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Precipitation during homogenization cooling in AlMgSi alloys

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Abstract: Precipitation during the industrial cool down takes place predominantly above 300 °C in the EN AW−6082 and 6005 alloys. The phase precipitation throughout cooling is equilibrium β phase. A considerable capacity is retained after the cool down for further precipitation during a subsequent heating cycle. The β-Mg_2Si is once again the predominant phase that forms during a scan heating cycle employed in exactly the same manner with the industrial billet preheating operation. The precipitation in the 6060 alloy, on the other hand, occurs predominantly below 300 °C with additionally β'-Mg_2Si particles formed below 200 °C.
Key words: aluminium alloys; extrusion; precipitation; homogenization

1 Introduction

Aluminium extrusions are used in a variety of structural applications ranging from building and automotive to aerospace industries [1]. AlMgSi alloys claim over a 90% share of the total extruded volume owing to an attractive combination of mechanical properties, corrosion resistance, extrudability and an excellent response to surface finishing operations [2].

The processing of AlMgSi billets always starts with a homogenization cycle since the homogenized billets are extruded easier and faster and give better surface finish as well as higher tensile properties than as-cast billets [3]. Heating to the homogenization temperature is relative routine and must be sufficiently slow to avoid the melting of coarse eutectics of the cast billet. The rest of homogenization treatment consists of two critical steps: soaking followed by cooling at a controlled rate [4]. The interdendritic network of β-AlFeSi plates is replaced by round α-AlFeSi particles [5−8]; Mg_2Si precipitates and coarse eutectics are solutionized [6,9,10] and the coring inherited from the as-cast state is levelled out in favour of a homogeneous distribution of solute Mg and Si during soaking.

The cooling of billets to room temperature at the end of soaking, the so called "cool down" step of the homogenization treatment, is just as critical as it impacts the extrudability and section properties. The extrudability is improved by an increasing cooling rate after homogenisation [11]. The formation of coarse Mg_2Si particles must be avoided as they take much longer time and/or higher temperature to dissolve during preheating and tend to melt during extrusion once they survive the preheating step. It is of great technological interest to identify the range of temperature over which such Mg_2Si particles form. The present work was undertaken to identify the critical temperature range for precipitation in three popular Al−Mg−Si alloys, namely EN AW−6082, EN AW−6005 and EN AW−6060 alloys, in order to design more efficient cooling cycles for better extrudability.

2 Experimental

The EN AW−6082, EN AW−6005 and EN AW−6060 alloys used in the present investigation were cast industrially with a vertical DC caster, the dimensions are d203 mm×6 m, and the compositions are listed in Table 1. Samples for homogenization experiments were sectioned from a transverse slice of the billet, at least 10 mm away from the surface to avoid possible microstructural and compositional variations from one sample to the other. The homogenization treatment involved heating the billet samples at a rate of 250 °C/h to 580 °C and soaking for 8 h. This heating rate was selected to avoid the premature melting of eutectic phases of the cast billets. Soaked samples were cooled

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Table 1 Compositions of AlMgSi alloys (mass fraction, %)

Alloy	Composition/%							
	Si	Fe	Mn	Mg	Cr	Dispersoid formers (Mn+Cr)	Si_{ex}	Mg_2Si
6082	0.985	0.222	0.423	0.599	0.091	0.514	0.424	0.928
6005	0.631	0.209	0.127	0.458	−	0.127	0.254	0.726
6060	0.455	0.218	0.039	0.414	−	0.039	−	0.653

to room temperature within approximately 200 min. The temperature vs time curve is shown in Fig. 1. This cooling cycle was adapted from the industrial homogenization practice and gave an average cooling rate of approximately 250 °C/h over the critical temperature range of 500−200 °C. Different sets of soaked EN AW−6082, EN AW−6005 and EN AW−6060 billet samples were quenched in water at 400, 350, 300, 250, 200 and 150 °C during cooling in order to identify the critical temperature range for precipitation activities. Two additional sets of samples were produced in addition to those quenched in water while cooling from the soak temperature. The first set was water-quenched right after soaking directly from 580 °C while the second set was cooled inside the furnace within 18 h at an average cooling rate of approximately 30 °C/h.

