Intergranular Fracture of Al–5%Mg Alloys Containing a High Amount of Sodium and Its Suppression by Bismuth or Indium Additions

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The effect of high amounts of sodium on intergranular fracture of Al–5% Mg alloys without and with additional bismuth or indium was studied under different heat treatment conditions. A set of experiments made it evident that the intergranular fracture occurred even at room temperature when the amount of sodium in the Al–5%Mg alloy exceeded 23 ppm under homogenization treatment. On the contrary, Al–5%Mg alloy with large amounts of sodium (23 and 200 ppm) did not show intergranular fracture at 300°C under homogenization treatment. In addition, the Al–5%Mg alloy containing 4 ppm of sodium showed obvious intergranular fracture when the alloy was pre-deformed and subjected to the solution heat treatment. This suggests that the effect of sodium on the intergranular fracture of the Al–Mg alloys varies according to the sodium concentration, heat treatment, and testing temperature. We have also clarified that the room-temperature intergranular fracture caused by 200 ppm of sodium in the Al–5%Mg alloys was suppressed by 0.1%-ordered additional elements such as bismuth or indium. It is presumed that the suppression of the intergranular fracture by the addition of bismuth or indium was caused by the formation of sodium-bearing compounds in the Al–5%Mg alloys, leading to scavenging of sodium from GBs at room temperature.

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Keywords: Al–Mg alloy, grain boundary fracture, segregation, sodium, bismuth, indium

1. Introduction

It is widely known that the Al–Mg base alloys containing a high amount of magnesium (~5 mass%) show better workability at room temperature, while these alloys show grain boundary (GB) embrittlement at higher temperatures ranging from 200–500°C, depending on the grain size1,2 (Otsuka, 1984), sodium impurity level3,4 (Ransley, 1959, Okada, 1997, Horikawa, 1998, 2001) and strain testing rate5,6 (Yamada, 2012). In the case of the coarse-grained Al–5% Mg alloys (~300 μm), only 2 mass ppm of sodium causes severe GB fracture around 300°C; however, the Al–5% Mg-2 ppm alloys do not show intergranular fracture when tested at room temperature. It has also been shown that the high temperature GB embrittlement caused by 2 ppm of sodium is suppressed by the additional elements, such as bismuth (Talbot, 1995),7,8 antimony (Ueda, 1997),9 indium10 (Horikawa, 2012) and silicon.11 Based on this knowledge, it can be concluded that the GB embrittlement of the Al–Mg alloys at high temperatures is attributed to the synergy effects of GB segregation of atomic sodium and GB sliding. In the case of the GB embrittlement of the Al–Mg alloys, the involvement of low melting point metallic phases has also been pointed out previously (Lynch, 2002),12 on the basis of the GB embrittlement at specific temperatures above the melting point of sodium. To date, the effects of high amount of sodium addition (~2 ppm) on the intergranular fracture in the Al–Mg alloys have not been fully investigated. In this study, the effect of 100 ppm-ordered sodium on the GB fracture of the Al–5%Mg alloys was examined mainly at room temperature, together with the effect of other additional elements, such as bismuth and indium.

2. Experimental Procedure

High purity aluminum of 99.999% purity, magnesium of 99.98% purity, and sodium of 99% purity were used to prepare the Al–5 mass%Mg alloys (‘mass%’ is expressed as ‘%’, hereinafter) without and with sodium in an argon atmosphere. In order to examine the effect of the additional elements, Al–5% Mg–200 ppm Na–0.15% Bi and Al–5% Mg–200 ppm Na–0.69% In alloys were also made using the Al–Bi and Al–In master alloys. Chemical composition of the alloys is shown in Table 1. All the alloy ingots were homogenized at 430°C for 18 h in an argon atmosphere and further cooled in a furnace (HT conditions). After the homogenization treatment, some of the alloys were cold-sweated by 35% and were further solution heat treated at 510°C for 0.5 h in air, followed by quenching in water (SW conditions). The average grain size after the heat treatment is shown in Table 2. The phase transformation in the alloys was studied using differential scanning calorimetry (DSC, Rigaku, DSC-8231C) at a heating rate of 10°C/min in argon. After the heat treatment, round tensile test pieces of 4 mm diameter and 10 mm gauge length were machined. Tensile test was performed at temperatures from 25°C (RT) to 500°C with an initial strain rate of 8.3 × 10⁻⁴ s⁻¹. The fracture surfaces of the test pieces after the tensile tests were observed.

