

Influence of Pre-straining and Pre-ageing on the Age-hardening Response of Al-Mg-Si Alloys

Yong Yan^{1,a*}, Zeqin Liang^{1,b} and John Banhart^{1,2,c}

¹ Helmholtz-Centre Berlin, Hahn-Meitner-Platz 1, Berlin, 14109, Germany

² Technische Universität Berlin, Hardenbergstr. 36, Berlin, 10623, Germany

^ayong.yan@helmholtz-berlin.de, ^bzeqing.liang@novelis.com, ^cjohn.banhart@tu-berlin.de

Keywords: Al-Mg-Si, pre-ageing, pre-straining, negative effect

Abstract. The effect of pre-straining (PS) and pre-ageing (PA) on the age hardening response of Al-0.6 wt.%Mg-0.8 wt.%Si alloy is studied by Vickers hardness measurement and differential scanning calorimetry (DSC). It is found that PA can suppress the formation of undesired clusters and keeps the structure stable for a certain period. A PA treatment can effectively reduce or avoid the negative effect of natural ageing on artificial ageing and even produce a positive effect. Cluster formation can also be reduced by PS, but the kinetics of clustering is still similar to that of the as-quenched condition. In contrast, after PS, the peak positions of β'' and β' move to lower temperatures and peak hardness is achieved in a shorter time, indicating that the formation of β'' and β' is accelerated by PS. However, the negative effect of natural ageing still persists after PS. PS before PA can take advantage of both techniques and produce a positive strength response. PS after PA tends to destabilize the structure created by PA and can reactivate the clustering process, which has a negative effect on subsequent artificial ageing.

Introduction

Most technologically important 6XXX (Al-Mg-Si-based) alloys suffer from the negative effect of natural pre-ageing (NA) after quenching on subsequent artificial ageing (AA). It is known that pre-ageing can alleviate the effect. Moreover, pre-straining can also be beneficial. We study the effects of pre-ageing and pre-straining on the AA response of a pure ternary Al-Mg-Si alloy both individually and in two combinations. A pre-ageing treatment shorter than usually used in practice is chosen in order to be able to investigate the failure of the treatment after extended natural ageing.

Experimental

The alloy employed is pure Al-0.6 wt.%Mg-0.8 wt.%Si and has been used and described in previous studies [1]. It is solutionised at 540 °C for 1 h and quenched into iced water. DSC is carried out in a Netzsch 204 Phoenix F1. Micro(Vickers)hardness is measured applying a load of 1 N for 10 s.

Results and Discussion

The effects of pre-ageing (PA) or pre-straining (PS). The evolution of hardness during NA at 20 °C directly after quenching (Q), after Q+PA and after Q+PS is given in Fig. 1(a). NA directly after quenching (black) gives rise to a continuous hardness increase with a decreasing rate. 10 min of PA directly after quenching (blue) increases hardness by ~7 HV and introduces an incubation time of ~1 d, during which the hardness remains constant, but after which it increases throughout the following 70 d of NA. Pre-straining increases hardness by 15 HV, after which it increases slowly without an incubation time (red).

If the samples are AA after quenching, PA or PS, the hardness evolves as shown in Fig. 1(b). The solid black line (direct AA after Q) serves as a reference line. After PA for 10 min at 140 °C prior to AA (solid blue) the hardness starts from a higher level but merges into the course of the

directly aged sample after 20 min. The pre-strained sample (solid red) also starts from a higher level and its hardness evolves fast up to 30 min, after which hardening slows down and the peak hardness is reached after just 2 h, at a level much lower than for the other two treatments.