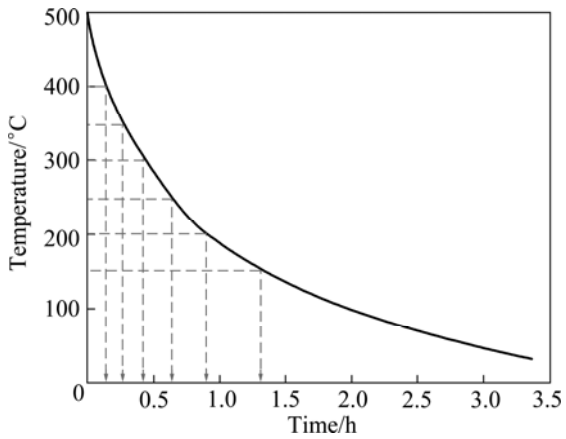

Fig. 1 Change in temperature with time during a typical industrial homogenization treatment. The T vs. t data was recorded after the billet cooled to 500 °C

Water-quenched samples were prepared with standard metallographic techniques, ground with SiC paper, polished with 3 μm diamond paste and finished with colloidal silica. They were examined after etching with 0.5% HF solution using a Olympus BX51M model optical microscope. The XRD patterns were recorded with a Shimadzu XRD 6000 diffractometer equipped with Cu K_α radiation operated at a very low scanning rate (<0.5 (°)/min) to increase the counting frequency. A Sigma test unit was used to measure the electrical conductivity of the quenched samples for the investigation of the progress of the precipitation activities. Differential scanning calorimetry (DSC) experiments were also performed using a Setaram Labsys model DSC unit by placing the sample disc in the sample pan and super purity aluminium of equal mass in the reference pan of the cell. The cell was equilibrated at 20 °C and then heated to 600 °C at 10 °C/min under flowing argon (1 L/h). The heat effects associated with precipitation reactions were then obtained by subtracting a super purity Al baseline run from a given heat flow curve.

3 Results and discussion

The samples directly quenched in water from the soaking temperature exhibit a supersaturated solid solution while a fully precipitated state with a Mg- and Si-depleted matrix is produced in samples cooled inside the furnace. The electrical conductivities of the former are measured to be 23.3, 26.2 and 28.0 MS/m while those of the furnace-cooled samples are 28.85, 29.15 and 29.95 MS/m for EN AW−6082, EN AW−6005 and EN AW−6060 alloys, respectively. The difference between the electrical conductivities of the supersaturated and fully depleted solid solutions is a sound measure of the maximum precipitation capacity, i.e. achieved at the maximum cooling rate, and is estimated to be 5.55, 2.95 and 1.95 MS/m for EN AW−6082, EN AW−6005 and EN AW−6060 alloys, respectively. These values are consistent with the solute capacities dictated by the chemical compositions of the respective alloys and imply that the precipitation capacity is the largest for EN AW−6082 alloy and the smallest for the EN AW−6060 alloy.

The electrical conductivity change of samples as a function of the quench temperature during quenching is shown in Fig. 2(a). The fractions precipitated during cooling are estimated from these electrical conductivity measurements. This was done by comparing the change in electrical conductivity until quenching at each quench temperature with the maximum precipitation capacity of respective alloys. The electrical conductivity of the EN AW−6082 sample quenched at 400 °C for instance is 24.8 MS/m, evidencing an increase of 1.5 MS/m with

respect to the supersaturated state of 23.3 MS/m, due to partial precipitation during cooling to 400 °C. The same calculations were performed for the rest of the samples quenched at lower temperatures. The precipitated fraction obtained are plotted as a function of quench temperature to illustrate the evolution of precipitation during the cool down, as shown in Fig. 2(b).

