Understanding the High Creep Resistance of MRI 230D Magnesium Alloy through Nanoindentation and Atom Probe Tomography

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Abstract: Due to their low density, magnesium alloys are very appealing for light-weight constructions. However, the use of the most common magnesium alloy, AZ91 (Mg 9 wt.% Al, 1 wt.% Zn), is limited to temperatures below 150 °C due to creep failure. Several alloys with an improved creep resistance have been developed in the past, for example the alloy MRI 230D or Ca-alloyed AZ91 variants. However, there is an ongoing discussion in the literature regarding the mechanisms of the improved creep resistance. One factor claimed to be responsible for the improved creep resistance is the intermetallic phases which form during casting. Another possible explanation is an increased creep resistance due to the formation of precipitates. To gain more insight into the improved creep resistance of MRI 230D, nanoindentation measurements have been performed on the different phases of as-cast, creep-deformed and heat-treated samples of MRI 230D and Ca-alloyed AZ91 variants. These nanoindentation measurements clearly show that the intermetallic phase (IP) of the alloy MRI 230D does not lose strength during creep deformation in contrast to the Ca-alloyed AZ91 variants. High-temperature nanoindentation measurements performed at 200 °C clearly show that the intermetallic phases of the MRI 230D alloy maintain their strength. This is in clear contrast to the Ca-alloyed AZ91 variants, where the IP is significantly softer at 200 °C than at room temperature. Atom probe measurements have been used to gain insight into the differences in terms of chemical composition between the IPs of MRI 230D and the Ca-alloyed AZ91 variants in order to understand the dissimilar behaviour in terms of strength loss with increasing temperature.

Keywords: creep; magnesium alloy; intermetallic phase; mechanical properties; nanoindentation; atom probe tomography

1. Introduction

Since vehicle mass is a key contributor to fuel efficiency, the use of lightweight materials can have a significant impact on their CO₂ emissions. The increased use of magnesium alloys is therefore very appealing, as magnesium is the least dense metal regularly used in structural applications. However, the most widely used magnesium alloys are based on the Mg–Al system and their application is limited to temperatures below approximately 150 °C as a result of the low creep strength of these alloys [1–3]. Conversely, e.g., for automotive powertrain applications, alloys with an increased creep strength for use up to 200 °C under long-term loading conditions are needed. Several successful attempts have been made to increase the creep strength of Mg–Al alloys by adding rare earth elements or alkaline earth elements, see for example [4–8]. However, there is a lack of understanding and an ongoing debate in the literature on the mechanisms responsible for the increased creep strength. The microstructure of all derivatives of the above-mentioned Mg–Al-alloy family shows a skeleton-like structure of hard intermetallic phases (IP) in which the Mg grains...
are embedded. In several publications, it is proposed that the skeleton of hard IPs is responsible for the improved creep strength of these alloys, see [9–16]. For Ca-alloyed A91 variants it could be shown that an increased interconnectivity of the IP network results in an increased creep strength [17]. This is supported by the works of Zubair et al. [18,19] where the skeleton of hard IPs was claimed to be responsible for the improved creep properties of the investigated Mg–Al-Ca alloys. Their microstructural investigations of creep-deformed specimens clearly showed strain localizations at the interfaces of $\alpha$-Mg and IPs and a fracture of the IP in areas of high strain localization [18,19].

However, a comparison of the Ca-alloyed AZ91 variants [17,20] with the commercial alloy MRI 230D shows that the alloy MRI 230D has an improved creep strength over similar Ca-alloyed AZ91 variants. Even an AZ91 alloy with 5 wt.% Ca addition (AXZ951) has a lower creep strength compared to MRI 230D, especially in a regime of low creep rates [17]. This is quite surprising, considering MRI 230D has a lower content of Ca, only about 2 wt.% compared to approximately 5 wt.% in the case of the alloy AXZ951, i.e., a smaller amount of IP. The quantification of the interconnectivity of the IP skeleton additionally revealed that the interconnectivity is less pronounced than in the case of the alloy AXZ951; the interconnectivity of the IP of the alloy MRI 230D is more equal to that of the alloy AXZ931 with 3 wt.% of Ca—see [17]. Since the creep rate of the alloy AXZ931 is more than one order of magnitude higher than the creep rate of the alloy MRI 230D under identical conditions [17], the question about the origin of the improved creep strength of MRI 230D arises. Recently, the increased creep strength of the Mg grains due to precipitation was investigated by Lamm et al. [21]. They showed that MRI 230D has much more thermally stable nano-sized precipitates in the Mg grains, at least partially explaining the increased creep resistance. What is however still unclear is if the IP network also behaves differently in MRI 230D vs. the AZ91 variants.

