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Influence of Strontium, Silicon and Calcium Additions on the Properties of the AM50 Alloy

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Abstract

The increasing use of heat resistant magnesium alloys for automotive applications is expected to influence the chemical composition of upcoming post consumer scrap. Therefore it would be useful to define alloys that resemble the future composition of the material. For this purpose a matrix of potential recycling systems has been set up. AM50 was used as a base material to which decisive amounts of strontium, silicon and calcium were added. The basic heat resistant alloy systems AJ, AS, and AX have been investigated closely. This work deals with combinations of the three above mentioned elements. Some essential observations shall be presented concerning the development of the microstructure and its influence on the materials properties. For combined additions of strontium, silicon and calcium the formation of a new ternary phase has been observed. The compound has a positive influence on the fracture elongation and the corrosion rate in the salt spray test.

Introduction

Cost competitive, heat resistant magnesium alloys use the AM-system as a base material. The heat resistance is achieved by additions of strontium, silicon and calcium. The AS-system contains 1.8-5.0\% aluminium and 0.5-1.5\% silicon, see ASTM B94, the AX-system covers 5-8\% aluminium and 1-3\% calcium \cite{1} and finally the AJ-system is composed of 4.5-6.6\% aluminium and 1.7-2.8\% strontium, see ASTM B94. These alloys are increasingly used for components of the automotive drive train and upcoming post consumer scrap is going to be contaminated from the three above mentioned elements. In search of an attractive magnesium recycling system a matrix of alloys based on the AM50 alloy has been prepared. The base material was modified with up to 2\% of strontium, 1\% of silicon and 0.2\% of calcium. Several investigations of the material have been accomplished and promising alloys have already been fabricated via high pressure die casting \cite{2}. However, the strontium-silicon-rich magnesium alloys were not studied. Microstructure and properties of these materials have not been reported in literature.

Experimental

The alloy matrix was prepared via permanent mould casting. Sectioned ingots of primary AM50 were molten at 730\degree C. A mixture of argon and 0.2vol-\% SF\textsubscript{6} was used to prevent melt oxidation. The alloying elements were added in their pure form. After 30 minutes of stirring and 15 minutes of settling the melt was poured into a permanent mould preheated to 400\degree C. Ceramic foam filters supplied by FOSECO were used to slow down the melt before entering the mould and thereby prevent the formation of air entrapments. The chemical composition was investigated using a Spark Emission Analyser, Spectrolab9 from SPECTRO (OES). Microstructural investigations and phase analysis were performed using optical microscopy, scanning electron microscopy and X-ray diffraction. Round tensile specimens for mechanical testing were prepared and tested on a ZWICK Z050 tensile testing machine according to ASTM B557M. Round cylindrical specimens with a diameter of 6mm and a length of 15mm were machined for compression creep tests. Tests were
carried out on ATS Lever Arm Testers for 200h at 80MPa and 150°C. Salt spray tests were performed according to ASTM B117. Corrosion specimens were ground with silicon carbide paper, 1200grit and cleaned in ethanol prior to testing. Tests were performed for 48h with a 5% NaCl solution, pH7. All tests were repeated three times and the average values with their standard deviation are presented.

Results

Table 1 shows the chemical composition of the prepared alloys. It can be seen that the level of impurities is below the required thresholds for the alloy AM50. XRD-patterns in Figure 1 reveal the presence of magnesium and Mg₁₇Al₁₂ for the AM50 alloy. Addition of 1% strontium causes the formation of Al₃Sr and the disappearance of Mg₁₇Al₁₂. With increasing the strontium content to 2%, additional peaks of Mg₁₃Al₃Sr are observed. These results are in accordance with literature [3, 4]. Figure 2 shows XRD-patterns of the same alloys but with additions of 0.2% calcium and 1% silicon. In contrast to AM50, the Mg₂Si-phase forms in the ASMX51 alloy. With the addition of 1% of strontium a new compound is emerging which has been identified as Sr₆.₃₃Mg₁₆.₆₇Si₁₃. The maxima of Mg₂Si show a reduced intensity. The material containing 2% strontium and 1% silicon – AJSMX521 – exhibits increased maxima of Sr₆.₃₃Mg₁₆.₆₇Si₁₃. Traces of the Al₃Sr-phase are visible but no peaks of Mg₁₃Al₃Sr or Mg₂Si occur. In contrast to AJM51 and AJM52 the β-phase was detected in the AJSMX511 and the AJSMX521 alloys.

