EFFECTS OF TRACES OF CALCIUM AND STRONTIUM ON HOT DUCTILITY OF AN Al-5.5mol%Mg ALLOY

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ABSTRACT

Hot ductility of an Al-5.5mol%Mg alloy is decreased by the addition of more than 2 molppm of calcium or strontium, though the effect of calcium or strontium per mole on this lowering is not as severe as that of sodium. Al-5.5mol%Mg binary alloy showed almost an transgranular fracture surface, while the surface of the same alloy containing calcium or strontium was intergranular. Auger electron spectroscopy revealed that calcium or strontium segregates at grain boundaries. These results indicate that the lowering of hot ductility is brought about calcium or strontium segregation to grain boundaries.

INTRODUCTION

It has been reported that an Al-5.5mol%Mg alloy shows high temperature embrittlement based on intergranular fracture at around 300°C depending on strain rate(1)(2). Recently, one of the authors reported that this embrittlement is caused by a trace amount of sodium of 0.6massppm (0.7molppm) in a coarse-grained Al-5.5mol%Mg alloy using high purity ingots(3). Sodium is a common impurity in primary aluminum and magnesium ingots of commercial grade and in an alumina crucible of 99mass% purity(4), so that a trace amount of sodium in an Al-Mg alloy is not unusual.

Numerous of studies have been made on the effect of sodium, little is known about the effect of alkali and alkaline-earth elements other than sodium. However, unusual impurities may inevitably creep in the recycling process in future. For example, it is reported that Al-Mg alloy is contaminated by calcium through the ceramic tube filter used during melting and casting(5)(6), and strontium is used commercially as an additional element of an Al-Si alloy. Hence, aluminum alloys made using recycled stock may be contaminated at least by traces of calcium and strontium. The purpose of this study is to crarify the effect of traces of calcium or strontium on hot ductility of an Al-5.5mol%Mg alloy.

EXPERIMENTAL PROCEDURE

Al-5.5mol%Mg alloys with and without trace amounts of calcium, strontium or sodium were melted in a graphite crucible by a high frequency induction melting method under argon atmosphere of 10^5Pa (Table 1). Aluminum of 99.999mass% purity, magnesium of 99.98mass%

purity and master alloys such as Al-2.5mol%Ca, Al-0.94mol%Sr and Al-0.07mol%Na which were made in our laboratory by using high purity materials were used. Ingots were homogenized at 430°C for 18hr in argon of 10^5Pa, cold-swaged by 70% and machined into round tensile specimens with a gage length of 10mm and a diameter of 4mm. Sheet specimens with a gage length of 10mm, a width of 4mm and a thickness of 1mm were also made. These specimens were annealed at 510°C for 0.5-18hr so that the grain size of the specimens was about 0.3mm.

Tensile tests were performed at temperatures ranging from ambient temperature to 400°C at an initial strain rate of $8.3\times10^{-4}s^{-1}$. Surface of the specimens for optical microscopy were electrolytically polished in a mixture of perchloric acid and ethanol after the annealing. Ductility was assessed by measuring the reduction in area. Analyses of trace elements were made by emission spectrochemical analysis. After the tensile tests, fracture surfaces were observed by a scanning electron microscope (SEM), and were analyzed to examine impurity segregation at grain boundaries using an auger electron spectroscope (AES).

Table 1 Chemical Composition of Al-5.5mol%Mg Alloys

Alloy	Mg (mol%)	Ca*	Sr*	Na*	Si*	Fe*	Al
Base	5.52	<1	<1	<1	14	<1	Bal.
2-Sr	5.41	<1	2	<1	18	2	Bal.
10-Sr	5.41	<1	11	<1	14	<1	Bal.
2-Ca	5.52	2	<1	<1	23	<1	Bal.
10-Ca	5.41	13	<1	<1	14	<1	Bal.
2-Na	5.52	<1	<1	2	13	3	Bal.