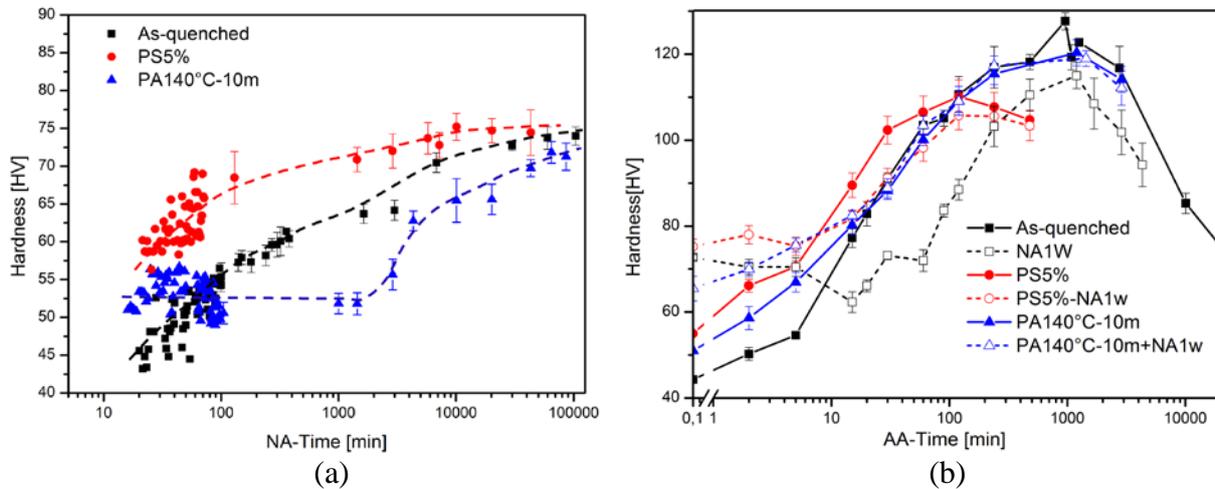


Fig. 1. (a) NA hardness evolution after quenching (Q), after Q and pre-ageing (PA) at 140 °C for 10 min and after Q and pre-straining (PS) by 5%. Hardness values for short times < 100 min are individual measurements, otherwise averages of 10 measurements. (b) AA hardness evolution for the three conditions in (a), each also with an additional week of NA before AA (broken lines).

To study the negative effect of NA, the samples are stored at 20 °C for 1 week before AA. Fig. 1(b) shows that this has a very strong negative effect if done directly after quenching (broken black line). The hardness increases to 72 HV during NA, but reverts to 61 HV after. The subsequent re-increase is rather sluggish (note logarithmic time scale). In contrast, PA for 10 min at 140 °C prevents this effect (broken blue). Hardness, which has increased to 65 HV during PA, continues to increase during AA. Especially the important paint bake hardness after 20–30 min of AA is the same as for the sample without NA. PS, however, cannot prevent the negative effect (broken red). After hardness has increased to 75 HV during NA, there is a stage of sluggishness and the peak hardness reached is even lower than for the sample aged directly after PS.

Fig. 2 shows thermograms for all the 6 cases displayed in Fig. 1(b). The as-quenched sample (a, full) shows the usual features detected in such alloys [2], namely a clustering double-peak (1), the formation of zones (2), a dissolution trough (7), a pre- β'' reaction (3), precipitation of the main hardening phase β'' (4), the formation of β' (5) and the formation of β (6). NA before DSC (a, broken) eliminates most of peak 1 because the associated clusters have formed already before DSC [2, 3]. This also causes the hardness increase in Fig. 1(a). Instead, the dissolution trough 7 is much more pronounced, indicating that at least some of the clusters formed before DSC are not stable and dissolve, whereas the clusters formed during the DSC run (full line) dissolve only to a small part. The strong hardness decrease within the first 15 min of AA, see Fig. 1(b), also points at a pronounced dissolution of clusters after 1 week of NA. The pre- β'' peak is still there, but the β'' -peak is shifted to a higher temperature and has become higher.