Table 1. Chemical composition of the permanent mould cast alloys in wt-%.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Al</th>
<th>Mn</th>
<th>Sr</th>
<th>Si</th>
<th>Ca</th>
<th>Zn</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Be</th>
</tr>
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<tbody>
<tr>
<td>AM50</td>
<td>4.97</td>
<td>0.302</td>
<td>&lt;0.002</td>
<td>0.017</td>
<td>0.001</td>
<td>0.011</td>
<td>0.0005</td>
<td>0.0023</td>
<td>0.0008</td>
<td>0.0010</td>
</tr>
<tr>
<td>ASMX51</td>
<td>4.92</td>
<td>0.297</td>
<td>&lt;0.002</td>
<td>1.05</td>
<td>0.128</td>
<td>0.012</td>
<td>0.0006</td>
<td>0.0027</td>
<td>0.0005</td>
<td>0.0011</td>
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<tr>
<td>AJM51</td>
<td>5.07</td>
<td>0.307</td>
<td>0.939</td>
<td>0.017</td>
<td>0.001</td>
<td>0.012</td>
<td>0.0006</td>
<td>0.0024</td>
<td>0.0008</td>
<td>0.0006</td>
</tr>
<tr>
<td>AJMX51</td>
<td>5.08</td>
<td>0.310</td>
<td>0.992</td>
<td>0.019</td>
<td>0.132</td>
<td>0.011</td>
<td>0.0007</td>
<td>0.0029</td>
<td>0.0007</td>
<td>0.0004</td>
</tr>
<tr>
<td>AJSMX511</td>
<td>5.17</td>
<td>0.264</td>
<td>0.803</td>
<td>0.932</td>
<td>0.130</td>
<td>0.013</td>
<td>0.0006</td>
<td>0.0020</td>
<td>0.0005</td>
<td>0.0006</td>
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<td>AJM52</td>
<td>5.18</td>
<td>0.340</td>
<td>1.87</td>
<td>0.015</td>
<td>0.001</td>
<td>0.011</td>
<td>0.0007</td>
<td>0.0028</td>
<td>0.0006</td>
<td>0.0016</td>
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<tr>
<td>AJMX52</td>
<td>5.06</td>
<td>0.321</td>
<td>1.94</td>
<td>0.018</td>
<td>0.137</td>
<td>0.012</td>
<td>0.0008</td>
<td>0.0031</td>
<td>0.0008</td>
<td>0.0004</td>
</tr>
<tr>
<td>AJSMX521</td>
<td>5.12</td>
<td>0.316</td>
<td>1.98</td>
<td>1.14</td>
<td>0.136</td>
<td>0.011</td>
<td>0.0007</td>
<td>0.0029</td>
<td>0.0005</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

Figure 1. XRD-pattern of the silicon-and calcium-free alloys.

Figure 2. XRD-pattern of the silicon- and calcium-containing alloys.

