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DSC ANALYSIS OF THE PRECIPITATION REACTIONS IN THE ALLOY AA6082
Effect of sample preparation

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The deformation introduced during the sample preparation had a high impact on the response of the alloy AA6082 to heating in the DSC cell. The DSC curve was strikingly different when DSC samples of this alloy were punched after the solution treatment. Dislocations introduced by punching have annihilated the quenched-in vacancies and have suppressed clustering initially. Dislocations have also provided heterogeneous nucleation sites for the GP-1 zones that readily grew to become stable nuclei for the β″ phase owing to the enhanced atomic transport. β″ as well as the β′ precipitation kinetics were thus accelerated leading to a substantial change in the DSC peak arrangement. Deformation introduced during sample preparation by gentle grinding alone, on the other hand, did not suffice to alter the precipitation sequence, producing a DSC curve very similar to that obtained with samples punched before the solution treatment.

Keywords: *Al–Mg–Si, characterisation methods, differential scanning calorimetry, metals and alloys*

Introduction

Differential scanning calorimetry (DSC) is a thermal analysis method that measures the heat evolution from a sample under a controlled temperature scan and is under continuous development [1]. DSC has been applied extensively for the analysis of precipitation and dissolution activities and to relate microstructure to processing and properties in age-hardenable Al–Mg–Si alloys [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 [7–15] which can be readily identified by the peak arrangement in the DSC curve.

While deformation is known to have a substantial effect on the precipitation process [16–20], punching of disc samples for DSC experiments is a widely used practice. The deformation inherited from punching operation was shown to influence the precipitation reactions in Al–Cu, Al–Cu–Mg–Li–Zr and Al–Mg–Si alloys [21–24]. The effect of sample preparation on the DSC analysis of aluminium alloys was discussed by Starink in a recent review [25]. The present work was undertaken to illustrate the effect of deformation introduced by punching disc samples on the response to DSC heating of a structural extrusion alloy AA6082. As the alloy AA6082 is known to be quench-sensitive, punching disc samples for its DSC analysis before the solution treatment, to erase punching deformation, presents other problems since the post-solutionizing cooling rates in this case are far greater than those experienced by the extrusions in an industrial environment. An attempt was thus made to identify a sound sample preparation practice for this alloy.

Experimental

The alloy AA6082 used in the present work was cast industrially with a hot top air-slip vertical billet caster in the form of 7400 mm long, 178 mm diameter billet containing 1.06% Si, 0.78% Mg, 0.21% Fe, 0.74% Mn (mass%). The billet was homogenized and extruded into a tube profile (inner and outer diameters were 12 and 26 mm, respectively) and was supplied in T4 temper. The laboratory processing involved solutionizing at 560°C for 1 h and water-quenching before DSC experiments.

Sample preparation for DSC experiments involved sectioning a 1.2 mm thick slice from the as-received profile with a precision saw, grinding this slice 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 employed both after and before the solution heat treatment to produce two sets of DSC samples with and without deformation, respectively. 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 heat treatment in the latter set. When the disc samples were punched before the solution heat treatment, they were heat treated after they were placed in a

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3.5 mm diameter, 10 mm deep hole drilled in the tube profile, in order to avoid post-solutionizing cooling rates which were much higher than those encountered by the samples punched after the solution treatment. A third procedure was employed for the preparation of DSC samples to avoid deformation effects without a subsequent high-temperature anneal. A 8×8 mm square piece was first cut from the 1.2 mm thick slice. The square piece was ground manually to a thickness of 1 mm and then was rounded of by gently grinding its edges until it was reduced to a disc of 3 mm diameter. This procedure was employed when the DSC samples were to be prepared after solutionizing to avoid higher than usual cooling rates.

DSC analyses were performed using a Setaram Labsys model DSC unit by placing the sample disc in the sample pan and a super purity aluminum 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}). The heat effects associated with precipitation/dissolution reactions were then obtained by subtracting a super purity Al baseline run from a given heat flow curve. The DSC curves thus obtained were highly reproducible. Two separate sets of samples were heated in the DSC cell, under the conditions described above, to a range of temperatures with 10–25°C increments and subsequently quenched. A Future Tech FM-700E model microhardness tester was employed to investigate the evolution of hardness during DSC heating, in AA6082 samples punched before and after the solution heat treatment. A low testing load of 500 g was used to allow several indentations to be performed on small disc samples. Hardness measurements were performed within 15 min of quenching.

Results and discussion

The DSC curve of the 6082 sample punched before the solution treatment revealed a total of 8 enthalpic effects, 5 of which were exothermic (Fig. 1). The relatively high supersaturation owing to the water-quenching employed in its processing, together with some excess silicon are believed to be responsible for the extensive clustering activity below 100°C in this alloy. Excess silicon is known to promote clustering process at low temperatures [26]. The relatively weak exothermic signal between 150 and 200°C was linked to the formation of GP-1 zones (effect 2). A fraction of the clusters and zones thus formed were reverted at still higher temperatures thus producing a dissolution trough shortly after 200°C (effect 3). Precipitation continued first with the formation of the β″ (effect 4), and then its transformation to the β′ phase (effect 5), producing the two neighbouring exothermic peaks between approximately 220 and 320°C. An endothermic signal followed (effect 6) and was linked to the dissolution of the β′ phase (Fig. 1). The last two peaks were of exothermic and endothermic character (effects 7 and 8) and were associated with the precipitation and dissolution of the equilibrium β phase, respectively. It can thus be concluded that the response to DSC heating of the present alloy agreed reasonably well with the precipitation sequence reported for AlMgSi alloys: supersaturated solid solution (SSSS)→solute clusters→GP zones→β″ (needle)→β′ (rod)→β [7–15].