| Table 1 Chemical composition of Al–5%Mg alloys. |
|---|---|---|---|---|---|
| 0.1 Na | 5.10 | - | - | <0.0001 | Bal. |
| 4 Na | 5.10 | - | - | 0.0004 | Bal. |
| 20 Na | 4.90 | - | - | 0.0023 | Bal. |
| 200 Na | 4.95 | - | - | 0.0165 | Bal. |
| 200 Na-Bi | 4.95 | 0.150 | - | 0.0110 | Bal. |
| 200 Na-In | 4.95 | - | 0.651 | 0.0200 | Bal. |

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with a scanning electron microscope (SEM, JOEL, JSM-6335). Elemental analysis on the fracture surfaces was carried out using an energy dispersive X-ray spectrometry (EDXs) accessory attached to the SEM. The segregation of sodium at the GB was examined with Auger electron microscopy (AES, PHI 680 Auger Nanoprobe) using the fractured test piece.

3. Results

3.1 Effect of sodium on room temperature GB fracture

Figure 1 shows the room temperature stress-strain curves of the Al–5% Mg alloys containing sodium in the range of 0.1–200 ppm. The decrease of elongation is obvious when the alloy contains more than 23 ppm of sodium. The tensile strength decreases as the sodium content increases from 4 to 200 ppm. The fracture surfaces indicate that the decrease in the room temperature ductility is caused by the change of the fracture mode from the transgranular to GB fracture, as shown in Fig. 2. The GB fracture surfaces observed in 200 Na are covered with ledge patterns, representing the interaction between the planer slip lines and GBs. EDXs revealed that the particles partly visible on the GB fracture surface in 200 Na are sodium particles, as shown in Fig. 3. In order to make the sodium segregation at the GB more evident, the GB fracture surface fractured at room temperature was examined using AES, and the results are shown in Fig. 4. The appearance of sodium peak in the AES spectra indicates the sodium segregation at the GB fracture surface in 200 Na. In addition, a higher sodium concentration is observed for the sodium particles compared to that for the regular GB surface. After sputter etching on the GB fracture surface with argon ions, the sodium peak disappears. The depth of the sodium segregation at the GB is estimated to be about 3.5 nm, regardless of the locations. This set of results

<table>
<thead>
<tr>
<th>Nominal stress (MPa)</th>
<th>Nominal strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 Na (HT)</td>
<td>3.1</td>
</tr>
<tr>
<td>0.1 Na (SW)</td>
<td>3.1</td>
</tr>
<tr>
<td>4 Na (HT)</td>
<td>6.2</td>
</tr>
<tr>
<td>4 Na (SW)</td>
<td>6.2</td>
</tr>
<tr>
<td>23 Na (HT)</td>
<td>6.2</td>
</tr>
<tr>
<td>200 Na (HT)</td>
<td>6.2</td>
</tr>
<tr>
<td>200 Na (SW)</td>
<td>6.2</td>
</tr>
<tr>
<td>200 Na-Bi</td>
<td>6.2</td>
</tr>
<tr>
<td>200 Na-In</td>
<td>6.2</td>
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</tbody>
</table>

Fig. 1 Effect of sodium content on stress-strain curves of Al–5% Mg alloys tested at RT at a strain rate of $8.3 \times 10^{-4}$ s$^{-1}$.

Fig. 2 Fracture surfaces of Al–5% Mg alloys (HT) without and with sodium (a) 0.1 Na, RT, (b) 200 Na, RT.

Fig. 3 Magnified image on room temperature GB fracture surface and EDX analysis of an Al–5% Mg alloy, 200 Na (HT), tested at RT.
suggests that the room temperature GB fracture observed in 200 Na is caused by the segregation of the sodium particles at the GBs.

Figure 5 shows the DSC plots of 0.1 Na and 200 Na after the homogenization treatment (HT). An endothermic peak is observed around 98°C only in 200 Na, while it is not observed in 0.1 Na. Because the melting point of sodium is 97.8°C, the endothermic peak at approximately 98°C observed in 200 Na seems to represent the melting of solid sodium phases. In addition, at temperatures ranging from 250–420°C, both the alloys show the endothermic peak, which suggests the dissolution of the β-phase (Al₃Mg₂) in these alloys. It is obvious that sodium phases in 200 Na exist in the solid state at room temperature.

### 3.2 Effect of sodium on high temperature GB fracture

Figure 6 shows the stress-strain curves of the Al–5% Mg alloys tested at 300°C. Under the HT conditions, the slight decrease in the ductility of the 23 Na and 200 Na alloys is still obvious at 300°C. In addition, the detrimental effect of sodium on the ductility is weaker than that observed at room temperature. Interestingly, the decrease of hot ductility at
300°C is more prominent in the 0.1 Na and 4 Na alloys under SW conditions than that in 200 Na under the HT conditions. The fracture surfaces of 0.1 Na and 4 Na tested at 300°C are shown in Fig. 7. It is clear that GB fracture occurs particularly in 4 Na (SW) at 300°C under the SW conditions. In accordance with our previous study,6) the high temperature GB fracture observed in 4 Na indicates HTE, which is caused by the synergy effects of the atomic sodium segregation and GB sliding.

