In Situ Synchrotron Tomography of the Solidification of an Elektron 21 Mg Alloy

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The directional solidification of an Elektron 21 magnesium alloy is investigated by in situ synchrotron radiation tomography. To visualize the solidification process, samples of Elektron 21 are first heated to 800 °C, and the melt is held at this temperature for 5 min, to ensure temperature homogeneity. Subsequently, the samples are cooled with a cooling rate of 10 K min⁻¹, while for every 35 s, one full tomogram is acquired. The evolution of the microstructure can be followed in 3D on the reconstructed tomograms. The contrast between rare-earth metals and Mg enables to quantitatively analyze the changes in the morphology of the dendritic structure during solidification. At the onset of the detection, the growth of secondary dendrite arms occurs, which ends at the dendritic coherency point. From this temperature on, only the coarsening and coalescence of existing dendrite arms occurs.

1. Introduction

Mg-based materials are becoming increasingly attractive as structural materials due to their light weight, high specific strength, and good castability. These properties enable them to substitute heavier counterparts in applications, where weight reduction and the consequent improvement in fuel efficiency is of importance.[1] Furthermore, biocompatible Mg alloys, when their corrosion rate is controlled, can be used in degradable implant applications, eliminating the need for a second, implant removal surgery.[2] During the development of Mg alloys for structural applications, one of the aims is to increase the generally poor creep resistance that impedes their use in fields where elevated temperature strength is required. A possible solution to overcome this disadvantage is the alloying with rare-earth (RE) metals, where even a relatively low alloying addition has a beneficial effect.[3–5] The Elektron 21 alloy (Mg–Nd(2.6–3.1)–Gd(1–1.7)–Zn(0.2–0.5)–Zr(sat.) all values in wt%) was developed to service aerospace applications including those at elevated temperatures.[6–7] In addition to its good corrosion resistance, it possesses superior creep properties in comparison with Mg alloys containing Al as an alloying element,[8,9] due to the grain refinement effects of Zr and the intermetallic Mg–RE phases which are stable at elevated temperatures. Further improvement of the mechanical properties was achieved by the addition of nanoparticle reinforcement during casting as reported in previous studies.[10,11] In addition to its use in structural applications, investigations related to biodegradability were also carried out.[12] The microstructure consists of α-Mg dendrites and intermetallic particles, which were reported by Kiebus to be the Mg12RE phase.[13] Easton et al. found that for Nd the stable phase, Mg41Nd5, could only form following a long heat treatment time.[14] Tolnai et al. reported that the presence of Zn stabilizes the Mg12RE phase in Mg–Nd–Zn alloys[15] that was also found to be the case in Elektron 21.[11]

The processing of Mg components usually involves a casting step, where a liquid–solid transformation takes place. The internal architecture of the phases plays a vital role in the macroscopic mechanical properties.[16] Thus, the quantification of the spatial distribution of the phases as a function of the temperature and cooling rate is crucial for alloy development. The development of X-ray imaging can be used to follow the evolution of the microstructure during solidification in situ by X-ray radiography[17–19] with the necessary time–temperature resolution of the process in multiphase materials. Due to the continuous improvement in the acquisition rate of detectors and the stability of the experimental setup, it became possible to capture the solidification in 3D by rotating the sample and acquiring tomograms.[20] At the early stages of the method development, predominantly, Al alloys were investigated due to the relatively easy handling of the sample, because neither protective atmosphere nor additional sample holder is necessary.[21,22] However, experimental setups were then developed for the safe handling of Mg alloys in special nonreactive crucibles under a protective atmosphere.[23] The high-speed imaging of microstructural processes often require a compromise between speed and image quality, which ultimately can have a detrimental effect on the contrast-to-noise ratio of the images. Therefore,
to obtain a clear image of the developing dendritic structure materials with large quantity of absorbing elements such as zinc are often used for the investigations.\cite{24–27}

The aim of this study is to investigate the phase formation during solidification in a commercial Elektron 21 alloy with in situ synchrotron radiation tomography and to quantify the morphological changes of the dendritic structure during the process.

