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Tolnai, D.; Szakacs, G.; Requena, G..; Stark, A.; Schell, N.; Kainer, K.U.; Hort, N.:

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Materials Science Forum, Light Metals Technology Conference, LMT 2013 (2013)
Trans Tech Publications

DOI: 10.4028/www.scientific.net/MSF.765.286

Materials Science Forum Vol. 765 (2013) pp 286-290
© (2013) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/MSF.765.286

Study of the Solidification of AS Alloys Combining in situ Synchrotron Diffraction and Differential Scanning Calorimetry

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Keywords: In situ synchrotron diffraction, Differential Scanning Calorimetry, Mg-Al-Si alloys

Abstract. In situ synchrotron diffraction experiments were performed during Differential Scanning Calorimetry (DSC) of AS31, AS33 and AS35 alloys. The samples were encapsulated in stainless steel crucibles during the measurement using an empty crucible as the reference. The samples were heated up to 680°C, melted and solidified in the beginning of the experiment in order to fill the crucible. This short cycle was followed by three subsequent cycles between 400°C and 680°C with 5, 10 and 20 K/min heating and cooling rates with 5 min of holding time in the molten state. The diffraction patterns were recorded every 6 s during the DSC program by a Perkin-Elmer XRD 1622 Flatpanel detector including an acquisition time of 3 s and the collection of reference images. The endothermic and exothermic peaks are in correlation with the dissolution and formation of new diffraction patterns, respectively. During cooling from the liquid state, first, α-Mg dendrites solidify, followed by the formation of Mg_2Si and $Mg_{17}Al_{12}$ intermetallics. The results are correlated with those obtained by thermodynamic simulations performed with the software Pandat.

Introduction

Mg-Al alloys contain the Mg matrix with Al in solid solution and the so-called beta-phase, $Mg_{17}Al_{12}$. The strength increases with growing Al content because of solution and precipitation hardening [1]. Although a relatively high strength (~230 MPa [1]) can be achieved at room temperature by the addition of Al, the mechanical properties at higher temperatures, especially the creep resistance [2-4] undergo a rapid degradation. This can be attributed to the low melting point of $Mg_{17}Al_{12}$. As a consequence their application is limited to $T \leq 120$ °C [5]. The solution is to add further alloying elements, which either form intermetallic compounds with Al and, therefore, hinder the formation of $Mg_{17}Al_{12}$, or with Mg to improve the mechanical properties at elevated temperature. Introducing Si into the Mg-Al system results in the formation of the rigid Mg_2Si phase, which contributes to higher creep resistance due to its stability at elevated temperature [6]. In addition, the lower Al content compared with that of AZ61 and AZ91 alloys results in a lower volume fraction of $Mg_{17}Al_{12}$, which improves the creep resistance. As a disadvantage, the castability of this type of alloy is reduced [1]. The production of these alloys starts with casting, thus their microstructure and consequently their macroscopic mechanical properties are determined during solidification and the following thermo-mechanical processing. Formerly, the evolution of the internal phases during solidification could only be investigated by *ex situ* methods, i.e. interrupting the solidification at different temperatures (different stages of microstructure development) by quenching the sample to perform the characterization [7]. Although this is a simple method it has the disadvantage of lacking time-temperature resolution and requires that no new phases are formed during quenching. The development of the acquisition systems and the high brilliance of the beam at synchrotron sources allow characterizing the phase formation and evolution *in situ* by X-ray diffraction [8]. The measurement can be complemented by detecting the

DSC (Differential Scanning Calorimetry) signal during the solidification. The DSC can detect the temperatures of the formation of the phases even if the phase volume fraction is not large enough to be detected by diffraction. On the other hand, the phases formed can be determined from the diffraction spectra to determine the correct sequence of formation/dissolution of phases.

The aim of this investigation is to determine solidification sequence of AS31, A33 and AS35 alloys by *in situ* DSC measurements.

Experimental Methods

The experiments were carried out at the P07 HEMS beamline of the synchrotron facility PETRA III at the Deutsches Elektronen-Synchrotron (DESY). The experiments were performed in the chamber of a dilatometer DIL 805A/D (Bähr-Thermoanalyse GmbH, Hüllhorst, Germany). The experimental setup is shown in Fig. 1.

