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# DSC ANALYSIS OF THE PRECIPITATION REACTION IN AA6005 ALLOY

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DSC analysis is applied to investigate the precipitation reaction in the AA6005 extrusion alloy for different heat treatment practices often presented in commercial production. The quenching practice is shown to have a big impact on the response of the AA6005 alloy to an artificial ageing treatment. The range of β'' precipitation is displaced to lower temperatures in samples quenched in air following the solution treatment. This acceleration, however, does not produce a favorable effect on age hardening capacity since much of the solute Mg and Si is removed from the solid solution before the principal hardening phase can precipitate. The DSC results are in good agreement with the age hardening curves. Natural ageing before artificial ageing promotes clustering activities during a subsequent thermal exposure and produces a strong delay in β'' precipitation.

***Keywords:*** *Al–Mg–Si, alloys, characterisation methods, DSC, metals*

## Introduction

Differential scanning calorimetry (DSC) precisely measures the heat exchange of a sample submitted to a controlled temperature scan [1]. It has been widely used to relate microstructure to processing and properties in age-hardening Al–Mg–Si alloys as it provides valuable information on exothermic precipitation and endothermic dissolution reactions [2–6]. Age hardening in Al–Mg–Si alloys occurs due to precipitation of metastable precursors of the equilibrium β-$Mg_2Si$ phase in a particular sequence [7–18] which can be readily identified by the peak arrangement in the DSC curve.

DSC analysis was used in the present work to investigate the precipitation reaction in the AA6005 extrusion alloy for different heat treatment practices often encountered in commercial production. AA6005 is a medium strength, heat treatable commercial alloy with excellent corrosion resistance and good weldability. It offers higher strength than 6063 and 6060, and better extrusion characteristics than 6082 and 6061 for complex cross sections. 6005 is widely used in structural applications, in the form of intricate extrusions for railway and bus profile structures, platforms and pipelines. The artificial ageing treatment, which provides the required strength via precipitation strengthening in this alloy, is thus technologically very important. The effect of quenching practice of solution heat treatment and natural ageing on the response of this alloy to artificial ageing, were investigated in the present work using DSC.

## Experimental

Small pieces taken from the as-received AA6005 profile with 0.74% Si, 0.44% Mg, 0.18% Fe (mass%), were solutionized at 560°C for 1 h and subsequently quenched in air and in water. The precipitation sequence of these samples was investigated by means of DSC. A second set of samples were naturally aged, before being tested with DSC, in order to assess the impact of natural ageing on the artificial ageing response. Microhardness and electrical conductivity measurements were also performed to identify artificial and natural ageing behavior.

Sample preparation for DSC experiments involved sectioning the as-received profile with a precision saw, grinding the slice obtained with a 600 grade SiC paper to a thickness of 1 mm and finally punching 3 mm diameter discs from the ground slice. This procedure was applied before solution heat treatment, in order to erase the effect of deformation introduced by punching which was recently shown to have a significant impact on the DSC results [19, 20]. The disc samples were heat-treated after placed in a 3.5 mm diameter, 10 mm deep hole drilled in the original tube profile, a measure taken to achieve post-solutionizing cooling rates encountered in commercial practice [21]. DSC analyses were performed by placing the sample disc in the sample pan and a super-purity aluminium of equal mass in the reference pan of the cell. The cell was heated to 600°C at 10°C $min^{-1}$ in a dynamic argon atmosphere (1 L $h^{-1}$). A second scan was performed by placing super-purity aluminium discs of equal

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mass in both pans in order to obtain a baseline. The heat effects associated with precipitation/dissolution reactions were obtained by subtracting the baseline thus obtained from a given heat flow curve.