2. Results and Discussion

The initial microstructure of the Elektron 21 alloy was investigated by scanning electron microscopy (SEM). The backscattered electron (BSE) micrographs are shown in Figure 1.

The microstructure of the alloy consists of $\alpha$-Mg dendrites, intermetallic particles in the interdendritic space, and regions near the grain boundaries, segregated areas, where the concentration of solute atoms is higher than in the middle of the grains. The composition of the intermetallic particles is dependent on the cooling rate and the alloying elements. As a result of this processing route, the intermetallic particles are Mg$_3$RE.\cite{11}

The tomographic slices from the middle section of the sample perpendicular to the temperature gradient are shown in Figure 2.

The liquidus temperature of Elektron 21 is $\approx$640 °C with a solidification range of 120 °C.\cite{15} The first slice depicts an already advanced state of dendritic solidification approximately at a temperature of 620 °C. The images before this state cannot be properly reconstructed and segmented due to the movement of dendrites being fast when compared with the acquisition time for a full tomogram and due to the poor contrast between the dendrites and the melt at the onset of solidification. As the solidifying dendrites decreases the amount of molten Mg in the melt, the spatial contrast and the intensity contrast between melt and dendrites gradually improve and the image quality becomes sufficient for segmentation, which we consider to be reliable from 602 °C onward. The segmented dendritic structure in 3D is shown in Figure 3. Nevertheless, we would like to emphasize that the interface between the phases remains still blurred, i.e., segmentation can only approximate an in between state. Thus, we provide alternative segmentations, illustrating the uncertainty at any given temperature during the experiment (shown in Figure 4a).

The time series of the dendritic structure shows how the solidification front passes through the region of interest. During the solidification, the dendrites grow and the microstructure becomes coarser. The change in volume fraction during solidification is shown in Figure 4a.

In the initial recorded image stack, the volume fraction of the dendrites is 46 %, and it gradually increases until reaching the solid phase at a volume fraction of 84 %. Conversely, the volume fraction of the melt decreases and at the end of solidification, it freezes as eutectic with the RE containing intermetallic. The volume fraction of the intermetallics at the last step is 16 %, which is higher than the volume fraction measured by other techniques in the case of Elektron 21.\cite{28} This can be attributed to the coarse structure as a result of the relatively low cooling rate in the experiments and to the presence of segregated areas that during the segmentation being classified as the intermetallic volume fraction based on their absorption thus increasing the measured volume fraction of the secondary phase.

Until $\approx$595 °C, the growth of the dendrites is dominated by the formation of additional dendritic fingers which can be deducted from the rapidly increasing connectivity density in the dendrite phase (shown in Figure 4d). From there on, existing dendrites keep gaining in thickness almost linearly, whereas the spacing between them decreases markedly slower (shown in Figure 4c). This indicates that existing dendritic fingers are being merged and

Figure 1. BSE micrographs of Elektron 21 showing an overview of the microstructure, the grain boundaries, and the detailed morphology of the intermetallic particles.

Figure 2. Time series of synchrotron radiation-based $\mu$CT slices acquired during the solidification of Elektron 21.
connections between them are being smoothed out which is also evident from a stabilizing relative standard deviation and peeking connectivity density around 585 °C (shown in Figure 4c,d).

The distribution of mean and Gaussian curvature (the mean value and the product of the principal curvatures) of the surface points of the α-Mg dendritic structure during the solidification process is shown in Figure 5. The characteristic morphologies for each part of the diagram and the scale of the axes are indicated schematically in the upper left panel, whereas the frequency is represented by the color scale.