After 10 min of PA (c, full), no clusters exist prior to DSC or form during DSC as there is neither a peak 1 nor a dissolution trough 7. PA produces a microstructure that is stable at low temperatures at least temporarily, as the extended incubation time for NA in Fig. 1(a) shows. A broad exothermic reaction ranges from 130 °C to a peak at 228 °C, indicating an enhanced pre- β'' precipitation reaction. Precipitation of β'' is observed at a lower temperature than without PA. If the sample is NA for 1 week between PA and DSC (c, broken), the effect of PA is partially reversed. The pre- β'' peak has disappeared and β'' has moved to a higher temperature again. Instead, a small and broad precipitation peak centered around 130 °C has appeared. A dissolution trough of clusters is observed, indicating that clusters formed during NA dissolve during DSC. However, there is no hardness decrease in the first 20 min of AA, just a lower hardening rate compared to PA without

NA, see Fig. 1(b). This means that PA removes the negative effect of NA caused by cluster dissolution taking place during AA.

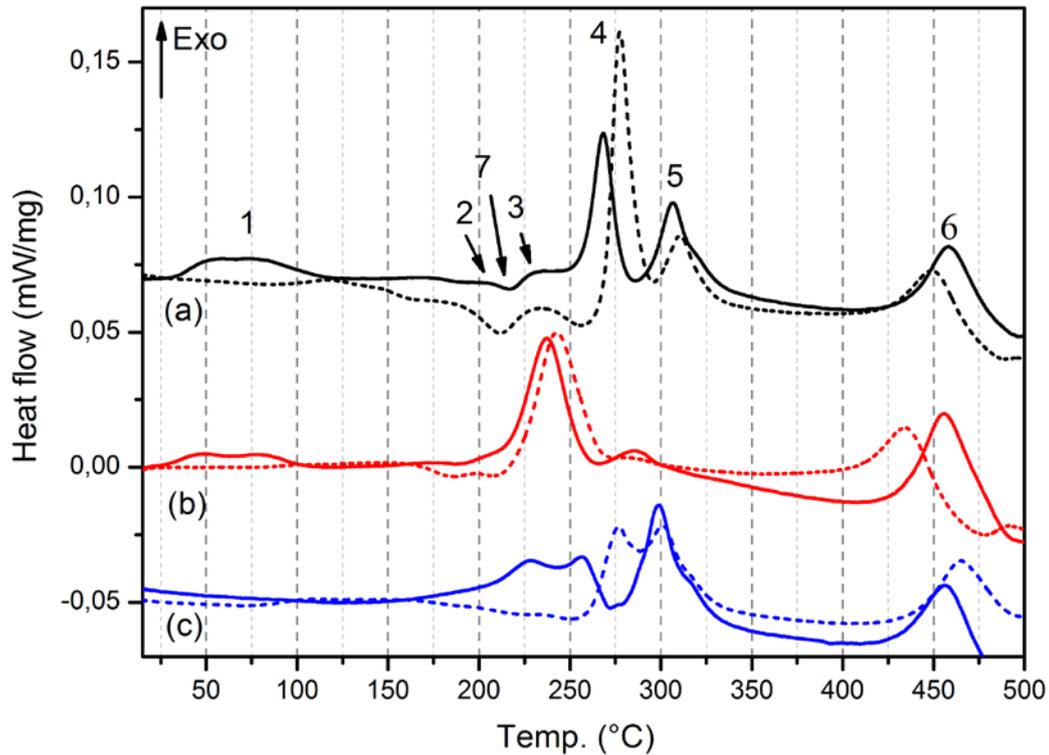


Fig. 2. DSC thermograms at a heating rate of 10 K/min for: (a) the as-quenched condition (b) after pre-straining by 5%, (c) after pre-ageing at 140 °C for 10 min. Each sample is measured without (full line) and with 1 week of NA (broken) before the DSC measurement. The offset of the curves in (a) and (c) is 0.07 and -0.05 W/g, resp.