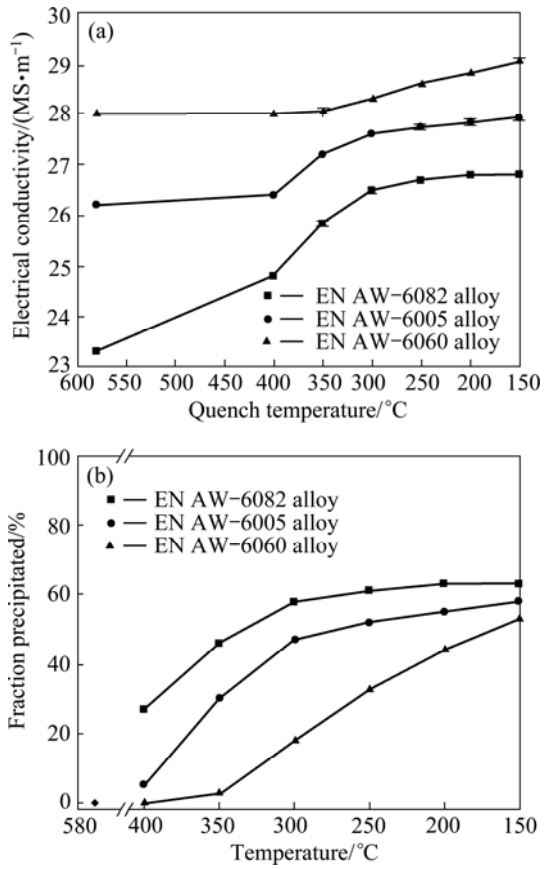

Fig. 2 Electrical conductivity (a) and fraction precipitated (b) of samples quenched in water during homogenization at cooling rate of 250 °C/h

As seen from Fig. 2(b), nearly a quarter of the available capacity already precipitates at 400 °C in the 6082 alloy. The precipitation fraction increases with decreasing temperature at a decreasing rate and levels out at 200 °C where it is estimated to be 63%. It is thus fair to claim that only two thirds of the available capacity is precipitated by the time when the temperature of the 6082 billet drops to 150 °C during an industrial cool down. The temperature ranges of the precipitation activities in 6005 and 6060 alloys are evidently displaced to lower temperatures. There appears to be hardly any precipitation before 400 °C in the case of the former and before 350 °C for the 6060 alloy. This is believed to be linked with the dispersoid concentration of the respective alloys which decreases in the order of 6082, 6005 and 6060 alloys (Table 1). While relatively delayed, the evolution of precipitation in 6005 alloy is very similar to that in 6082 alloy. The response of the 6060 alloy to the same cooling cycle is markedly different. The precipitated fraction still exhibits an increasing trend at 150 °C in the 6060 alloy partly owing to a late start, while the precipitation activities of 6082 and 6005 alloys are almost terminated at 200 °C. The precipitating phase is identified by XRD analysis of quenched samples to be predominantly the β-Mg_2Si phase in 6082 and 6005 alloys while weak β'-Mg_2Si reflections are also noted in the XRD spectrum of 6060. A substantial capacity for precipitation is nevertheless retained in all alloys at the end of the homogenization cooling.

The microstructures of samples quenched in water during cooling are illustrated in Fig. 3. The precipitates in these micrographs are equilibrium β-Mg_2Si. The change in microstructural features with decreasing temperature is consistent with the electrical conductivity measurements. There is a significant amount of β precipitated already at 400 °C in the case of 6082 alloy. Both the size and number of β precipitates increase with decreasing temperature. The increase in precipitation is remarkable from 400 to 350 °C but fades with decreasing quench temperature. The progress of the precipitation activities in the 6005 alloy is slightly delayed but nevertheless shows a similar trend. While there is hardly any precipitation at 400 °C, the amount of precipitate is considerable at 350 °C and increases with decreasing temperature. The precipitate features in the samples quenched at 200 °C are not much different from those quenched at 250 °C, suggesting that the precipitation process is near completion at 200 °C during the cooling down. The evolution of precipitation in the 6060 alloy, on the other hand, is markedly different. Precipitation is delayed further as inferred from the micrographs of samples quenched above 300 °C. Precipitates are noted at 300 °C for the first time. Both the size and number of the precipitates increase with decreasing temperature. It is inferred from the marked change in microstructural features from 250 °C to 200 °C and from Fig. 2(b) that the precipitation is still in progress below 200 °C. The extent of precipitation in each alloy is in reasonable agreement with the precipitation capacities estimated from the electrical conductivity measurements.