A number of changes were noted in the DSC curve of those samples punched after the solution treatment (Fig. 2). The low-temperature exothermic signal produced by the formation of clusters was smaller (effect 1) and the dissolution trough associated with their reversion was entirely missing in these samples. The first major exothermic peak, that was linked to the precipitation of the metastable β″ phase in the 6082 sample punched before the solution treatment, has moved to lower temperatures by about 20°C (effect 3). The exothermic peak centering around 300°C associated with the β′ phase in Fig. 1, on the other hand, has disappeared completely. A similar effect regarding the β′ peak was reported in a 6061 sample punched after the solution treatment, prior to heating in the DSC [24]. Both the precipitation and the dissolution of the equilibrium β phase were accelerated as inferred from the shift of their peaks to lower temperatures (effects 4 and 5).

The DSC features summarized above imply a number of changes in the response of the alloy 6082 to DSC heating when punching is performed after solutionizing thereby introducing nonnegligible deformation. Clustering was largely suppressed in the deformed sample as inferred from the decrease in size of the exothermic signal below 100°C and the absence of a dissolution trough near 200°C (Fig. 2). Clusters and zones form homogeneously and are affected only little by the presence of dislocations, which, however, act as vacancy sinks and thus annihilate quenched-in vacan-

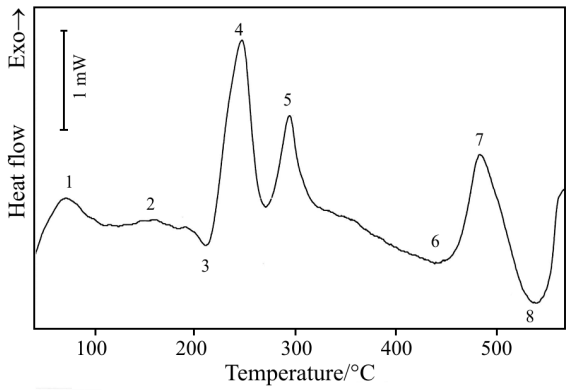

Fig. 1 DSC curve of AA6082 disc samples punched before the solution treatment, obtained by heating at 10°C min^{-1}

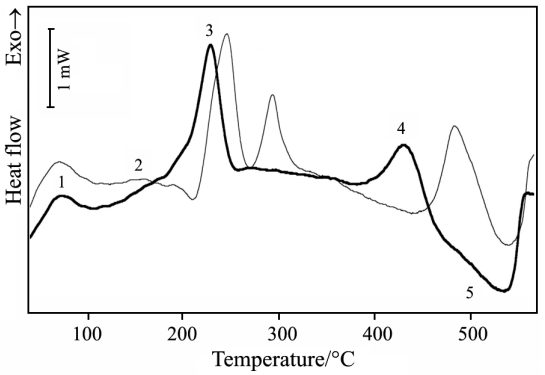

Fig. 2 DSC curve of AA6082 disc samples punched after the solution treatment obtained by heating at 10°C min^{-1}, shown superimposed on the DSC curve of disc samples punched before the solution heat treatment

cies [16]. As the clustering activities rely on the quenched-in vacancy population [27], the reduced vacancy population is held responsible for the suppression of clustering at low temperatures [25]. Mg and Si were thus largely retained in solution early in DSC heating and the GP-1 zones started to form early and served as stable nuclei for the β″ phase as inferred from the exothermic character of the leading portion of the β″ peak (effect 2 in Fig. 2). Hence, β″ precipitation was accelerated as evidenced by the shift of the major exothermic peak to lower temperatures. The presence of dislocations is well established to lead to an acceleration in precipitation kinetics at high temperatures both in monolithic Al–Mg–Si alloys and in their particulate-reinforced composite counterparts [17, 28, 29].

The removal of the β′ peak centering around 300°C (Fig. 2), may imply that deformation prior to DSC heating somehow stabilizes the β″ phase and thus suppresses its transformation to the semi-coherent β′ phase. While such an account sounds plausible in view of the peak arrangement in the deformed sample, it is not supported by the microhardness measurements performed on samples heated in the DSC cell to a range of temperatures and subsequently quenched. The hardness evolution during DSC heating of the 6082 samples punched before and after the solution heat treatment are illustrated in Fig. 3 along with their respective DSC curves. The peak hardness in samples punched before the solution heat treatment, i.e. without deformation (Fig. 3a), coincides with the onset of the β′ peak (Fig. 3b), suggesting that the hardness starts to drop as soon as the β″ to β′ transformation is underway.

