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In situ natural ageing of Al-Cu-(Mg) alloys: the effect of In and Sn on the very early stages of decomposition

Frank Lotter^{1,*}, Danny Petschke¹, Frédéric De Geuser², Mohamed Elsayed^{3,4}, Gerhard SEXTL^{1,5}
and Torsten E.M. Staab¹

¹University Wuerzburg, Dep. of Chemistry, LCTM, Roentgenring 11, 97070 Wuerzburg, Germany

²Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMAP, 38000 Grenoble, France

³Martin Luther University Halle, Dep. of Physics, 06120 Halle, Germany

⁴Minia University, Dep. of Physics, Faculty of Science, 61519 Minia, Egypt

⁵Fraunhofer ISC, Neunerplatz 2, 97082 Wuerzburg, Germany

*corresponding author: frank.lotter@uni-wuerzburg.de; tel.: +49931-3188942

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Abstract

The influence of trace elements (0.01 at.% In/Sn) on the decomposition process of Al-Cu-(Mg) alloys during the very early stages of natural ageing has been investigated in situ by small angle X-ray scattering supported with differential scanning calorimetry and hardness measurements. In the binary Al-Cu alloy quenched-in vacancies are bound to In or Sn, resulting in a suppressed Cu clustering process. In Al-Cu-Mg room temperature hardening occurs much faster due to Mg entering clusters. However, the influence of In or Sn is negligible. **Cu and Mg possibly form complexes with quenched-in vacancies before they can reach a trace element atom.**

The positive effect of trace additions like Sn, In, Cd or even Ag and Au to alloys of the Al-Cu system is still a matter of active research [1–7] since first discovered in the 1950th [8–10]. In

Al-Cu, for example, it is known that small amounts (~100 ppm) of Sn, In or Cd have a strong influence on the ageing behavior at temperatures of 150-200°C. There, the alloys show a significantly increased hardening response by preferably forming finely dispersed θ' precipitates, which can block the dislocation movement more effectively than in the binary Al-Cu alloy [11,12]. The trace elements play a key role in assisting the θ' formation, possibly by lowering the interfacial energy between the particle and the matrix [2] or as heterogeneous nucleation sites [11].

The influence of trace elements has also been discovered in other alloy systems, such as Al-Si-Mg [13–15] and in the here investigated Al-Cu-Mg system [16].

Nevertheless, most of the here listed publications make use of imaging methods like transmission electron microscopy (TEM) or 3D atom probe tomography (3DAP) and therefore focus more on the ageing process at elevated temperatures (150-200°C). With these methods it is hard to access the very early stages of decomposition in the alloy, especially during natural ageing (RT), due to the time consuming sample preparation.

Typical trace elements, like Sn/In/Cd are known to have a strong binding energy to vacancies (0.2 – 0.25 eV) [6,17,18] and thus suppress cluster/precipitate formation during natural ageing. Hence, in the present study in situ small angle X-ray scattering (SAXS) is used to follow the decomposition process at room temperature directly after quenching the alloys. SAXS has proven to be a powerful tool for the characterization of precipitates or clusters in Al alloys, particularly for mapping or in situ experiments due to the short measuring times [19–25]. The SAXS data are supported by Vickers hardness and DSC measurements to get a better understanding of the types of clusters/precipitates that form during the ageing process.

Therefore two base alloy systems with a nominal composition of Al-1.7%-Cu and Al-1.7%Cu-1.3%Mg (all in at.%) were investigated. Additionally 0.01 at.% of trace elements (in this case In and Sn, respectively) were added to each base alloy. The alloys were cast as small