The DSC analysis provides further evidence for the account given above in view of the conductivity measurements and the microstructural analysis (Fig. 4). The DSC spectrum of the EN AW−6082 sample quenched directly at the end of soaking reveals the full precipitation sequence owing to a supersaturated matrix, as shown in Fig. 4(a). The precipitation sequence in AlMgSi alloys is well established to be SSSS→G.P. zones→β''→β'→Si→β [12−20]. Hence, the first weak exothermic signal centered at approximately 160 °C is

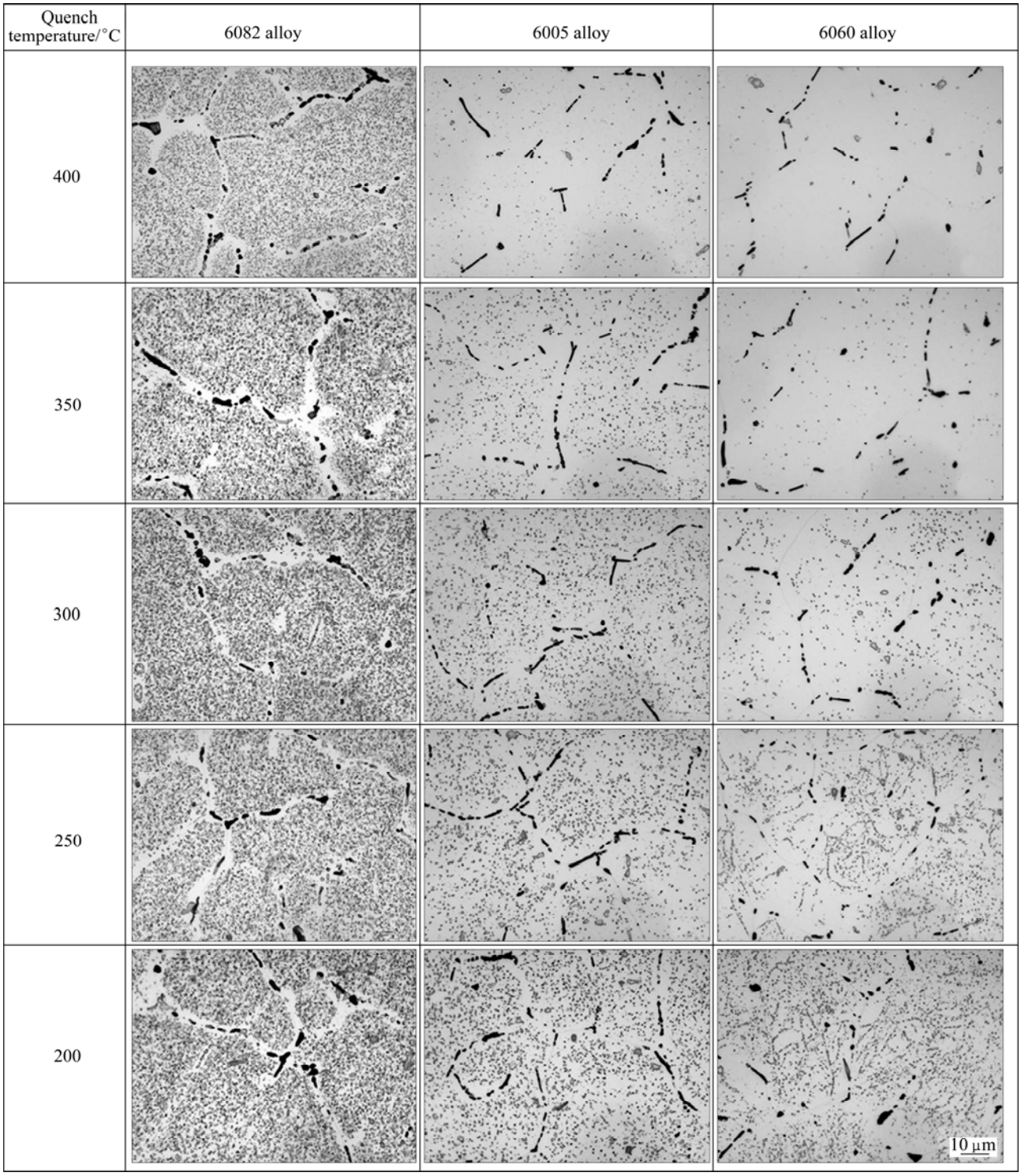

Fig. 3 Micrographs of samples quenched in water at different temperatures while cooling to room temperature at rate of 250 °C/h

assigned to the formation of G.P. zones while the following weak endothermic signal to their dissolution. The first major exothermic peak centered