Effects of Cd and Sn on double-peak age-hardening behaviors of Al-Si-Cu-Mg cast alloys

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Abstract: The effects of trace elements Cd and Sn on precipitation process of Al-Si-Cu-Mg cast alloys were investigated in the present research. It is shown that the addition of Cd and Sn not only increases remarkably the aging peak hardness and reduces the time to reach aging peak, but also eliminates the double-aging-peak phenomenon which appears in Al-Si-Cu-Mg alloys. In Al-Si-Cu-Mg alloys the first aging peak corresponds to GP zones (especially GP II), and the second one is caused by metastable phases. The obvious time interval of transition from GP II to metastable phases associates with the double-aging-peak phenomenon. The results of DSC and TEM show that Cd/Sn elements suppress the formation of GP I zone, stimulate the formation of θ'', θ' and θ phases, and then shorten remarkably the temperature intervals of each exothermic peak. Because the transition interval between GP II zone and metastable phases is shortened by Cd/Sn in Al-Si-Cu-Mg cast alloys, θ' phase coexists with θ'' phase in matrix of ageing peak condition, which causes effective hardening on the alloys, and at the same time, eliminates the double-aging-peak phenomenon.

Key words: Al-Si-Cu-Mg cast alloys; Cd /Sn addition; age-hardening; precipitation

Among the commercial aluminum cast alloys, Al-Si-Cu-Mg alloys are extensively used mainly because of its good castability and excellent mechanical properties in the heat-treated condition [1,2]. It is accepted that precipitation sequence of α is mainly responsible for the precipitation hardening of Al-Si-Cuq-Mg alloy [2-4], namely: α→GP zones→θ''→θ'→θ phase, where GP zones are Cu/Mg Guinier-Preston zones, θ'' and θ' are metastable phases, and θ is equilibrium phase.

In recent years, the double-peak aging behaviors of Al-Si-Cu-Mg alloys were noticed [5-7], and it was also found that the first peak is higher than the second one. The age hardening behavior is related to the precipitation sequence of alloys. Li, et al. [5] proposed that in Al-Si-Cu-Mg alloys the first aging peak is the result from the high-density GP zone (especially GP II zones), while the second one is attributed to metastable phases. The obvious interval during the transition from GP zones to metastable phases, which are caused by dissolution of GP zones and the nucleation of metastable phases on dislocation, may be the main reason for the formation of the double aging peaks.

On the other hand, micro-alloying addition such as Sn, Cd or In is known to change the precipitation sequence of θ in Al-Cu alloys from α→(GP →GP II→θ''→θ) to α→(GP→θ'+ Cd'→θ'+ Cd'→θ + Cd) [8-9]. The addition of Sn, Cd and In results in an extremely fine and uniform dispersion of θ' precipitates which effectively strengthen the alloys. Various mechanisms have been proposed to explain this phenomenon. Sankaren and Laird [10] suggested that the trace elements segregate to the edges of the θ' precipitates and thereby reduces the total interfacial energy. Bondan [11] proposed that dislocation loops are formed by the condensation of vacancies during quenching immediately following the solution treatment, which provides heterogeneous nucleation sites for θ'.

However, there are few published data describing the influence of trace elements of Cd (Sn and In) on aging behavior of Al-Si-Cu-Mg alloys although such alloys have extensive industrial applications. Therefore, the present investigation has examined the effect of Cd/Sn on mechanical properties and precipitation processes of Al-Si-Cu-Mg cast alloys by means of transmission electron microscope (TEM), differential scanning calorimeter (DSC) and scanning electron microscope (SEM).

1 Experimental details

The experimental alloys listed in Table 1 were prepared from 99.99% pure aluminum, 99.98% pure Mg, Cd and Sn, and Al-25.98%Si, Al-4.01%Ti, Al-9.84%Mn and Al-29.98%Cu
master alloys. The alloys were melted in an electric (resistance) furnace, modified using ternary sodium–salts modifier, then cast in a preheated mold with an inner cavity of φ 12 mm × 60 mm. All alloys were solution treated at 525±5 °C for 12 hours in a high-temperature furnace with smart numerical control system under nitrogen gas, followed by water quenched to room temperature. The subsequent age treatment was kept in dried oven at 175 °C for 0 – 24 hours. At least five (5) test bars were used in each individual treatment.

