Substitution of Rare Earths in Magnesium Alloys

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Abstract. Magnesium alloys containing rare earth elements have better properties in terms of formability, strength and corrosion resistance. Due to the tight supply situation these elements should be substituted partially or complete, for example by calcium. Microstructural studies of cast alloys of new compositions, and the influence of various heat treatments on their microstructure are investigated. The mechanical properties of the rolled materials are also presented and discussed. The works presented in this paper are results of the ongoing BMBF project SubSEEMag.

Introduction

The application of rare earth elements in Magnesium alloys leads to a significant increase of strength, ductility, creep resistance and corrosion resistance compared to classic alloys like the AZ31 [1]. Because of the strategic importance of these elements, which leads to economical dependencies, they are classified as a critical resource group. In addition there are environmental problems producing these elements which should be avoided in terms of sustainability. Aim of this project is to design new alloys which meet the properties of rare earth containing alloys or even surpass them. There is a special view on the capability of sheet material to be plastically deformed at room temperature. The poor plastic deformability of common magnesium sheet materials is caused by its pronounced rolling texture and is the reason why until now there are only a few applications of magnesium sheets especially in the automotive industry. The reason for this is the limited number of deformation systems that could be activated in magnesium crystals for plastic deformation at low temperatures [2, 3]. Rare earth elements containing magnesium alloys show the demanded randomized texture and fine-grained microstructure [4-6]. There are already applications of magnesium parts in a car. Some of them like wheels and housings are cast parts as they are well known. Others like the roof are sheet applications. These sheet components are not easy to produce with the standard AZ31-alloy. It is time- and therefore cost intensive to deform flat sheet material of this alloy to the finished product.

In consequence rare earth free magnesium alloys with a weaker rolling texture have to be found to meet the demands of the automotive industry. In cooperation with the project partners there are a number of alloys selected to be tested [Table 1]. Most of them are calcium containing alloys, because adding Ca to Mg-Zn containing Mg-alloys leads to a texture evolution similar to RE containing alloys [7,8]. Additionally the common AZ31-alloy was tested as a benchmark. These alloys were cast in laboratory scale. The billets with a size of 105 mm in diameter and a length of 220 mm were cast in a modified gravity casting process.

Table 1: Alloy composition and heat treatment

Alloy	Alloy composition	Heat treatment
ZMX210	2 m% Zn, 1 m% Mn, < 1 m% Ca	350°C/16h
ZAX210	2 m% Zn, 1 m% Al, < 1 m% Ca	450°C/16h
MX20	2 m% Mn, < 1 m% Ca	450°C/16h
MX21	2 m% Mn, 1 m% Ca	450°C/16h
ZA21	2 m% Zn, 1 m% Al	400°C/16h
AZ31	3 m% Al, 1m% Zn	450°C/16h

For each alloy there was a tailored heat treatment found, that leads to an optimized microstructure where precipitations especially at the grain boundaries are gone in solid solution and dendritic structures in the grains disappeared. In table 1 there are all these alloys listed up with its composition and heat treatment. After the heat treatment all these alloys were rolled to sheets and mechanical tests were performed to determine the mechanical properties. The tests were performed according to ISO 6892-1. The microstructure and texture of the tested specimen were analyzed and the results discussed in terms of their influence on the observed mechanical properties.

