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# CHARACTERIZATION OF PRECIPITATES IN ALUMINUM BASED ALLOY AW 6016

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***Key words***: AW 6016 aluminium alloy, microstructure, TEM, 3DAP, micro-hardness

## Abstract

The aluminium based engineering alloy AW 6016 of nominal composition 98.44 Al - 0.45 Mg - 0.96 Si - 0.11 Fe - 0.034 Mn - 0.0054 Zn - 0.0038 Cr was investigated (all values are given in at. %). Heat treatment of solutionized and quenched alloys leads to an increase in hardness which is due to the formation of small precipitates of nano-meter scale size. Two complementary high resolution methods, namely transmission electron microscopy (TEM) and three - dimensional atom probe (3 DAP), are used for investigations of the precipitate evolution after annealing at 185°C and 235°C. At very early stages, i.e. after 5 min at 185°C, Mg-rich, Si-rich and Mg-Si co-clusters are observed. They are spherical and their diameter is between 1 and 3 nm. The number density of clusters as measured by 3 DAP is 9 x $10^{23}/m^3$. After ageing for 25 min and 90 min at 185°C GP zones and the needle-like β'' phase are formed. Both are rich in Mg and Si. The concentration ratio of Mg to Si of the precipitates is approximately 1. The number density of all precipitates after 90 min annealing time at 185°C is 6 x $10^{23}/m^3$. The needle-like β'' precipitates at this ageing stage are about 4 nm in diameter and longer than 10 nm.

The precipitates formed at 235°C after 10 min are much larger than compared to those at 185°C. They are rod-shaped and have an average size as measured by TEM, about 50 nm in length and 3-4 nm in cross-section. The concentration ratio between Mg and Si as measured by 3 DAP is about 1.

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## Introduction

The aluminium based engineering alloy AW 6016 is used as sheet material for car body applications due to its good mechanical properties, easy formability and its favourable corrosion behaviour. The strength of 6xxx series alloy is mainly caused by very fine precipitates, containing both Mg and Si, embedded in a solid solution matrix. Age hardening is very important for optimum alloy application. Precipitation formation and precipitation sequence [1-3], early stages of precipitate nucleation and their structure [1, 4-8], correlation between hardness and microstructure [1, 4], quantitative analyses of early stage precipitates and clusters [1, 6, 9] and precipitate evolution after isothermal heat treatment [10] have been investigated thoroughly during the past few years.

The generally accepted precipitation sequence in Al-Mg-Si alloys during heat treatment is:

Super saturated solid solution $\rightarrow$ atomic clusters $\rightarrow$ GP zones $\rightarrow$ β" $\rightarrow$ β' $\rightarrow$ β ($Mg_2Si$).

Evidence for the presence of Mg-, Si- and co-cluster of Mg and Si after solid solution and during aging at 70°C using atom probe field ion microscopy (APFIM) and three - dimensional atom probe (3 DAP) technique was reported by [1, 8, 9]. It was shown that the Mg:Si ratio for co-clusters and the β" phase is close to 1:1 for Si excess alloys [1, 9] while it is 2:1 [9] for balanced alloys. In the case of Si-excess alloys the amount of Si seems to play an important role for the composition of the precipitates.

The alloy used in this study is AW 6016 which is being used in car body applications [11]. A common problem with such alloys is that of limited shelf life: If these alloys are stored at room temperature for an extended time after quenching from solutionizing, the subsequent ageing leads to an increase of hardness which is much lower compared to ageing directly after quenching without any delay. By applying intermediate heat treatments after quenching one can minimize this effect. The exact reasons, however, for these phenomena are not yet known which is a future challenge for our work. In this work we intend to characterize the evolution of precipitates during ageing. In a first step we considered heat treatments without delays at room temperature in order to obtain information on undisturbed precipitation formation. The data of interest is the size, morphology and composition of precipitates emerging during ageing. The latter information is of paramount interest since only some years ago it was discovered that precipitates in Al-Mg-Si alloys have much higher silicon and aluminium contents than

previously assumed. Still, in the literature the data especially on the ratio Mg:Si is scarce and sometimes contradictory which calls for some additional studies.
The quantitative analysis of precipitates and their change in composition with annealing time were carried out by employing the 3 DAP method. This technique is especially effective in characterizing small precipitates in real space with near-atomic resolution [12, 13]. In addition to these investigations transmission electron microscopy (TEM) and hardness measurements were carried out.