1 rods with a diameter of about 10 mm from high purity materials (Al 5N5 and Cu/Mg/In/Sn
2 4N). The alloys were then homogenized at 520°C for 24h.
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4 Vickers hardness testing was done on a Innovatest Falcon 600 micro hardness tester using a
5 load level of 500 gf. For DSC square shaped samples with a mass of about 45 mg were cut
6 with a SiC saw. To ensure a good contact with the Al crucible one side of the specimen was
7 polished. The samples were then solution heat treated at 520°C for 1h and rapidly quenched to
8 ice water. Ageing took place at room temperature (25°C) for the given times with the “as
9 quenched” sample being measured immediately after quenching (< 2 min at RT). The
10 measurements were carried out in a Netzsch 204 F1 Phoenix heat flux DSC apparatus with a
11 heating rate of 20 K/min in a range of -20°C to 530°C under nitrogen atmosphere. Pure Al
12 (5N) was used as a reference and for baseline correction.
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26 For SAXS the samples were prepared as disks with a diameter of about 10mm and a thickness
27 of about 100 µm by gradual grinding with SiC paper (#500 - #2000). All samples were then
28 solution heat treated and quenched as stated above. To freeze out the diffusion processes the
29 samples were stored on dry ice throughout the transportation to the synchrotron facility and
30 then kept in liquid nitrogen until the in situ measurement took place. The in situ SAXS
31 experiments were conducted at the BM02 beamline at the European Synchrotron Radiation
32 Facility (ESRF) in Grenoble, France. The beam energy was set to 8 keV with a beam size of
33 about 200 µm. The distance of the 2D XPAD hybrid pixel detector to the sample was about
34 400 mm. The samples were then naturally aged in situ (25°C) while constantly recording
35 scattering images every 20 seconds. After detector and background corrections all scattering
36 images are integrated and normalized to absolute units using glassy carbon as a secondary
37 calibration sample.
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55 For the analysis of the data the model by Ivanov et al. [22] is used, who model the scattering
56 intensity by a more statistical description of concentration fluctuations, i.e. small clusters, in
57 the Al matrix. The Intensity can be written as
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$$I(q) = I_{cluster}(q) + Pq^{-4} + B$$

with a Porod contribution (Pq^{-4}) from large objects as well as a constant background B.

From this model on the one hand the correlation length ξ , a measurement corresponding to the size of the clusters, and on the other hand the mean number of excess Cu atoms, which is representative for the number of Cu atoms incorporated in the clusters, can be extracted. It is

very important to note that, because of the small difference in X-ray scattering contrast between Al and Mg, the contribution of Mg to the scattering signal can be neglected in this experiment. To access the excess in Mg for the Al-Cu-Mg alloys a combined approach of X-ray and neutron scattering would be necessary [22]. The contrast difference very well exists for In and Sn but considering their small concentration, their contribution is negligible. In **Fig. 1** an example for the measured and fitted scattering curves during in situ natural ageing of the Al-Cu and Al-Cu-Sn alloy is shown. For a detailed explanation of the model we refer the reader to [22].

Fig. 2 presents the evolution of the Vickers hardness for the investigated alloys during natural ageing. The base Al-Cu alloy starts at a value of 67.4 ± 1.4 HV in the as quenched state. After about 20 min of ageing a hardness increase can be observed, which continues to develop up to 3 h of ageing time to about 85 HV. In both the Al-Cu-In and Al-Cu-Sn alloys an almost identical behavior can be observed. The as quenched value for both alloys is about 56 ± 2 and a very small rise in hardness can be detected during the first hours of natural ageing. This suggests the suppression of Cu agglomeration to clusters and/or small GP zones in the presence of the trace elements.

The Al-Cu-Mg alloys on the other hand show a clearly increased hardening response compared to the Al-Cu system, regardless of the trace additions. The alloys start at hardness values between 74 ± 2 and 87 ± 2 in the quenched condition, which is significantly higher than the binary Al-Cu alloys and indicates a higher degree of solid solution strengthening in the

Mg containing alloys [24]. During further natural ageing all three alloys show a continuous strengthening, which becomes even more pronounced after 20 min, up to about 116 ± 5 HV. The for the Al-Cu-In/Sn alloy observed suppression effect is surprisingly not achieved in Al-Cu-Mg. Additionally, hardness data after 24 h have been recorded to get an idea of the hardness progression for longer terms of natural ageing. It becomes clear that the most significant hardness increase happens indeed during the first 2-3 h.