### 3.3 Effect of additional elements on GB fracture caused by 200 ppm of sodium

Figure 8 shows the effect of the additional elements on the room temperature stress-strain curves of the Al–5%Mg alloys containing 200 ppm of sodium. It is clear that the room temperature ductility increases in the alloy with 200 ppm of sodium by the addition of bismuth (0.15%) or indium (0.65%). The positive effect on the ductility is much higher in the bismuth containing alloys than the indium containing alloys. At 300 and 500°C, additional bismuth increases the hot ductility, while indium decreases the hot ductility. It is noted that the effect of additional elements on the ductility of the high-sodium Al–Mg alloys depends on the type of additional elements and testing temperature.

Figure 9 shows the fracture surfaces of 200 Na, 200 Na–Bi and 200 Na–In tested at various temperatures. At room temperature, the GB fracture is suppressed in 200 Na–Bi and 200 Na–In; however, the surface of 200 Na–In shows partially smooth planes, similar to those in a quasi-cleavage like fracture. At 300°C, a ductile transgranular fracture is observed in 200 Na and 200 Na–Bi, while 200 Na–In shows mixed brittle fracture surfaces with quasi-cleavage and intergranular fractures. In 200 Na–Bi, the suppression of the GB embrittlement is still visible at 500°C. On the contrary, 200 Na and 200 Na–In show brittle fractures at 500°C. In addition, the fracture of 200 Na is apparently different from ordinal GB fracture, while that of 200 Na–In is complete GB fracture.
4. Discussion

4.1 Room temperature GB embrittlement by sodium

As previously discussed in 3.1, it is found that addition of high amounts of sodium (>23 ppm) causes the GB embrittlement even at room temperature. Based on the set of results obtained from DSC and AES analyses, it is apparent that the embrittlement is brought about by the segregation of the solid sodium particles at the GBs. In particular, this embrittlement is clearly different from the liquid metal embrittlement (LME) reported previously,14) because the melting point of sodium, 97.8°C, is above the room temperature. The additional sodium amount causing the room temperature GB embrittlement was more than 23 ppm, and this additional amount is close to the value of maximum solubility of sodium (25 ppm) in aluminum.15) In 23 Na and 200 Na, the sodium concentrations at the GBs are believed to be saturated, considering the sodium concentration and its grain size of ~1000 µm. Thus, it is supposed that a large fraction of the sodium atoms, particularly in 200 Na, decomposes at room temperature as solid sodium phases in grains and sodium rich phases segregated at the GBs. Based on the Al–Na phase diagram reported,15) sodium phases observed in 200 Na would have body centered cubic (bcc) structure. In fact, the sodium phases were partly observed at the GBs after room temperature GB fracture in 200 Na. In addition, these phases were randomly distributed. On the GB surface, the ledge patterns, which were associated with localized slips in grains, were also visible. Based on these observations, the GB fracture observed in 200 Na at room temperature seems to be in agreement with the solid metal induced embrittlement (SMIE) mechanism proposed in previous studies.16–18) The SMIE mechanism explains that adsorption of solute atoms on the GB surfaces or crack tips results in the changes in electron density18) and weakening of interatomic bonding. In the case of the decrease in the electron density at the GBs in aluminum, the first-principles calculation predicts that the sodium atom significantly lowers the electron density at the GBs in aluminum.19) The formation of the sodium particles at the GBs could be associated with the transport of the sodium atoms to the GB crack tips by a surface diffusion process during SMIE, as schematically illustrated in Fig. 10(a).

4.2 High-temperature GB embrittlement by sodium

As previously discussed in 3.2, the GB fracture at 300°C appeared only in the alloy containing traces of sodium, 4 Na (SW), while 200 Na (HT) did not show the GB fracture. In 0.1 Na or 4 Na (SW), sodium might have been segregated at the grain boundaries in an atomic state. This is based on the consideration of trace sodium concentration (<4 ppm) and coarse grain size (400 µm). Atomic sodium segregation might have led to the weakening of GB bonding based on the decrease in electron density at the GBs in aluminum,19) which is similar to SMIE. At high temperature deformation of the Al–5% Mg–2 ppm Na alloys at approximately 300°C, it has been reported that serration and sliding of the GBs occurs at the same time,20) which generate nuclei of GB cavities. Thus, the mechanism of the high temperature GB fracture of the Al–5% Mg alloy might have been caused by the synergy of
atomic sodium segregation at GB and GB serration/sliding in the same manner as explained in our previous studies.