## Experiment

The aluminium based alloy AW 6016 was supplied as sheet material of 1.2 mm thickness by Hydro Aluminium. The chemical composition of this alloy given in at. % is: 98.44 Al - 0.45 Mg - 0.96 Si - 0.11 Fe - 0.034 Mn - 0.0054 Zn - 0.0038 Cr. This alloy was solution treated at 540°C for 1 h and subsequently water quenched. The solution treated specimens were aged at various temperatures for different durations. Micro-hardness measurements were carried out on specimens annealed between 5 min and 74 h and between 120°C and 235°C. In order to observe the sequence of microstructural evolution, samples were investigated after ageing at 185°C for 5 min, 20 min, 90 min and at 235°C for 10 min. Microstructure was characterized by high resolution TEM in a Philips CM30 microscope operated with 300 kV. Thin foil suitable for TEM investigations were prepared by electrochemically jet polishing using $HNO_3$-$CH_3OH$ electrolyte. For microchemical analysis 3 DAP (TAP, CAMECA) was employed in the present study. 3 DAP specimens were first cut into rods of 0.2 x 0.2 x 10 $mm^3$. These samples were prepared by electrolytically polishing at room temperature with 7 V DC in a solution of $HNO_3$ in methanol. 3 DAP analysis was performed at a temperature of about 60 K with the fraction of pulse voltage to standing sample voltage of 0.2 and with a pulse penetration frequency of 1000 Hz.

## Results and discussion

Fig. 1 shows the micro-hardness evolution as a function of annealing time at different temperatures. The reference value for a non-annealed alloy is also given. The micro-

hardness curves show a peak after heat treatment at 185°C, 205°C, 225°C and 235°C. For higher temperatures the peak appears at shorter annealing times with smaller amplitude. For example the hardness maximum after annealing at 185°C was achieved after about 3 h whereas at 235°C the peak hardness was reached after 10 min already. This is the typical behavior observed in most alloys. As the macroscopic mechanical properties are correlated to the microscopically observed phases the microstructure of samples at 185°C and at 235°C was investigated in detail.

*Aging at 185°C*

Fig. 2 shows a typical atom probe mass spectrum obtained from an AW 6016 alloy using the linear detector. Aluminium atoms were mainly detected as $^{27}Al^{+}$ at 27 amu whereby the small amount of detected atoms can also be observed at 13.5 amu as $^{27}Al^{2+}$ and at 28 or 29 amu as $(AlH)^{+}$ and as $(AlH_2)^{+}$, respectively. Magnesium and silicon were detected as doubly charged ions. Both elements, Mg ($^{24}Mg^{2+}$, $^{25}Mg^{2+}$, $^{26}Mg^{2+}$) - and Si ($^{28}Si^{2+}$, $^{29}Si^{2+}$, $^{30}Si^{2+}$)- isotopes in the region between 12 and 16 amu can clearly be separated in this mass spectrum. Iron atom distributions could not be determined because of the peak overlap between $Fe^{2+}$ (main isotope of Fe), $Si^{+}$ and $(AlH)^{+}$ ions at 28 amu. No manganese ions ($Mn^{2+}$ at 27.5 amu) could be resolved because of the overlap with the $^{27}Al^{+}$ peak. Due to the very small amount of chromium and zinc in the alloy, they were not taken into consideration for this work. The average composition of Mg and Si as derived from the complete data set involving 1,8 x $10^6$ atoms is given in Table 1, where the quoted errors represent 2σ standard deviation. These measurements are in agreement within the error limits with those of the nominal composition as can be seen in Table 1. Therefore, concentrations of Mg and Si given in the following were calculated from double charged ions only.

Fig. 3 shows a 3 - dimensional reconstruction of a) Mg-rich and b)Si-rich small particle positions within the analysed volume of 6 x 6 x 62 $nm^3$ using a cluster-search module developed by the FIM grope in Rouen [14]. This figure represents only a part of the complete experimental data involving 5 x $10^5$ ions of specimen annealed at 185°C for 5 min. The particle information is estimated from a very small volume (average number of detected atoms in the particle was ~ 120) with a radius of about 1.0 nm. The Mg-rich particles shown in Fig. 3a have Mg concentrations ≥ 3.5 at.%. The average chemical

composition of these particles has been determined 5.1 ± 1.7 at.% Mg and 1.5 ± 0.9 at.% Si. In addition, some Mg particles free of Si were also observed. Their average Mg concentration is about 6.7 at.%. The Si-rich particles shown in Fig. 3b have Si concentrations ≥ 4 at.%. They contain 6.5 ± 2.2 at.% Si and 2.2 ± 1.3 at.% Mg, whereas Si particles (Mg free) contain about 9 at.% of Si. We therefore find four types of clusters: pure Mg- and Si clusters and co-clusters of Mg and Si with a ratio Mg:Si of either 1:3 or 3:1. The number density of all particles at this ageing state as measured by 3DAP is 9 x $10^{23}/m^3$. The size of such particles is very small (1- 3 nm diameter) which is in agreement with measurements by neutron small angle scattering (SANS) [10]. Their shape could be considered spherical. The small increase in micro-hardness from ~ 55 after quenching to ~ 65 after ageing at 185°C for 5 min indicates a small change in the microstructure which results in the formation of small particles. Because of their composition they are most probably clusters important for nucleation of subsequent phases, i.e. precipitates such as GP zones.