The simultaneous analysis of the sign (positive, 0, or negative) of the mean- and Gaussian-curvatures enables to classify the surface section into different shapes and, thus to quantitatively describe the changes in the dendritic morphology during solidification. At the onset of the detection, the dendritic structure mostly has a shape constructed from spherical- and rod-like parts as the distribution has its maximum in the positive–positive quadrant. As the solidification proceeds, this maximum stretches toward higher mean- and Gaussian-curvature values, indicating the increase in the spheroid-like sections. This can be attributed to the formation of the secondary dendrite arms with sharp tips. In the middle stages of the solidification (608 °C – 578 °C) in addition to maintaining this high value at the positive–positive quadrant, a maximum of the distribution emerges between the flat and the rod-like surface parts as these secondary dendrite arms also grow. In the later stages, there is an increased probability of pit-like and saddle-like surface parts while the probability of spheroid parts decreases. This is due to the coarsening and coalescence of the dendritic structure, as the arms grow together and the tips disappear while divots get filled with melt form. Elektron 21 is not prone to the formation of hot tears and the used measurement setup with directional solidification also hinders the formation of closed cavities. Consequently, there were no hot cracks observed as there was a sufficient amount of liquid being feed into the cracks throughout the solidification process.

The displacement of the dendrite tips in z-direction during solidification is shown with respect to the previous scan in Figure 6, where z coincides with the axis of rotation during scanning and the direction of dendritic growth. Like the segmentation, it becomes reliable after the third scan.

Figure 6 shows a visualization of the solidification velocity \( \bar{u}_z \) in the molten alloy. The parameter is derived as the average axial displacement between two consecutive scans as determined by digital volume correlation (DVC) tracking. The mapping is generally more reliable in feature rich image regions like...
the interface surface and interpolates homogeneous regions found in the bulk of the phases. Thus, the determined apparent motion of objects equates to a surface velocity. While in the first detected volume around 617 °C, the dendrites grew more than 30 μm per scan into the melt, this growth is already slowed to below 10 μm per scan after 587 °C and the time required for halving the growth speed slows down. With the growth rates determined the morphological features that are shown in Figure 4 with respect to temperature/time can now be expressed in terms of growth rate in between two scans. This reveals that the growth speed of the dendrites becomes proportional to their spacing and thereby available magnesium (shown in Figure 6c) when the dendrite tip velocity approaches zero. The abscissa of a linear fit for $u_z$ and dendrite spacing is located at 18 μm, indicating the spacing in the final solidified structure.

3. Conclusions

In situ tomography was carried out during the solidification of an Elektron 21 alloy with a furnace constructed for directional solidification. The following conclusions can be drawn from the obtained results. 1) At the beginning after reaching the detection limit, the dendritic structure consists of spheroidal and cylindrical surface shapes attributed to dendrite arms. 2) Shortly afterward the spheroidal-shaped parts increase and a maximum in the distribution appears at the cylindrical surfaces which can be associated with the formation and growth of secondary arms. 3) At the end of solidification, the dendrite arms coalesce and the dendritic structure coarsens. 4) Monitoring the penetration of the dendrites into the cell via DVC provided an expression for the state of the solidification process and revealed a linear relationship between dendrite spacing and growth rate from.
Figure 5. Change in the curvature distribution of the $\alpha$-Mg dendrites during solidification; the characteristic morphologies of surfaces and the scales of curvature values are shown in the upper left panel, the frequency is represented by the color scale.

Figure 6. a) Growth rate of dendritic structures along the axis of rotation of the imaging cell ($u_z$) evaluated from the average phase displacement between two consecutive scans. b–d) Consistency of the determined displacement field was evaluated by performing additional DVC runs with increased smoothing and on surfaces, i.e., interfaces, only. $u_z$ was then used to express time-dependent morphological parameters shown in Figure 4 in terms of growth rate.
4. Experimental Section

The commercial Elektron 21 alloy for this study was produced by the Magnesium Elektron Ltd at Manchester, UK, with a composition of Mg–2.85Nd–0.92Gd–0.41Zr–0.29Zn (in wt%). The ingots were melted in an electric resistance furnace under protective atmosphere of 2 vol% SF₆ and Ar. During mixing, the melt was held at 720 °C for 10 min and then was poured into a steel mold preheated to 660 °C. After 5 min isothermal holding, the mold was quenched into water at a rate of 10 mm s⁻¹ until the top of the melt was in line with the cooling water level.