AZ31

The AZ31 alloy was tested as a benchmark. The experimental proceeding will be shown here as it was done to all the alloys tested in this project. Out of the cast billet rolling specimen were prepared with dimensions of 20 mm thickness by 70 mm with and 140 mm in length. Those heat treated slabs were rolled down from 140 mm in rolling direction and 20 mm thickness to final gauge of app. 1.7 mm. The rolling temperature was equal to the annealing temperature. In this case it was 450 °C. Before the first rolling pass the specimen were heated up for 30 minutes. Between each rolling step they were heated up again starting with duration of 15 minutes for each period. After step #8 the thickness of the strip was below 7 mm and therefore the heating duration could be reduced to 10 minutes. The initial deformation grade at this rolling procedure was $\varphi = 0.1$ and it was increased to $\varphi = 0.2$ at step 5 and finally to $\varphi = 0.3$ from step 12 on. After rolling the microstructure of the produced sheet material was inspected using optical microscopy. Standard metallographic sample preparation techniques were employed and an etchant based on picric acid was used to reveal grains and grain boundaries [9] (Fig. 1). Specimens for texture measurements were prepared out of the rolled sheet. Using a Panalytical X-ray diffractometer the pole figures were measured up to a tilt of 70°. This allowed recalculation of full pole figures based on an MTEX software routine [10]. The (0001) and $(10\bar{1}0)$ pole figures were used in this work to present the texture of the strips at the mid plane of the sheet. The AZ31 alloy shows the typical pronounced rolling texture with a maximum of 9.6 in the (0001) pole figure (Fig. 2a).
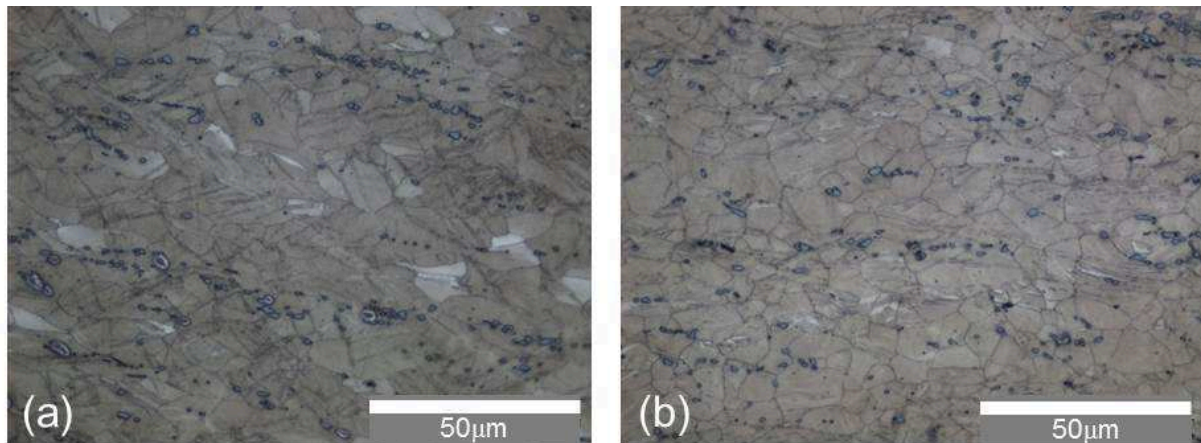

Figure 1: Microstructure of AZ31, rolling temperature 450 °C in rolling direction (a) and transverse direction (b)

Tensile test specimen were prepared out of the rolled sheet with dimensions of 12.5 mm by 50 mm according to DIN 50125-H. Before performing tests on those specimen they were heat treated for 1h at the same temperature the sheet was rolled before. The uniaxial tensile test was performed according to ISO6892-1 at room temperature with a strain rate of $d/dt = 10^{-3}$ s^{-1}. In these tests performed on two specimen the AZ31 shows the expected behavior with an average flow stress of 154 MPa, ultimate stress of 253 MPa at 14.2 % elongation and an average plastic fracture strain of 14.9 % (Fig. 2b).
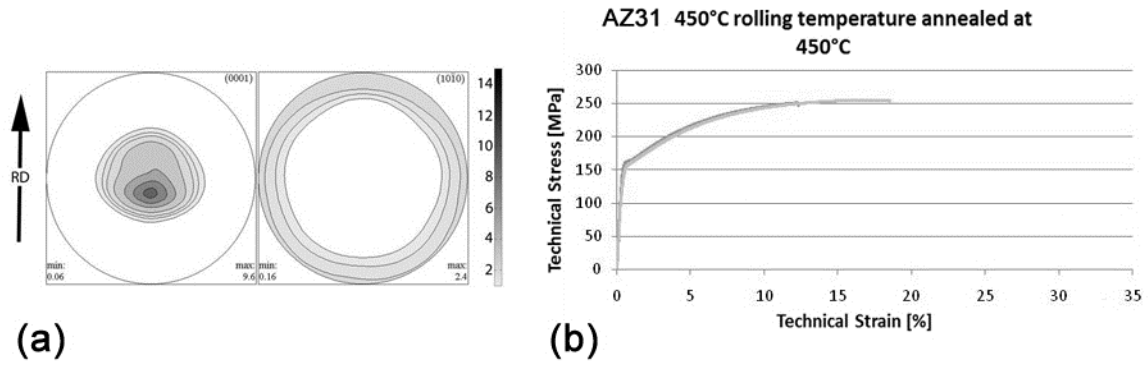
Figure 2: Texture of the AZ31 sheets rolled at 450 °C (a) and stress-strain curves of AZ31. Both specimen rolled at 450 °C and annealed at 450 °C (b)

