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Investigations on microstructure and mechanical properties of non-flammable Mg-Al-Zn-Ca-Y extruded alloys

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Abstract
Among commercial structural metals, magnesium alloys feature the lowest absolute density, showing specific strength values superior to other structural materials such as aluminum alloys and steels. While the inherent, high weight- and hence CO2-saving potential conduce to applications of magnesium alloys to mobile components, most of them suffer from high oxidation affinity and insufficient chemical and mechanical stability at elevated temperatures. It is known that the oxidation behavior can be improved by addition of specific elements such as calcium and yttrium. Mg-Al based alloys (e.g. AZ alloys) are commercially dominating, as they show good mechanical properties, eutectic behavior and include cast- as well as wrought alloys. Hence in this work, four Mg-Al-Ca-Y alloys with Al contents ranging from 3 wt. % to 9 wt. % were produced and compared to two standard AZ-type alloys (AZ31 and AZ91). The alloys were cast into small billets, homogenized and finally extruded. Mechanical properties in the extruded state, microstructure and processability were investigated at room temperature and at elevated temperatures.

1. Introduction

Increasing environmental awareness and the need for reduced fuel consumption in the field of transportation pushes aircraft and automobile manufacturers to enforce weight saving measures in their products. Using materials with high specific strength offers the opportunity to decrease components' weight without compromising its overall strength. Magnesium is one of the most promising materials for this application due to its low density. Compared to aluminium it is 35% lighter and possesses advantages in strength values when normalized with density. While typical die cast aluminium alloys like A226 (AlSi9Cu3(Fe)) show specific yield strength values of 51 Nm/g and a specific ultimate tensile strength of 87 Nm/g, typical values for the standard magnesium alloy AZ91 reaches values of 88 Nm/g and 127 Nm/g, respectively.

A key negative aspect of magnesium is its high chemical reactivity associated with low corrosion resistance and high oxidation tendency. In commercial aviation, the primary concern is the flammability performance of magnesium. While the use of magnesium in passenger airplane cabins was prohibited for many years, the Society of Automotive Engineers (SAE) recently cleared magnesium for aircraft seats, "provided the materials are tested to and meet the flammability performance requirements" in a specialized test [1,2].

Up to date, few magnesium alloys have passed this test, e.g. alloys containing several weight percent rare earth elements, like WE43 and Elektron 21. Cheaper alternatives which already passed the test are alloys based on the Mg-Al-Ca and Mg-Al-Ca-Y systems, which are currently under development [3–6]. In the present work, the processability and the resulting mechanical properties of four non-flammable Mg-Al-Ca-Y-(Zn,Mn) alloys were investigated and compared to two commercial available Mg-Al-Zn alloys, namely AZ31 and AZ91.

2. Methodology

Six AZ-type magnesium alloys were produced. Four alloys included small additions of calcium and yttrium whereas two alloys represented commercial AZ alloys. The nominal chemical compositions of the alloys can be seen in table 1.

Table 1: Nominal chemical compositions of the used alloys

Alloy	Al	Zn	Mn	Ca	Y	Mg
AZ31B	2.5 – 3.5	0.7 - 1.3	> 0.2	0.0	0.0	Bal.
AZ91D	8.5 – 9.5	0.45 – 0.9	> 0.17	0.0	0.0	Bal.
AZXW3100	3.0	0.8	0.1	0.5	0.2	Bal.
AZXW6000	6.0	0.3	0.1	0.5	0.2	Bal.
AZXW8000	8.0	0.3	0.1	0.3	0.2	Bal.
AZXW9100	9.0	0.8	0.1	0.3	0.2	Bal.

All alloys were produced using commercial Mg ingot (99.8 wt. %), Al ingot (99.9 wt. %), Zn ingot (99.8 wt. %), calcium granules (99.6 wt. %), manganese chloride and a commercial magnesium-30 wt. % yttrium master alloy. Billets with a diameter of 50 mm and a length of 200 mm were cast using a cooled graphite mold [7]. Melt temperature during holding and casting was 720°C and melt coverage was provided by protective gas atmosphere (Ar mixed with 1 % sulfur hexafluoride (SF6)). Following casting, the alloys were solution heat treated for 24 hours to dissolve the magnesium-aluminium eutectic at temperatures between 425°C and 440°C, depending on the inherent aluminium content of the billets. Microstructures were analyzed before and after the solution heat treatment step.