A Tescan Vega Scanning Electron Microscope with accelerating voltage of 15 kV was used to investigate the microstructure of Elektron 21. BSE imaging was used to clearly resolve the intermetallic particles at grain boundaries. The samples were prepared for electron microscopy investigation by the standard metallography techniques of grinding with SiC paper to 2000 grit and then polishing using oxide polishing suspension (OPS) water-free suspension and 0.1 μm diamond paste.

The in situ tomography of the solidification was carried out at the imaging beamline P05 (IBL) operated by Helmholtz–Zentrum Hereon at PETRA III on the decile of voxels with the steepest intensity gradient. Good matching qualities were achieved from after 600 °C onward with cross-correlation above 0.98 after DVC.

For the quantification of morphological parameters, the denoised images were segmented by Otsu thresholding. Connectivity density, local thickness, and related relative standard deviation were then evaluated using the Bonej plugin for ImageJ. Stability of the estimated volume fractions was additionally evaluated from a segmentation acquired with maximum entropy thresholding and a custom-seeded watershed segmentation. Seeds for fore- and background used in the latter segmentation technique were assigned by fitting a bi-Gaussian mixture model to the histogram of each image stack and selecting voxels that could be assigned with 99.8% probability to one of the fitted Gaussian distribution functions.

Figure 8. Arbitrary slices through the reconstructed sample volume at 578 °C before and after applying iterative nonlocal means denoising. The region around the center of rotation was excluded from analysis for being reconstructed unreliably.
considering the neighboring triangles up to the fifth order. The local radii of these curves were averaged five times with the radii of direct neighboring triangles before the curvature was calculated. To prevent the influence of the phases cut by the boundaries of the region of interest, surfaces that simultaneously exhibited zero values for mean and Gaussian curvatures (i.e., perfectly flat) were excluded from further evaluation.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