Figure 3 and Figure 4 show the results of the tensile tests. The relatively low amount of nominal 0.2% calcium reduces the yield strength while subsequent silicon additions increased the value again. In case of the AJSMX521 alloy the yield strength is lower compared to AJM52. After silicon additions in case of AJSMX511 the yield strength increases above the level of AJM51. It is interesting to note that the fracture elongation rises in both cases after the silicon additions.
The minimum creep rate was calculated from the last ten hours of the creep tests, see Figure 5. Strontium generally reduces the creep rate compared to the base material. The addition of 0.2% calcium results in a further improved creep resistance. After the silicon addition the creep rate exceeds the level of the only strontium containing alloys. Materials with 2% of strontium generally show a higher creep resistance. Figure 6 displays the results of the salt spray tests. In any case calcium has a detrimental influence on the corrosion resistance. Subsequent addition of silicon reduces the corrosion rate. AJSMX511 even shows a slightly lower corrosion rate than AM50.

Discussion

The AJ52 and the AS41 alloys have been developed for elevated temperature applications. Silicon is believed to provide high temperature strength via Mg$_2$Si precipitates that block the dislocation movement [5]. Strontium suppresses the Mg$_{17}$Al$_{12}$-phase by the formation of Al$_4$Sr and Mg$_{13}$Al$_3$Sr [6]. When strontium, silicon and calcium are present in the AM50 alloy the new ternary compound Sr$_{6.33}$Mg$_{16.67}$Si$_{13}$ is formed preferentially instead of Mg$_2$Si, Al$_4$Sr and Mg$_{13}$Al$_3$Sr. A possible influence of calcium has still to be investigated. Calculating the ratio of the weight-fractions Sr/Si results in a value of 1.52. This would mean that for the alloy AJSMX511 not all silicon is bound in Sr$_{6.33}$Mg$_{16.67}$Si$_{13}$, while for the AJSMX521 alloy a remainder of strontium is available for the formation of aluminium-strontium-phases. This calculation is supported by Figure 2. No aluminium is needed for the new compound which explains the observed peaks of the β-phase in Figure 2. Discontinuous precipitates of Mg$_{17}$Al$_{12}$ and the low strength of existing β-phase particles are reported to promote creep deformation. Sr$_{6.33}$Mg$_{16.67}$Si$_{13}$ is thermally stable up to 1380 K [7]. The increased minimum creep rates of AJSMX511 and AJSMX521 are therefore probably caused by an increased amount of aluminium not bound in aluminium-strontium-phases.
The increased fracture elongations of AJSMX511 and AJSMX521 may be due to the replacement of $\text{Al}_4\text{Sr}$ and $\text{Mg}_{13}\text{Al}_3\text{Sr}$ by $\text{Sr}_{6.33}\text{Mg}_{16.67}\text{Si}_{13}$. The increased amount of $\text{Mg}_{17}\text{Al}_{12}$ or aluminium in solid solution does not seem to be a probable reason. A higher aluminium content is rather found to decrease the deformability in case of AM- and AS-alloys, see ASTM94. The AS41 alloy in the die cast state has a lower fracture elongation compared to AJ52, see ASTM94. The addition of silicon and calcium to the AJM52 alloy doubles the fracture elongation for the permanent mould cast material.

The Zintl-phase $\text{Sr}_{6.33}\text{Mg}_{16.67}\text{Si}_{13}$ most likely has a positive influence on the alloy’s corrosion resistance. Die cast AS41 was reported to have a reduced corrosion resistance in the salt spray test compared to AJ52x [4]. Low contents of Calcium have been reported to increase the corrosion rate of the die cast AM50 alloy [8]. The results show better corrosion performance for the AJSMX511 alloy compared to AJM52, most likely due to the reduced amount of $\text{Al}_4\text{Sr}$. Further studies are required to identify the mechanisms.

Conclusions

Combined additions of strontium, silicon and calcium to the AM50 alloy lead to the formation of the ternary Zintl-Phase $\text{Sr}_{6.33}\text{Mg}_{16.67}\text{Si}_{13}$. To the best knowledge of the authors the phase has yet not been reported in magnesium alloys. It has a positive influence on the fracture elongation and the materials corrosion rate in the salt spray test. Further investigations are required to find out about the influence of calcium on the phase formation.

References