After heat treatment, billets were turned to a diameter of 48.5 mm and subsequently extrusion pressed to circular and flat profiles. Extrusion pressing was done using a laboratory scale extrusion press with a container diameter of 50 mm and an extrusion force of 1,5 MN at extrusion parameters provided in table 2. Figure 1 shows the extrusion pressing process with the extrudate.

Figure 1: Extrusion pressing of Ø 10 mm profiles

Table 2: Extrusion pressing parameters

Billet temperature	Billet heating	Die temperature	Billet length	Ram speed	Profile diameter
390°C	Inductive	390°C	180 mm	1.0 mm/s	Ø 10 mm

Tensile test samples according to DIN EN 50125 with a gauge length of 30 mm and a diameter of 6 mm were machined from the extruded profiles. The testing speed was 0.006 s^{-1} at temperatures of 25°C, 50°C, 100°C, 150°C and 200°C, respectively.

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3. Results and Discussion

3.1 Casting

The alloys containing Ca and Y produced a more stable oxide layer on the melt during holding and stirring. Therefore the amount of cover gas needed for melt protection could be reduced dramatically. Moreover, this robust oxide film also leads to increased surface quality of cast parts due to reduced oxygen access.

3.2 Microstructure

Figure 2 shows the microstructure of AZ31 alloy before solution heat treatment (as cast condition). Besides the typical, blocky and needle-shaped Al-Mn-phases, small fractions of β-phase ($Mg_{17}Al_{12}$) can be found in the sample - although the Mg-Al-phase diagram suggests the phase to appear only at higher Al-contents. However, this is caused by the low diffusion speed of aluminium in magnesium and non-equilibrium casting conditions [8]. In the solution heat treated sample, the eutectic phase was found to be completely dissolved which is preferable for forming processes.

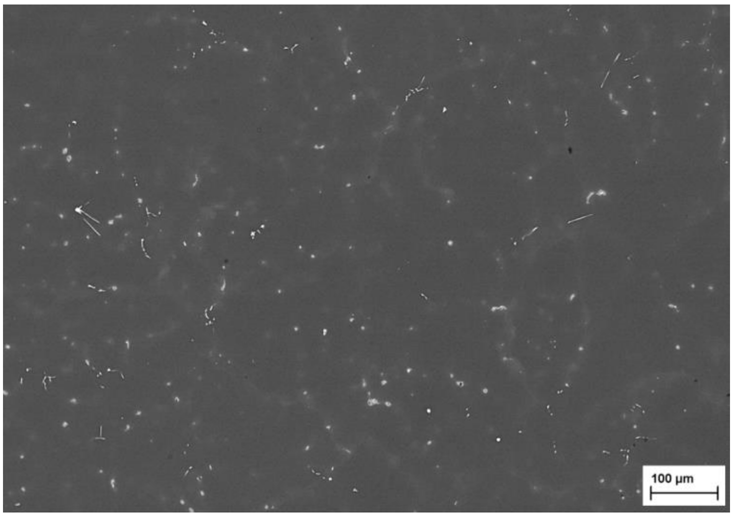

Figure 2: Microstructure of AZ31 alloy - as cast condition

Figure 3 shows the microstructure of the AZ91 alloy produced in this work in as-cast condition. The amount of eutectic phase is greatly increased compared to the AZ31 due to the higher aluminium content.