Light microscopy images of the microstructure of the investigated alloys are summarized in Figure 1. The microstructure of all alloys consists of $\alpha$ magnesium grains (light grey) surrounded by intermetallic phases (dark grey). The IP shows an increasing interconnectivity with increasing Ca content. Due to the lower thixomolding temperature of the alloy MRI 230D, primary solid $\alpha$-Mg can be found in the microstructure. A detailed analysis of the microstructure of the investigated alloys including the reproducibility of the microstructural observations as well as the quantification of the interconnectivity can be found in [17].

As known from previous work, the creep resistance of AZ91 alloy variants increases with increasing Ca content; see for example [1,17,20,22–25]. The alloys tested in this work show the same behaviour, as depicted in Figure 2, where their respective creep curves are shown. The observed strain rate $\epsilon$ decreases significantly with an increasing Ca content. An increase in the Ca content from 1 wt.% to 3 wt.% leads to a decrease in the measured minimum creep rate of about one order of magnitude. A further increase in the Ca content to approximately 5 wt.% further decreases the minimum creep rate by more than one order of magnitude. The creep rate of MRI 230D is comparable to that of AZ91 with 5 wt.% Ca addition, although the Ca content of MRI 230D is much lower with only about 2 wt.%; see also [17]. As the ductility of AZ91 decreases with increasing Ca content (see [22]) the tensile elongation of the alloy with 5 wt.% of Ca is below 1%. A lower Ca content of the alloys is therefore beneficial for structural applications.

Other works show that a combined addition of Ca and Sr to Mg–Al alloys leads to improved creep properties when compared with the addition of only Sr or Ca [26,27], but no reasons for these improved properties due to a combined addition of Sr and Ca are given.
To gain more insight into the mechanisms responsible for the enhanced creep resistance, in this work the mechanical properties of the individual phases have been determined via nanoindentation. To this end, a commercially sourced sample of MRI 230D has been investigated in different states of creep deformation, namely as-cast, at minimum creep rate and after long-term creep loading at a typical service temperature of 200 °C (approximately 250 h). These results are compared with a series of experimental AZ91 alloy variants with Ca additions varying from 1–5 wt.%. The nanoindentation measurements have been performed at room temperature and at 200 °C. Measuring the local mechanical properties of the individual phases is a new approach to gain more insight into the origins of the creep resistance of magnesium alloys, especially in order to understand the high creep strength of the alloy MRI 230D.
In the case of the Ca-alloyed AZ91 variants, the IP mainly consists of Mg$_{17}$Al$_{12}$, Al$_2$Ca and (Mg, Al)$_2$Ca; see for example [28–30]. X-ray diffraction measurements from Aghion et al. [31] revealed only the presence of $\alpha$-Mg and Al$_2$Ca in the case of the alloy MRI 230D. Other groups report ternary MgAlSrCa phase compositions in Mg-Al-Ca-Sr alloys; see for example [32–35].

2. Experimental Section

A commercially available alloy, MRI 230D, was investigated and compared with Ca-alloyed AZ91 alloys with nominally 1, 3, and 5 wt.% of added Ca, named AXZ911, AXZ931 and AXZ951, respectively, according to ASTM B275 standard. All alloys were thixomolded by Neue Materialien Fürth GmbH on a Japan Steel Works machine with a closing force of 220 t. The cooling rate in thixomolding is rather high, comparable with the cooling rate of high-pressure die casting, and should be comparable for all alloys investigated in this work. In the case of the Ca-alloyed AZ91 variants, a thixomolding temperature of 605 $^\circ$C was used, so these alloys were cast in a fully liquid state. For the alloy MRI 230D the thixomolding temperature was 590 $^\circ$C, so the alloy was cast in semi-solid state. Due to this, primary $\alpha$-Mg can be found in the microstructure; see also Figure 1. Comparative measurements showed no significant influence of the thixomolding temperature on the hardness of the individual phases. The chemical composition for all investigated alloys as measured by GDOES (Glow Discharge Optical Emission Spectroscopy) is summarized in Table 1.