at 230 °C is linked with the precipitation of the metastable β' phase that is responsible for the peak hardness values obtained in 6082 alloys artificially aged to the T6 temper [21]. The neighbouring peak is produced by the formation of β' phase. This peak merges with a relatively small one accounted for by the precipitation of excess Si. The last exothermic peak is produced by the formation of equilibrium β phase while the next endothermic trough is linked with its dissolution.

The peak configuration in Fig. 4(a) and the corresponding precipitation sequence is largely retained

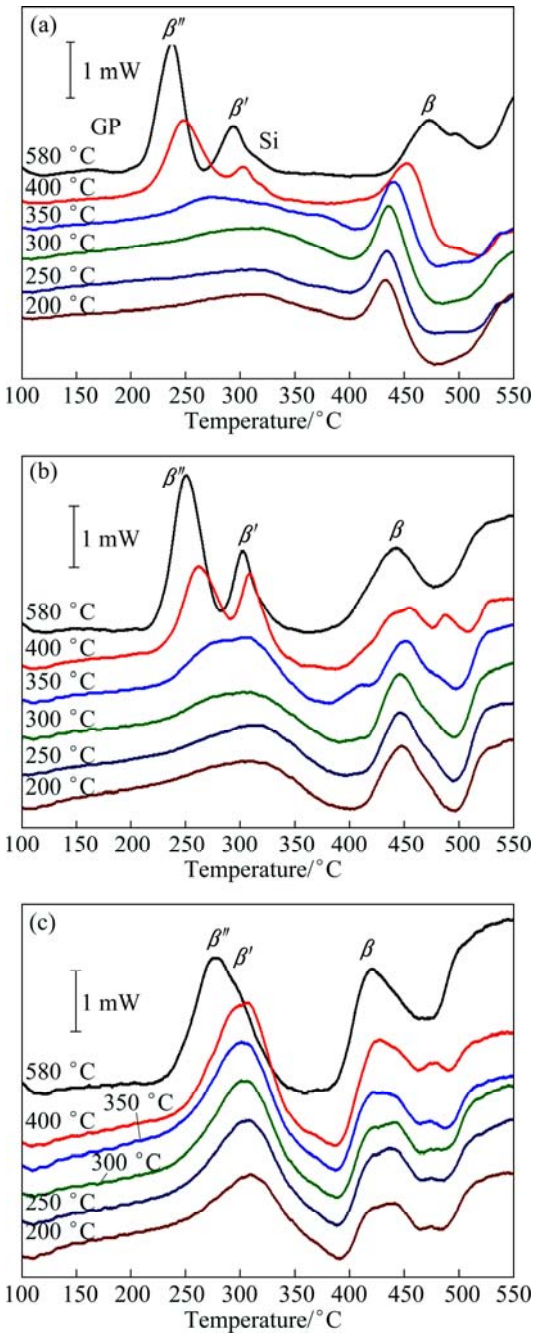

Fig. 4 DSC spectra of samples cooled down in water at different temperatures while cooling to room temperature at rate of 250 °C/h: (a) EN AW−6082 alloy; (b) EN AW−6005 alloy; (c) EN AW−6060 alloys