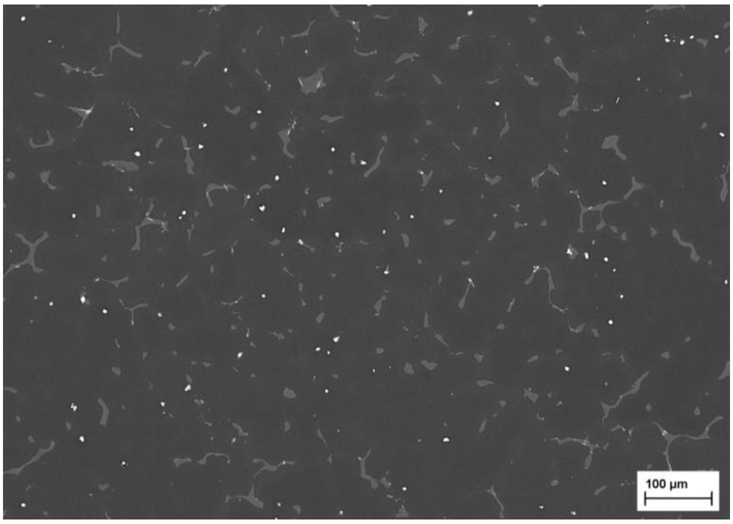

Figure 3: Microstructure of AZ91 alloy – as cast condition

Figure 4 shows the microstructure of the heat treated AZ91 alloy. The eutectic phase was completely dissolved while the other phases were not influenced.

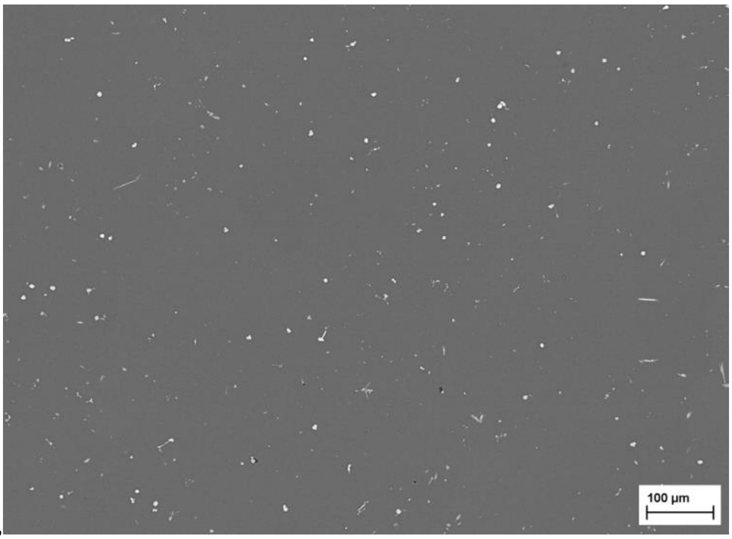

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Figure 4: Microstructure of AZ91 alloy – heat treated condition

The microstructure of as cast AZXW9100 alloy, as depicted in Figure 5, is comparable to the microstructure of the AZ91 alloy but with a higher amount of β-phase. EDS analyses confirm that calcium is mainly found in the eutectic phase. Additionally to the typical Al-Mn phases, Al-Y as well as Al-Mn-Y phases could be detected. Compared to AZ91, the eutectic phase of AZXW9100 possesses a higher thermal stability owing to the calcium content of this phase [5,9]. By comparing microstructures to results presented from Wang et al. [10], Suzuki et al. [11], Zhang et al. [12] and Nami et al. [13], the phases present in this works alloys can be identified as Al_8Mn_5, Al_2Y and $Al_{10}Mn_2Y$. Other possible phases for the system Mg-Al-Zn-Ca-Y like Al-Ca-phases (Al_2Ca and Al_4Ca), Mg_2Ca and Al_3RE_{11} could not be identified.

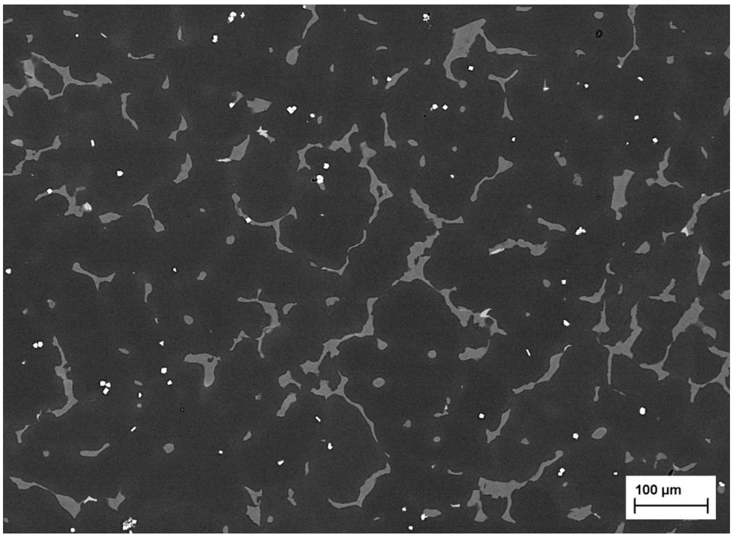

Figure 5: Microstructure of AZXW9100 alloy – as cast condition

Figure 6 shows the same alloy after heat treatment. It can be seen, that the eutectic phase was not fully dissolved and remainders are still present in the alloy. Al-Mn, Al-Y and Al-Mn-Y phases were not dissolved.

