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The effect of sample preparation on the DSC analysis of 6061 alloy

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Deformation introduced by punching had a big impact on the response of the 6061 alloy to DSC heating. Clustering at low temperatures was suppressed while the precipitation of the metastable precursors of the equilibrium β-Mg_2Si phase were accelerated. The β'' peak in the DSC curve has transformed into a doublet when the samples were punched after the solution treatment. This change in the peak arrangement was accounted for by the operation of two distinct mechanisms for the formation of the β'' phase. While a fraction of the β'' needles has formed through evolution of the GP-1 zones, the rest had to form in the solid solution matrix. Acceleration in the kinetics of β'' precipitation and its transformation to β' was confirmed by hardness measurements.

1. Introduction

Differential Scanning Calorimetry (DSC) is a powerful technique for the study of phase transformations and is widely employed to relate microstructure and properties to ageing process in Al-Mg-Si alloys [1–6]. Age hardening in these alloys occurs due to precipitation of metastable precursors of the equilibrium β-Mg_2Si phase in a particular sequence which can be identified by the peak arrangement in the DSC curve and detailed Transmission Electron Microscopy (TEM) studies [7–10]. While deformation is known to have a substantial effect on the precipitation process by providing heterogeneous nucleation sites for precipitates and by annihilating quenched-in excess vacancies [11–13], grinding and punching of disc samples for DSC experiments are almost a standard practice [14]. The deformation introduced during sample preparation was shown to have an impact on the precipitation reactions in Al-Cu-Mg-Li-Zr, Al-Cu and Al-Mg-Si alloys [14–18], and dislocations generated by the thermal expansion coefficient mismatch between the ceramic reinforcements and the matrix are known to lead to accelerated ageing in aluminium composites without altering the precipitation sequence [19–24]. The present work offers further evidence to illustrate how deformation introduced by punching DSC disc samples affects the response of high-strength structural 6061 extrusion alloy to DSC heating.

2. Experimental

6061 extrusion alloy, with 0.70% Si, 0.87% Mg, 0.23% Fe, 0.21% Cu and 0.07% Cr (wt%), was extruded into a 2.8 mm thick plate and was supplied in T4 temper. The laboratory processing involved solutionizing of the as-received plate at 560°C for 1 h and quenching in water before DSC experiments. Sample preparation for the DSC experiments involved cutting square pieces from the as-received plate, grinding these pieces with a 600 grade SiC paper to a thickness of 1 mm and finally punching 3 mm diameter discs. One set of discs was prepared before the solution heat treatment to produce DSC samples without deformation while the second set was prepared by grinding and punching after the solution treatment. The disc size was kept small intentionally in order to exaggerate the effect of punching deformation which was believed to be completely erased during the solution treatment in the first set. As the preparation of the DSC samples after the solution treatment took nearly 20 min, samples punched before the solution treatment were kept at room temperature for 20 min before they were heated in the DSC cell to account for the natural ageing in the former practice and thus to allow a fair comparison between the two procedures. DSC analyses were performed using a Setaram Labsys model DSC unit by placing the sample disc in the sample pan and a high purity aluminium of equal mass in the reference pan of the cell. The cell was heated to 600°C at 10°C/min in a dynamic argon atmosphere (1l/h). A second scan was performed by placing high purity aluminium discs of equal mass in both pans this time, in order to obtain a baseline. The heat effects associated with precipitation/dissolution reactions were then obtained by subtracting the high purity Al baseline run from a given heat flow curve. The DSC curves obtained from both groups of samples were highly reproducible.

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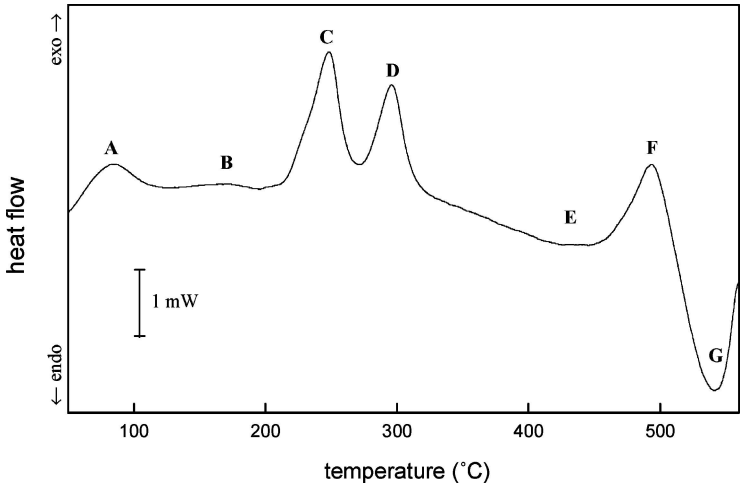


Figure 1 The DSC curve of the AA6061 alloy obtained by heating at 10°C/min of disc samples punched before the solution treatment.