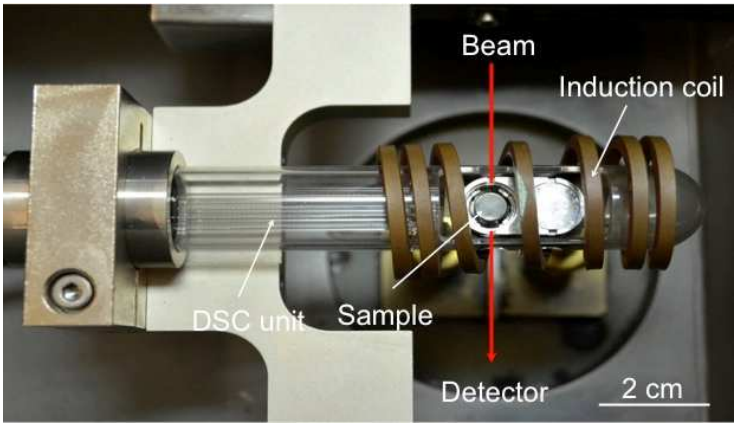

Fig. 1. Experimental setup of the *in situ* DSC unit.

The samples were encapsulated in stainless steel crucibles during the experiment using an empty crucible as the reference. The DSC unit was placed inside the heating induction coil of the dilatometer, which is modified so the beam only passes through the sample [9]. The samples were heated up to 680°C, melted and solidified in the beginning of the experiment in order to fill the crucible. This short cycle was followed by three subsequent cycles between 400 °C and 680 °C with 5, 10 and 20 K/min heating and cooling rates with 5 min of holding time in the molten state. The *in situ* diffraction experiment was done in transmission geometry using a beam cross section of 1x1 mm^2. High-energy X-rays with a photon energy of 100 keV, corresponding to a wavelength of $\lambda = 0.0124$ nm were used to penetrate the sample and to obtain low 2θ values and, thus, acquire several complete Debye-Scherrer rings. The diffraction patterns were recorded every 6 s during the DSC program by a Perkin-Elmer XRD 1622 Flatpanel detector with an acquisition time of 3 s. Reference dark field images where acquired for every frame. The sample-to-detector-distance was set to 1918.95 mm. LaB_6 powder was used as a reference sample. Line profiles were obtained by the azimuthal integration of the Debye-Scherrer rings through 360°. The identification of the phases present at each temperature was performed based on the software Carine Crystallography allowing the determination of the solidification sequence.

Results and Discussion

The T(t) program and the resulting DSC curves are shown in Fig. 2.

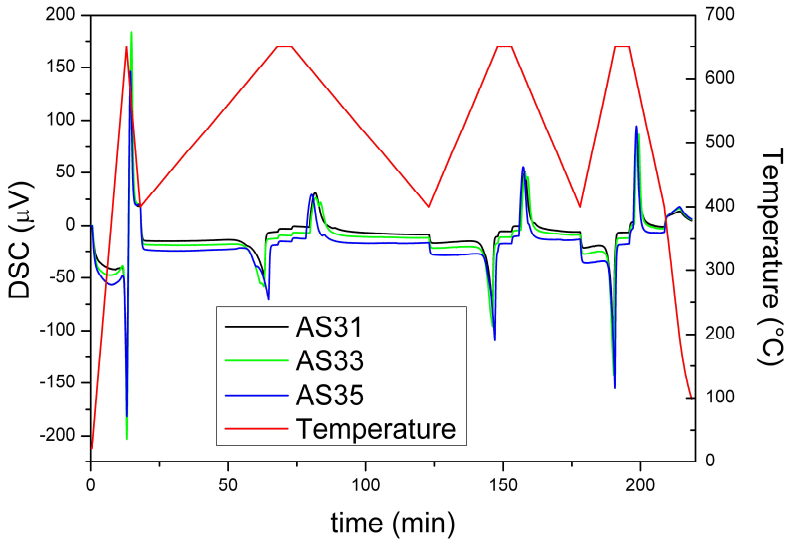

Fig. 2. T(t) program of the experiments and the resulting DSC curves.

The temperatures of formation of phases during solidification of the investigated alloys can be determined based on the DSC signal. In AS31 the solidification starts at 617 °C followed by another exothermic peak at 565°C. In the case of AS33 these temperatures are 620 °C and 584 °C, while in the case of AS35 these temperatures are 614 °C and 587° C, respectively for a cooling rate of 20 K/min.

Diffraction patterns recorded at different temperatures during solidification of AS31 with a cooling rate of 20 K/min are shown in Fig. 3.

