The role of Zn on the elevated temperature compression behavior of Mg5Nd: an *in situ*
synchrotron radiation diffraction study

D. Tolnai^{1*}, R.H. Buzolin¹, F. D'Elia¹, T. Subroto¹, S. Gavras¹, A. Stark¹, N. Schell¹, K.U. Kainer¹, N. Hort¹

¹*Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Germany*

Max-Planck-Straße 1,

D 21502, Geesthacht, Germany

(*Corresponding author: domonkos.tolnai@hzg.de)

Keywords: Magnesium alloys, deformation behaviour, elevated temperature, *in situ* synchrotron diffraction

ABSTRACT

As-cast Mg5Nd, Mg5Nd3Zn, Mg5Nd5Zn and Mg5Nd7Zn alloys were investigated with *in situ* synchrotron radiation diffraction during compression at 350 °C. The results and the post mortem microscopy investigations suggest that during deformation twinning was active, the most pronounced in the binary alloy whereas in the ternary alloys grain rotation could be observed. Sub-grain formation could be detected in all the alloys. The reinforcing capacity of the intermetallic network was the largest in Mg5Nd and Mg5Nd3Zn.

Introduction

During the development of high strength Mg alloys two approaches can be pursued; altering the composition by selecting alloying elements to generate secondary phases with reinforcing characteristics and/or modifying the microstructure using thermo-mechanical processing to obtain ultrafine structures. The combination of a transition metal such as Zn with Rare Earth (RE) metals is an effective way to enhance the mechanical property profile of Mg alloys [1]. Zn accelerates the age hardening response and increases the peak strength for binary Mg alloys containing RE elements due to the uniformly distributed basal precipitates [2-4]. The addition of RE metals results in improved castability and elevated temperature strength [5], and weaker anisotropy [6-8] that leads to improved ductility of Mg alloys.

The high brilliance of the available beam in synchrotron sources allows for fast acquisition times and performing experiments with the necessary temporal resolution [9, 10]. *In situ* high energy synchrotron radiation diffraction is a unique method to follow dynamic microstructural processes during the thermo-mechanical loading of polycrystalline materials [11]. Azimuthal angle – time plots can be constructed from the 2D Debye-Scherrer patterns taken during the experiment. These plots give information on grain size evolution, grain imperfection, grain rotation, and grain orientation, texture evolution, strain and strain anisotropy [12]. This information can be correlated with dislocation slip, sub-grain formation, twinning [13], recovery, recrystallization [14-16] and grain growth [17,18]. The disadvantage of the limited sampling volume originating from the cross section and the penetration depth of the synchrotron beam can be overcome by neutron diffraction [19-21], however synchrotron radiation diffraction provides the better time resolution.

The aim of this work is to investigate the influence of Zn addition on Mg5Nd during *in situ* compression at 350 °C, which is a typical extrusion temperature for Mg-Zn alloys, using

synchrotron radiation to investigate the dynamic microstructural changes during high temperature deformation.

Experimental Procedures

The alloys were prepared by permanent mould indirect chill casting [22]. Pure magnesium was melted in an electric resistance furnace under protective atmosphere of 2 vol.% SF₆ and Ar. The Zn and Nd were added as pure elements under continuous stirring. The melt was held at 750 °C for 10 min then poured into a steel mould preheated to 660 °C. After 15 min holding time at 660 °C the mould was lowered into water at a rate of 10 mm s⁻¹. For the *in situ* compression experiments cylindrical specimens were machined from the ingots with a length of 10 mm and diameter of 5 mm.

For the metallographic characterisation the samples were mounted in epoxy and ground using SiC paper and finally polished with OPS solution as the last step of polishing. The microstructures for optical microscopy (OM) were etched with acetic-picral solution. The specimens for electron backscattered diffraction studies (EBSD) were washed with 0.5 vol.% nitric acid in ethanol solution for 5 seconds and cleaned with ethanol.

The optical microscopic analysis was performed using a Leica DMI 5000 light optical microscope. The average grain size of each alloy was determined using the line intercept method on at least 100 grains from four optical micrographs per alloy. Microstructural investigation was performed using a TESCAN Vega SB-U III scanning electron microscope (SEM) in backscatter electron (BSE) mode. An accelerating voltage of 15 kV and working distance of 15 mm were used to obtain the SEM micrographs.