The very early stages of precipitating have been discussed in the literature [1, 2, 8]. Formation of Mg-rich, Si-rich and of co-clusters was found in the specimens after long time natural ageing [2, 8] or in specimens after ageing at 70°C for 8 h and 60 h [1]. Some regions with significantly higher Mg concentration than the average concentration of the alloy were also found in as-quenched alloys, which was attributed to Mg clusters [2]. The ratio of Mg:Si in co-clusters was found to be 1:1 in the literature [1, 2, 8], which is in contradiction to our measurements which yield Mg:Si = 3 or Si:Mg = 3.

Fig. 4 shows 3 - dimensional reconstruction of Mg and Si atom positions in an investigated volume 5.5 x 5.5 x 198 $nm^3$ of an AW 6016 specimen aged at 185°C for 25 min. Regions enriched in Mg and Si are clearly visible in this volume which is only a part of complete measurement extending over 1.6 μm (1.8 x $10^6$ atoms). Using the same cluster-search procedure as above with a concentration threshold of Mg ≥ 6 at. % the average amount of Mg and Si in the particles was estimated to be 14.8 ± 6 at.% and 12.6 ± 4.6 at.%, respectively. The atomic ratio of Mg:Si in these particles therefore is about 1:1. Comparing Fig. 3 and Fig. 4, it is evident that the morphology and the size of particles have changed during heat treatment. Some particles have an elongated morphology. The structure of the fine precipitates formed during early stages of ageing were observed by several authors [1, 7-9]. Such fine precipitates were designated as GP zones and as β'' phase.

Fig. 5 shows a TEM bright field image and the corresponding selected area electron diffraction (SAED) pattern obtained from the AW 6016 alloy aged for 90 min at 185°C. This aging stage produces a microstructure which corresponds to a state close to peak hardness, see Fig. 1. A dark contrast arising from the fine needle-like precipitates imaged along their axis which are homogeneously distributed in the Al matrix is observed in Fig. 5. The [001] SAED image of the aluminium matrix shows additional diffuse features which are generated by the precipitates. The high resolution TEM (HRTEM) image of one precipitate embedded in the matrix is shown in Fig. 5b. Its cross-sectional diameter lies between 2.5 and 3.5 nm.

Fig. 6a shows a 3 - dimensional reconstruction of Mg atom positions in an investigated volume of 10 x 10 x 247 $nm^3$ in a sample annealed at 185°C for 90 min. The presence of several areas enriched in Mg is evident from the elemental map. The same areas are also enriched in Si, but this is not shown in the figure. The shape of the Mg enriched zones can be observed by rotating the region of interest. In Fig. 6b one part of the same investigated volume is presented with four precipitates in two different orientations. One of them is a needle-like β'' precipitate, about 10 nm long and ~ 4 nm in diameter. The morphology of the other Mg-rich areas cannot be determined because they are intercepted by the boundary of the measurement volume. Therefore, they could be GP zones or β'' phases. The particle density of β'' phase and GP zones as measured by 3 DAP in the present work is 6 x $10^{23}/m^3$. The needle-like precipitates β'' contain 14.2 ± 1.8 at.% Mg and 13.3 ± 1.8 at.% Si when a Mg concentration ≥ 8 at. % is used for the cluster-search calculation. The atomic ratio of Mg to Si therefore is approximately 1. A significant increase in micro-hardness after this ageing proves the role of the β'' phase. It is widely accepted that the β'' phase is the most effective age-hardening phase [15, 16]. Precipitates with similar compositions of Mg and Si were also observed in an alloy with Si excess aged at 70°C for 16 h [8].

*Aging at 235°C*

A bright field TEM image of the typical microstructure of AW 6016 alloy annealed at 235°C for 10 min (close to peak hardness) is shown in Fig. 7a. The rod-shaped precipitates with a cross-section of about 3 x 4 $nm^2$ and about 50 nm in length are homogeneously distributed in the matrix. A high resolution image of one of the precipitates in the cross-section is presented in Fig 7b. The elongated precipitates are

always aligned to one of the <100> Al directions. The [001] SAED pattern obtained from this image is shown in the inset of Fig. 7a. The microstructure formed at this aging stage is responsible for peak hardness. The presence of at least two different kinds of precipitates is also supported by small angle neutron scattering (SANS) measurements [10] for an equivalent sample aged under the same conditions. One kind of precipitate is spherical with about 4 nm in diameter [10]. The calculation of the size of the other type is in progress.