Pre-straining (Fig. 2(b), full) reduces the height of the cluster peak 1 by about 40%. The partial suppression of clustering might be either due to a lowering of vacancy concentration during straining as vacancies annihilate in the newly generated dislocations or by premature clustering induced by rolling. Corresponding to this partial suppression of clustering, the increase of hardness during NA after PS is just 16 HV, compared to 28 HV increase without PS, see Fig. 1(a). The corresponding dissolution trough is hardly visible since it overlaps with an exothermic feature, which appears as a pre- β'' reaction and has moved down in temperature to ~ 170 °C. This early onset explains the fast AA hardening in Fig. 1(b), which, however, slows down after 30 min. The reason for faster AA after PS can be either the easier nucleation of precipitates at dislocations and the faster supply of solute atoms to the growing precipitates by pipe diffusion [4], or the higher solute supersaturation of the matrix caused by the faster annihilation of vacancies and the associated reduction of cluster formation. It has been reported that after PS, β' is precipitated instead of β'' [5] and, indeed, the original β' peak 5 has become very small, so that peak 4 might contain a mixed β'' and β' reaction. If the sample is NA for 1 week between PS and DSC (b, broken), the DSC trace shows no clustering peak but a pronounced dissolution trough of the clusters formed during 1 week of NA. Correspondingly, during AA ageing, see Fig. 1(b), a stage of stagnant hardness is observed for the first 5 min. The formation of clusters is related to the hardness increase, see Fig. 1(a), which after 1 week has reached a maximum. The β'' -peak is higher in temperature than in the sample pre-strained only, indicating a delayed formation of the strengthening phase. Still, a slightly negative effect of 1 week of NA is observed, see Fig. 1(b), although smaller than for the samples neither exposed to PS nor to PA.

The combination of pre-ageing (PA) and pre-straining (PS). Fig. 3 (a) displays the NA hardness response of quenched samples that have been exposed to both PA and PS, not just to one treatment as in Fig. 1(a). Combined PS and PA lead to an initial hardness of 62 or 65 HV, depending on the order, see Fig. 3(a), which is in both cases higher than for PA or PS alone, see Fig. 1(a). PS after PA leads to the higher hardness throughout subsequent NA. In both cases, an incubation time for the NA hardness increase is observed that is inherited from the PA step since PS alone does not show it, see Fig. 1(b). PS after PA markedly shortens this incubation period.

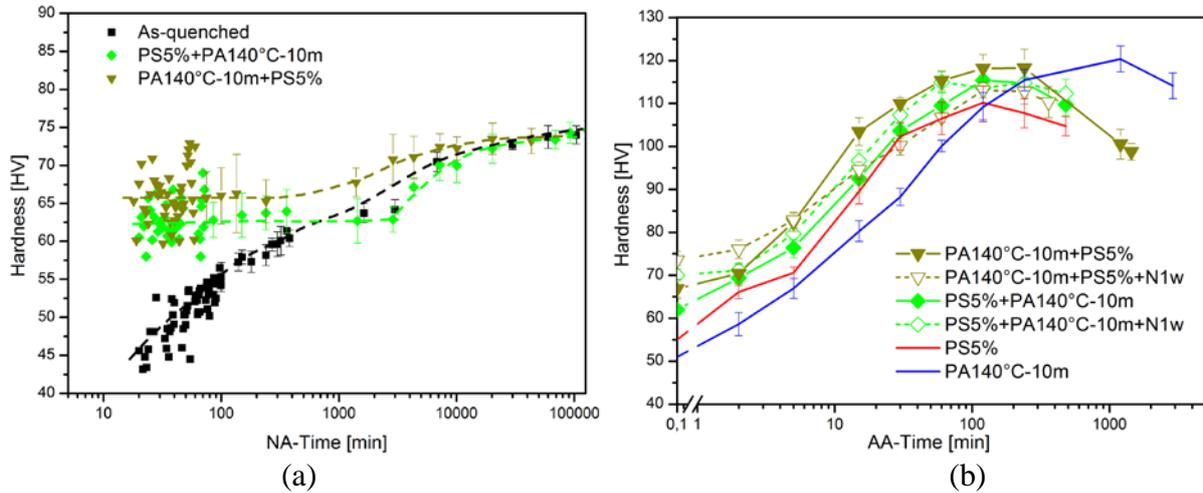


Fig. 3. (a) NA hardness evolution for specimens exposed to pre-ageing at 140 °C for 10 min and pre-straining by 5% in both orders. Individual hardness values are given for short times, for $t > 100$ min averages of 10 measurements. (b) AA hardness evolution for PS+PA and PA+PS, each with and without 1 week of NA before AA. Curves for PA and PS only are taken from Fig. 1(b).

