ATOMIC RESOLUTION IN-SITU HR(S)TEM INVESTIGATION OF THE GRAIN-BOUNDARY SEGREGATION BEHAVIOUR OF CA IN BINARY, TERNARY AND QUATERNARY MY-AL-CA-MN SYSTEM

LI Jiehua, Chair of Casting Research, University of Leoben
ZHU Jianing, Chair of Casting Research, University of Leoben
WANG Huiyuan, Jilin University
WANG Cheng, Jilin University

Research background

The grain boundaries have a significant impact on the mechanical response of crystalline materials, which has been recognized ever since the concept of dislocation as carrier of plasticity in metals had been established. The migration of grain boundaries has been well-accepted to be one of the most dominant factors affecting microstructure evolutions and thereby mechanical properties. More importantly, the solute segregation to grain boundaries very often occurs, which also modulates the properties of a metallic alloy.

Mg alloy, as the lightest structural metal material, offers irreplaceable opportunity of significant weight reduction of the structural components. However, Mg belongs to hexagonal close-packed (hcp) structure. Less slip systems are, therefore, available for the plastic deformation compared with Al with cubic (fcc) structure. How to improve the formability of Mg alloy is one of the major international problems in the field of Mg alloys. It is well-accepted that micro-alloying (e.g. rare earth elements) can be used to weaken the texture and thereby improve the formability of Mg alloy due to the solute segregation to grain boundaries. For example, in Mg-Gd binary alloy, Gd-solute clustering and grain boundary segregation has been reported to modify and weaken the overall texture. In Mg-Y binary alloy, clustering of Y on the grain boundaries was also observed to change the texture. However, in Mg-Nd binary alloy, no texture change and no segregation was observed, strongly indicating that different alloying elements may behalf differently. Furthermore, in Mg-Gd-Zn ternary alloy, co-segregation of Gd and Zn atoms was observed in the as-quenched condition. The segregation of Gd to the twin boundaries was also reported, indicating that there is a strong interaction among different solutes. Similarly, in Mg-Y-Zn ternary alloy, Zn atoms were found to preferentially segregate to the deformation induced symmetrical kink boundaries (KBs) in the long period stacking ordered (LPSO) structures and sandwiched Mg layers, while only a small amount of Y atoms concentrate at KB in LPSO structure, again indicating that different solutes may have different segregation behaviours to grain boundaries.

However, as described above, to date, previous investigations are mainly focused on Mg alloys containing rare elements (e.g. Gd, Y) due to the fact that the higher atomic number of rare elements (Gd (64), Y (39)) compared with Mg (12) makes it very suitable for high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). However, for alloying elements with a lower atomic number (e.g. Al (13), Ca (20), Mn (25)), there still lacks a detailed investigation on the solute segregation to grain boundaries.

In fact, these alloying elements (e.g. Al, Ca, Mn) play a very important role for strengthening commercial Mg alloys (e.g. AZ91, AZ31, AM60). For example, Al is one of most dominant alloying elements in Mg-Al based alloys, while Ca and Mn can significantly improve properties of Mg-Al based alloys. More importantly, the physical and thermodynamic mechanism about the solute segregation to grain boundaries in Mg-Al-Ca-Mn alloy system still remains to be explored. Especially, an atomic scale in-situ HR(S)TEM investigation is of great necessity to elucidate the physical and thermodynamic mechanism about the solute segregation to grain boundaries in Mg-Al-Ca-Mn alloy system.

The present proposal is, therefore, aimed to elucidate the solute segregation to grain boundaries in binary, ternary and quaternary Mg-Al-Ca-Mn alloy system by an atomic scale in-situ HR(S)TEM investigation. The obtained fundamental knowledge can be used to optimize the microstructure evolution and thereby improve the performance of Mg alloys in service.

Research instruments

Chair of Casting Research in Montanuniversität Leoben has a great strength on the melting and casting of Mg alloys. It hosts a lot of melting and casting instruments.

- DSC, optical microscopy, SEM (including EBSD and FIB) and TEM (CM12 and JEOL-2100F FEG TEM in cooperation with Erich Schmid Institute of Materials Science), which are available for this project to characterize the microstructure evolution.
- JEOL-2100F FEG TEM with the Double Tilt Specimen Heating Holder is available for this project to perform the in-situ TEM heating experiments.

More importantly, during the past eight years, these experimental instruments have been widely used to investigate the microstructure evolution of high performance Mg alloys. Therefore, Chair of Casting Research in Montanuniversität Leoben is eligible to perform the proposed research works on bulk Mg alloys.