|        | Mg   | Al   | Zn   | Ca   | Mn   | Sr   | Sn   |
|--------|------|------|------|------|------|------|------|
| AXZ911 | 88.72| 8.98 | 0.60 | 1.27 | 0.22 | -    | -    |
| AXZ931 | 88.04| 8.02 | 0.55 | 2.96 | 0.22 | -    | -    |
| AXZ951 | 86.81| 7.88 | 0.54 | 4.35 | 0.22 | -    | -    |
| MRI230D| 89.16| 6.76 | 0.27 | 1.94 | 0.38 | 0.48 | 1.1  |

Throughout this work, great care has been taken to take the samples out of the centre of the casting plates and to avoid taking samples out of the regions of the casting skin.

Creep tests were performed in compression mode at a temperature of 200 $^\circ$C under constant true stress of 100 MPa on samples of approximately 5.5 mm height and about 20 mm$^2$ in cross-section. The cylindrical samples were ground to a parallelism of better than 10 $\mu$m. The solid cross-section, where casting porosity has been taken into account, is calculated from the sample mass m and the sample height $h_{0,RT}$ (averaged over five measurements) as $A_{0,RT} = m / (\rho h_{0,RT})$. A constant solid density $\rho = 1.811$ g/cm$^3$ was assumed for all alloys. For the calculation of the sample cross-section at the elevated test temperature of 200 $^\circ$C the thermal expansion was accounted for with a thermal expansion coefficient of $2.6 \times 10^{-5}$ K$^{-1}$.

The compressive constant true stress experiments were carried out using a lever-arm creep-testing machine, with the height change $\Delta h$ measured by a tube–rod extensometer system based on a linear variable differential transformer. Compressive strain is determined as $\varepsilon = -\ln(1 + \Delta h / h_0)$. Compressive stress is calculated as $\sigma = -F / A_0 \times \exp(-\varepsilon)$ from the force, F, measured by a load cell with a maximum capacity of 20 kN. Please note that for reasons of clarity in this work for compressive strains and stresses absolute values are used. For all creep tests in this work a temperature of 200 $^\circ$C and a stress of 100 MPa has been used.

For microstructural investigations and nanoindentation measurements, samples were cut out of the castings or the creep-deformed samples and ground and polished with diamond suspension. The last preparation step was polishing with colloidal SiO$_2$ suspension (OPS, Struers, Denmark) to ensure high surface quality with low residual deformation. To prevent corrosion, water-free isopropyl alcohol was used as a lubricant for all polishing
steps. In the case of the creep deformed samples, a surface parallel to the deformation direction was investigated.

The nanoindentation measurements at room temperature (meaning a temperature range of 18 °C–25 °C) were performed on an Agilent Nanoindenter XP. For the measurements at 200 °C a G200 from Surface equipped with a heating stage was used. To prevent the oxidation of the samples, measurements at 200 °C were performed under a protective argon atmosphere. All nanoindentation experiments used a Berkovich indenter tip and continuous stiffness mode (CSM). Due to the limited size of the intermetallic phase, the maximum indentation depth was 250 nm and the hardness for each measurement was averaged over a depth range between 200 and 250 nm. Figure 2 shows exemplarily indents in a sample of the alloy AXZ911 which has crept to the minimum creep rate.