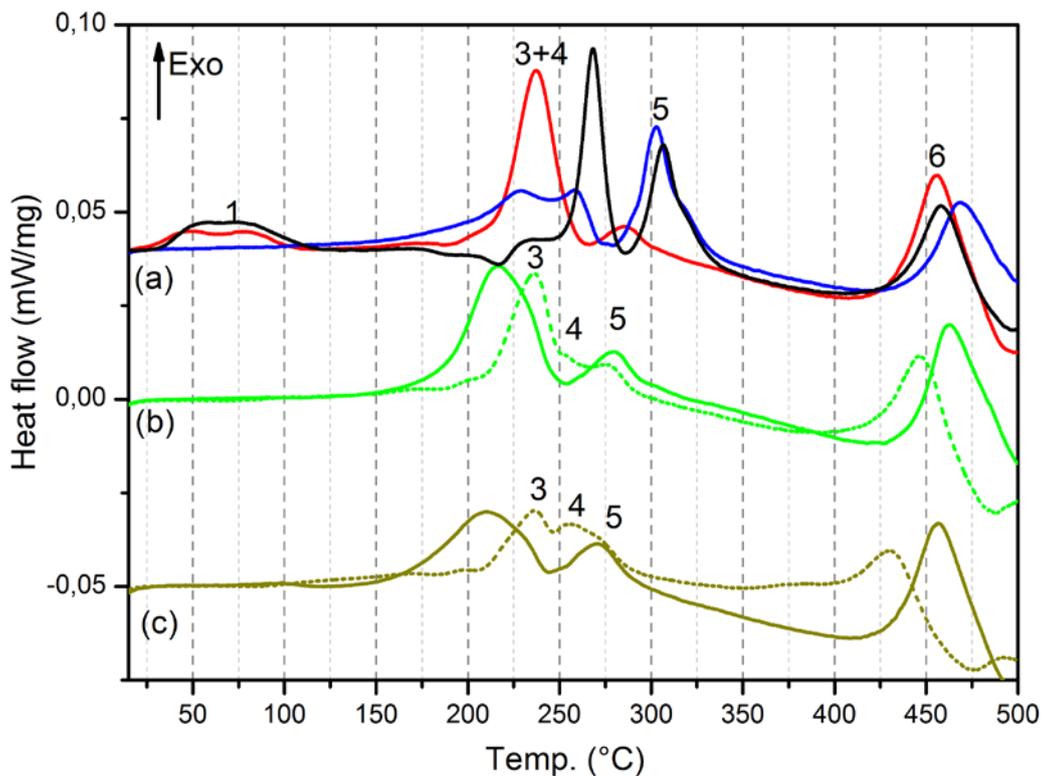


Fig. 4. DSC thermograms at a heating rate of 10 K/min for combined treatments of pre-straining (PS) and pre-ageing (PA): (b) PS by 5% + PA at 140 °C for 10 min, (c) PA at 140 °C for 10 min + PS by 5%. Each sample is measured without (full line) and with 1 week of NA (broken) before the DSC measurement. (a) reproduced from Fig. 2 for comparison: As-quenched (black), PS only (red), PA only (blue), all without NA. The offset of the curves in (a) and (c) is 0.04 and -0.05 W/g, resp.

AA after combined PA and PS, see Fig. 3(b), gives rise to continuously rising hardnesses (full green and olive lines) which are higher than those of the individual pre-treatments alone (red, blue). If PS is after PA the hardness remains higher than for the opposite order throughout ageing. In both cases the hardness maximum is reached after 2 to 4 h, i.e., the hardening kinetics are dominated by PS and not by PA since for PA alone it takes 1 d to reach peak hardness (Fig. 3(b), blue line). NA before AA for 1 week increases the initial hardness by the values given in Fig. 3(a), but during subsequent AA the order of PA and PS plays an important role: For PS after PA there is a cross-over of the curves with and without NA after 5 min of AA – i.e. NA has a negative effect on AA. For PA after PS, the hardness of the sample with 1 week of NA before AA remains above the sample without such treatment and also reaches peak hardness slightly faster than without NA – i.e. NA before AA has a slight positive effect on AA. This finding is in accordance to [6]. The maximum of the ageing curve is achieved after 2 h, again dominated by the acceleration of kinetics by PS.