*molppm

RESULTS

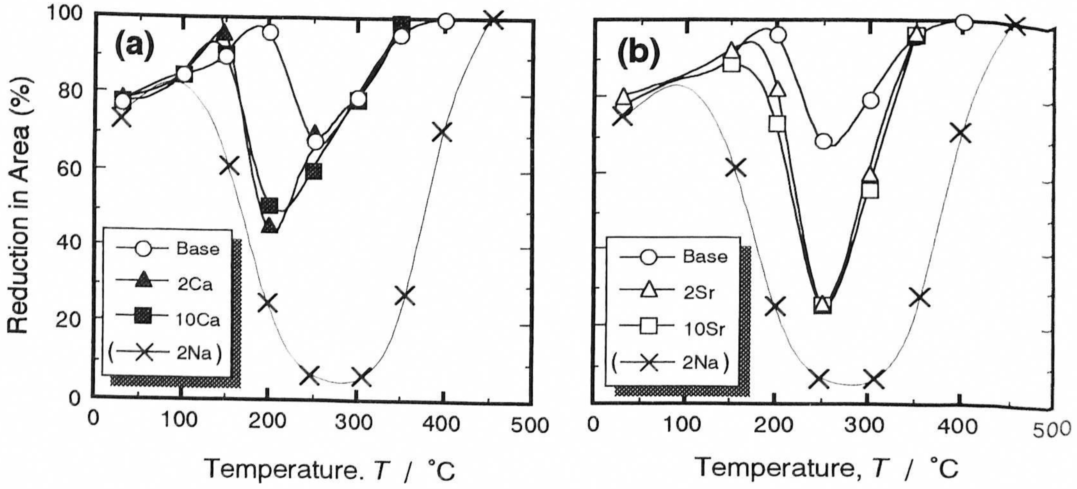

Figure 1 Effect of traces of calcium or strontium on hot ductility of an Al-5.5mol%Mg alloy.
(a): Effect of calcium, (b): Effect of strontium

Effects of calcium or strontium on reduction in area vs. temperature curves of the Al-Mg alloy are shown in Figures 1. Hot ductility of the base alloy is decreased by the addition of trace amounts of either calcium or strontium, and there is a similarity between Ca and Sr-added alloys: the hot ductility is not changed by the difference in added contents between 2 and 10molppm. However, there is some difference of the lowering effect between Ca and Sr-added alloys. First, the reduction in area of Ca-added alloys at the bottom of the ductility trough is as low as 50%, while that of Sr-added alloys is about 25% that is, the ductility trough which appears in the Ca-added alloy is much shallower than that in the Sr-added alloy. Secondly, the temperature at the bottom of the ductility trough of the Ca-added alloy shifts to low temperature, while that of the Sr-added alloy does not.

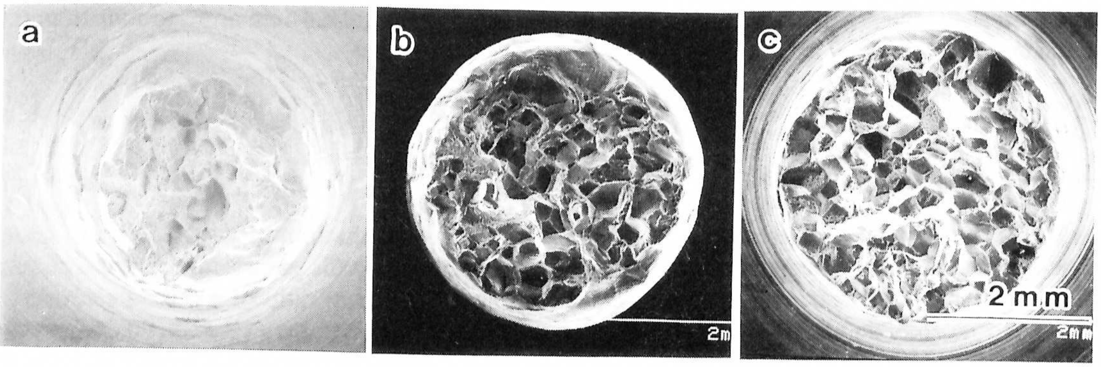

Figure 2 SEM fractographs of the base (a), the 10-Ca (b) and the 10-Sr (c) specimens after being tensile tested at 250°C (a), (c), and 200°C (b).

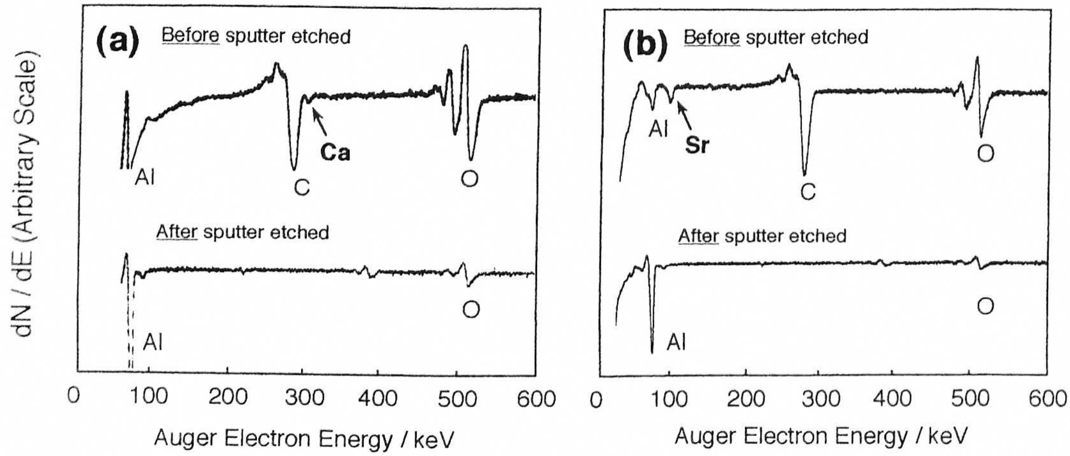

Figure 3 AES spectra obtained from a fracture surface of the 10-Ca (a), and the 10-Sr (b) specimens after being tensile tested at 200°C (a) and 250°C (b).