The EBSD was performed using a Zeiss FEG-SEM Ultra 55 attached with a Hikari detector and a TSL-OIM software package. The EBSD measurements on compressed samples were

conducted on an area of 800 μm x 360 μm with step size of 0.65 μm close to the centre of the deformed specimen to ensure a similar area to that measured during *in situ* diffraction analysis.

The *in situ* synchrotron radiation diffraction was performed at the P07 beamline of PETRA III, DESY (Deutsches Elektronen-Synchrotron). A monochromatic beam with the energy of 100 keV ($\lambda=0.0124$ nm) was used as the optics yield a sufficient flux at this energy. The maximum available beam cross section of 1.1 mm x 1.1 mm was used to illuminate a volume, containing between 10 and 150 grains depending on the alloys in this study. Diffraction patterns were recorded with a PerkinElmer 1622 Flatpanel with a pixel size of (200 μm)² which was placed at a sample-to-detector distance of 1603 mm from the specimen (calibrated with a LaB₆ standard powder sample). The acquisition time for each image was 1 s. The specimens were compressed in a DIL 805A/D (Bähr-Thermoanalyse GmbH, Hüllhorst, Germany) dilatometer, combined with a modified induction coil so the beam passes only the sample [23]. The specimens were heated to 350 °C at a rate of 50 Kmin⁻¹ and held at this temperature for 5 min before the compression started to ensure temperature homogeneity. The specimens were compressed with an initial strain rate of $1.1 \times 10^{-3} \text{ s}^{-1}$. The tests were terminated at a strain of 0.3. After the compression the samples were held at the same temperature for 15 min to relax and then gas-quenched in order to preserve the microstructure. The morphology of the Debye-Scherrer rings was analysed using Fit2D[®] software and converted into azimuthal-angle time (AT) plots by using the ImageJ[®] software package.

Results

The as-cast microstructures of the investigated alloys are shown in Figure 1/a-d prior to the deformation. The intermetallic particles build a semi-continuous intermetallic network along

the grain boundaries. The grain sizes are measured as 0.99 ± 0.14 mm for Mg5Nd, 0.56 ± 0.03 mm for Mg5Nd3Zn, 0.36 ± 0.02 mm for Mg5Nd5Zn and 0.2 ± 0.02 mm for Mg5Nd7Zn, respectively. The True Stress – True Strain curves from the *in situ* compression experiments are shown in Figure 2. The periodic noise on the measurement curves originates from the compression setup. The compressive strength of the materials were measured as 54.6 MPa for Mg5Nd, 61.2 MPa for Mg5Nd3Zn, 45.3 MPa for Mg5Nd5Zn and 41.7 MPa for Mg5Nd7Zn, respectively.

The azimuthal angle – time plots are shown in Figure 3. For the Mg5Nd the broadening of the timelines can be observed which can be attributed to sub-grain formation during the deformation. From the disappearance of the timelines and appearance on the other reflection it can be concluded that twinning also played an important role during the deformation. In the case of Mg5Nd3Zn the broadening of the timelines also suggests sub-grain formation, but unlike in the case of the binary alloy, the inclination of the timelines can also be observed. This indicates the rotation of the grains during compression. The same deformation behaviour can be observed in the case of Mg5Nd5Zn and Mg5Nd7Zn as well. Due to the large grain sizes in the microstructure and the resulting poor statistics the evaluation of the load transfer was not possible.

The microstructures after 10% of deformation at 350 °C are shown in Figure 4. The microstructure of Mg5Nd (Figure 4/a) shows a significant amount of twins in some of the grains, while the other alloys seem unaffected by twinning. In the case of Mg5Nd3Zn (Figure 4/b) some twinning also can be observed but the amount of twins is lower than in the binary alloy. In the Mg5Nd5Zn (Figure 4/c) and Mg5Nd7Zn (Figure 4/d) a very low amount of twins and no twinning can be detected.

