and solute elements has strongly decreased
due to the RT ageing. The low initial number of
vacancies limits the formation of pre-\( \beta^n \) and \( \beta^n \) par-
ticles. Thus, for the RT stored specimens, during
ageing, transportation of the Mg and Si atoms
(from cluster to pre-\( \beta^n \) nuclei and from the solid
solution to pre-\( \beta^n \) nuclei) will be much slower.
This reduced diffusion delays the formation of pre-
\( \beta^n \) particles. As a consequence the pre-\( \beta^n \) number
density is almost five times lower in the 7/150 °C
series than in the 0/150 °C (Table 1). Continuing
in time, the newly formed pre-\( \beta^n \) increase in size,
and (like in the 0 RT aged specimens) when
enough Al from their composition is replaced by
Mg and Si the pre-\( \beta^n \) particles become unstable and
transform into the \( \beta^n \)-phase.

The observed spread in the sizes of the pre-\( \beta^n \)
and \( \beta^n \) precipitates and the coexistence of these two
phases over a relatively large time interval also
suggests that the initial atomic clusters vary in size
and surroundings.

In the series 0/125 and 0/150 °C the transform-
ation of a large amount of pre-\( \beta^n \) into \( \beta^n \) resulted
in a plateau of constant or little increase in hard-
ness. In contrast, for the 7/125 and 7/150 °C series
no plateau is present indicating that there is no
strict time interval at which the pre-\( \beta^n \) precipitates
transform into \( \beta^n \) particles. This is the case when
the process: clusters\( \rightarrow \)pre-\( \beta^n \)\( \rightarrow \)\( \beta^n \) is continuous and the hardness increases at a constant rate.
med, indicating that for the given composition and pre-aging conditions this temperature is too low to form $\beta^\prime$. Annealing at 100 °C produces a microstructure consisting of a very fine distribution of pre-β precipitates.

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