ZA21

In the as cast state the ZA21 alloy shows a globular microstructure with large grains, and a high amount of small precipitates which are homogenous distributed inside the grains. After the heat treatment for 16 h at 400 °C the grain size did not change significantly, but the precipitations disappeared nearly completely. Rolling the ZA21 at 350 °C resulted in a sheet with small cracks at the edges, but with the temperature increased to 400 °C they did not show up again. The microstructure shows severe plastic deformation localized mainly in the center of the sheet resulting in very fine grains by the effect of dynamic recrystallization. The (0001) pole figure of the ZA21 shows a basal texture with a double peak in rolling direction (Fig. 3a). The strain test results in a flow stress of about 96 MPa, an ultimate stress of 214 MPa at 18 % elongation and a fracture elongation of 19 % (Fig. 3b).
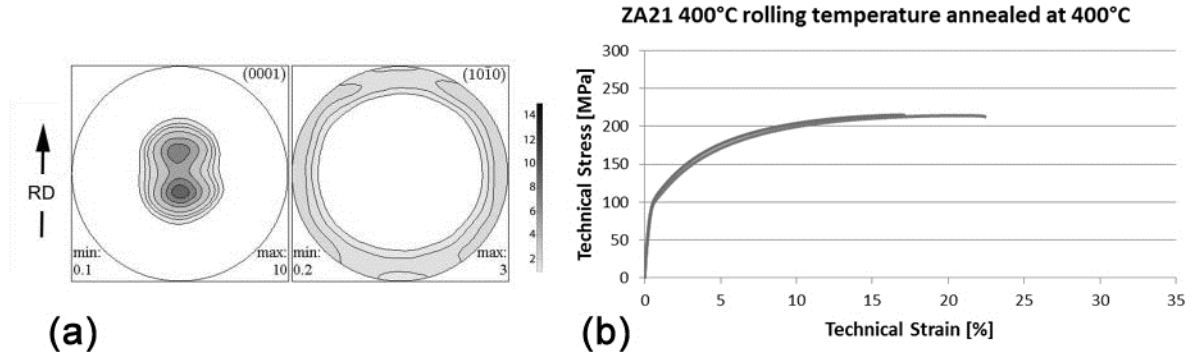

Figure 3:Texture (a) and stress-strain curves of ZA21. Both specimen rolled at 400 °C and annealed at 400 °C (b)

ZAX210

The alloy ZAX210 which differs from the before described ZA21 only by a small amount of Calcium added, shows nearly the same microstructure in the as cast condition. The coarse microstructure with grains even bigger than 1mm and a big amount of small precipitations inside these grains changes the same way during the 16 h/450 °C heat treatment. The number of precipitations decreases significantly but those remaining grow slightly. Dendritic structures observed inside the grains have as well disappeared afterwards. After a not successful first rolling trial at 450 °C the temperature was reduced down to 350 °C. This trial was successful, but because of some hot cracks at the sides of the strip the temperature was finally reduced to 300 °C and so the number of hot cracks was reduced.
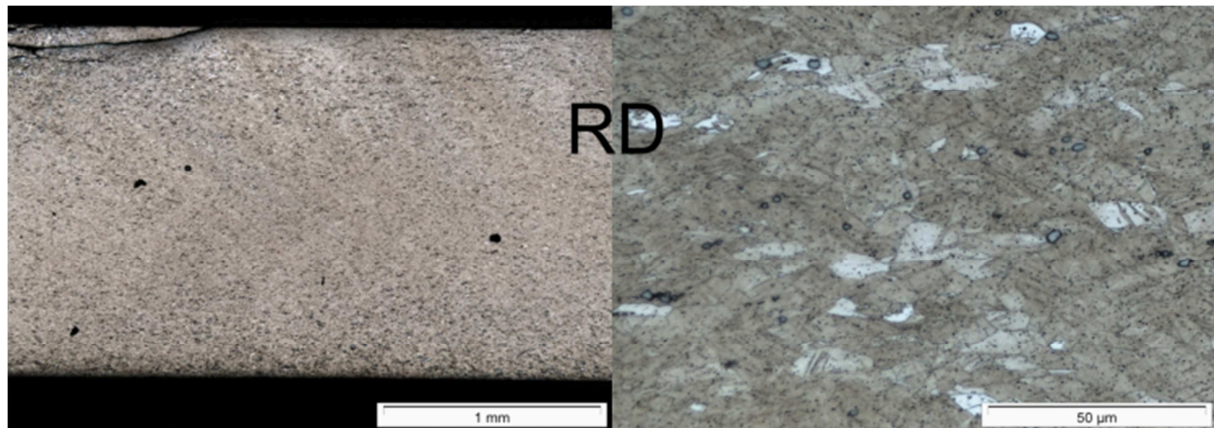
Figure 4: Microstructure of the ZAX210 sheets rolled at 350°C

