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In situ synchrotron diffraction of the solidification of Mg₄Y₃Nd

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Abstract

In situ synchrotron diffraction experiments were performed during the solidification of a Mg₄Y₃Nd alloy. The material was melted and solidified inside a sealed stainless steel crucible in the chamber of a Bähr 805A/D dilatometer. The sample was heated up to 680 °C and kept at this temperature for 5 min to ensure it is molten. Afterwards it was cooled down to the fully solidified state with a cooling rate of 10 K/min. During the T(t) program diffraction patterns were acquired continuously in every 25 s (~5 K). The forming phases were identified as α -Mg at 625 °C, Mg₁₂Nd and Mg₁₄Y₄Nd at 545 °C, and Mg₂₄Y₅ at 320 °C. The experimental results were correlated with simulations based on thermodynamic databases.

Keywords: Mg alloys; Solidification; In situ; Synchrotron diffraction.

1. Introduction

Mg-RE based alloys are attractive for structural [1] as well as for biomaterial applications [2] due to the good combination of mechanical and corrosion properties. Commercial Mg-Y-Nd based alloys, such as WE43 and WE54 form an important class of alloys used in elevated temperature applications with superior mechanical properties at both room and elevated temperatures [3]. The WE54 and WE43 alloys are conventionally used in the T6 condition. The age hardening response as well as the precipitation sequence and crystal structures of the resultant phases investigated previously [4-7]. The intermetallic particles found in the as-cast Mg5Y2Nd (wt%) and Mg4Y2Nd (wt%) alloys have been characterized, with transmission electron microscopy to be a ternary phase with a face centered cubic crystal structure with $a = 2.223$ nm and a composition of $Mg_{14}Nd_2Y$ [8] or $Mg_{15}Nd_2Y$ [7]. The macroscopic mechanical properties of multiphase materials depend strongly on the chemical composition, volume fraction and spatial distribution of the intermetallic phases [9]. The thermodynamic databases and binary phase diagrams [10] provide information on the presumed solidification paths of the simple alloy systems. Based on these databases, the resultant microstructure can be modeled [11]. The majority of the commercial Mg alloys are not binary, but containing more than one alloying addition resulting in complex intermetallics. For these complex phases the information in the simulation databases is limited. Thus the simulation of the experimentally observed microstructure and modeling of the solidification sequence is not feasible in every case due to the lack of available data.

The continuous development of the X-ray acquisition systems at synchrotron sources provides a unique tool to characterize the phase formation and evolution during the

solidification *in situ*. Recording the diffraction patterns while cooling the alloy system down, allows identifying the internal phases, to determine their solidification sequence [12,13] and to use these results as experimental validation of the existing thermodynamic databases and in certain cases contribute to their further development.

The present study reports results on the *in situ* synchrotron diffraction during solidification of a Mg₄Y₃Nd alloy, and their comparison with the existing thermodynamic data on this system.

2. Materials and Methods

The alloy Mg₄Y₃Nd (wt.%) was chosen for the experiments, as it is of particular interest in structural and in biomaterial applications. The microstructure of the direct chill cast alloy was examined with a Carl Zeiss Gemini Ultra 55 scanning electron microscope (SEM) operating at 15kV.

The samples for the synchrotron diffraction measurements were cut into small cubes and encapsulated in steel crucibles. The experiments were carried out at the HARWI II beamline of the Hamburger Synchrotronstrahlungslabor (HASYLAB) at the Deutsches Elektronen-Synchrotron (DESY). The measurements were performed in the chamber of a DIL 805A/D (Bähr-Thermoanalyse GmbH, Hüllhorst, Germany) dilatometer the experimental setup is shown in Figure 1. During the tests the samples were held in a sealed stainless steel crucible in order to hold the molten metal and to isolate it from the surrounding atmosphere. The dilatometer has been modified to meet the requirements of *in situ* synchrotron measurements. The two windows on the sides are covered by Kapton foils, to prevent interference with the X-ray beam. The induction coil is modified so the

beam to only pass through the sample [14]. The temperature was regulated by a type S thermocouple welded on the steel crucible containing the sample.