Figs. 8(a) and (b) show 3 DAP elemental maps of Mg and Si atoms obtained from the specimen aged at 235°C for 10 min. Five areas enriched in Mg and Si are marked in these maps. The rod-shaped precipitate with a cross-section of about 2 x 3 $nm^2$ (see Fig. 8c Mg and Si maps) and a length of minimum 46 nm is entirely visible, whereas the other four precipitates are truncated by the boundary of the given volume of interest. Precipitates contain ~17 at.% Mg and ~19 at.% Si. These results are in good agreement with recent observations of comparable alloys with Si-excess [4, 9].

The experimental data measured in this work are summarized in Table 2.

## Conclusions

- It was found that 3 DAP yields reliable values for the content of Mg and Si in the precipitates.
- Heat treatment of solutionized and quenched AW 6016 alloys at 185°C for 5 min leads to the formation of various types of nm-sized spherical clusters: pure Mg, pure Si and co-clusters of Mg and Si with both ratios 1:3 and 3:1 (previously not observed).
- After 25 min and even more after 90 min at 185°C elongated and needle-shaped precipitates ( GP zones and β'') are formed in which the Mg:Si ratio is ~ 1.
- Heat treatment at 235°C produces very long rod-shaped precipitates (~ 50 nm ) with a cross-section of 3 x 4 $nm^2$ which contain the same amount of Mg and Si.

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## References

1. G.A. Edwards, K. Stiller, G.L. Dunlop and M. Couper, Acta Mater. 46, (1998) 3893

2. M. Murayama, K. Hono, M. Saga and M. Kikuchi, Mater. Sci. and Eng. A250 (1998) 127

3. L. Zhen, W.D. Fei, S.B. Kang and H.W Kim, J. Mater. Sci. 32 (1997) 1895

4. C.D. Marioara, S.J. Andersen, J. Jansen and H.W. Zandbergen, Acta Mater. 49 (2001) 321

5. P. Donnadieu, M. Roux-Michollet and V. Chastagnier, Phil. Mag. A 79, (1999) 1347

6. J.P. Lynch, L.M. Brown and M.H. Jacobs, Acta Metall. 301 (1982) 389

7. P. Donnadieu, F.Carsughi, A. Redjaimia, C. Diot and G. Lapasset, J. Appl. Cryst. 31 (1998) 212

8. A. Morley, MEng thesis, University of Oxford, 2004

9. M. Murayama, and K. Hono, Acta Mater. 47 (1999) 1537

10. R. Schiffmann, J. Haug, J. Banhart, Proceedings of the 9th Int. Conf. on Al alloys (2004), Ed.: J.F. Nie, A.J. Morton and B.C. Muddle, 604

11. Vom Werkstoff zum Bauteilsystem H. Kaufmann, A. Wahlen, P.J. Uggowitzer, ISBN 3902092017, LKR-Verlag, 2002

12. A. Cerezo, T.J. Godfrey and G.D.W. Smith, Rev. Scient. Instrum. 59 (1988), 862

13. D. Blavette, B. Deconihout, A. Bostel, J.M. Sarrau, M. Bouet and A. Menand, Rev. Scient. Instrum. 64 (1993) 2911

14. X. Sauvage, G. Dacosta and R.Z. Valiev, Proceedings of Ultrafine Grained Materials III, TMS 2004 Annual Meeting, Ed.: Y.T. Zhu, T.G. Langdon, R.Z. Valiev, S.L. Semiatin, D.H. Shin and T.C. Lowe, 31