In comparison to the before discussed ZA21 alloy the microstructure of the ZAX210 rolled at 350 °C is very fine grained and homogenous without any signs of local deformation. The microstructure seems not to be fully recrystallized during the rolling process (Fig. 4). The texture measured after rolling is weaker compared to those of AZ31 and ZA21. It has a (0001) maximum of 7.6, two peaks along the rolling direction (RD) and is enlarged in the transversal direction (TD) (Fig. 5a). This is similar to textures observed at rare earth containing Mg alloys like the ZE10. Performing tensile tests on this material, the ZAX210 shows the good formability that is expected because of the mentioned texture. The addition of a small amount of Ca to the ZA21 improves the formability without even lowering the strength. With a flow stress of 154 MPa, an ultimate stress of 245 MPa at 18.5 % elongation and a fracture elongation of 27.1 % (Fig. 5b), this alloy outperformed all the other inspected alloys. This makes it one of the most promising candidates for the further project.
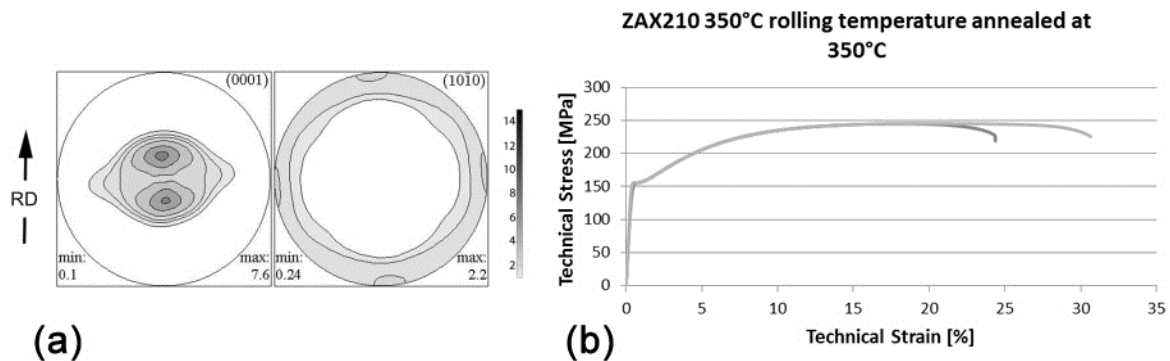

Figure 5: Texture (a) and stress-strain curves of ZAX210. Both specimen rolled at 350 °C and annealed at 350 °C (b)

ZMX210

In the ZMX 210 alloy compared to the ZAX210 aluminum is replaced by manganese. The micrograph shows a fine grained homogenous microstructure. After heat treatment at 350 °C for 16 h the precipitates located at the grain boundaries and inside the grains are reduced. The grain size is not influenced by the temperature. The slap was destroyed during the first rolling pass at 400 °C because of hot cracks. Reducing the rolling temperature to 300 °C gives same result. This is probably because of the existence of the $Mg_6Ca_2Zn_3$ phase in this material. This phase has a melting point of around 400 °C, so that the additional energy induced by the severe plastic deformation during the rolling process could lead to hot cracks.