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[1] M. Pekguleryuz, K. U. Kainer, A. Kaya, Fundamentals of Magnesium Alloy Metallurgy, Woodhead, Philadelphia, PA 2013.
[2] F. Feyerabend, J. Fischer, J. Holtz, F. Witte, R. Willumeit, H. Drücker, C. Vogt, N. Hort, Acta Biomater. 2010, 6, 1834.
[3] S. Gavras, S. M. Zhu, J. F. Nie, M. A. Gibson, M. A. Easton, Mater. Sci. Eng., A 2016, 675, 65.
[4] S. M. Zhu, M. A. Gibson, M. A. Easton, J. F. Nie, Scr. Mater. 2010, 63, 698.
[5] C. J. Bettles, M. A. Gibson, S. M. Zhu, Mater. Sci. Eng., A 2009, 505, 67.
[6] N. Jacl, Adv. Mater. Processes 2005, 163, 65.
[7] P. Lyon, I. Syed, S. Heaney, Adv. Eng. Mater. 2007, 9, 793.
[8] A. Bell, V. Srivastava, C. W. Greenwood, H. Jones, Z. Metall./Mater. Res. Adva. Techn. 2004, 95, 369.
[9] D. Thomas-Whittington, V. Srivastava, C. W. Greenwood, H. Jones, Inte. J. Mater. Res. 2006, 97, 156.
[10] M. Garrido, L. Davoust, R. Daudin, L. Salvo, W. Sillekens, Y. Fautrelle, Metall. Res. Technol. 2020, 117, 203.
[11] H. Yang, Y. Huang, D. Tolnai, K. U. Kainer, H. Dieringa, Mater. Sci. Eng., A 2019, 764, 138215.
[12] M. Omasta, B. Hadzima, Manuf. Technol. 2015, 15, 656.
[13] A. Kielbus, Solid State Phenomena 2007, 130, 175.
[14] M. A. Easton, M. A. Gibson, D. Qiu, S. M. Zhu, J. Gröbner, R. Schmid-Fetzer, J. F. Nie, M. X. Zhang, Acta Mater. 2012, 60, 4420.
[15] D. Tolnai, T. Subroto, S. Gavras, R. Buzolin, A. Stark, N. Schell, N. Hort, Materials 2018, 11, 1637.
[16] G. Requena, G. Garcés, M. Rodriguez, T. Pirling, P. Cloetens, Adv. Eng. Mater. 2009, 11, 1007.
[17] R. H. Mathiesen, L. Anrberg, H. Nguyen-Thi, B. Billia, JOM, 2012, 64, 76.
[18] D. Casari, W. U. Mirihanage, K. V. Falch, I. G. Ringdalen, J. Friis, R. Schmid-Fetzer, D. Zhao, Y. Li, W. H. Sillekens, R. H. Mathiesen, Acta Mater. 2016, 116, 177.
[19] A. G. Murphy, W. U. Mirihanage, D. J. Browne, R. H. Mathiesen, Acta Mater. 2015, 95, 83.
[20] O. Ludwig, M. DiMichiel, L. Salvo, M. Suéry, P. Falus, Mater. Trans. A. 2005, 36, 1515.
[21] N. Limodin, L. Salvo, E. Boller, M. Suéry, M. Felberbaum, S. Gailleguë, K. Madi, Acta Mater. 2009, 57, 2300.
[22] D. Tolnai, P. Townsend, G. Requena, L. Salvo, J. Lendvai, H. P. Degischer, Acta Mater. 2012, 60, 2568.
[23] W. H. Sillekens, D. Casari, W. U. Mirihanage, S. Terzi, R. H. Mathiesen, L. Salvo, R. Daudin, P. Lhuissier, E. Guo, P. D. Lee, JOM 2016, 68 3042.
[24] S. Nie, B. Gao, X. Wang, Z. Cao, E. Guo, T. Wang, Metals 2019, 9, 420.
[25] S. Shuai, E. Guo, J. Wang, A. B. Phillion, T. Jing, Z. Ren, P. D. Lee, Acta Mater. 2018, 156, 287.
[26] E. Guo, S. Shuai, D. Kazantssev, S. Karagadde, A. B. Phillion, T. Jing, W. Li, P. D. Lee, Acta Mater. 2018, 152, 127.
[27] E. Guo, A. B. Phillion, B. Cai, S. Shuai, D. Kazantssev, T. Jing, P. D. Lee, Acta Mater. 2017, 123, 373.
[28] A. Kielbus, in Magnesium Alloys Design, Processing and Properties (Eds.: F. Czerwinski), IntechOpen, London 2011.
[29] F. Wilde, M. Ogurreck, I. Greving, J. U. Hammel, F. Beckmann, A. Hipp, L. Lottermoser, I. Khokhriakov, P. Lytaev, T. Dose, H. Burmester, M. Müller, A. Schreyer, AIP Conf. Proc. 2016, 1741, 030035.
[30] J. Moosmann, A. Ershov, V. Weinhardt, T. Baumbach, M. S. Prasad, C. LaBonne, X. Xiao, J. Kashef, R. Hoffmann, Nat. Protocols 2014, 9, 294.
[31] W. van Aarle, W. J. Palenstijn, J. Cant, E. Janssens, F. Bleichrodt, in Lecture Notes on Computer Science, Vol. 3024, Springer, Berlin, Heidelberg 2004.
[32] W. van Aarle, W. J. Palenstijn, J. De Beenhouwer, K. J. Batenburg, J. Sijbers, Opt. Express 2016, 24, 25129.
[33] W. van Aarle, W. J. Palenstijn, J. De Beenhouwer, T. Altantzis, S. Bals, K. J. Batenburg, J. Sijbers, Ultramicroscopy 2015, 157, 35.
[34] W. J. Palenstijn, K. J. Batenburg, J. Sijbers, J. Struct. Biol. 2011, 176, 250.
[35] T. Brox, A. Bruhn, N. Papenberg, J. Weickert, in Lecture Notes on Computer Science, Vol. 3024, Springer, Berlin, Heidelberg 2004.
[36] C. Liu, Doctoral Thesis, Massachusetts Institute of Technology. 2009.
[37] S. Bruns, S. L. S. Stipp, H. O. Sørensen, Adv. Water Resour. 2017, 105, 96.
[38] R. Domander, A. A. Felder, M. Doube, Wellcome Open Res. 2021, 6, 37.
[39] C. A. Schneider, W. S. Rasband, K. W. Elcei, Nat. Methods 2012, 9, 671.