Atom probe tomography (APT) experiments were carried out in a Cameca LEAP 4000X HR (Cameca Instruments Inc., Madison, WI, USA) with a reflectron detector system offering 37% detection efficiency. The samples were prepared via FIB lift-out in a FEI Helios 660i (FEI, Hillsboro, FL, USA) and a Zeiss Crossbeam 1540 EsB (Carl Zeiss AG, Oberkochen, Germany). While the lift-out process was done with a 30 kV Ga-beam, the shaping of the samples as soon as they were smaller than 1 µm was carried out under reduced acceleration voltage of 10 kV. This eliminates spurious ion irradiation damage within the investigated volumes caused by ion channelling. For the final milling step, the ion energy was reduced to 5 kV. A more precise description of the lift-out procedures is given in Refs. [36–38]. All APT measurements were performed using high voltage pulses with a repetition frequency of 200 kHz to trigger field evaporation with the sample bias voltage regulated to achieve an average detection rate of 2 kHz. The temperature of the tips was 40–45 K and the pulse amplitude was 20% of the bias voltage.

3. Results
3.1. Creep Behaviour

The creep curves showing the creep rate over the strain of the investigated alloys in as-cast condition can be seen in Figure 3. Although several samples (minimum two experiments each) have been tested, only one creep curve for each alloy is shown for the sake of clarity. The creep tests showed a reproducibility in the strain rate within a factor of two.

![Creep curves](image-url)

Figure 3. Creep curves of the different alloys measured at a temperature of 200 °C and a compressive stress of 100 MPa; creep data for the alloy MRI 230D are taken from [17].

The creep strength of the alloys significantly increases with an increase in Ca content, which is in accordance with literature. The creep rate of the alloy MRI 230D is approximately
the same as the creep rate of the alloy AXZ951, although the Ca content of the alloy MRI 230D is much lower than that of the alloy AXZ951.

3.2. Nanoindentation

In order to assess the mechanical properties of the individual intermetallic phases in the different alloys, we performed nanoindentation. The results at room temperature of these nanoindentation measurements are summarized in Figure 4. The room temperature hardness of the $\alpha$-Mg is similar for all alloys and all creep states. The measured hardness of the $\alpha$-Mg in as-cast condition increases slightly with the increasing Ca content of the alloy, so the hardness is lowest for AXZ911 and highest for AXZ951. However, the differences in hardness are rather small. The hardness of the $\alpha$-Mg phase of the alloy MRI 230D equals approximately the hardness in the alloy AXZ951.

![Figure 4. Room temperature hardness of the $\alpha$-Mg (a) and the IP (b) for the different alloys measured at various conditions.](image)

A comparison of the hardness of the $\alpha$-Mg phase for the different creep states reveals no clear trend concerning the hardness evolution during creep testing in the case of the alloys AXZ911, AXZ931 and AXZ951. The differences in hardness for the different alloy conditions do not exceed the experimental scatter and there is no systematic evolution of the hardness with increasing creep testing time of the samples. In the case of the alloy MRI 230D one can observe that the hardness of the $\alpha$-Mg phase decreases with increasing creep deformation, e.g., time at elevated temperature (see also Lamm et al. [21]).

In the case of the Ca-alloyed AZ91 variants, the hardness of the IP increases with the Ca content of the alloy, i.e., the room temperature hardness of the IP of the alloy AXZ951 is highest for all alloys investigated in this work. The hardness of the IP of the Ca-alloyed AZ91 variants AXZ911, AXZ931 and AXZ951 does not change significantly during creep deformation. Remarkably, this is different for MRI 230D, where the room temperature hardness of the IP significantly increases during creep deformation. The hardness of the IP of MRI 230D is comparably low in the as-cast condition, but in the sample which has been creep deformed to the minimum creep rate, the hardness of the IP has significantly increased. Further creep deformation leads to a further increase in the hardness of the IP. Although the IP of MRI 230D in as-cast condition is significantly softer than the IP of the alloys AXZ911, AXZ931 and AXZ951, after creep deformation the IP of the alloy MRI 230D has approximately the same hardness as the IP of the alloys AXZ931 and AXZ951 and is significantly harder than the IP of the alloy AXZ911.