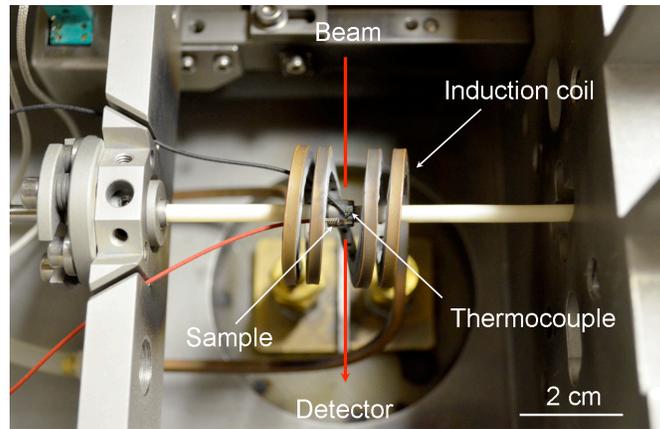


Figure 1 Experimental setup of the *in situ* solidification experiment inside the chamber of a Bähr 805A/D dilatometer modified for *in situ* synchrotron measurements. The windows on the sides are covered by Kapton foil, while the coil is opened, for the beam to pass through the sample.

The heating and cooling was performed in Ar flow. To melt the samples the system was heated up to 680 °C, held for 5 min and then cooled to 180 °C at a cooling rate of 10 K/min. The *in situ* diffraction experiment was done in transmission geometry using a beam cross section of 1x1 mm². In order to penetrate the sample, high-energy X-rays were used with a photon energy of 100 keV, corresponding to a wavelength of $\lambda = 0.0124$ nm. During the experiment the Debye-Scherrer diffraction rings were recorded in every 25 s (~ 5 K) with an acquisition time of 2 seconds by a mar555 flatpanel detector (Marresearch GmbH, Norderstedt, Germany) with an area of 3070×2560 pixels with a pixel size of 140 μm^2 . Conventional diffraction patterns (line profiles) were achieved by an azimuthal integration of the Debye-Scherrer rings. The line profiles were indexed based on the peak positions obtained by CaRIne Crystallography 3.1. The thermodynamic simulation of the solidification was carried out with the software Pandat 8.1.

3. Results and Discussion

The secondary electron micrograph is shown in Figure 2. The microstructure consists of α -Mg dendrites and intermetallic particles with Y and Nd.

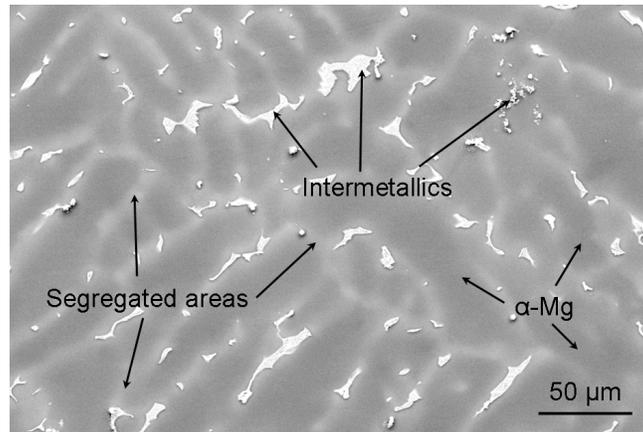


Figure 2 Secondary electron micrograph of the investigated Mg4Y3Nd alloy in as-cast condition.

The XRD line diagrams resulting from the azimuthal integration of the 2D diffraction patterns are shown in Figure 3. Based on the peak positions the solidification sequence of the phases can be determined with a temperature resolution of $\sim 5^\circ\text{C}$.

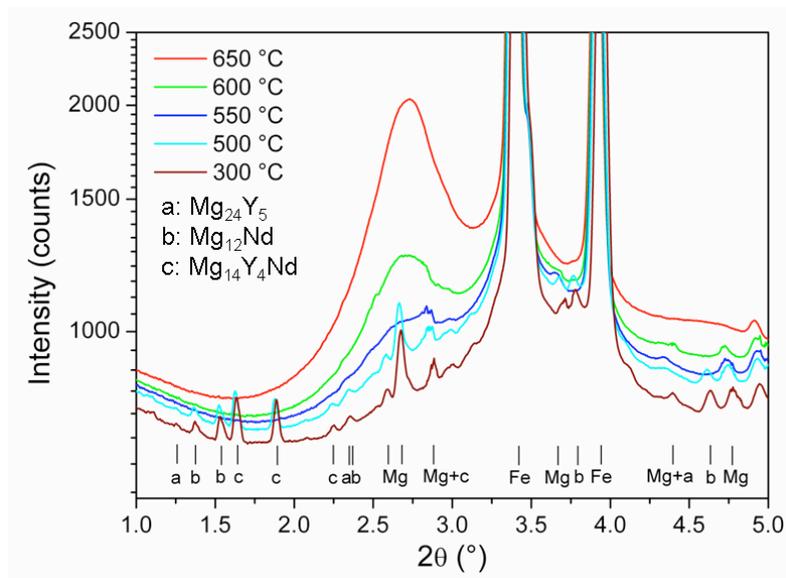


Figure 3 Sequence of XRD line diagrams at different temperatures obtained by the integration of the diffraction patterns recorded during solidification. (Wavelength $\lambda = 0.0124 \text{ nm}$)