3. Results

A typical DSC curve of the 6061 samples punched before the solution treatment is shown in Fig. 1. The response of these samples to DSC heating without punching deformation agrees reasonably well with the precipitation sequence reported for the 6061 alloy [20–26]. The DSC curve starts with a prominent exothermic peak (peak A) which centers around 80°C and is linked with the formation of vacancy-Si clusters [23, 26]. A very weak and broad exothermic signal (peak B) is noted between 120°C and 190°C and is believed to be associated with the formation of GP-1 zones. The much smaller size of peak B with respect to peak A implies that the majority of the GP-1 zones form through evolution of Si clusters. Precipitation of the β'' phase, and its transformation to the β' phase, produced the two neighbouring exothermic peaks between approximately 220°C and 320°C (peaks C and D). This identification of the two major exothermic peaks is consistent with those suggested in previous studies on AA6061 monolithic and composite alloys [20, 22, 26]. The endothermic trough (effect E) is linked with the dissolution of the β' phase. The last two peaks of the DSC curve in Fig. 1 (peaks F and G) are of exothermic and endothermic character and are associated with the precipitation and dissolution of the equilibrium β phase, respectively.

A typical DSC curve of the samples punched after the solution treatment is shown in Fig. 2, superimposed on the DSC curve of the sample punched before the solution treatment. A number of changes are noted in the former (Fig. 2). The low-temperature exothermic signal produced by the formation of clusters (peak A in Fig. 1) is almost completely missing. The weak and broad exothermic peak B is replaced by an exothermic signal which grows continuously until the onset of the precipitation of the principal hardening phase. The first of the two major exothermic peaks, peak C, ascribed to the formation of β'' phase has turned into an unresolved doublet suggesting that it actually consists of two superimposed peaks (peaks C1 and C2) when punching was performed after the solution treatment. Among earlier studies which have employed the DSC technique to study the precipitation process in 6061 alloy [19–22, 24, 26], that by Dutta and Allen [26] appears to be the only one where such a feature has been reported for this particular peak. This variation in peak configuration is believed to result from different sample preparation procedures. It is also worth noting that both peaks C1 and C2 occur at lower temperatures with respect to peak C. The neighbouring exothermic peak (peak D), linked to the formation of the β' phase, was also displaced to lower temperatures. The change in size of the latter was substantial when punching of the DSC sample followed the solution heat treatment. Both the precipitation and the dissolution of the equilibrium β phase were accelerated as inferred from the shift of their peaks (peaks F and G) to lower temperatures. The β precipitation peak was smaller in the sample punched after the solution treatment.

4. Discussion

The DSC features summarized above imply a number of changes in the response of the 6061 alloy to DSC heating when punching is performed after solutionizing. The removal of the exothermic signal centering around 80°C suggests that low-temperature clustering is largely suppressed in deformed samples (Fig. 2). Dislocations, introduced during sample preparation by punching apparently act as vacancy sinks and annihilate quenched-in vacancies [11]. As the clustering activities very much rely on the quenched-in vacancy population, the annihilation of vacancies is claimed to be responsible for the suppression of clustering at low temperatures [27]. As there are practically no clusters to evolve to GP-1 zones, GP-1 zones are on their own and form in the solid solution matrix, producing a prominent heat effect, as inferred from a subsequent deviation from the baseline in the exothermic direction which grows continously and connects directly to peak C1. Dislocations introduced by punching evidently provide heterogeneous nucleation sites and thus promote the formation of GP-1 zones which is judged to be extensive as Mg and Si are largely retained in solution early in DSC heating owing to the suppresion of clustering.