15. M. Takeda, F. Ohkubo, T. Shirai, K. Fukui, J. Mat. Sci. 33 (1998) 2385

16. L. Zhen and S.B. Kang, Mat. Sci. & Tech. 14 (1998) 317

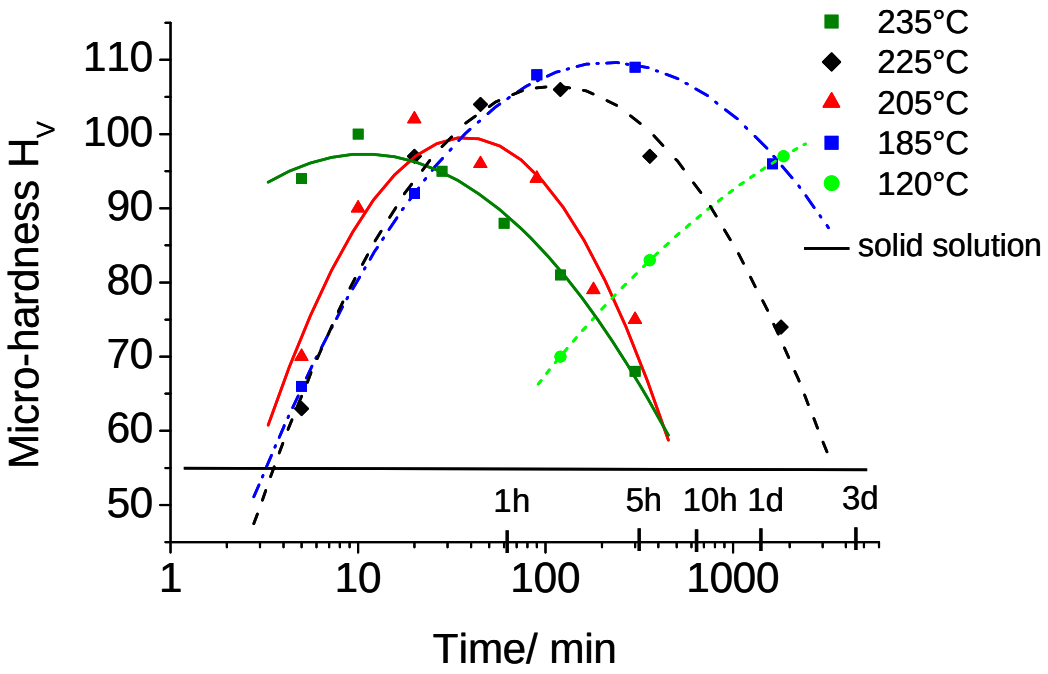



**Fig. 1.** Vickers hardness as a function of isothermal annealing time at various temperatures. The micro-hardness of the solid solution (solutionized and quenched only) is indicated as a horizontal line.