The time resolved results of the fitted small angle scattering data are displayed in **Fig.3**. The left column shows the data for the binary Al-Cu system with and without trace additions of tin and indium, while on the right the respective results for the Al-Cu-Mg alloy is presented. For the Al-Cu system one can immediately notice the immense difference in cluster size and excess Cu for the base alloy and the ones with trace elements. The cluster size in the base alloy is with about 4 Å in the beginning and about 5 Å in the end more than twice as big compared to the Al-Cu-In/Sn alloy. Regarding the number in excess Cu atoms the difference is even more than one order of magnitude. Directly after quenching we already observe significant clustering in the Al-Cu base alloy with numbers in excess Cu over 20 nm^{-3} . For Al-Cu-In and Al-Cu-Sn, which behave nearly identical, almost no correlation can be observed during the first 20 min of ageing, leading to cluster sizes $< 2 \text{ Å}$ and excess Cu atoms $< 2 \text{ nm}^{-3}$. After 3h at room temperature we measure cluster sizes of about 2.5 Å with about 2 excess Cu atoms per nm^3 . This, in correlation with the hardness data in **Fig. 2**, clearly underlines the suppression of Cu diffusion and cluster/GP-zone formation in Al-Cu due to the high binding energy of In and Sn to quenched-in vacancies, which has been calculated [17] and experimentally observed several times in the literature [5,6,8–10,18] but never been quantified during the very early stages of decomposition in a time resolved manner. In [6] the authors propose the existence of In and Sn vacancy complexes, which are stable up to 150°C . It is noteworthy that the clustering process is not completely frozen out, since the vacancy trapping has to be seen as a more dynamical process as suggested in [24]. So, the vacancies

1 spend most their time in the vicinity of an In or Sn atom but sometimes can help a copper
2 atom to diffuse further in the lattice. This also becomes evident in the DSC curves presented
3 in **Fig. 4**. In the Al-Cu alloy the evolution of the endothermal peak in the temperature range of
4 50°C to 100°C, corresponding to the dissolution of Cu clusters that formed during natural
5 aeging, is much more prominent than in the alloys with trace additions.
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10 The picture becomes completely different if Mg is added to the alloy system. If we compare
11 the results of the Al-Cu-Mg alloy, displayed in the right column of **Fig. 3**, with the binary Al-
12 Cu, the data show much smaller clusters as well as significantly fewer excess Cu atoms. It is
13 again after about 15 to 20 min until the main cluster process starts, indicated by the growth of
14 the clusters and rise in the excess Cu to about 15 nm^{-3} after 3h, which is still by a factor of 4
15 lower than in the binary Al-Cu alloy, where we reach a value of $>55 \text{ nm}^{-3}$. The Reason for this
16 has to be the for the X-rays invisible Mg atoms entering the clusters quite early in the process.
17 Ivanov et al. [24] report comparable results in excess Cu and rise in excess Mg atoms, due to
18 the access to neutron scattering, for an Al-Cu-Mg alloy of similar composition after about 20
19 min of natural ageing. This observation is also in good agreement with the hardness curves in
20 **Fig. 2**, where the major strengthening starts in the same time frame. The much higher
21 hardness achieved in Al-Cu-Mg compared to Al-Cu suggests a different composition of the
22 clusters in the Mg system. The DSC measurements (**Fig. 4**) can confirm this as well. In the
23 AQ state of the Al-Cu-Mg alloys we observe a formation peak at 75°C, which can be
24 attributed to the cluster formation [24–28]. This is followed by a wide dissolution region in
25 the temperature range of 120° and 250°C compared to 50°-100°C in the Al-Cu alloy. The
26 higher thermal stability also indicates a different composition of the clusters.
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53 The next very surprising observation that can be made is the almost negligible influence of
54 indium and tin added to the Al-Cu-Mg system in all data sets. This suggests that the addition
55 of Mg to the Al-Cu system somehow compensates the (in Al-Cu) strong influence of In and
56 Sn, which is in contrast to the observations of Poon et al. [16], who propose a strong
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1 interaction between tin and vacancies at 150°C ageing temperature due to fewer dislocation
2 loops observed in HRTEM. In their study the authors also report a higher hardness of the Al-
3 Cu-Mg-Sn alloy compared to its base alloy possibly due to a finer and more uniform
4 distribution of S phase. These findings might lead to the assumption that at room temperature
5 Mg competes with In or Sn in localizing the vacancies. However, in Al-Mg-Si with Sn
6 additions alloys many authors report a retarded natural ageing [13–15,29], so Mg alone might
7 not be the decisive factor.