Dutta and Allen, in their work on the DSC analysis of a 6061 alloy, have claimed that the first of the

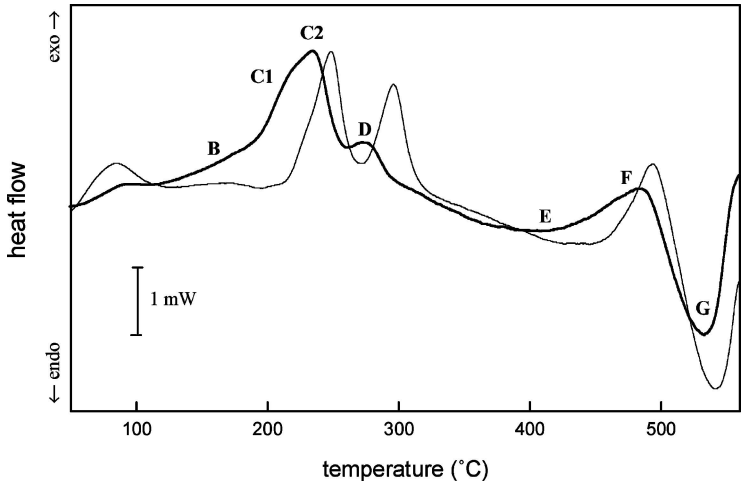


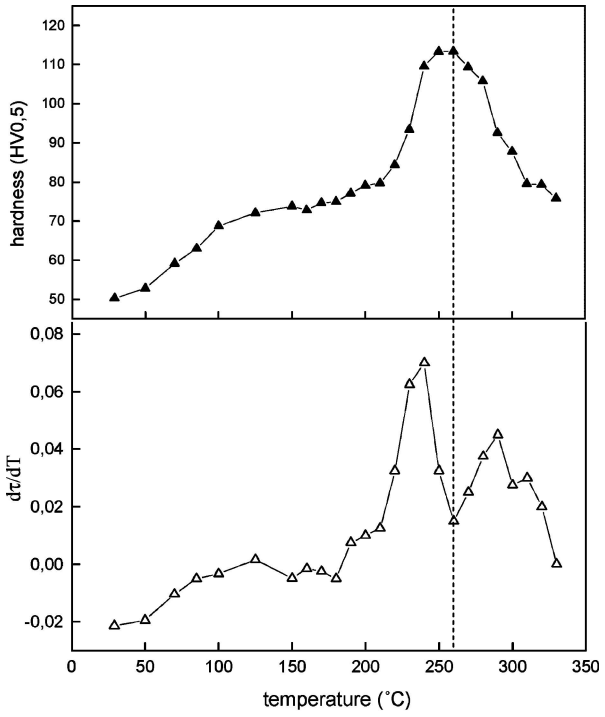
Figure 2 The DSC curve of the AA6061 alloy obtained by heating at 10°C/min of disc samples punched after the solution treatment, shown superimposed on the DSC curve obtained by heating at 10°C/min of disc samples punched before the solution treatment.

two superimposed peaks, peak C1, was associated with the formation of very tiny GP-1 zones based on their TEM observations [26]. The temperature range estimated for peak C1 (200°C–230°C), however, is considerably higher than that often reported for the formation of GP-1 zones [28]. Two superimposed peaks replacing peak C are better accounted for by the operation of two distinct mechanisms for the formation of β'' needles in the deformed samples. GP-1 zones might have evolved with increasing temperatures to become β'' needles and are believed to be responsible, at least in part, for the transformation of peak C into two superimposed peaks (peaks C1 and C2). This process relied on the availability of a large number of GP-1 zones, and was easier and thus took place earlier, shifting peak C1 to lower temperatures. The majority of the β'' needles, on the other hand, formed in the solid solution matrix which was partially depleted of Mg and Si. The latter process had to overcome a larger energy barrier and was thus relatively retarded. The formation of β'' needles in the solid solution matrix was also accelerated owing to the presence of dislocations introduced during sample preparation as evidenced by the displacement of peak C2 to lower temperatures. The relative enthalpies of the two peaks are dictated by the extent to which one of these two mechanisms is dominating. The overall acceleration in β'' precipitation kinetics is consistent with earlier work where the presence of dislocations was reported to lead to accelerated precipitation at high temperatures both in monolithic Al-Mg-Si alloys and in their particulate-reinforced composite counterparts [19–22, 24, 26, 29].