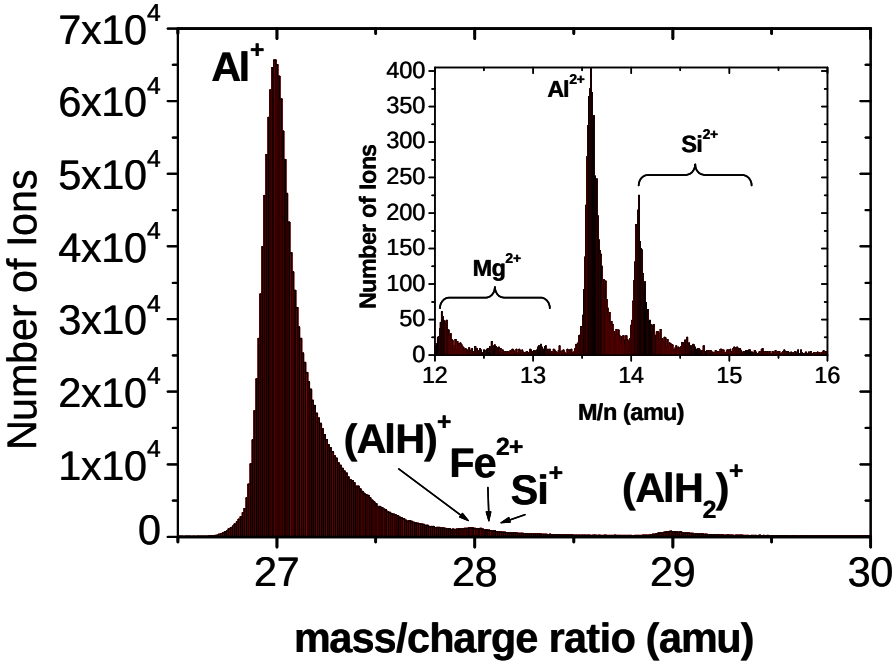



**Fig. 2.** Atom probe mass spectrum obtained from an AW 6016 alloy using the linear detector.

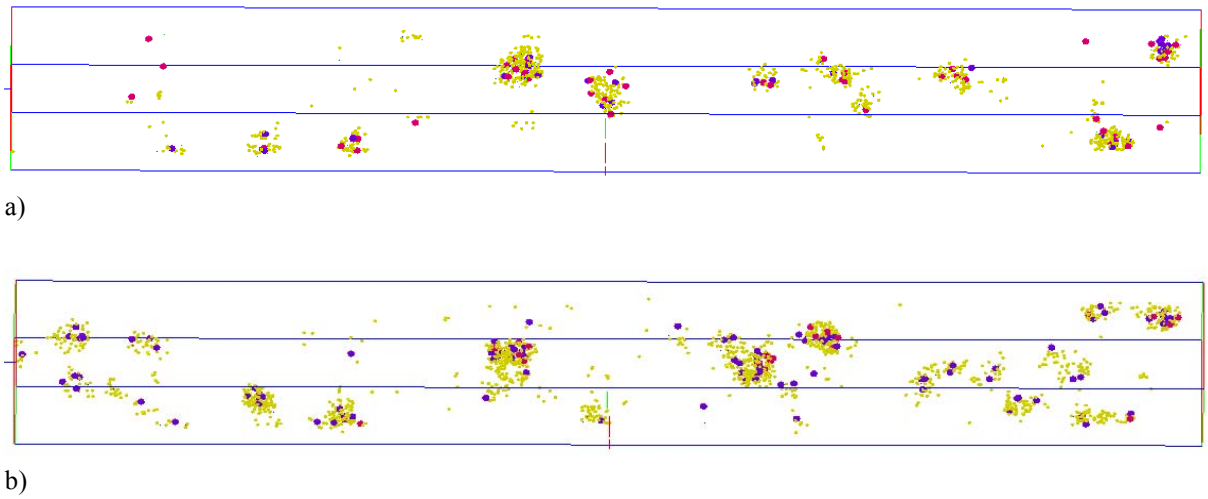



**Fig. 3.** 3 - dimensional reconstruction of a) Mg-rich and b)Si-rich clusters within the analysed volume of 6 x 6 x 62 $nm^3$ obtained from the specimen aged at 185°C for 5 min using a cluster-search module. Threshold for Mg clusters > 3.5 at.%, for Si clusters > 4 at.%.

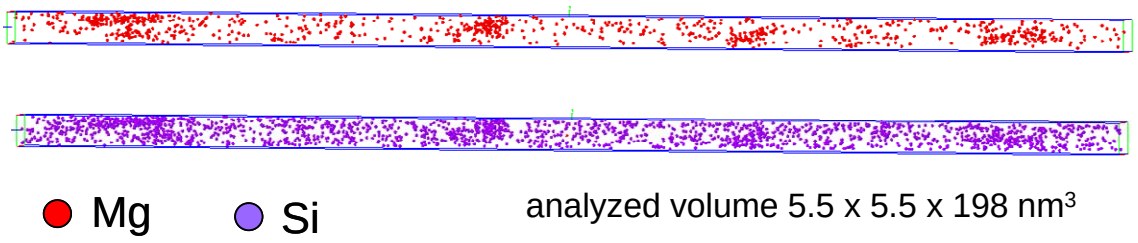



**Fig. 4.** 3 - dimensional reconstruction of Mg and Si atom positions in an investigated volume 5.5 x 5.5 x 197 $nm^3$ of a specimen aged at 185°C for 25 min.

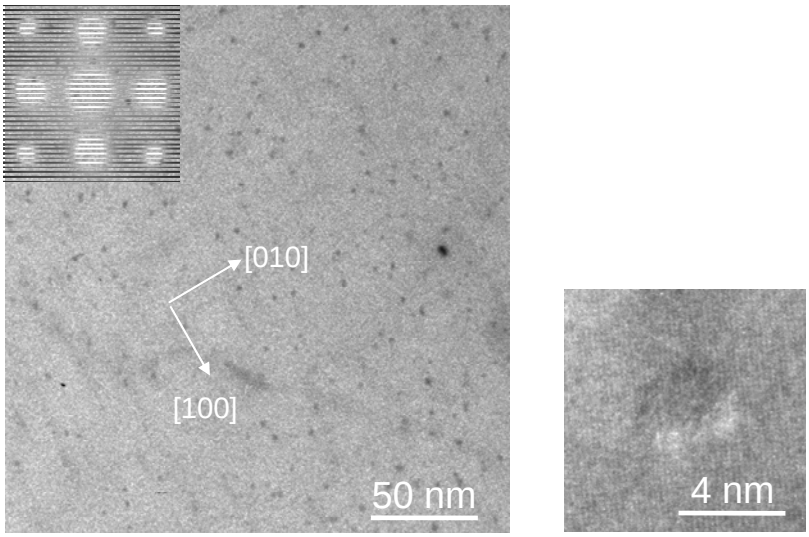



**Fig. 5.** a) TEM bright field image and selected area electron diffraction patterns for the specimen aged at 185°C for 90 min, b) high resolution image of one typical precipitate in the cross-section.

