Effects of particle reinforcement and ECAP on the precipitation kinetics of an Al-Cu alloy

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Abstract. The precipitation kinetics of Al-Cu alloys have recently been revisited in various studies, considering either the effect of severe plastic deformation (e.g., by equal-channel angular pressing – ECAP), or the effect of particle reinforcements. However, it is not clear how these effects interact when ECAP is performed on particle-reinforced alloys. In this study, we analyze how a combination of particle reinforcement and ECAP affects precipitation kinetics. After solution annealing, an AA2017 alloy (initial state: base material without particle reinforcement); AA2017 + 10 vol.-% Al2O3; and AA2017 + 10 vol.-% SiC were deformed in one pass in a 120° ECAP tool at a temperature of 140°C. Systematic differential scanning calorimetry (DSC) measurements of each condition were carried out. TEM specimens were prepared out of samples from additional DSC measurements, where the samples were immediately quenched in liquid nitrogen after reaching carefully selected temperatures. TEM analysis was performed to characterize the morphology of the different types of precipitates, and to directly relate microstructural information to the endo- and exothermic peaks in our DSC data. Our results show that both ECAP and particle reinforcement are associated with a shift of exothermic precipitation peaks towards lower temperatures. This effect is even more pronounced when ECAP and particle reinforcement are combined. The DSC data agrees well with our TEM observations of nucleation and morphology of different precipitates, indicating that DSC measurements are an appropriate tool for the analysis of how severe plastic deformation and particle reinforcement affect precipitation kinetics in Al-Cu alloys.

Keywords: Differential Scanning Calorimetry, DSC, Precipitation, equal channel angular pressing, ECAP, particle reinforcement, Al-Cu-alloy, microstructures, transmission electron microscopy

1. Introduction

Aluminium alloys offer great potential for lightweight constructions, where mechanical properties play an important role. To further improve the mechanical and wear properties, ceramic reinforcements (e.g. Al2O3 or SiC) can be used to produce aluminium matrix composites (AMCs) [1-2]. An alternative approach to improve the mechanical properties is severe plastic deformation (SPD), such as equal channel angular pressing (ECAP) [3-4]. Recent studies show that either the addition of reinforcing particles [1-3] or SPD processes (like ECAP [5] or high pressure torsion [6]) - generally alter the precipitation kinetics: precipitation is accelerated and specific steps in the precipitation sequence can be suppressed. It is, however, not known how a combination of these approaches (i.e., particle reinforcement and ECAP) affects precipitation.

In this study, we use differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) to document how both particle reinforcement and ECAP change the precipitation kinetics. We confirm that severe plastic deformation by ECAP and the addition of particles result in shifts of the DSC peaks corresponding to the formation of the $\theta$ and $\theta'$ phases towards lower temperatures. Most notably, we show that the combination of both leads to an even more pronounced acceleration of the precipitation kinetics and a further shift of the DSC peaks to lower temperatures.
2. Experimental

2.1 Materials and processing

The base material in this study is an Al-Cu alloy (AA2017). The chemical composition is given in Table 1. The base material was ground mechanically and mixed with the particle powders (10 vol.-% Al₂O₃ or 10 vol.-% SiC). The size of particles was less than 2 \( \mu \)m. Hot isostatic pressing (HIP) and extrusion of the mixed powders was performed at Powder Light Metals GmbH in Gladbeck, Germany. The different batches of base and reinforced materials were then solution annealed at 505 °C for 60 min.

ECAP was performed at 140 °C on selected billets (both of the base material and reinforced AMCs) in a tool with an internal angle of 120° and at a pressing velocity of 20 mm/min. Further details on our ECAP tools are e.g. given in [3-4].

| Table 1: Composition of base material AA2017 (wt.-%). |
|---|---|---|---|---|---|---|
| Al | Cu | Mn | Mg | Fe | Si | Zn |
| >94.1 | 4.1 | 0.84 | 0.58 | 0.22 | 0.08 | <0.01 |

2.2 DSC measurements and microstructural analysis

In a first series of DSC measurements, the different material conditions were heated from room temperature to 500 °C with a heating rate of 10 K/min. The resulting DSC curves (see also Fig. 1) exhibit characteristic peaks that are directly related to different steps in the precipitation sequence and that can be used to qualitatively analyze the precipitation behavior. A second series of DSC measurements was then used to heat DSC specimens of the different material conditions up to the previously determined peak temperatures. Once a peak temperature was reached, the DSC measurement was interrupted, the specimen was removed from the DSC apparatus and immediately quenched in liquid nitrogen to preserve the specific ageing condition of the specimen.