The hardness evolution in 6082 samples punched after the solution treatment is almost identical, but is shifted to lower temperatures by nearly as much as the major exothermic peak is displaced in the DSC curves (Fig. 3). The higher hardness of these samples below 150°C is claimed to be associated with the deformation hardening introduced by punching.

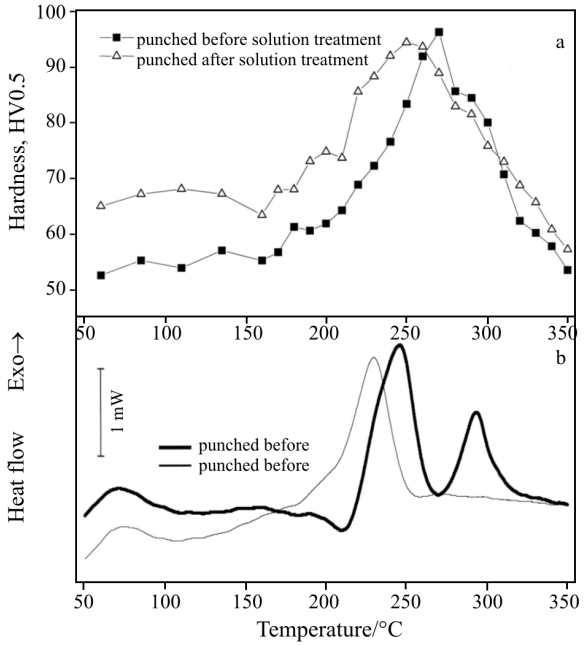

Fig. 3 a – The evolution of hardness in 6082 samples, punched before and after the solution treatment, heated in the DSC cell at a rate of 10°C min^{-1} and subsequently quenched; b – corresponding DSC curves

The peak hardness level is similar to that measured in the case of punching before and cannot be accounted for by the semi-coherent β′ phase. It is thus fair to conclude that the β″ phase has indeed formed and is largely responsible for the major exothermic peak when punching was performed after the solution treatment. The peak hardness was achieved faster but was not maintained evidencing acceleration not only in the kinetics of β″ precipitation but also in the kinetics of its transformation to β′. The β″ phase loses its coherency with the matrix and transforms to the β′ phase as soon as it precipitates owing to the availability of a rather high dislocation density introduced by punching during sample preparation. In other words, the precipitation of β″ and its transformation to β′ are taking place simultaneously when deformation is in-

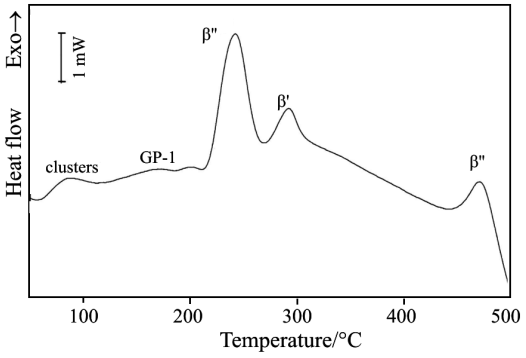

Fig. 4 DSC curve obtained by heating at 10°C min^{-1}, of AA6082 disc samples prepared by manual grinding alone after the solution heat treatment

troduced after the solution treatment. This account is consistent with an earlier work, where ageing following deformation was claimed to favor the formation of the more stable phases [18].

The DSC curve obtained from 6082 samples, prepared by gentle grinding alone, is illustrated in Fig. 4. The peak arrangement in this case, which did not involve punching, is very similar to that given in Fig. 1, implying that the deformation introduced during gentle grinding did not suffice to alter the precipitation sequence. Some deformation was nevertheless inherited from grinding operation in spite of the extra caution exercised, as inferred from the relatively smaller size of the β′ peak. A small fraction of the β″ to β′ phase transformation is believed to have taken place at lower temperatures, under the β″ peak, owing to the availability of dislocations generated by grinding. It can be speculated that the rest of the β″ needles had to wait for the temperature to increase to transform to β′ rods as usual, thus producing the usual yet relatively smaller β′ peak in the DSC curve (Fig. 4).

Conclusions

Deformation introduced by punching was shown to have a big impact on the DSC analysis of the alloy AA6082. The DSC curve was strikingly different when DSC samples were punched after the solution treatment and thus inherited nonnegligible deformation from the punching operation. Clustering at low temperatures was suppressed while the precipitation of the metastable precursors of the equilibrium phase, β-Mg_2Si and the β-Mg_2Si phase itself were all accelerated. The dislocations introduced by punching have annihilated the quenched-in vacancies and were thus responsible for the suppression of clustering initially. Dislocations have also provided heterogeneous nucleation sites for the GP-1 zones that readily grow to become stable nuclei for the β″ phase owing to the enhanced atomic transport. The β″ as well as the β′ precipitation kinetics were thus accelerated leading to a substantial change in the DSC peak arrangement. The DSC curve obtained from 6082 samples, prepared by gentle grinding alone, on the other hand, was very similar to that of the 6082 sample punched before the solution treatment, implying that the deformation introduced did not suffice to alter the precipitation process.

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