On the other hand, 200 Na (HT) did not show the GB fracture at 300°C. Sodium atoms in 200 Na (HT) might have been present in a liquid state in the grains as well as at the GBs at 300°C because the temperature was above the melting point of sodium. It has been reported that large amounts of liquid phases at the GB in the aluminum alloys enhance the elongation during the high temperature deformation because the liquid phases at the GBs play a role in the accommodation of stress relaxation and delay in cavitation. Therefore, it is assumed that the disappearance of the high temperature GB fracture in 200 Na (HT) might have been caused by such stress relaxation effect of the liquid sodium phases at the GBs during the high temperature deformation. The mechanism of high temperature GB embrittlement by the traces of sodium and its suppression by high sodium (200 ppm) is summarized in Fig. 11.

4.3 Suppression of GB fracture by additional elements

This study also revealed that the addition of bismuth or indium suppressed the room temperature GB embrittlement caused by 200 ppm of sodium at room temperature. To understand the suppression of the GB fracture, the fracture surfaces of 200 Na–Bi and 200 Na–In were analyzed by EDXs, as shown in Fig. 12. It is observed that sodium bearing compounds are formed at transgranular dimples in both the alloys. Hence, the suppression mechanism could be related to the formation of the sodium bearing compounds in grains, which leads to decrease in the concentration of sodium at the GBs. This is similar to the suppression of the HTE explained in our previous study. The suppression of the room temperature GB embrittlement by additional elements, bismuth or indium, is summarized in Fig. 10.

The effects of additional elements (i.e., bismuth and indium) on the suppression of GB embrittlement differ from each other at high temperatures. In particular, the suppression of GB embrittlement by bismuth addition is effective even at 500°C. On the contrary, such positive effect was not seen in the case of indium addition. One reason for the difference could be related to the thermal stability of the sodium-bearing compounds formed with bismuth or indium. Table 3 shows the sodium bearing compounds with bismuth or indium and their melting points. Because additional bismuth suppresses the high temperature GB embrittlement by sodium at 500°C, sodium-bearing compounds with high melting point (Na3Bi, Tm = 775°C) might have been formed. On the contrary, the low melting point compounds (Na2In, Tm = 286°C) might have been formed in the case of indium addition. This is because the GB fractures were observed in 200 Na–In, when tested at 300°C and 500°C. It is also presumed that the suppression of the room temperature GB
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embrittlement was caused by the formation of Na₃Bi or Na₂In based compounds like Fig. 10, based on the comparison with the fracture morphology shown in Fig. 9.

Further, additional indium suppressed the room temperature GB fracture in 200 Na–In, and the total elongation was not fully recovered compared to 0.1 Na (HT). In addition, the fracture surface of 200 Na–In showed partially smooth planes, similar to a quasi-cleavage like fracture at room temperature. Because indium has been reported to induce SMIE (23) or LME (14) in the aluminum alloys, the cleavage like fracture observed at room temperature in 200 Na–In could be associated with the effect of the solid indium phases in the grain interior by SMIE. Besides, the high temperature GB embrittlement observed at 500°C in 200 Na–In could be attributed to the LME by liquid indium at the GBs.

5. Conclusions

The conclusions of this study can be summarized as follows:

(1) The Al–5%Mg alloys containing 23 ppm or 200 ppm of sodium show GB fracture at room temperature. In addition, the detrimental effect of 200 ppm Na on the room temperature ductility loss is brought about by the segregation of the solid sodium phases at the GBs. The liquid phase does not contribute to the room temperature ductility loss.

(2) The room temperature GB fracture caused by 200 ppm of sodium might have been due to the metal induced embrittlement by the sodium particles at the GBs.

(3) The effect of sodium on the GB embrittlement of the Al–5%Mg alloys varies according to the sodium concentration, heat treatment, and testing temperature.

(4) The mechanism of the room temperature GB embrittlement observed in high sodium alloys could be related to SMIE.

(5) The mechanism of high temperature GB embrittlement observed in low sodium alloys is related to the synergy effect of atomic sodium segregation at the GBs and the dynamic change of the GB microstructures.

(6) The room temperature GB fracture caused by 200 ppm Na is suppressed by the addition of bismuth or indium in the Al–5%Mg alloys after the homogenization treatment.

(7) The suppression of the room temperature GB embrittlement by bismuth or indium addition in the high sodium alloys is based on the formation of the sodium-bearing compounds with the additional elements.

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REFERENCES