For subsequent microstructural analysis, the DSC specimens were prepared for TEM investigations by grinding, mechanical thinning and electro-polishing. TEM analysis was performed using a TEM Hitachi H8100 with an accelerating voltage of 200 kV.

3. Results and Discussion

3.1 Initial condition AA2017

In Fig. 1 the DSC curves of the base material AA2017 are shown for two different ageing conditions. The “T4” condition represents a material aged at room temperature after solution annealing. The “T6” condition corresponds to a material peak-aged at 170°C for 30 minutes after solution annealing. Note that the T4 condition exhibits a peak at low temperatures while the T6 condition does not. This first peak (observed in T4) corresponds to the formation of Guinier-Preston zones (GP zones) [1]. Ageing at temperatures above 100 °C causes a complete formation of GP zones [1]; because this process is already completed prior to DSC testing in the case of T6 ageing, no additional peak is observed in the DSC curve. At temperatures above 170 °C, the DSC curves of T4 and T6 are very similar. Three characteristic peaks can be observed, labeled as peak 2 (endothermic), peak 3 (exothermic) and peak 4 (exothermic). The endothermic peak 2 is associated with the dissolution of the GP-zones and of the θ’ phase, [1]. The exothermic peaks 3 and 4 are associated with the formation of the θ’ phase and of the θ phase, respectively, [1]. At higher temperatures (labeled region 5 in Fig. 1) only the equilibrium θ phase remains present.
Fig. 1: DSC curves of AA2017 in cold-aged condition (T4) and warm-aged condition (T6); heating rate 10 K/min. Four characteristic peaks can be observed. Peak 1 (present in T4 but suppressed in T6) is associated with the formation of GP zones. Peak 2 is endothermic and associated with the dissolution of GP zones and the $\theta''$ phase. Peak 3 corresponds to the formation of the $\theta'$ phase. Peak 4 is associated with the formation of the $\theta$ phase.

Our experimental observations and our interpretation of the DSC data is well in line with previous studies; to further confirm these results, we consider microstructural information from the TEM analysis of different samples taken from the interrupted DSC tests. Fig. 2a shows a TEM micrograph of the microstructure in a specimen that was heated up to peak 1. Because the typical average size of GP zones is 10 nm, they cannot be observed directly in our bright field images; the black circle in Fig. 2a highlights a region where these zones (and the meta-stable $\theta''$-phase) are likely to be present. The microstructure after heating to peak 3 (Fig. 2b) is characterized by the occurrence of the $\theta'$-phase and have also been observed under similar conditions in previous studies [2]. The $\theta'$-phase is also present after heating to peak 4 (Fig. 2c). Moreover, white arrows mark the $\Omega$-phase. This phase develops along the [100]-plane and has a well-defined [010]-orientation, [7]. These precipitates are nucleated in magnesium-rich regions in the matrix [8-10]. Besides the well-known precipitation sequence in the Al-Cu system (GP-zone, $\theta''$, $\theta'$, $\theta$), the corresponding precipitation sequence has been observed [8-10] as:

supersaturated solid system $\rightarrow$ Mg clusters $\rightarrow$ $\Omega$ $\rightarrow$ $\theta$.

The $\Omega$ precipitates with typical lengths of 300-550 nm have also observed in former studies [9-10]. Furthermore, the black arrows in Fig. 2c mark small precipitates that signify the equilibrium $\theta$ phase. These precipitates can be clearly distinguished by their more compact shape. During further ageing and with increasing temperature, the $\theta$ phase precipitates grow as shown in Fig. 2d (corresponding to region 5).
Fig. 2: TEM micrographs of the AA2017 base material from the interrupted DSC scans at (a) peak 1 (T4 condition), (b) peak 3, (c) peak 4 and (d) region 5 of AA2017-T6. The black circle in (a) highlights a region where GP zones may well be present; open black arrows mark examples of $\theta'$ precipitates; white arrows indicate $\Omega$ phase and black arrows highlight $\theta$ phase precipitates.

3.2 AA2017 with a 10 vol.-% reinforcement of Al$_2$O$_3$ or SiC

In Fig. 3 the DSC curves of the material reinforced with 10 vol.-% Al$_2$O$_3$ is compared to the reference material (T6 condition). The curve of the reinforced material differs from the reference curve: The formation of GP-zones (peak 1 in Fig. 1) is suppressed, which confirms earlier studies [2, 11]. The peaks associated with the formation of $\theta'$ and $\theta$ phase (peaks 3 and 4) overlap. Such overlapping peaks have also been observed in [1]. Most importantly, all peaks are shifted to lower temperatures compared to the reference condition. The endothermic peak (peak 2 in Fig. 1) and the exothermic peaks (peaks 3+4 in Fig. 1) occur at about 20-30 K below the peak temperatures of AA2017-T6. Such an acceleration of the precipitation behavior has been rationalized by an increased dislocation density resulting from different thermal expansion coefficients of the particles and the aluminium matrix, [1]. This increased dislocation density can facilitate faster diffusion (by, e.g., pipe diffusion) and hence accelerate nucleation and precipitation, [12].