Jilin University has a great strength on the alloy design and rolling deformation of Mg alloy. It hosts a lot of melting, casting and deformation instruments.

- Induction melting is available for this project to prepare the bulk Mg alloy.
- Rolling instrument is available for this project to prepare the rolled sheets.
- Heat treatment instrument is available for this project to anneal the rolled sheets.

Since 2016, Montanuniversität Leoben and Jilin University have worked together on Mg alloys. A very strong cooperation has been established. A very promising progress has been made. On this previous basis, in this project, by working together with Jilin University, Chair of Casting Research in Montanuniversität Leoben will become more skilled with the design and engineering of high performance Mg alloys, in particular to the rolling deformation of Mg sheets. This collaboration will enhance the linking between Jilin University and Chair of Casting Research in Montanuniversität Leoben.

Research plans

The present proposal focuses on the segregation of Ca to grain boundaries in binary, ternary and quaternary Mg-Al-Ca-Mn alloys. Starting alloy to be analysed will be Mg-3Al-1Ca-1Mn (wt. %). Ternary and binary variations will be respectively investigated if required to clarify the segregation behaviour of individual elements, based on the results obtained for the quaternary starting alloy. Main purpose of the project is the in-situ heating experiments aiming on the in-situ observation of evolution of Ca segregation to grain boundaries as a function of annealing temperature and time. More especially, the dynamic precipitations from Ca-rich clustering to (Mg,Al)2Ca Lavas phase along grain boundaries will be highlighted. Also, ex-situ heat-treated material will be investigated as a reference to compare the ex-situ and in-situ behaviour. In particular, the as-cast and annealed materials will be considered.

The in-situ TEM heating sample is the rolled sample. Special grain boundaries with defined orientation relationship (i.e. tilting grain boundaries) will be selected using EBSD and FIB. In-situ HR(S)TEM investigation will be performed at 175°C up to 1.5 h, which is similar to the annealing treatment. However, it should be noted that there is a significant difference on the diffusion behaviour between TEM thin foil and bulk samples. In fact, even within the TEM thin foil, there may be also a significant difference on the diffusion behaviour at different regions with different thickness. The key point for in-situ HR(S)TEM investigation is the segregation of Ca to grain boundaries. However, other important issues should be also taken into consideration, i.e. the precipitation within Mg matrix, dislocation evolution. The obtained in-situ HR(S)TEM results can be used to compare with that obtained in the ex-situ rolled and annealed sample in order to elucidate the effect of thickness on the diffusion behaviour and thereby the microstructure evolution.

First group of the ex-situ samples include the as-cast materials. In this case, a significant segregation of Ca to grain boundaries occurs due to the high Ca concentration (1 wt. %) and the strong partitioning potency of Ca. It should be noted here that the grain size in the as-cast sample is about 50 µm, which makes is feasible to select special grain boundaries with defined orientation relationship (i.e. tilting grain boundaries) using EBSD and FIB. The as-cast ex-situ sample will be used as the reference for comparison with the rolled and annealed samples.

The second group of ex-situ samples are the rolled sample. Before rolling, the as-cast samples were heat treated at 430 °C for 3 h. The rolling was performed at 300-350 °C with a reduction of 10-20% for 13 passes. There is a significant microstructure change after rolling as a function of rolling deformation and temperatures. Indeed, the grain size in the rolled sample is less than 1 µm. Furthermore, dislocations and deformation bands with a higher density are present. Similar to the as-cast sample, special grain boundaries with defined orientation relationship (i.e. tilting grain boundaries) will be selected using EBSD and FIB. Subsequently, the segregation of Ca to these grain boundaries will be investigated using ex-situ methodology.

The third ex-situ sample is the rolled and annealed sample. After rolling, a necessary annealing treatment will be performed at 175 °C for 1.5 h. During annealing, recrystallization occurs and the segregation of Ca also enhances. Possible Lavas phases (i.e. Mg2Ca, or (Mg,Al)2Ca) could be present with increasing annealing time. Similar to the as-cast and rolled samples, special grain boundaries with defined orientation relationship (i.e. tilting grain boundaries) will be selected using EBSD and FIB. It should be noted here that this sample is the key point for this proposal and can provide necessary information for subsequent in-situ HR(S)TEM investigation. The in-situ HR(S)TEM investigation will be mainly focused on this annealing process.