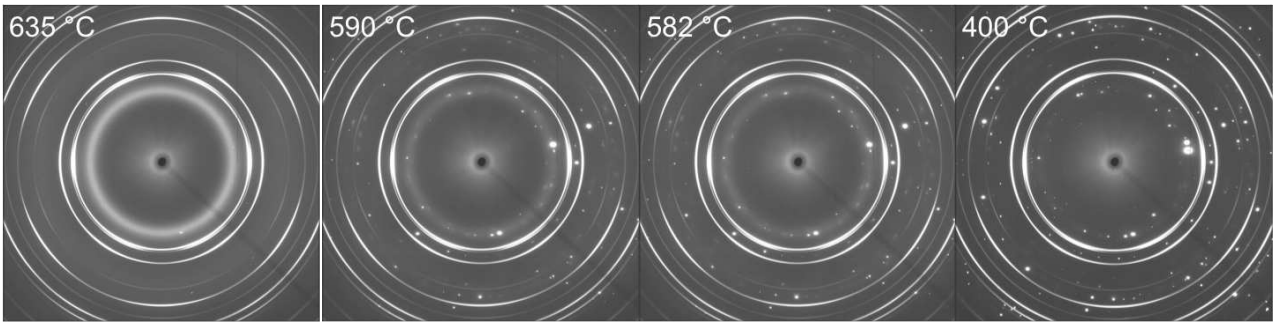

Fig. 3. Diffraction patterns recorded at different temperatures for the AS31 solidified using a cooling rate of 20 K/min.

At 635 °C, besides the diffuse ring originating from the melt and the diffraction rings of the steel crucible, the first diffraction spots corresponding to α-Mg grains appear. Below 590 °C the spots of the Mg grains remain in the same position indicating that the system has reached the dendritic coherency temperature (DCT), which is the temperature at which a stable dendritic skeleton builds up. At 582 °C the first diffraction spots of Mg_2Si appear approximately at the same temperature as the spots of $Mg_{17}Al_{12}$. At 400 °C at the end of the T(t) program the sample is fully solidified.

The line profiles obtained by azimuthal integration of the diffraction patterns at different temperatures during solidification of AS31 with 20 K/min are shown in Fig. 4.

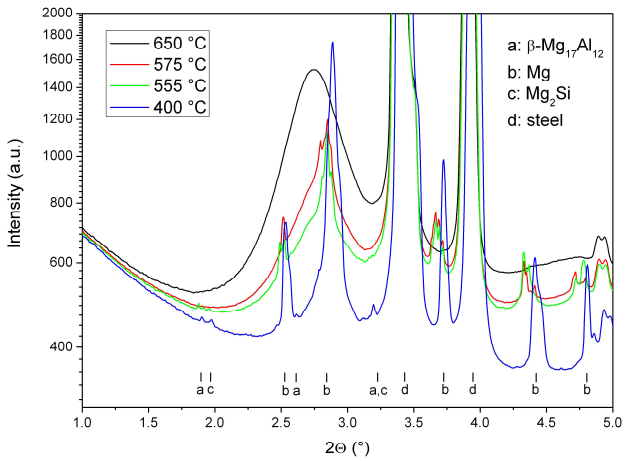

Fig. 4. Line profiles at different temperatures during the solidification of AS31 with a cooling rate of 20 K/min.

The phases are identified based on the Pearson's Crystal Structure Database [10]. The temperatures at which the phases are first observed during the solidification by the DSC and the *in situ* diffraction measurement, complemented with results obtained by Pandat, are summarized in Table 1.

Table. 1. Temperatures of the solidification of the phases measured by DSC, *in situ* diffraction and calculated by Pandat.

	Calorimetry	*In situ* diffraction	Pandat
		AS 31	
α-Mg	617 °C	635 °C	627 °C
DCT	-	590 °C	-
Mg_2Si	565 °C	582 °C	619 °C
$Mg_{17}Al_{12}$	Overlap	582 °C	-
		AS 33	
α-Mg	620 °C	609 °C	622 °C
DCT	-	585 °C	-
Mg_2Si	584 °C	581 °C	700 °C
$Mg_{17}Al_{12}$	Overlap	581 °C	-
		AS 35	
α-Mg	614 °C	638 °C	622 °C
DCT	-	603 °C	-
Mg_2Si	587 °C	590 °C	762 °C
$Mg_{17}Al_{12}$	Overlap	590 °C	-

The experimental setup has some limitations. The DSC pan is open for the beam to pass through; therefore, the measurement cannot be as precise as in the case of laboratory DSC devices. During *in situ* diffraction the sample is fixed. This limits the possibility of detecting the formed phases if the grains are orientated so that they do not fulfill the Bragg condition. Considering these restrictions the temperatures obtained by DSC, diffraction and Pandat simulations correlate reasonably well.

Summary

In situ synchrotron diffraction experiments were performed during the solidification of AS31, AS33 and AS35 alloys in a DSC unit constructed to be used in a Bähr DIL 805 A/D dilatometer. The temperatures of the solidification of the phases were determined independently from the DSC curves, the diffraction patterns and simulations performed with Pandat. The results correlate reasonably well taking into account the limitations of the methods in this experimental setup.

Acknowledgements

The authors would like to thank the Deutsches Elektronen-Synchrotron (DESY) for the provision of synchrotron radiation facilities at beamline P07 in the framework of proposal I-20120285EC.

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