Fig. 3: DSC curves of AA2017 + 10 vol.-% Al$_2$O$_3$ and AA2017 (T6, used as reference). Only two characteristic peaks can be observed for the reinforced condition. Peak 1 (see Fig. 1) is suppressed. Peak 2 is endothermic and associated with the dissolution of GP zones and $\theta''$ phase. Peak 3 is associated with the formation of the $\theta'$ phase. Peak 4 is related to the
formation of the $\theta$ phase. Peaks 3 and 4 exhibit an overlap. Compared to the base material, peaks 2-4 are shifted towards lower temperatures.

The microstructure of the material reinforced with Al$_2$O$_3$ was analyzed in the TEM after interrupted DSC scans at peaks 3+4 (~270 °C, Fig. 4a) and in region 5 (Fig. 4b), respectively. Open black arrows mark $\theta'$ particles in Fig. 4a. In addition, some small $\theta$ precipitates can be observed (black arrows), which clearly demonstrates that the overlapping of peaks 3+4 can be related to the almost simultaneous formation of $\theta'$ and $\theta$ phases. When the temperature is increased (Fig. 4b), the $\theta$ phase particles are further coarsened.

![Fig. 4: TEM micrographs of AA2017 + 10 vol.-% Al$_2$O$_3$. (a) Microstructure after an interruption of the DSC test at peaks 3+4; (b) microstructure in region 5 (see also Fig. 3). Open black arrows indicate $\theta'$; black arrows indicate $\theta$ phase.](image)

The DSC data and TEM micrographs for the material reinforced with 10 vol.-% SiC (Figs. 5 and 6) hardly differs from the data discussed above (Figs. 3 and 4): The DSC curve of the particle reinforced material is characterized by a suppression of GP zone formation, by overlapping peaks 3+4 related to the precipitation of $\theta'$ and $\theta$ phase (indeed, only a single broad peak is observed), and by a shift of all peaks towards lower temperatures. This shift is somewhat more pronounced (30-40 K) compared to the material reinforced with Al$_2$O$_3$, but since the DSC peaks cover a wide temperature range, this minor difference is almost negligible. Again, the TEM micrographs clearly show the presence of both $\theta'$ and $\theta$ phases in the region of the peak labeled 3+4, which demonstrates that the single broad peak is in fact a signature of these two distinct precipitation processes. The $\theta$ precipitates are coarsened considerably as temperature is increased (region 5; Fig. 6b).

![Fig. 5: DSC curves for AA2017 + 10 vol.-% SiC and for AA2017-T6 as reference. Only two characteristic peaks can be observed for the reinforced material.](image)
3.3 Base material AA2017 after ECAP

In Fig. 7, we compare the DSC curve of the AA2017 base material after one pass of ECAP and the reference condition AA2017-T6. Quite similar to what was observed in both particle-reinforced materials, the ECAPed base material is characterized by a suppression of peak 1 (i.e., no formation of GP zones can be observed), by overlapping peaks 3+4, and by a general shift of the characteristic DSC peaks towards lower temperatures. These findings are in line with previous studies on the precipitation kinetics of ultrafine-grained aluminium [5]. Following a similar scenario as in the case of the particle-reinforced materials, the accelerated precipitation kinetics of ECAPed material can be related to faster diffusion promoted by larger numbers of vacancies [13], dislocations [12] and grain boundaries [14-16].

In Fig. 8a, we present a TEM image of material quenched near 260°C (labeled peak 3+4 in Fig. 7). The high dislocation density is well known in materials deformed by SPD processes such as ECAP and is likely to be the main factor contributing to the acceleration of precipitation processes in this material condition. Again, θ phase precipitates are considerably coarsened at higher temperatures (region 5; Fig. 8b).
3.4 Combination of ECAP and particle reinforcements

We now present our results on how the combination of both particle reinforcement and SPD by ECAP affect the precipitation kinetics in the Al-Cu alloy. DSC data and TEM micrographs are of AA2017 + 10 vol.-% Al₂O₃ after one pass of ECAP are given in Figs. 9 and 10, respectively. For comparison, the DSC curves of the reference base material (AA2017-T6) and after ECAP (AA2017 E1) are also included in Fig. 9. The curve of the AA2017 reinforced with Al₂O₃ after ECAP differs from both curves. The endothermic peak (peak 2 in Fig. 1) cannot be detected. This peak is associated with the dissolution of the GP zones and of the θ'' phase. The formation of GP zones is suppressed in particle-reinforced Al-Cu alloys, [1], and the dissolution of the θ'' phase is most likely masked by the onset of the combined peaks 3+4 that are shifted towards even lower temperatures (compared to the AA2017-T6 condition the peak 3+4 is about 70-80 K lower).