Fig. 4 shows thermograms for all the four cases displayed in Fig. 3(b). Fig. 5 shows magnifications of the cluster formation regime for the two combinations of PA and PS and various NA times before AA. PS after PA (Fig. 4(c), full line) gives rise to a very small clustering event at $\sim 100^\circ\text{C}$, see left arrow in Fig. 5(a). The reason might be that PS shears the clusters formed during PA and the fragments facilitate clustering during DSC. Other changes are the shift of both β'' and β' to lower temperatures. β'' precipitation now peaks at 209°C , which is much lower than for PA or PS only and the peak is so broad that it may also include some signal from GP zone and pre- β'' formation. If there is 1 week of NA prior to DSC (Fig. 4(c), broken line) the low-lying peak moves to a higher temperature again and splits into three subpeaks that can be assigned to pre- β'' , β'' and β' formation. In the temperature region around 100°C one observes a peak if NA for 1 d, see broken cyan line in Fig. 5(a), but after NA for 1 week this peak has gone. This implies that during NA the sheared fragments first grow to a size at which they are efficient nuclei for cluster formation during DSC, but that for even longer NA this cluster growth takes place already before DSC so that no clustering is observed during DSC any more. Instead, some precipitation in the range $120\text{--}170^\circ\text{C}$ is observed. In addition, cluster dissolution is present, but superimposed with the precipitation signal at $\sim 180^\circ\text{C}$, see right arrow in Fig. 5(b). This results in slower hardening during AA and to the observed negative strength response (Fig. 3(b), olive lines).

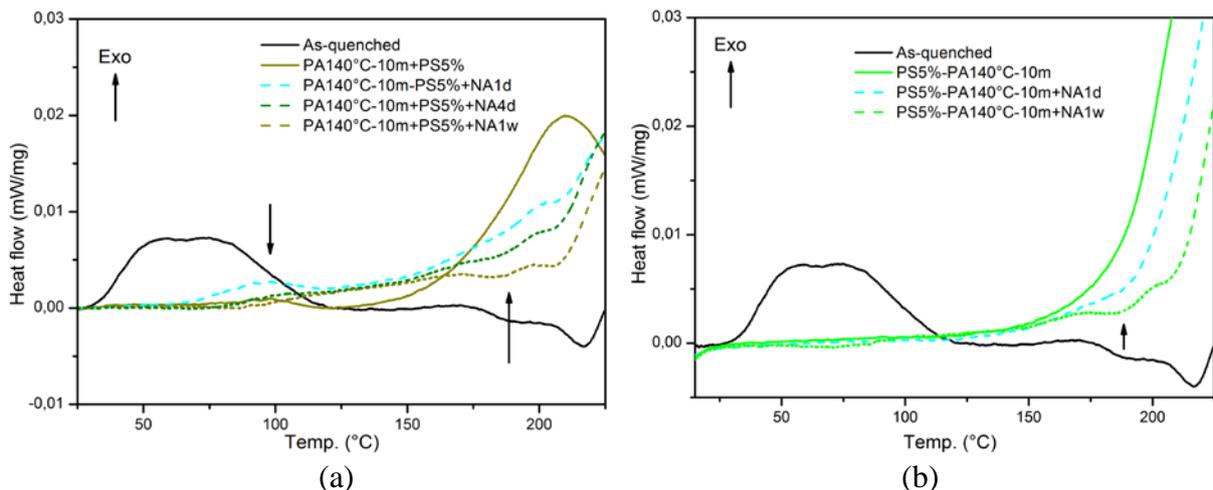


Fig. 5. DSC thermograms at a heating rate of 10 K/min for combined treatments of pre-straining (PS) and pre-aging (PA) and various NA times before AA: (a) PS by 5% + PA at 140°C for 10 min, (b) PA at 140°C for 10 min + PS by 5%. A temperature range in which cluster formation and dissolution takes place has been selected for this figure.