## Results and discussion

A total of seven enthalpic signals, five of which are exothermic, are identified in the DSC spectrum of the 6005 sample quenched in water following the solution heat treatment (Fig. 1). The small exothermic peak centering around 80°C (effect 1) is best accounted for by low temperature clustering activities. It is inferred from the size of this peak that clustering is very limited in the water-quenched sample in spite of a large number of quenched-in vacancies expected in this sample, a relatively high supersaturation and excess silicon known to promote clustering. There appears to be another weak exothermic signal between 122 and 212°C (effect 2) which, in 6XXX alloys in this temperature range, implies formation of GP-I zones. The very small endothermic signal at approximately 215°C (effect 3) is produced by the dissolutionizing of the few clusters which have formed below 120°C. The major exothermic peak which follows right after and lasts until 275°C (effect 4) is clearly linked with the precipitation of the principal hardening phase, $\beta''$. The $\beta''$ peak is skewed on the leading edge, implying that $\beta''$ precipitation is promoted by precursor GP-I zones. The neighbouring exothermic peak between approximately 275 and 340°C (effect 5) is produced by the transformation of $\beta''$ to $\beta'$. The last two peaks are exothermic and endothermic (effects 6 and 7) and are associated with the precipitation and dissolution of the equilibrium $\beta$-Mg$_2$Si phase, respectively. It is fair to claim, in view of the foregoing, that the response to DSC heating of the present alloy in the water-quenched state agrees reasonably well with the precipitation sequence reported for Al–Mg–Si alloys: supersaturated solid solution (SSSS)$\rightarrow$solute clusters$\rightarrow$GP-I zones$\rightarrow\beta''\rightarrow\beta'\rightarrow\beta$ [7–15]. Lack of endothermic signals in between exothermic peaks for the formation of $\beta''$, $\beta'$ and $\beta$-Mg$_2$Si phase implies that the transition from one to the other is merely a transformation reaction and does not involve a measurable dissolution activity.

The DSC response of the sample quenched in air following the solution heat treatment is also shown in Fig. 1, superimposed on the DSC scan of the water-quenched sample. The low-temperature exothermic signal produced by the formation of clusters (effect 1) and the dissolution trough associated with their reversion (effect 3) are almost entirely missing in this sample. The exothermic signal of GP-I zones which is barely identified in the water-quenched sample (effect 2), on the other hand, grows larger with increasing temperatures until it merges with the $\beta''$ peak. The latter is displaced to lower temperatures by about 20°C and is much smaller. The $\beta'$ peak is also displaced to lower temperatures but is unchanged otherwise. The rest of the DSC features at higher temperatures are almost identical to those observed in the water-quenched sample.

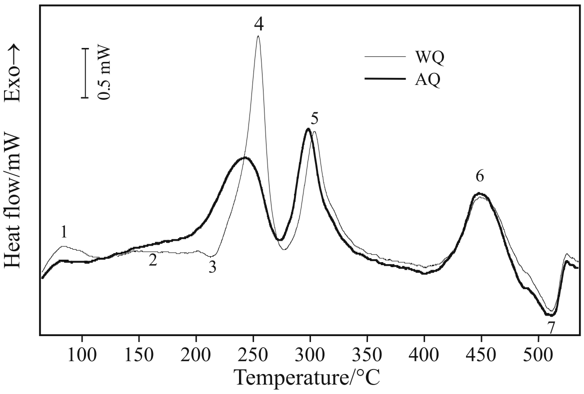

**Fig. 1** DSC curves of AA6005 disc samples quenched in water (WQ) and in air (AQ) after the solution treatment

The DSC features summarized above imply a number of changes in the response of the 6005 alloy to DSC heating when air, instead of water, quenching is employed after the solution heat treatment. Clustering activities are largely suppressed in the air-quenched sample as inferred from the missing enthalpic signals produced by the formation and dissolution of clusters. This could be accounted for by the formation of zones already during air-quenching owing to the much slower cooling rates with respect to water-quenching, thereby largely removing the solute Mg and Si from the solid solution leaving only a small fraction for clustering activities. Further relaxation of the supersaturation of the matrix during heating in the DSC cell occurs by the evolution of these zones and clusters into stable GP-1 zones. This process is easier with respect to the direct formation of GP-I zones from the supersaturated solid solution and thus produces an exothermic signal which grows with increasing temperature until it merges with the $\beta''$ peak. These GP-I zones serve as stable nuclei for the $\beta''$ phase as inferred from the exothermic character of the leading edge of the $\beta''$ peak. The much smaller size of the $\beta''$ peak in the air-quenched sample is blamed on extensive zone formation which largely consumes the solute Mg and Si and thus leaves only a fraction for the principal hardening $\beta''$ phase. So, the number of $\beta''$ needles forming at the artificial ageing temperature is relatively less which thus suffers a low age hardening capacity. Such an account provides a plausible explanation for the lower hardness in air-quenched sample in spite of the overall acceleration in precipitation kinetics.