One notable difference is the evolution of the DSC curve at temperatures beyond 300 °C. In contrast to the reference conditions (E1 and T6) the curve of the reinforced AA2017 material after ECAP increases, suggesting exothermic reactions. It is reasonable to assume that this feature of the heat flow in the DSC curve indicates recovery of the material that is characterized by a high dislocation density after ECAP.

Fig. 9: DSC curves of AA2017 + 10 vol.-% Al₂O₃ after one pass of ECAP, AA2017 after one pass of ECAP and AA2017-T6 as reference. Only one characteristic peak ("3+4") can be observed for the reinforced condition.

Fig. 10a shows the TEM micrograph of the microstructure after a DSC scan that was interrupted at peaks 3+4. The high dislocation density associated with ECAP can be observed. It proved difficult to identify precipitates in this strongly deformed microstructure; the open black arrows highlight some θ’ precipitate and the black arrow points out a small but coarsened θ precipitate. Clearly, both precipitation steps occur simultaneously in the temperature range covered by peaks 3+4.

We note that the size of θ’ and θ precipitates is smaller than in the previously discussed material conditions. In contrast, the amount of dislocations and vacancies is further increased. These defects
provide additional sites for nucleation. An increase in defect density therefore results in more nuclei, and a larger number of nuclei leads to the formation more (and finer) precipitates. Our results demonstrate that the combination of particle reinforcement with Al₂O₃ and ECAP leads to further accelerated precipitation kinetics, with the additional benefit of smaller precipitates. Fig. 10b shows that, at higher temperatures (region 5), the equilibrium θ phase is also coarsened. Moreover, the much lower dislocation density in Fig. 10b confirms that recovery processes can contribute to the increasing heat flow in this temperature range.

Finally, Figs. 11 and 12 demonstrate that particle-reinforcement with SiC leads to similar DSC curves and microstructural features as reinforcement with Al₂O₃. While recovery processes are not directly obvious from the DSC data at temperatures beyond 300 °C, they can be inferred from the decreasing dislocation density between peaks 3+4 and region 5 (Fig. 12).

![Fig. 10: TEM micrographs of AA2017 + 10 vol.-% Al₂O₃ after one pass of ECAP. (a) Material after heating to peaks 3+4, and (b) in region 5. Open black arrows highlight θ' phase; black arrows indicate θ phase.](image)

![Fig. 11: DSC curves of AA2017 + 10 vol.-% SiC after one pass of ECAP, AA2017 after one pass of ECAP and AA2017-T6. Only one characteristic peak can be observed for the reinforced condition.](image)

![Fig. 12: TEM micrographs of AA2017 + 10 vol.-% SiC after one pass of ECAP, at (a) peak 3+4, and (b) region 5. Open black arrows indicate θ' phase, black arrows indicate θ phase.](image)
4. Summary and Conclusions

Using DSC measurements and TEM analysis, we have analyzed how particle reinforcement (either using Al$_2$O$_3$ or SiC), severe plastic deformation by ECAP, or a combination of both, affect precipitation kinetics in an AA2017 alloy. Our results show that particle reinforcement of AA2017 suppresses the formation of GP zones. Furthermore, an overlapping of the formation of the $\theta'$ and $\theta$ phases can be documented. Particle reinforcement also leads to a pronounced shift of peak temperatures towards lower temperatures: the precipitation kinetics are considerably accelerated irrespective of the type of reinforcing particles.

SPD by ECAP also suppresses the formation of GP zones, leads to an overlapping of the formation of the $\theta'$ and $\theta$ phase and shifts the peak temperatures towards lower temperatures. When particle-reinforcement and ECAP are combined, the formation of GP zones is suppressed and the endothermic peak related to the dissolution of the $\theta''$ phase is not observed because the peak(s) associated with the formation of $\theta'$ and $\theta$ phases is shifted to even lower temperatures. Compared to the reference AA2017-T6, the shift of these peaks for both reinforced materials after ECAP is about 70-80 K – the most pronounced acceleration of precipitation kinetics observed in this systematic study. These findings can be rationalized by considering the strong increase of dislocation density during ECAP: both the high dislocation density and the large number of grain boundaries in the ultrafine-grained microstructures subsequently allow for faster diffusion processes.

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