PA after PS (Fig. 4(b), full line) eliminates the cluster peak and the corresponding dissolution trough that would have been visible for PS only (Fig. 2(b), broken line). We have seen that PA alone produces a microstructure that is stable at low temperatures and PS+PA also does this, see the long stage of constant hardness in Fig. 3(a), green line. The effect of pre-treatment is very similar

for the two cases PA+PS and PS+PA, concerning peak positions, but the low lying precipitation peak comprising a superposition of GP zones, pre- β'' and β'' formation is larger for PS+PA. If there is NA prior to DSC, unlike PA+PS, no cluster peak is observed for PS+PA, see Fig. 5(b). It is possible that a cluster peak would have been detected between ~2 d – end of constant stage in Fig. 3(a) – and 1 week, but no measurements are available. The formation of clusters is responsible for the hardness increase during NA, see Fig. 3(a). For 1 week of NA, see Fig. 4(b), broken line, the low lying precipitation peak moves to a higher temperature and narrows. Moreover, it splits into three peaks with two small satellites around 210 °C and 260 °C. In addition, a small signal of dissolution can be observed, see arrow in Fig. 5(b). This results in a short plateau in the initial first 2 min of AA in Fig. 3(b) (green dashed line) and retards β'' precipitation in the matrix, see Fig. 4(b), peak 4. However, due to the higher supersaturation in the matrix, some large clusters formed during NA tend to grow during AA. Therefore, hardness remains higher throughout AA longer than 2 min, see broken green line in Fig. 3(b). AA hardness is unaffected by the dissolution of clusters and shows a higher value compared to that of PS+PA without NA before AA. Thus, the negative effect of NA has been eliminated, see broken green line in Fig. 3(b).

Summary

Different pre-treatments including pre-ageing for 10 min at 140 °C (PA), pre-straining by 5% (PS) and combinations of the two in both orders were applied to a Al-0.6 wt.%Mg-0.8wt.% Si alloy and the influence of such treatments on subsequent natural ageing (NA), artificial ageing (AA) and DSC scans studied. It was found that

- AA directly after quenching gives rise to a strong hardening effect, but NA before AA causes the well-known “negative effect” of natural ageing.
- PA leads to a state that is stable at 20 °C for 1 d, during which cluster formation is suppressed. NA sets in after but has no immediate negative effect on subsequent AA that peaks after 1 day.
- PS increases the hardness level during AA, but after 30 min, the hardening rate sharply decreases and peak hardness is reached already after 2 h but at a lower level than after PA.
- Combinations of PA and PS inherit the fast hardening to a maximum from PS, but achieve a higher level due to PA. If PS is carried out first, there is no negative effect of 1 week of NA prior to AA. A peak value almost as high as for the as-quenched and PA samples is reached, but after 2 h instead of 1 day.

Acknowledgements

Funding of Deutsche Forschungsgemeinschaft (DFG grant Ba 1170/22-1) and support by M. Liu (HZB) and C.S.T. Chang (TU) Berlin are gratefully acknowledged.

References

- [1] J. Banhart, M.D.H. Lay, C.S.T. Chang, A.J. Hill, *Physical Review B*, 83 (2011).
- [2] A.K. Gupta, D.J. Lloyd, *Metall Mater Trans A*, 30 (1999) 879-884.
- [3] C.S.T. Chang, J. Banhart, *Metall Mater Trans A*, 42A (2011) 1960-1964.
- [4] A. Deschamps, F. Livet, Y. Brechet, *Acta Materialia*, 47 (1998) 281-292.
- [5] K. Teichmann, C.D. Marioara, S.J. Andersen, K.O. Pedersen, S. Gulbrandsen-Dahl, M. Kolar, R. Holmestad, K. Marthinsen, *Philosophical Magazine*, 91 (2011) 3744-3754.
- [6] T. Masuda, Y. Takaki, T. Sakurai, S. Hirosawa, *Mater Trans*, 51 (2010) 325-332.