Figure 2 shows SEM fractographs of the base, the 10-Ca and the 10-Sr alloy at the bottom of ductility troughs. The base alloy exhibits an almost transgranular fracture, while the fracture mode is changed to an intergranular fracture by the addition of traces of calcium or strontium. Since intergranular fracture is brought about by the addition of trace strontium, strontium may segregate to grain boundaries leading to a reduction of grain boundary strength. To confirm this hypothesis, the fracture surfaces of a 10-Ca and a 10-Sr alloy which were fractured in advance at the bottom of ductility troughs were analyzed by AES.

Figures 3 show AES spectra obtained from intergranular fracture surfaces of the 10-Ca and the 10-Sr alloy. Peaks of calcium or strontium appeared in the spectra together with carbon and oxygen. The reason carbon and oxygen are detected is that specimens were exposed to air before their insertions to the AES equipment. After sputter etching on the intergranular fracture surface with argon ions for 0.5hr, the peak of calcium or strontium disappeared. The sets of results make it clear that the intergranular fracture is caused by the segregation of calcium or strontium to grain boundaries.

DISCUSSION

Since the intergranular fracture was shown to be caused by the impurity segregation to grain boundaries, the value of reduction in area may be closely related to the grain boundary enrichment ratio of the added elements. As a rule, the grain boundary enrichment ratio of a certain element is related to its solid solubility limit(7). Calcium or strontium exhibit quite a low(8) (<0.01mass%) solid solubility limit in pure aluminum. Thus, the grain boundary enrichment ratio of calcium or strontium is thought to be high. In the present study, the value of reduction in area however is not changed by the difference of additions between 2 and 10molppm as indicated in Figures 1. This implies that the amount of calcium or strontium at grain boundaries is saturated by the addition of more than 2molppm.

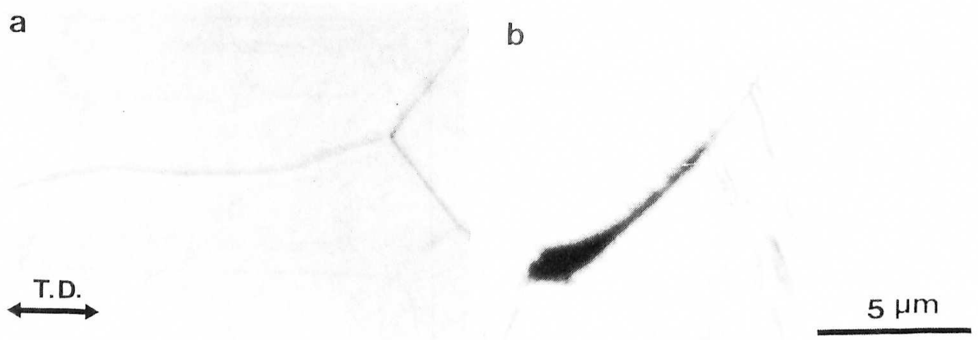

Figure 4 Optical microscopic images of specimens of the base (a) and the 10-Ca (b) which are deformed by 9% at 200°C

The temperature at the bottom of the ductility trough of the Ca-added alloy shifted to a lower temperature than that of the base alloy. Otsuka and Horiuchi(2) claimed that high stress concentration could develop to grain boundaries near 200°C in an Al-5%Mg alloy, since grain boundary sliding and serration of grain boundary occur simultaneously. Since confirmation was needed on whether the sliding and serration of the grain boundary occur at the bottom temperature of the ductility trough, the microstructure adjacent to grain boundaries in the base and 10-Ca alloys which were deformed by 9% at 200°C were performed as shown in Figure 4. Wedge-type cracking has already been produced in the stage of the uniform deformation mainly at triple grain junctions of the 10-Ca alloy. Grain boundary sliding had occurred in both the base and the 10-Ca alloys even at 200°C, though the remarkable serrated grain boundary around the crack could not be observed in the 10-Ca alloy. These results indicate that the initiation of the wedge-type cracking is not always accompanied by the serration of grain boundaries. There was also little difference in the morphology of slip bands developed inside grains between the 10-Ca and the base alloy. It may be possible in the shift of the ductility trough of Ca-added alloys to a low temperature that the grain boundary sliding is accelerated by the grain boundary segregation of calcium. There is however, room for further quantitative investigations to verify this supposition.

SUMMARY

From a series of experiments, it is shown that calcium or strontium brings about high temperature embrittlement. The detrimental effect of calcium is weaker than that of strontium, while the effect of calcium or strontium per mol on hot ductility is milder than sodium. The AES studies reveal that the embrittlement caused by calcium or strontium is related to its grain boundary segregation.

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