The solidification starts with the nucleation and growth of the α -Mg dendrites at a measured temperature of 625 °C. As the cooling advances the dendrites are followed by the Nd containing intermetallic phases. The binary Mg_{12}Nd and the ternary $\text{Mg}_{14}\text{Y}_4\text{Nd}$ phases are first observed at 545 °C. Finally, solidification of Mg_{24}Y_5 can be observed at 320 °C.

The resulting section of the ternary phase diagram obtained by Pandat at an Nd content of 3 wt.% is shown in Figure 4. The vertical line corresponds to a Y content of 4 wt.%. According to the thermodynamic database the α -Mg dendrites initiate at 639 °C. They are followed by the $\text{Mg}_{41}\text{Nd}_5$ phase at 538 °C, while the solidification ends with the Mg_{24}Y_5 phase at 316 °C. The solidification of any ternary phase is not predicted to be an expected phase by the thermodynamic database.

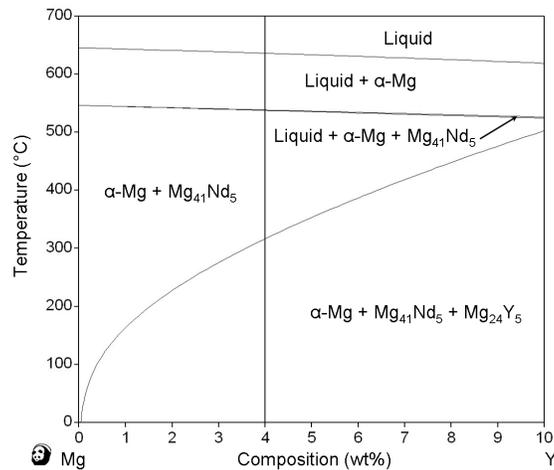


Figure 4 Section of the ternary Mg-Y-Nd phase diagram at a Nd content of 3 wt.%, calculated by Pandat 8.1.

The determination of the solidification sequence by *in situ* synchrotron diffraction has some limitations. A compromise must be made between the cooling rate and the acquisition time. The crystallographic orientation of the solidifying grains plays a vital

role. As these grains float in the melt without fixed orientation their detection is difficult. It is likely that the α -Mg grains can be detected for the first time as the system reaches the dendrites coherency point, the temperature where a continuous dendrite skeleton is built up. Despite these limitations, the onset temperatures, obtained experimentally by *in situ* diffraction and that predicted theoretically from the thermodynamic calculations, for the solidification of different phases correlate reasonably well. Instead of $\text{Mg}_{41}\text{Nd}_5$, Mg_{12}Nd was found, while the ternary intermetallic phase $\text{Mg}_{14}\text{Y}_4\text{Nd}$ was only shown experimentally and not predicted by the thermodynamic simulations performed with Pandat software. This can be attributed to either the limited information available in the database, or the $\text{Mg}_{14}\text{Y}_4\text{Nd}$ phase is thermodynamically meta-stable.

4. Conclusions

In conclusion, *in situ* solidification experiments were performed with a Bähr 805 A/D dilatometer, on a $\text{Mg}_4\text{Y}_3\text{Nd}$ alloy by synchrotron diffraction, for the first time. During cooling with 10 K/min from 680 °C to 180 °C, the solidification sequence could be determined experimentally. First α -Mg solidifies at a temperature of 625 °C followed by the solidification of the intermetallic particles; Mg_{12}Nd and $\text{Mg}_{14}\text{Y}_4\text{Nd}$ at 545 °C and finally the Mg_{24}Y_5 phase at a temperature of 320 °C. The results are in correlation with the results obtained by the thermodynamic calculations performed with Pandat 8.1. *In situ* synchrotron diffraction reveals the presence of the ternary $\text{Mg}_{14}\text{Y}_4\text{Nd}$ phase and the onset of its solidification at 545 °C which could not be predicted by the simulations.

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