Hardness specimens were lightly polished with SiC paper and aluminum powder polishing cloths. Hardness measurement was performed using a Brinell hardness tester with a load of 250 kg and a dwell time of 30 s. The Brinell hardness value at each state was an average of at least six (6) measurements.

Samples for TEM and HRTEM were cut into 3 mm diameter discs. Thin foils of TEM were mechanically polished to 70 μm, and further polished with the twin electrolytic jet polishing technique using a 30 vol% nitric acid and 70 vol% methanol etchant maintained at – 20 °C. TEM images were observed under a PHILIPS EM 420 unit operated at 100 kV, and high resolution microstructures were observed with PHILIPS EM2010 operated at 200 kV. The DSC analysis was performed at a scanning rate of 10 °C /min in a Perkin-Elmer 7 apparatus under protective argon atmosphere.

### Table 1 Chemical compositions of samples (wt %)

<table>
<thead>
<tr>
<th>No.</th>
<th>Si</th>
<th>Cu</th>
<th>Mg</th>
<th>Cd</th>
<th>Sn</th>
<th>Mn</th>
<th>Ti</th>
<th>Fe</th>
<th>Al</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>9.85</td>
<td>1.48</td>
<td>0.42</td>
<td>—</td>
<td>0.18</td>
<td>0.20</td>
<td>0.18</td>
<td>bal.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>9.82</td>
<td>1.55</td>
<td>0.45</td>
<td>0.10</td>
<td>—</td>
<td>0.18</td>
<td>0.18</td>
<td>0.17</td>
<td>bal.</td>
</tr>
<tr>
<td>3</td>
<td>9.78</td>
<td>1.51</td>
<td>0.43</td>
<td>0.28</td>
<td>—</td>
<td>0.18</td>
<td>0.19</td>
<td>0.19</td>
<td>bal.</td>
</tr>
<tr>
<td>4</td>
<td>9.85</td>
<td>1.50</td>
<td>0.41</td>
<td>0.57</td>
<td>—</td>
<td>0.15</td>
<td>0.18</td>
<td>0.15</td>
<td>bal.</td>
</tr>
<tr>
<td>5</td>
<td>9.56</td>
<td>1.48</td>
<td>0.38</td>
<td>—</td>
<td>0.09</td>
<td>0.19</td>
<td>0.18</td>
<td>0.17</td>
<td>bal.</td>
</tr>
<tr>
<td>6</td>
<td>9.60</td>
<td>1.45</td>
<td>0.40</td>
<td>—</td>
<td>0.21</td>
<td>0.16</td>
<td>0.17</td>
<td>0.16</td>
<td>bal.</td>
</tr>
</tbody>
</table>

### 2 Results

#### 2.1 Aging-hardening of alloys

The effect of Cd and Sn on the age-hardening ability of Al-Si-Cu-Mg alloys is shown in Fig.1. It can be seen that there is an obvious double aging-peak phenomenon in Al-Si-Cu-Mg alloys aged at 175 °C as researchers had previously reported [5-6]. In which the first peak appears at the 6-hour aging mark, and the second one at the 12-hour mark. With the addition of Cd and Sn, the second aging peak disappears, resulting in only one aging peak which appears after aged for 4 hours in the hardness curve of Al-Si-Cu-Mg-Cd/Sn alloys.

In addition, Fig.1 shows that the rate of hardening of Cd/Sn containing alloys is faster and that a significantly higher level of hardness is possible. However, this promotion of age-hardening ability by Cd/Sn improves at first and then tends to drop with the further increase of Cd and Sn contents in the alloys. The optimal contents of Cd and Sn in Al-Si-Cu-Mg alloys are at about 0.3wt% and 0.1wt%, respectively.

#### 2.2 DSC analysis

In this paper, the phenomena of the nucleation and growth of precipitation phases in Cd/Sn free alloy and in the Al-Si-Cu-Mg alloys respectively containing 0.28wt%Cd and 0.09wt%Sn were investigated by DSC with a heating rate of 10 °C/min at the as-quenched state as shown in Fig. 2.