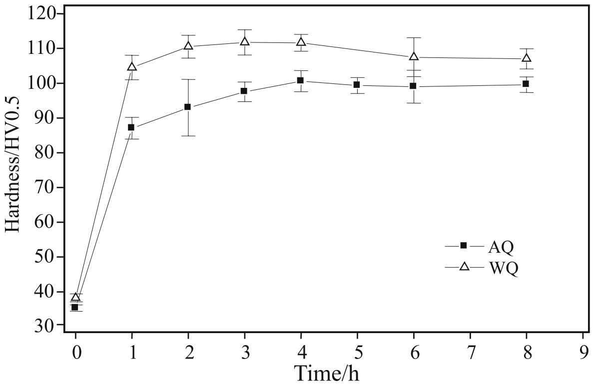

**Fig. 2** Artificial age hardening curves of AA6005 samples, quenched in water (WQ) and in air (AQ) after the solution treatment

Samples artificially aged at 185°C reach higher hardness levels when they are quenched in water following the solution heat treatment (Fig. 2).

Effect of natural ageing is also investigated in the present work using DSC since artificial ageing is rarely applied right after the solution treatment in commercial practice. Samples quenched in water and in air were heated in the DSC cell, several days and right after the solution treatment (i.e. with and without natural ageing). As the two sets of samples are solutionized in exactly the same fashion, any change in their response to a subsequent artificial ageing treatment are claimed to be due to natural ageing. Clustering is found to dominate during natural ageing, as inferred from the increase in hardness and the decrease in electrical conductivity with time at room temperature (Fig. 3). These changes are very prominent in the first couple of hours and level off upon further holding. It is interesting to note, however, that the conductivity of the water-quenched sample starts to increase after about 3 days at room temperature. More stable zones may start forming at this point in the water-quenched sample. DSC curves obtained from samples naturally aged for 3 days and for a full week are identical, however, implying that a 3-day natural ageing step suffices to illustrate the impact of natural ageing on artificial ageing response. The latter are thus not included in the discussion.

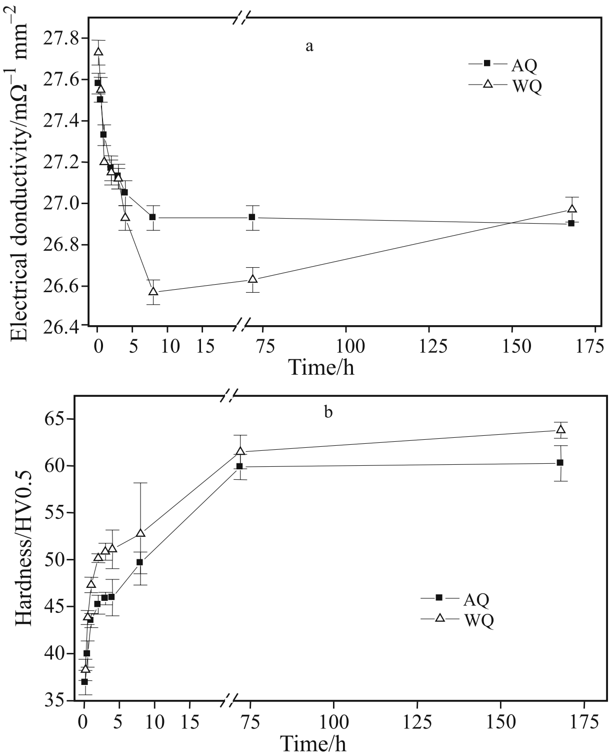

**Fig. 3** Change in a – electrical conductivity and b – hardness of AA6005 samples quenched in water (WQ) and in air (AQ) with time at room temperature after the solution treatment

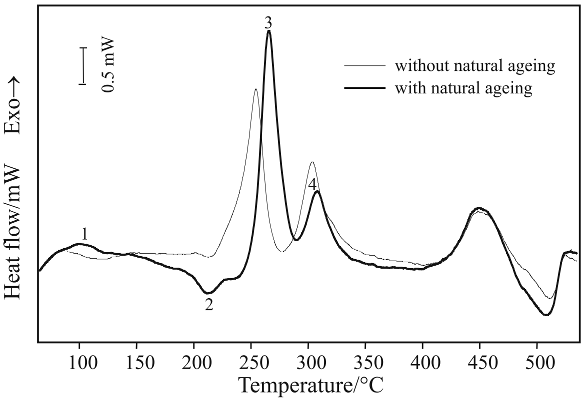

**Fig. 4** DSC curves of AA6005 disc samples quenched in water: DSC test employed right after (without natural ageing) and 3 days after the solution treatment (with natural ageing)