in the 6082 sample quenched in water at 400 °C during cooling down. The β'' and β' peaks, however, are relatively smaller and slightly displaced to higher temperatures, evidencing that some precipitation has already occurred during cooling to 400 °C. The β peak, on the other hand, has retained its size and shifted to lower temperatures. The displacement of β peak suggests that the precipitation of β is encouraged during a subsequent heating cycle, possibly owing to the β precipitates inherited from the cool down. β precipitation occurs readily via the deposition of solute Mg and Si on the pre-existing β precipitates. Marked changes are noted in the DSC spectra of samples quenched at lower temperatures. The β'' and β' peaks gradually disappear in spite of a strong β peak. The missing β'' and β' peaks seem to imply that the β'' and β' phases have already precipitated during post-soaking cooling. However, the hardness measurements on these samples and the XRD analysis fail to support such an account (Fig. 5). The hardness of 6082 samples quenched during the cooling down is about HV 45, which is too low to be linked with the precipitation of β'' and β' phases. It is concluded from the foregoing that there must be a critical level of supersaturation to facilitate the precipitation of the precursor phases during cooling to lower temperatures as well as during a subsequent heating cycle. When the precipitation capacity of the matrix falls below this critical level, the equilibrium β phase is the only phase that can precipitate. It is worth noting that β-Mg_2Si is solutionized at relatively lower temperatures in samples cooled at 250 °C/h than in water-quenched samples.

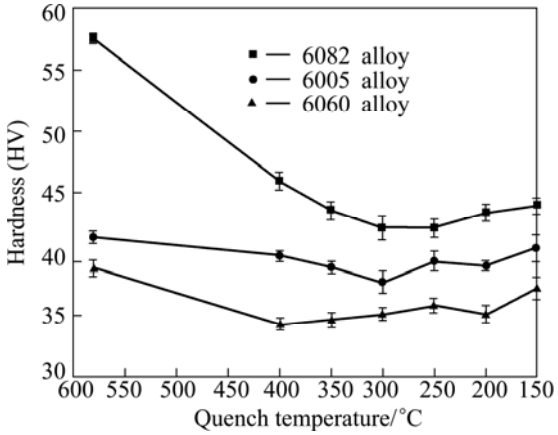

Fig. 5 Change in hardness of samples quenched in water directly at the end of soaking, i.e. at 580 °C, and at different temperatures while cooling to room temperature at a rate of 250 °C/h

The DSC spectra of the water-quenched EN AW−6005 samples show features similar to those of EN AW−6082 alloy regardless of the quench temperature, as shown in Fig. 4(b). The β'' and β' peaks, that have merged into a β''/β' doublet below 400 °C, however, are relatively bigger suggesting that less precipitation occurs in 6005 samples until each quench temperature during the cool down with respect to the 6082 counterparts, confirming that the precipitation process in the former is relatively delayed. This is more evident in the case of EN AW−6060 alloy. The DSC spectrum of the sample quenched at 400 °C is nearly identical to that quenched directly at the soaking temperature, evidencing that no precipitation has taken place at 400 °C. The β''/β' doublet

is still very strong with a substantial precipitation capacity until 250 °C, as shown in Fig. 4(c). This is essentially why the β peak in 6060 samples remains undisplaced contrasting the case of 6082 alloy where it moves to lower temperatures with decreasing quench temperatures. The lack of β' and β' precipitation during a subsequent heating cycle in the latter encourages β formation at relatively high temperatures.