Thermograms can be briefly described as follows:

Four distinct exothermic peaks marked as A, B, C and D corresponding respectively to the formation of GP zone, GP II zone (θ" phase), θ′ phase and θ phase (Al2Cu) [2-4] are visible in the DSC curves of tested alloys (No.1). The detailed characteristics of these peaks are reported in Table 2. It is noted that the temperatures corresponding to the exothermic peaks B, C and D obviously decrease with Cd / Sn addition,
especially the peaks C and D that decrease respectively by about 40 °C and 140 °C, as compared with the Cd/Sn free alloy. In contrast, the temperature corresponding to exothermic peak A increases by about 17 °C.

From the above results, it is revealed that the addition of Cd/Sn in Al-Si-Cu-Mg alloys strongly influences the precipitation phenomena of these alloys. Both the elements suppress the formation of GP zone and stimulate the formation of \( \theta'' \), \( \theta' \) and \( \theta \) phases, with stronger effect by the Cd element. The temperature intervals of each exothermic peak are remarkably shortened in the Cd/Sn containing alloys, such as the temperature interval between peaks B (corresponding to formation of \( \theta'' \) phase) and C (corresponding formation of \( \theta' \) phase) is shortened to 34.7 °C for Cd containing alloys and to 45.1 °C for Sn containing alloys from 64.4 °C for (the Cd/Sn free) Al-Si-Cu-Mg alloy.

### 2.3 TEM observation

Figure 3 shows the bright field (BF) TEM images of microstructures and corresponding selected-area diffraction pattern (SADP) of the Al-Si-Cu-Mg alloy (No.1), Al-Si-Cu-Mg-Cd alloys (No.3) and Al-Si-Cu-Mg-Sn alloys (No.5), all aged at 175 °C. The bright-field image of Al-Si-Cu-Mg alloy aged at 175 °C for 6 h (the first aging peak) is shown in Fig.3(a), in where the ultra fine and dense precipitates (~10 nm) appear as short rods which homogeneously disperse in the \( \alpha \) matrix. The corresponding [001] \( \alpha \) SADP inserted in the upper corner of the bright-field image reveals faint continuous streaking in <100> Al through {200} Al, the characteristics of which are representative of GP zone formation \[12\]. In the microstructure of Al-Si-Cu-Mg sample aged at 175 °C for 12 h (corresponding the second aging peak), there are numerous thin, needle-like precipitates in orientation along <100> \( \alpha \), which are 5 – 15 nm in thickness and 100–150 nm in length, as shown in Fig.3(b). The diffraction patterns of these precipitates are shown in Fig.4(a), with superlattice spots at (110) \( \alpha \), identical to those reported for \( \theta' \) phase by John et al \[13\]. The indexing of the diffraction pattern is presented in Fig.4 (b).

The microstructure of Cd/Sn-containing alloys aged for 4 h corresponding to aging peak contains more ultra fine highly-dense needle-like phase (at about 30–50 nm in length) than...
the Cd/Sn free alloy aged for 6 h (Fig.3(c) and (e)). The corresponding [001] Al SADP (inserted) shows weak spots of (020) \( \theta' \) and faint streaks along (001) Al, positively identifying them to be \( \theta'' \) phase and \( \theta' \) phase, respectively. After aged for 8 h numerous coarse plate-like \( \theta' \) and \( \theta \) phases precipitate in matrix, the size and distribution of which are larger than the precipitates in the Al-Si-Cu-Mg alloy aged for 12 h (Fig.3 (d) and (f)). However, the sizes of metastable phases which precipitate in Cd-containing alloys aged for 8 h appear to be slightly larger than those in Sn-containing alloys, which agrees with the DSC results that the precipitation of \( \theta' \) phase is accelerated more by Cd than Sn.

### 3 Discussions

The investigation findings reveal that the addition of Cd/Sn in Al-Si-Cu-Mg alloys strongly influences the precipitation phenomena of the alloys. Both elements suppress the formation of GP zone and stimulate the formation of \( \theta'' \), \( \theta' \) and \( \theta \) phases, leading to ultra fine structure and highly dense distribution of these phases and increased mechanical properties, with stronger effect by the Cd element.