Effect of natural ageing on the response of water-quenched samples to DSC heating is evident (Fig. 4). Clusters are claimed to be responsible for the exothermic peak centering around 100°C (effect 1). Clustering, shown by electrical conductivity and hardness measurements to have already started during natural ageing, is somehow promoted and continues to dominate during a subsequent thermal exposure until 150°C. Zone formation during DSC heating is thus suppressed in samples which are first naturally aged, possibly due to extensive clustering activity which exhausts the precipitation capacity. The clusters which form during natural ageing and in the early stages of DSC heating, however, are not stable and revert back into solid solution, starting at approximately 150°C, producing the descending enthalpic signal and finally the dissolution trough centering at 212°C (effect 2). The size of the dissolution trough is much larger since the naturally aged sample has many more clusters to be dissolved in the matrix. β'' precipitation has to wait until enough Mg and Si are put back into solution and is thus retarded (by nearly 30°C). While the β'' peak (effect 3) is relatively larger owing to the solute enrichment of the matrix by the reversion process, β' peak (effect 4) is smaller and is slightly displaced to higher temperatures. The rest of the DSC scan is identical to that obtained from the freshly solutionized sample. The DSC scans of the samples with and without prior natural ageing suggest that the delay in β'' precipitation in the former practice can be readily compensated for by selecting slightly higher artificial ageing temperatures (i.e. 195 instead of 185°C).

The effect of natural ageing on the response to DSC heating of the air-quenched sample is a similar one (Fig. 5). While the peak arrangement is the same, there are major changes in the DSC scan upon natural ageing not only before but also after β'' precipitation. The low temperature range (before β'' precipitation) where GP-I zone formation occurs in the freshly solutionized sample, is now dominated first by the formation (effect 1) and then the reversion of clusters (effect 2). The clustering activities is relatively restricted with respect to the water-quenched sample possibly due to the lower vacancy concentration in the former. So, the endothermic trough linked with the dissolution of these clusters (effect 2) is also smaller. The β'' peak in the naturally aged sample is much larger and is displaced to higher temperatures by about 40°C (effect 3). The β' peak occurs at the same temperature but, in contrast to the β'' peak, is relatively smaller (effect 4). The β'' and β' peaks which are independent in the freshly solutionized sample seem to have merged forming a resolvable doublet after natural ageing. In marked contrast to the water-quenched samples, the response to higher temperature range of the naturally aged air-quenched sample is also substantially different. Both precipitation and dissolution of the equilibrium β phase are shifted to lower temperatures (effects 5 and 6) and the latter is now clearly a doublet. This indicates a substantial acceleration in the formation of the equilibrium β phase and may have something to do with the phase(s) from which it forms. The change in the relative intensities of the β'' and β' peaks in favor of the former upon natural ageing may be taken to imply that the β'' phase is somehow stabilized and a fraction survives at higher temperatures. The equilibrium β phase, under these circumstances, forms via transformation of not only β' but also β''. Such an account may provide a plausible explanation for the acceleration in β precipitation as well as for the following endothermic trough. The β phase which forms from two different precursors may have different dissolutionizing characteristics producing a resolvable doublet.

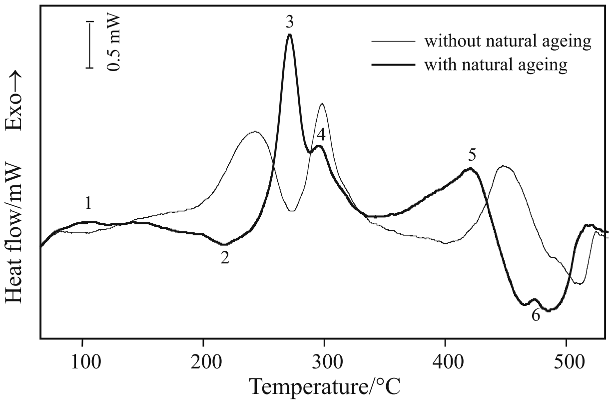

**Fig. 5** DSC curves of AA6005 disc samples quenched in air: DSC test employed right after (without natural ageing) and 3 days after the solution treatment (with natural ageing)

## Conclusions

The quenching practice is shown by DSC to have a big impact on the response of the AA6005 alloy to an artificial ageing treatment. The β'' precipitation is displaced to lower temperatures in samples quenched in air following the solution treatment. This acceleration, however, does not produce a favorable effect on age hardening capacity as much of the solute Mg and Si is removed from the solid solution before the principal hardening phase can precipitate, thereby reducing the population of β'' needles as inferred from the relatively smaller β'' peak. The DSC results are in good agreement with the age hardening curves which shows higher hardness levels for the water-quenched samples. Natural ageing before artificial ageing promotes clustering activities during a subsequent thermal exposure and produces a strong delay in β'' precipitation, as expected. The DSC scans of samples processed with natural ageing suggest, however, that the effect of natural ageing can be compensated for by selecting slightly higher artificial ageing temperatures.

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