8
9 Thermodynamic calculations in [15] show that an increasing Mg and Si content in Al-Mg-Si
10 reduces the solubility of Sn. It is noteworthy that Al-Cu-Mg-Sn shows a slightly higher initial
11 hardness compared to the other alloy (Fig. 2), what could be caused by undissolved Sn
12 precipitates. But at the same time the In solubility stays nearly unaffected in [15], which
13 suggests a sufficient amount of In in solution for thermal history of the samples. To allow a
14 more meaningful comparison future works should consider calculations on the Al-Cu-Mg
15 alloy system.

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17 While the interaction between Mg atoms and vacancies is still unclear, many authors report
18 Mg in the vicinity of vacancies [30], Mg-vacancy-complexes [31] or an attractive behavior
19 between Mg-Cu clusters and vacancies. This is also supported by Doppler broadening
20 spectroscopy measurements (not shown here) that reveal the same atomic surrounding of
21 vacancies in the Al-Cu-Mg and Al-Cu-Mg-In alloy, which is most likely Cu and Mg
22 dominated.

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24 Based on those findings a possible explanation would be that solute Mg and Cu act as a kind
25 of “fog” around the very early forming copper rich agglomerates. The combination of those
26 solute atoms might then have a strong tendency to form Mg-Cu-vacancy complexes. The
27 vacancies then become released, when the solute itself is transported to the clusters, leading to
28 this rapid and strong natural hardening response (Fig. 2). At higher temperatures such as
29 150°C the binding energy of those complexes might be too weak and the tin atoms start to

form Sn-vacancy complexes, which are stable up to 150°C [6].

In summary, we could follow the early stages of the natural ageing process of Al-Cu and Al-Cu-Mg and the influence of trace elements (In, Sn) added to the alloys using a combinatorial approach of in situ small angle X-ray scattering and differential scanning calorimetry. We draw the following conclusions:

- In the binary Al-Cu alloy rapid Cu clustering can be observed, which is dramatically suppressed by the addition of In or Sn. Reason for this is the strong interaction between vacancies and the trace element atoms.
- Al-Cu-Mg shows a significantly increased hardening response compared to Al-Cu due to the different composition of the clusters formed during ageing. The overall numbers in cluster size and excess Cu are much smaller than the binary alloy, but this is mainly due to the fact that the Mg contribution is neglected due to the very small difference in scattering contrast. The influence of indium and tin seems negligible at room temperature. This is most likely due to the formation of Mg-Cu-vacancy complexes capturing and localizing vacancies before they can find an In or Sn atom just because of their vast majority compared to the trace element atoms. This could be in combination with a reduced solubility of the trace elements in the presence of Mg.

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Fig. 1 Scattering curves of Al-Cu and Al-Cu-Sn with the respective model fits.

Fig. 2 Hardening curves for Al-Cu(-In/Sn) and Al-Cu-Mg(-In/Sn) alloys during the early stages of natural ageing. The dashed line marks the additional measurement after 24 h of ageing.

Fig. 3 Cluster development during the first hours of natural ageing of the Al-Cu (left) and Al-Cu-Mg (right) alloy systems with and without trace additions of In and Sn: the top figures display the evolution of the cluster size ξ and on the bottom the excess Cu in the clusters is shown.

Fig. 4 DSC thermograms of the Al-Cu-(In,Sn) and Al-Cu-Mg-(In,Sn) aged at room temperature for the given times. The arrows mark the cluster dissolution in Al-Cu as well as the cluster formation in Al-Cu-Mg.

Fig.1
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