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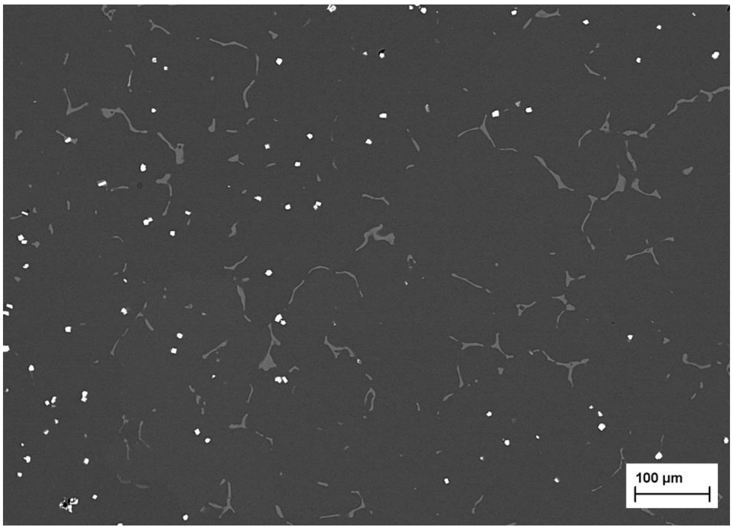

Figure 6: Microstructure of AZXW9100 alloy – heat treated condition

3.3 Extrusion pressing

Figure 7 shows a comparison of power/time curves of the extrusion press for selected alloys. While the AZXW alloys selected all have undissolved Al-Y phases present, AZ31 lacks these phases. As is evident from the maximum pressure values, the necessary extrusion force (pressure) increases with increasing aluminium content and furthermore with the addition of calcium and yttrium. Regarding required forces alone, commercial AZ31 seems to be better suited at standard extrusion temperatures of 390°C.
Yet, as discussed prior in microstructure analysis, the combined addition of Ca and Y reduces oxidation tendency and increases the eutectic temperature. These effects allow higher heat-treatment- and extrusion temperatures, the latter enabling operation at higher extrusion speeds and shorter heat treatment times due to the former. Hence, at full perspective, the beneficial effects of Ca and Y not only compensate for the increased expenditure but increase the cost-effectiveness of extrusion processing of these alloys overall.

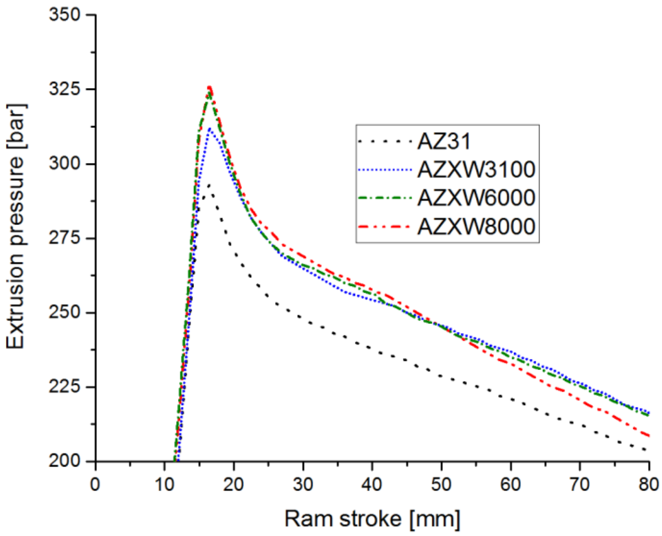

Figure 7: Energy consumption for deformation of the alloys

3.4 Tensile tests

Figure 8 and 9 show temperature dependent yield strength and ultimate tensile strength measurement results of the extrusion pressed material. As anticipated, the strength values increase with increasing aluminium content, coinciding with an increase in volume fraction of β-phase ($Mg_{17}Al_{12}$) [14]. It is noteworthy that the “flame resistant” alloys containing Ca and Y show no reduction in mechanical properties compared to the standard alloys. All alloys show reasonable stability in mechanical properties up to 100°C, which hence represent the upper limit temperature for potential applications. With further increase in temperature, strength decreases significantly. E.g. the alloys AZXW8000, AZXW9100 and AZ91 show a reduction of only 10 % in terms of YS and UTS between room temperature and 100°C. At 150°C the reduction is already 25 % and between 45 – 50 % at 200°C compared to room temperature. The decrease in mechanical properties is more distinct for the alloys with lower Al content.