EBSD inverse pole figure maps of the samples compressed at 350 °C are shown in Figure 5 after a relaxation time of 15 min at the deformation temperature. The binary Mg5Nd alloy (Figure 5/a) shows no traces of twinning after the relaxation. The grains are not completely recrystallized but contain a large amount of sub-grains. The Mg5Nd3Zn (Figure 5/b) also contain a high number of sub-grains and regions which seem to be twinned before the relaxation. The microstructure of Mg5Nd5Zn (Figure 5/c) contains as well sub-grains and a twin, while the Mg5Nd7Zn shows only the presence of sub-grains in the microstructure.

The cleavage of the intermetallic particles during deformation of the different alloys is shown in Figure 6. The network is destroyed mostly in the case of the binary Mg5Nd (Figure 6/a) where some fragments of the loose intermetallic particles were lost during the metallographic preparation. From the ternary alloys the Mg5Nd3Zn (Figure 6/b) also contains a large number of fragmented particles, which is not the case in the higher Zn content alloys (Figure 6/c-d).

Discussion

Although the grain size decreases with the Zn content, the addition of more than 3 wt.% Zn content was detrimental for the maximum compression strength [24]. Furthermore the softening of the samples can be observed with Zn containing alloys after reaching the maximum compressive strength. The micrographs of the intermetallic particles (Figure 6) suggests that the reinforcing capacity was the largest in the case of Mg5Nd and Mg5Nd3Zn because the intermetallic network shows a higher grade of fragmentation which is a sign of better load transfer between the phases, and can result in higher strength. During deformation the rotation of the grains and strong sub-grain formation can be observed in the case of the ternary alloys (Figure 3), while no rotation in the case of the binary alloys can be seen from the straight timelines. Furthermore the appearance and disappearance of timelines suggests that twinning took place at the onset of plastic deformation. The remaining twins can be seen

on the optical micrographs from the interrupted tests where the binary alloy shows the largest amount of twins while with increasing Zn content the amount of twins decreases (Figure 4). However twinning can be only seen in particular grains which suggests that their original orientation plays a vital role in their susceptibility to twinning [25]. The EBSD investigation of the relaxed samples (Figure 5) shows no sign of twinning in the binary alloy. This can be a result of the relaxation or that the growth of twins consumed the parent grains. The traces of moderate twinning can be observed in Mg5Nd3Zn; however the twinned regions seem recrystallized. In Mg5Nd5Zn a twin is still recognizable, that suggests that the Zn content plays an important role in the stability of the compressed microstructure.

Conclusions

From the *in situ* compression tests of Mg5Nd, Mg5Nd3Zn, Mg5Nd5Zn and Mg5Nd7Zn at 350 °C the following conclusions can be drawn:

- The addition of 3 wt.% Zn increased the compressive strength, but higher Zn contents were detrimental.
- The reinforcing capacity of the intermetallic network was the largest in Mg5Nd and Mg5Nd3Zn.
- During deformation twinning was observed in the binary alloy and less pronounced in the ternary alloy with the increasing Zn content.
- Unlike the Zn containing alloys, in the binary alloy no grain rotation could be observed during deformation.

Acknowledgements

The authors acknowledge the Deutsches Elektronen-Synchrotron for the provision of facilities within the framework of the proposal I-20150471 and the Deutsche

Forschungsgemeinschaft for the funding in the framework of the proposals TO817/4-1 and ME4487/1-1.

Figure 1 SEM micrographs of a) Mg5Nd, b) Mg5Nd3Zn, c) Mg5Nd5Zn and d) Mg5Nd7Zn in as-cast condition.

Figure 2 Compressive True Stress – True Strain curves from the *in situ* experiments.

Figure 3 Azimuthal angle – time plots obtained during compression of the alloys at 350 °C.

Figure 4 Optical micrographs after 10% deformation at 350 °C of a) Mg5Nd, (b) Mg5Nd3Zn c) Mg5Nd5Zn and d) Mg5Nd7Zn.

Figure 5 EBSD inverse pole figures after compression at 350 °C and 15 min recovery at deformation temperature of a) Mg5Nd, (b) MMg5Nd3Zn c) Mg5Nd5Zn and d) Mg5Nd7Zn.

Figure 6 SEM micrographs after deformation showing the cleavage of intermetallic particles a) Mg5Nd, (b) MMg5Nd3Zn c) Mg5Nd5Zn and d) Mg5Nd7Zn. The compression direction is aligned horizontally.