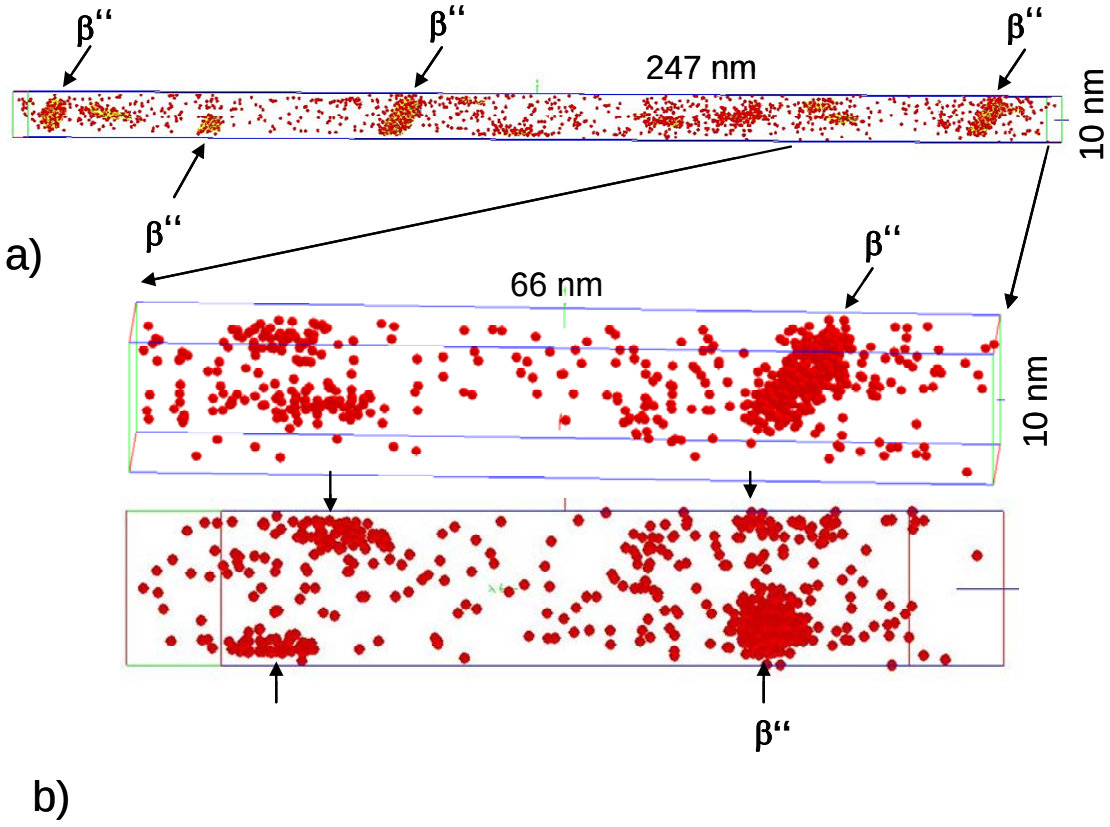
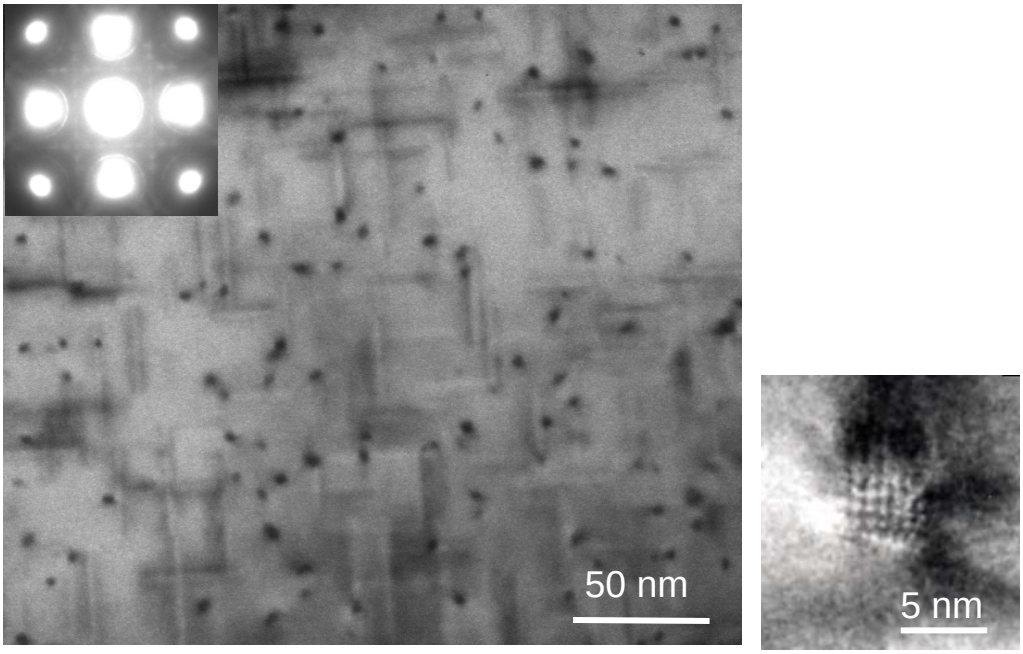



**Fig. 6**. 3 - dimensional reconstructed positions of Mg atoms (a) obtained from the specimen aged at 185°C for 90 min. The investigated volume is 10.8 x 10.8 x 247 $nm^3$. In order to observe the morphology of the particles, one part of the same investigated volume with four precipitates is presented in two different directions b).