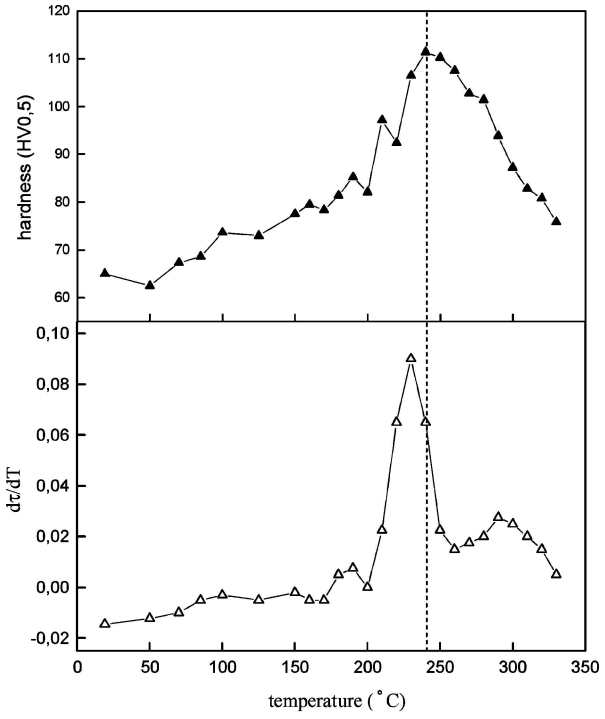
Another striking difference between the DSC curves of the 6061 samples punched before and after the solution treatment is the substantial change in the size of the β' peak (peak D) which is also displaced to lower temperatures. A much smaller β' peak may imply that deformation prior to DSC heating somehow stabilizes the β'' phase and suppresses its transformation to the semi-coherent β' phase. Another account of the change in the peak arrangement upon deformation was offered by Lee *et al.* [20], who claimed that the β' phase instead of the β'' phase was stabilized when deformation was introduced to the 6061 alloy before DSC heating.

If the β'' phase were, in fact, stabilized, high hardness levels associated with it would have to be retained until this phase eventually transformed to the equilibrium β-Mg_2Si phase. An attempt was made to identify the effect of deformation on the precipitation process in this temperature range by measuring the hardness of samples with and without deformation, heated to a range of temperatures, at a rate similar to that employed in the DSC experiments and then subsequently quenched. Since the DSC discs were rather small for hardness measurements, 2 cm × 2 cm square pieces of the same 6061 plate were used and the deformation introduced by punching DSC discs was approximated by cold rolling the extruded 6061 plate to a thickness reduction of 5%. The hardness of the regular and cold rolled samples was measured right after quenching to room temperature and was plotted as a function of temperature. As DSC analysis was not available for these larger samples, heated seperately in a laboratory furnace, the precipitation sequence was obtained by measuring their electrical conductivity values (τ) and taking the derivative of the electrical conductivity with respect to temperature ($d\tau/dT$). The evolution of hardness during heating is illustrated in Fig. 3 along with the respective $d\tau/dT$ vs T curves.

The temperature at which the peak hardness occurred in the samples without deformation marked the onset of the β' peak (peak D), suggesting that the hardness started to drop as soon as the $\beta'' \rightarrow \beta'$ transformation was underway (Fig. 3a). The higher initial hardness in the deformed samples (Fig. 3b) is associated with the deformation hardening introduced by cold rolling. The peak hardness in this sample was nearly the same as that obtained in the regular samples and cannot be accounted for by the semi-coherent β' phase. It is thus fair to conclude that the β'' phase has indeed formed when punching was performed after the solution treatment. The peak hardness was achieved faster but was not maintained suggesting acceleration not only in the



(a)



(b)

Figure 3 The change in hardness and in $d\tau/dT$ with temperature of 6061 plate samples which were heated at a rate of 4.3°C/min to a range of temperatures until 330°C and subsequently quenched: (a) samples with no deformation, (b) samples cold rolled 5%.

kinetics of β'' precipitation but also in the kinetics of its transformation to β'.

It is thus claimed that the β'' phase lost its coherency with the matrix and transformed to the β' phase shortly after it precipitated owing to the dislocations generated during punching. In other words, the precipitation of β'' and much of its transformation to β' were taking place in a rather narrow temperature range when deformation was introduced before the ageing treatment. So, precipitation of not only β'' but also its transformation to β' were responsible for peak C2 in the samples punched after the solution treatment.

5. Summary

Deformation introduced by punching had a big impact on the response of the 6061 alloy to DSC heating. Clustering at low temperatures was suppressed while the precipitation of the metastable precursors of the equilibrium phase, β-Mg_2Si were accelerated. The dislocations are believed to have provided heterogeneous nucleation sites for the GP-1 zones that evolved with increasing temperatures to become β'' needles. The precipitation of β'' and much of its transformation to β' were taking place in a narrow temperature range and were responsible for the second of the two superimposed exothermic peaks. This has reduced the β' formation peak into a small exothermic signal when deformation was introduced before the ageing treatment. The acceleration in the kinetics of β'' precipitation and its transformation to β' was confirmed by hardness measurements.

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