When comparing the nanoindentation results at room temperature with the measurements at creep temperature, a significant difference in behaviour between the alloy series emerges. The hardness of the IP at 200 °C of all AXZ alloys is significantly lower than at room temperature—by about 0.5 GPa; see Figure 5. This is completely different for MRI 230D, where the IP maintains its hardness. At room temperature, the hardness of the IP of
the alloy MRI 230D is lower than in the case of the Ca-alloyed AZ91 variants (compare also Figure 4) but at 200 °C the measurements show a completely different picture as the IP of the alloy MRI 230D is harder than the IP of the Ca-alloyed AZ91 variants.

![Figure 5. Hardness of the IPs of the different alloys in as-cast condition at 200 °C and at room temperature.](image)

The results clearly show that the local mechanical properties of the IPs are different for the individual alloys. The intermetallic phase network of the alloy MRI 230D nearly maintains its strength at 200 °C, whereas in the case of the Ca-alloyed AZ91 variants the IP exhibits significant strength loss at 200 °C.

### 3.3. APT Measurements

In order to assess the differences in composition, including minor elements, that may have led to such an improved high-temperature hardness of the IP in MRI 230D, we carried out atom probe measurements on the different IPs. The results of these are shown in Figure 6. These measurements clearly show that the IP in MRI 230D contains not only Al, Ca and Mg but also a significant amount of Sr. Sr is present as an alloying element in MRI 230D, but is absent in the AZ91 type alloys. This implies that Sr strengthens the IP of Mg-Al-Ca alloys. Even relatively small amounts of Sr seem to have an huge effect on the mechanical properties of the IP, as the overall amount of Sr in the alloy MRI 230D is only approximately 0.5 wt.% [17].

The APT measurements suggest that the IP in the alloy MRI 230D has a rather uniform composition where the elements Al, Ca, Sr, Zn and Mn segregate to the IP. A second APT measurement on the same alloy showed similar concentrations of the elements in the IP. Works from the literature report ternary MgAlSrCa phase compositions in the microstructure of Mg-Al-Ca-Sr alloys; see for example [32–35].

The results shown here hint that Sr plays an important role in the mechanical properties of the IP of MRI 230D. Sr is absent in the alloys AXZ911, AXZ931 and AXZ951 (see also Table 1) and the mechanical properties of the IP of these alloys suffer from degradation of their strength at 200 °C, whereas the IP of the alloy MRI 230D nearly maintains its strength at 200 °C compared to its strength at room temperature.
4. Discussion

4.1. Creep Behaviour

Interestingly, the alloy MRI 230D has approximately the same creep resistance as the alloy AXZ951, although the Ca content of the alloy MRI 230D is significantly lower, being only about 2 wt.%, than the Ca content of the alloy AXZ951. This has significant advantages as the ductility of the alloys decreases with increasing Ca content [22], so that the elongation to fracture of the alloy AXZ951 is below 1%; see [22]. Even when a Sr content of approximately 0.5 wt.% is added, the total content of alkaline earth elements Ca + Sr is significantly lower than 5 wt.% in the case of the alloy AXZ951. A comparison of the creep resistance of both alloys in a broader stress range [17] shows that the creep resistance of the alloy MRI 230D is even higher than the creep resistance of the alloy AXZ951, especially in a regime of low strain rates. This is even more surprising when one considers the connectivity of the skeleton-like structure of the IP, as the interconnectivity of the IP of the alloy AXZ951 is significantly higher than that of the alloy MRI 230D [17]. A quantification of the interconnectivities of the IPs reveals that the interconnectivity of the IP of the alloy MRI 230D is approximately the same as that of the IP of the alloy AXZ931 [17]. This clearly implies that the creep resistance of the alloys is not only governed by the interconnectivity of the IP, but that other factors are also important for creep resistance.