At an early stage of aging treatment, due to the high binding energies between the Cd/Sn atoms and vacancies (see Table 3), Cd/Sn -vacancy and Cd/Sn -Cu-vacancy clusters are formed, thus effectively reducing the number of free vacancies available to promote the diffusion of Cu atoms for the formation of GP zones, and consequently suppressing the formation of GP zone \([8]\). \( \theta'' \rightarrow \theta' \rightarrow \theta \)

On the other hand, the following reasons for stimulating the formation of \( \theta'' \), \( \theta' \) and \( \theta \) phases have been advanced. Firstly, the addition of Cd reduces the interfacial energy and the lattice mismatch for the \( \theta' \) - \( \alpha \) interface and hence stimulates \( \theta'' \), \( \theta' \) and \( \theta \) phase precipitation by providing better lattice matching \([10]\). Second, clustering of Cd and Sn elements, which have larger atomic volume than matrix aluminum (see Table 3), would create a compressive volume strain in the matrix, thus attracting a high concentration of vacancies and the smaller Cu atoms to the interfacial region, providing an excellent condition for the nucleation of \( \theta'' \), \( \theta' \) and \( \theta \) phases\([14]\).

It is noted that the effect of addition of Cd and Sn on precipitation phenomena not only strengthen effectively the alloy, but also eliminate the double-aging-peak phenomena of Al-Si-Cu-Mg alloys. Based on DSC results and observation of TEM micrographs, the precipitation process of the Al-Si-Cu-Mg alloys is likely to be as follows: supersaturated solid solution \( \rightarrow \) formation of GP zone \( \rightarrow \) dissolution of GP zone \( \rightarrow \) formation of metastable phase \( \rightarrow \) formation of equilibrium phase. The obvious interval during the transition from GP zone to metastable phase, which is caused by dissolution of GP zone and the nucleation of metastable phase on dislocation, may be the main reason for the formation of double aging peaks \([5]\).

From the DSC results, it is found that the enhancement of \( \theta' \) formation in Cd/Sn-containing alloys causes the shortening of the interval between GP II and metastable phase (Table 2). There is no obvious transition from GP II zone (\( \theta'' \)) to metastable phase (\( \theta' \)) in the Cd/Sn-containing alloys, and \( \theta' \) phase coexists with \( \theta'' \) phase in matrix during aging peak (shown in Fig.3(c) and (e)). It is well known that GP zones, especially GP II, and metastable phase can strengthen effectively alloys, as the result that those high-density and finely mixed \( \theta'' \) phase and \( \theta' \) phase homogeneously precipitate in \( \alpha \) matrix, causing stronger hardening on the alloy than any single one (phase and/or mechanism) and, at the same time, the elimination of the double aging-peak phenomenon.

### 4 Conclusions

(1) The addition of Cd/Sn increases remarkably the aging peak hardness and reduces the time required to reach the
aging peak in Al-Si-Cu-Mg alloys. The optimal addition of Cd and Sn in Al-Si-Cu-Mg cast alloys is about 0.3% and 0.1%, respectively.

(2) Cd/Sn elements suppress the formation of GP I zone and enhance the formation of θ″, θ′ and θ phases, with stronger effect by Cd. Moreover, the temperature intervals of each exothermic peak are also remarkably shortened in the Cd/Sn-containing alloys.

(3) The microstructure of Cd/Sn-containing alloys at peak hardness is the ultra fine and highly- dense needle-like θ′ phase coexisting with the θ″ phase (appearing as short lines) in matrix. After aged at 175 °C for 8 h, numerous coarse plate-like θ′ and θ phases precipitate in the matrix, the size and distribution of which are larger than the precipitates of the Al-Si-Cu-Mg alloy aged for 12 h.

(4) The Cd/Sn addition shortens the interval between GP I and metastable phase. In matrix under the aging peak condition, θ′ phase coexists with θ″ phase, and then causes effective hardening on the alloy, and at the same time, the double-aging-peak phenomenon can be eliminated.

References

[8] Sofyan B T, Raviprasad K, Ringer S P. Effects of microalloying with Cd and Ag on the precipitation process of Al-4Cu-0.3Mg(wt%) alloy at 200°C. Micron, 2001, 32: 851–856.