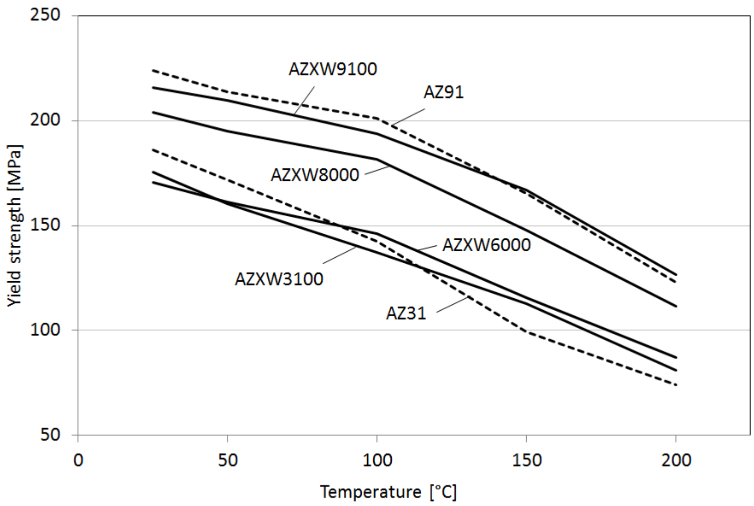

Figure 8: Temperature dependent yield strength of extrusion pressed alloys

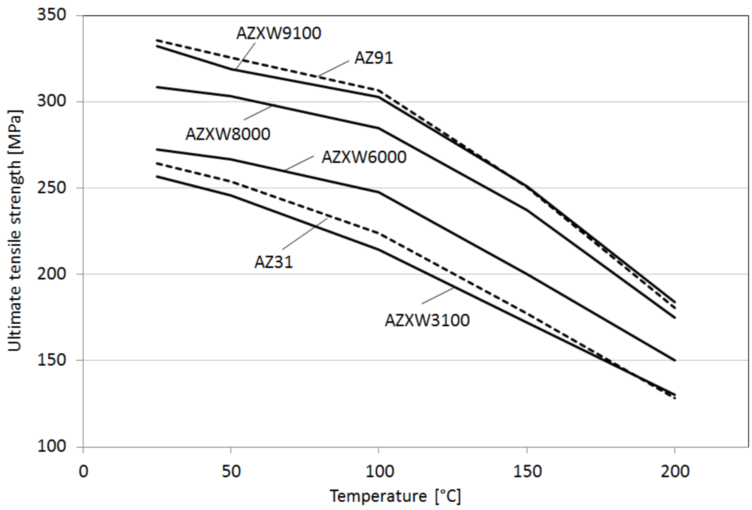

Figure 9: Temperature dependent ultimate tensile strength of extrusion pressed alloys

4. Conclusions

1. Adding calcium and yttrium to magnesium alloys leads to reduced melt reactivity and reduces the amount of cover gas needed for melt handling and casting. Especially calcium is very effective and, considering its low price, is capable of reducing the overall processing costs of magnesium alloys.
2. The addition of small amounts of calcium and yttrium to AZ-type magnesium alloys imposes no reduction to the mechanical properties of the alloys, while at the same time increasing the temperature regime applicable for forming operations. The increase in passivity against ignition in solid and molten state allow for higher heat treatment operation, and the stabilization of the eutectic phase due to Ca-additions leads to increased extrusion speeds.
3. AZ- and AZXW-alloys show good mechanical properties at room temperature. At elevated temperatures, mechanical strength decreases rapidly. For the use at higher temperatures, further efforts are necessary, e.g. stabilization of grain boundaries by addition of further elements.

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