4.2. Hardness of the $\alpha$-Mg

No significant differences in hardness of the $\alpha$-Mg for all investigated alloys and conditions could be found. The nanoindentation measurements in Figure 4 show a small decrease in hardness after creep exposure for about 250 h, however this decrease in hardness is within the range of the experimental scatter. Lamm et al. [21] found clusters rich in Ca, Mn and Al in the $\alpha$-Mg of the alloys AXZ931 and MRI 230D. Those clusters coarsen during high-temperature exposure, e.g., during aging or creep testing. In the case of the MRI 230D alloy the clusters stayed small during high-temperature exposure, whereas the clusters of the alloy AXZ931 grew significantly; see [21]. However, this did not seem to have an impact on the nanoindentation hardness of the $\alpha$-Mg. In both alloys, the hardness of the $\alpha$-Mg decreased when the samples were exposed to creep testing at 200 °C for approximately 250 h; see Figure 4. If the clusters found in [21] significantly contributed to the hardness.
of the α-Mg grains no drop in hardness of the α Mg would be expected in the case of the alloy MRI 230D after creep exposure, whereas in the case of the alloy AXZ931 a drop in hardness would be anticipated. Although it is not clear to what extent the clusters found in [21] contribute to the hardness of the α Mg, it appears to be reasonable that these very small clusters will not have a pronounced effect on hardness. To what extent these clusters influence the mechanical properties under creep conditions, e.g., long-term loading with low deformation velocities, cannot be determined from nanoindentation experiments.

4.3. Hardness of the IP

The hardness of the IP of the Ca-alloyed AZ91 variants does not change significantly during creep, as is shown in Figure 4. On the other hand, an increase in the measurement temperature to 200 °C leads to a significant softening of the IP of these alloys; see Figure 5. In contrast, the IP of the alloy MRI 230D shows a small increase in hardness after creep. By directly comparing the results of MRI 230D and AXZ951, which both revealed a very comparable creep behaviour, it becomes obvious that the higher Ca content of AXZ951 leads to a significantly higher strength of the IP at room temperature in the as-cast condition and after creep exposure to the minimum creep rate. However, as the Ca-content is rather similar, the strength of the IP of the alloy MRI 230D should be at the same level as the strength of the IP of the alloy AXZ931. Interestingly, this is not the case for the as-cast condition, where the hardness of the IP of the alloy MRI 230D is significantly lower than that of the alloy AXZ931. In contrast to the very small changes in the hardness of the IP in AXZ931 and AXZ951 when comparing the different conditions, e.g., as cast- and creep-loaded, the IP of the MRI 230D alloy behaves completely differently. A pronounced increase in hardness with increasing creep exposure time is noticed when the hardness at room temperature is considered.

Additionally, the results of the hardness tests of the IPs at 200 °C have to be taken into account. While pronounced softening was obtained for the AXZ-alloys when compared to the room-temperature hardness data, for the IP in MRI 230D no differences of the hardness at room temperature and at 200 °C were obtained. Moreover, at 200 °C, the IP in MRI 230D was notably harder than the IP of the comparable AXZ931 alloy and showed a comparable hardness to the IP of AXZ951. Interestingly, the hardness measured at the creep minima follows the same trend. The hardness of the α-Mg obviously does not play an important role, as the hardness of the AXZ931 and AXZ951 for the condition after exposure to the creep minimum is higher than that of MRI 230D, whereas the creep rates are worse or equivalent. Taking the APT results into account too, we can learn that the small Sr additions in MRI 230D lead to an increase in mechanical strength at an elevated temperature of the IPs when compared to AXZ931, which contains the same Ca content. From Figure 3 we also can see that long-term exposure to 200 °C leads to a further increase in the hardness of the IP, which is not observed in the case of AXZ931.

Bringing all these results together, it becomes obvious that creep behaviour in the Mg-Al-Ca-alloys is not only governed by the morphology of the skeleton structure of the hard IPs, but also by the high-temperature strength and thermal stability of the IPs.

5. Conclusions

Nanoindentation measurements revealed that the IP of the alloy MRI 230D is significantly harder at 200 °C than the IP of Ca-alloyed AZ91 variants, while the differences in the hardness between the alpha grains of the respective alloys even at high temperatures are low. This enhanced hardness of the IP at creep temperatures is likely a significant factor contributing to the high creep strength of MRI 230D compared to the Ca-containing AZ91 variants. This is surprising when taking into account that the IP of the MRI 230D alloy has a lower connectivity than the Ca-alloyed AZ91 variants. APT measurements show that the IP of the MRI 230D contains Sr, an alloying element which is absent in the Ca-alloyed AZ91 variants. It is thus likely that Sr has a creep-strengthening effect in MRI 230D.
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