-
- [1] T. Itoi T. Inzawa M. Yamazaki Y Kawamura and M. Hirohashi: *Mater Sci Eng A*, 560 216 (2013).
 - [2] J. F. Nie, X. Gao and S. M. Thu: *Scr. Mater.*, 53, 1049 (2005).
 - [3] T. T. Sasaki, K. Oh-ishi, T. Ohkubo and K. Hono: *Scripta. Mater.*, 55, 251 (2006).
 - [4] B.K. Park, J.H. Jun, and J.M. Kim: *Mat. Trans.*, 49, 931 (2008).
 - [5] Q. Li, Q. Wang, Y. Wang, X. Zeng and W. Ding: *J. Alloys Compd.*, 427, 115, (2007).
 - [6] N. Stanford, D. Atwell, A. Beer, C. Davies and M.R. Barnett: *Scripta. Mater.*, 59, 772, (2008).
 - [7] B. Langelier, A.M. Nasiri, S.Y. Lee, M.A. Gharghouri and S. Esmaeili: *Mat. Sci. Eng. A*, 620, 76, (2015).
 - [8] K. Yu, W.X. Li and R.C. Wang: *J. Cent. South Univ. Technol.*, 12, 499, (2005).
 - [9] D. Tolnai, P. Townsend, G. Requena, L. Salvo, J. Lendvai, and H.P. Degischer: *Acta Mater.*, 60, 2568, (2012).
 - [10] D. Tolnai, C.L. Mendis, A. Stark, G. Szakács, B. Wiese, K.U. Kainer and N. Hort: *Mater. Lett.*, 102-103, 62, (2013).
 - [11] K.-D. Liss and K. Yan: *Mater. Sci. Eng. A*, 528, 11, (2010).

-
- [12] D. Canelo-Yubero, G. Requena, F. Sket, C. Poletti, F. Warchomicka, J. Daniels, N. Schell and A. Stark; *Mater. Sci. Eng. A*, 657, 244, (2016).
- [13] K. Yan, D. Carr, M. Callaghan, K.-D. Liss, and H. Li: *Scripta. Mater.*, 62, 246, (2010).
- [14] R.H. Buzolin, D. Tolnai, C.L. Mendis, A. Stark, N. Schell, H. Pinto, K.U. Kainer and N. Hort: *Mat. Sci. Eng. A*, 640, 129 (2015).
- [15] R.H. Buzolin, C.L. Mendis, D. Tolnai, A. Stark, N. Schell, H. Pinto, K.U. Kainer and N. Hort *Mat. Sci. Eng. A*, 664, 2, (2016).
- [16] K.-D. Liss U. Garbe, H. Li, T. Schambron, J.D. Almer and K. Jan: *Adv. Eng. Mater.*, 11, 637, (2009).
- [17] K.-D. Liss K. Yan and M. Reid: *Mat. Sci. Eng. A*, 601, 78, (2014).
- [18] K. Yan, K.-D. Liss, U. Garbe, J. Daniels, O. Kirstein, H. Li and R. Dippenaar; *Adv. Eng. Mater.*, 11, 771, (2009).
- [19] T. Schmoelzer, K.-D. Liss, P. Staron, S. Mayer and H. Clemens: *Adv. Eng. Mater.*, 13, 685, (2011).
- [20] J. Čapek, K. Máthis, B. Clausen, J. Stráská, P. Beran and P. Lukáš: *Mat. Sci. Eng. A*, 602, 25, (2014).
- [21] K. Máthis, J. Čapek, B. Clausen, T. Krajňák and D. Nagarajan: *J. Alloys Compd.*, 642, 185, (2015).
- [22] F.R. Elsayed, N. Hort, M.A. Salgado-Ordorica and K. Kainer: *Mater Sci Forum*, 690, 65, (2011).
- [23] D. Tolnai, G. Szakács, G. Requena, A. Stark, N. Schell, K. Kainer and N. Hort: *Mater Sci Forum*, 765, 286, (2013).
- [24] S. Cai, T. Lei, N. Li and F. Feng: *Mat. Sci. Eng. C*, 32, 2570, (2012).
- [25] K Hazeli, J. Cuadra, F. Streller, C.M. Barr, M.L. Taheri, R.W. Carpick and A. Kontsos: *Scripta Mat.*, 100, 9, (2015).