A series of special DSC experiments were performed to follow the precipitation activities during the cooling down. The industrial homogenization conditions were reproduced inside the calorimeter for disc samples of approximately 50 mg. The cool down was performed at a rate higher than that employed in the industrial practice in order to improve the intensity of the exothermic signals associated with the precipitation process. This is considered to be a safe measure since the location of the precipitation signal was found to be rather insensitive to the cooling rate between 250 and 1000 °C/h. The DSC spectra of the three alloys recorded during cooling at 500 °C/h following a 2 h soaking step at 580 °C are shown in Fig. 6. The deviation from the baseline at approximately 425 °C marks the onset of precipitation in the 6082 alloy during the cool down. The precipitation reaction is accelerated shortly and is the most intense at approximately 391 °C where the exothermic signal goes through a peak, then slows down with decreasing temperatures. The onset of precipitation is displaced to approximately 405 and 355 °C for the 6005 and 6060 alloys, respectively. The precipitation reaction in the former is slow at first and reaches peak at approximately 350 °C. The amount of overall precipitates is much less in the 6060 alloy with respect to the former two alloys, giving a DSC trace that does not allow a sound analysis of the progress of precipitation at the present cooling rate. It would take much higher cooling rate to achieve a stronger signal for this particular alloy. The DSC spectra obtained are in perfect agreement with the electrical conductivity measurements and the microstructural analysis. It is fair to claim that one can obtain valuable information in the temperature range, and the progress of the precipitation reaction during a cooling cycle follows heating and soaking steps that are reproduced in a calorimeter in a manner similar to the industrial practice.

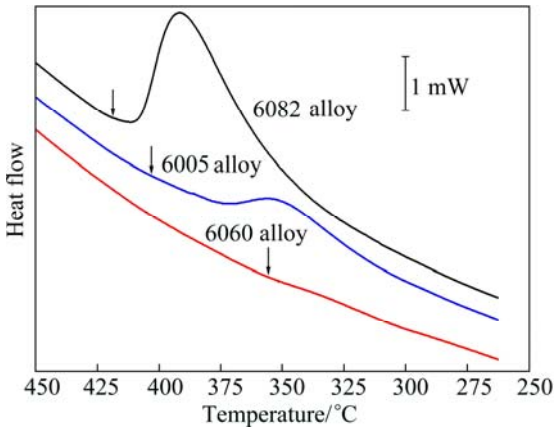

Fig. 6 DSC cooling scans of Al−Mg−Si alloys (Cooling rate in DSC unit was approximately 8 °C/min (500 °C/h))

4 Conclusions

1) The precipitation during the industrial cool down starts at approximately 425 °C and takes place predominantly above 300 °C in the EN AW−6082 alloy. The phase precipitating throughout cooling is the equilibrium β phase. A considerable capacity is retained after the cool down for further precipitation during a subsequent heating cycle.

2) The β-Mg_2Si is once again the predominant phase that forms during a scan heating cycle employed in exactly the same manner with the industrial billet preheating operation. It is fortunate that coarse β-Mg_2Si particles thus formed are solutionized at lower temperatures with respect to those in water-quenched samples. The precipitation temperature range is slightly displaced to lower temperatures in the 6005 alloy. Much of the precipitation reaction during cooling nevertheless takes place above 300 °C.

3) The overall response to homogenization cooling of the 6005 alloy is very similar to that of 6082 alloy. The precipitation in the 6060 alloy, on the other hand, occurs predominantly below 300 °C with additionally β'-Mg_2Si particles formed below 200 °C.

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AlMgSi 合金均匀化冷却处理过程中的沉淀析出

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摘　要：工业冷却处理 EN AW−6082 和 6005 合金，在 300 °C 以上发生析出。整个冷却过程中的析出相是平衡β 相。在冷却之后的加热环节，仍保持有相当的析出量。扫描加热与工业预热处理方式相同，期间β-Mg_2Si 还是主要形成相。而 6060 合金的析出主要发生在 300 °C 以下，并且在 200 °C 以下还伴有β'-Mg_2Si 颗粒的形成。

关键词：铝合金；挤压；沉淀析出；均匀化处理

(Edited by Jing-hua FANG)