MX20 / MX21

The last described magnesium alloys are manganese and calcium containing ones. They differ in the amount of calcium added. In case of the MX21 there is more than 1 m% of calcium added. In case of the MX20 the Ca-content is below 1 m%. The microstructure of the MX21 alloy is finer and more homogenous, but there are dendritic structures observed inside the grains. The precipitates in the MX21 are more located on the grain boundaries. After the heat treatment for 16 h at the temperature of 450 °C these precipitations are reduced and the dendritic structures could not be seen anymore. In both cases the grain size is the same after the heat treatment. Both alloys were rolled at 450 °C. There were no problems observed during this process, so both alloys could be rolled down to sheets with a thickness of 1.7 mm without any cracks. After rolling a fine grained homogenous microstructure was achieved in both alloys. Precipitates were found in both alloys, but there are more of them in the MX21 and they are aligned in small lines. A medium grain size of 15 µm in the MX20 alloy, and 26 µm in the MX21 was found (Fig. 6). The higher Ca content of the MX21 alloys reduces the intensity of the (0001) texture to a maximum of $I_{max} = 8.4$, which is slightly smaller than the maximum of $I_{max} = 9.1$ of the MX20 alloy (Fig. 7a). There are no great differences in the mechanical properties observed. Even though the MX21 had a weaker texture the MX20 shows a better deformability compared to the MX21 which had a fracture strain of 7.8 % (Fig. 7b). The finer microstructure of the MX21 did not result in a higher strength. It was absolutely comparable (213 MPa vs. 209 MPa).
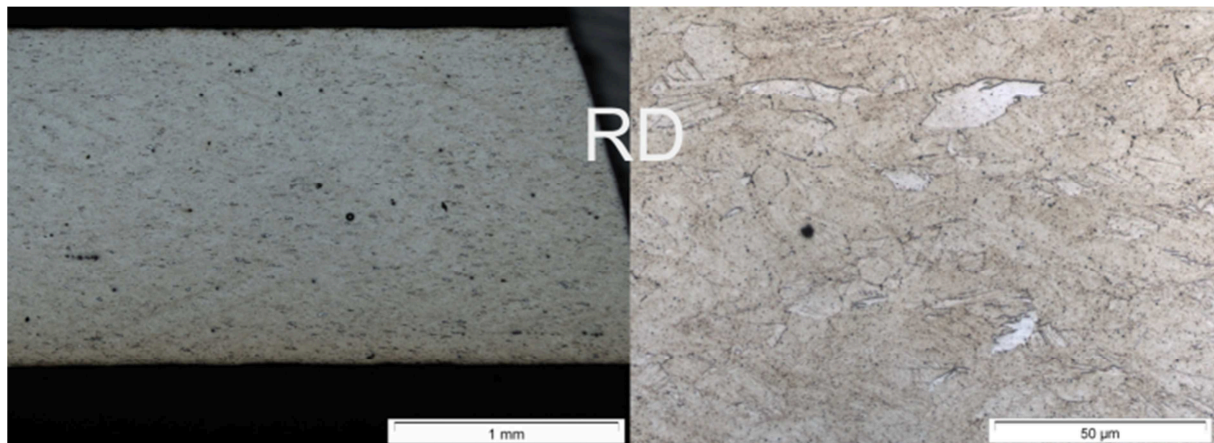

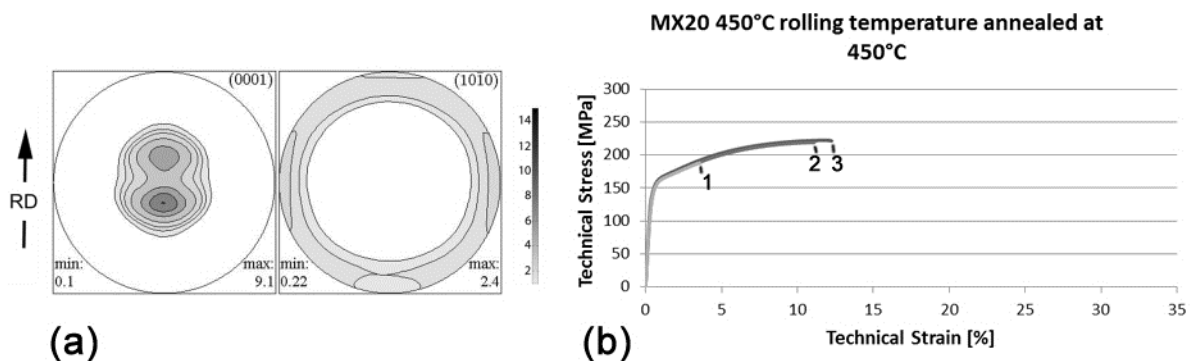Figure 6: Microstructure of the MX20 sheets rolled at 450 °C

Figure 7: Texture (a) and stress-strain curves of MX20. All three specimen rolled at 450 °C and annealed at 450 °C (b)

Conclusions

The heat treatment tests show the influence of different temperatures on the various microstructures in the as cast state. All the investigated alloys could be rolled except the Zn, Mn and Ca containing ZMX210, which probably results out of the existence on the $Mg_6Ca_2Zn_3$ phase in this alloy. Adding more than 1 m% of Ca to the Mn containing alloy MX21 does not result in better sheet properties compared to the MX20 with less than 1 m% of Ca. Around 1 m% of Ca added to the Al-Zn containing Mg-alloy ZAX210 leads to a texture close to those of rare earth Zn containing alloys like ZE10. The mechanical properties are as well comparable as they show high formability and a good strength. In the ongoing project two of the alloys (MX20 and ZAX210) will be processed via twin roll casting (TRC) and the process parameters will be tuned to optimize the resulting sheet properties.

Acknowledgements

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