**a)** **b)**

**Fig. 7.** TEM bright field image and selected area electron diffraction patterns for the specimen aged at 235°C for 10 min a), high resolution image of one of the precipitates in the cross-section b).

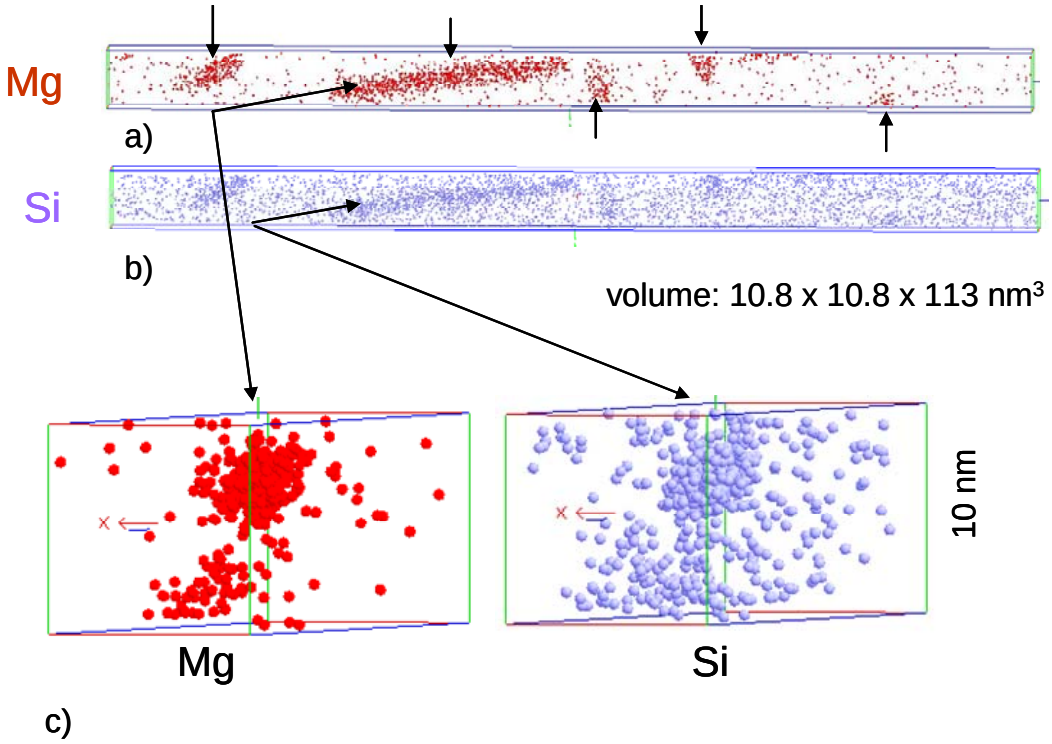



**Fig. 8.** 3 - dimensional reconstructed positions of Mg- (a) and Si atoms (b) obtained from the specimen aged at 235°C for 10 min. The investigated volume is 10.8 x 10.8 x 113 $nm^3$. The large precipitate shown in Fig. 8 a) and b) can be observed in the cross-section by Mg and Si maps in c).

**Table 1**

The calculated concentrations of Mg and Si of an AW 6016 specimen annealed at 185°C for 25 min as determined from the double charged ions only. The complete measurement involves a total of about 1,8 x $10^6$ atoms. The nominal composition of AW 6016 alloy is listed as well.

| | Al | Si | Mg | Fe | Mn | Cr | Zn |
|---|---|---|---|---|---|---|---|
| nom. comp. | balance | 0.96 | 0.45 | 0.11 | 0.034 | 0.0038 | 0.0054 |
| experiment | balance | 1.0±0.02 | 0.44±0.01 | | | | |

**Table 2**

Microstructural data obtained from an AW 6016 alloy after various heat treatments

| T / t | shape / size | |
|---|---|---|
| 185°C/5 min | spherical Ø1-3 nm | clusters: Mg-, Si-pure;<br>co-clusters Mg-Si, Mg:Si ≅ 1:3, 3:1 |
| /25 min | elongated | Mg/Si ≅ 1 |
| /90 min | needles / 3 DAP: Ø 4nm,<br>l > 10 nm<br>TEM: Ø 2.5 – 3.5 nm | Mg/Si ≅ 1 |
| 235°C/10 min | rods 3 DAP: 2 x 3 x 46 $nm^3$<br>TEM: 3 x 4 x 50 $nm^3$ | Mg/Si ≅ 1 |