Available online at www.sciencedirect.com

ScienceDirect

Procedia Technology 26 (2016) 35 – 42

Procedia Technology

3rd International Conference on System-integrated Intelligence: New Challenges for Product and Production Engineering, SysInt 2016

Microstructure and Magnetic Properties of Cobalt and Zinc Containing Magnesium Alloys

Christian Demminger[a]*, Christian Klose[a], Hans Jürgen Maier[a]

[a]*Institut für Werkstoffkunde (Materials Science), Leibniz Universität Hannover, An der Universität 2, D-30823 Garbsen, Germany*

Abstract

The magnetic properties of lightweight alloys based on magnesium and cobalt offer a novel way to measure mechanical loads throughout the entire structural component using the magnetoelastic effect. Since the solubility of cobalt in the magnesium matrix is negligible, the magnetic properties mainly originate from Co-rich precipitates. Size and distribution of the Co-containing phases within the alloy's microstructure can be influenced during the initial processing method of the alloy. Specifically, the cooling rate in the casting processes has a major influence on the resulting magnetic properties. In this study, Mg-Co-based alloys were produced by several casting methods which feature substantially different cooling rates, i.e. gravity sand casting, gravity die casting and high-pressure die casting. The differences between the manufactured alloys' micro- and phase structures are compared and the superior magnetic and mechanical properties of the high-pressure die cast material are demonstrated.

Peer-review under responsibility of the organizing committee of SysInt 2016

Keywords: magnesium; cobalt; magnetic materials; load-sensitive materials; die-casting; sand-casting; eddy-current measurements

1. Introduction

In mechanical engineering, strain gauges are commonly used to determine mechanical loads and stresses occurring during service of a structural component. Still, a limitation of conventional strain sensors is the spatially restricted measurement since only local strains directly at the measuring position are detected. Furthermore, strain gauges are typically applied to the component's surface, and thus, might be damaged by mechanical impacts. However, if the

* Corresponding author. Tel.: +49-511-762-18335; fax: +49-511-762-5245.
E-mail address: demminger@iw.uni-hannover.de

Peer-review under responsibility of the organizing committee of SysInt 2016
doi:10.1016/j.protcy.2016.08.006

structural component has material-inherent magnetic properties it can serve as a load sensor itself. The external mechanical forces temporarily change the preferred magnetization direction of the ferromagnetic material due to the reversible deformation of the material's crystal lattice [1]. This magnetoelastic effect leads to a detectable change of the magnetic properties on the macro scale [2]. This change can be monitored online by non-destructive component testing methods, such as the harmonic analysis of eddy-current signals, and the application of magnetoelastic force and torque sensors has been reported in literature (e.g. [3, 4]). However, these sensor elements are often made from ferromagnetic materials like metallic glasses, which are usually limited to the production of thin strips or wires in order to maintain an amorphous structure. Thus, a lightweight material with both high specific strength and usable magnetic properties that can be processed into various structural components is not yet available.

Magnetic magnesium alloys allow for an online-measurement of stresses acting on a structural component due to the changes of the material's magnetic properties under mechanical loading. The basic principle of the measuring system has been published by the authors in [5, 8]. Common magnesium alloys are, however, paramagnetic. To obtain magnesium alloys with ferromagnetic properties a magnesium melt was alloyed with cobalt, which is not among the usual alloying elements of magnesium alloys. Its high melting point and low solubility in magnesium are major challenges in the production of magnetic magnesium alloys by casting. Furthermore, information about the impact of a cobalt fraction in the range of a few percent on the magnetic and mechanical properties of Mg-Co alloys is rare in literature [5, 6]. In addition, the interactions of cobalt and nonmagnetic alloying elements like zinc, which is generally used in order to improve the mechanical strength of magnesium alloys [7], are hardly known.

Binary Mg-Co alloys manufactured by gravity die casting (GDC) were investigated earlier by the authors [8]. These alloys clearly exhibited a load-sensitive behavior in eddy-current measurements, but their mechanical strength was poor, featuring a low yield strength around 30 MPa. Especially the conditions of safety-critical components during operation are important to know and therefore these components are suitable for the adaption of magnetic magnesium alloys due to the detection of mechanical loads. On the other hand safety-critical structures require comparatively high mechanical strength. Both the yield strength and ultimate elongation values are important for energy adsorption in case of a system failure or accident.

Safety-critical components made from magnesium alloys are no standard solution in industrial automotive applications. The main goal of using magnesium instead of steel is the reduction of weight. For example, if a steel made strut tower should be substituted with a part made from magnesium, several tasks have to be carried out. Rafflenbeul investigated the weight reduction in a car body by using magnesium alloys instead of steel and analyzed the mechanical and economical requirements. He posited that the magnesium component he invented was suitable to use as a strut tower. Possible magnesium alloys to use are AZ91 or AM50 because of the advanced mechanical properties [9].

Therefore the current work emphasizes the improved magnetic and mechanical properties as well as the refined phase structure of a Mg-Co-Zn alloy produced by high-pressure die casting (HP-DC). In addition, the casting and solidification processes have been simulated to obtain information about the cooling rate, which defines the microstructure of thin-walled areas in casting geometries. Magnetic hysteresis curves were measured in order to compare the material's magnetic properties and the microstructure for both gravity sand casting (GSC) and the HP-DC process.

2. Experimental Procedure

In this study, the metal casting simulation tool Magma 5 (MAGMASOFT) was used to determine the casting's pouring, solidification and cooling conditions. The objective was to identify the relationship between the resulting properties and the local cooling rates depending on the casting process. Figure 1 shows the wire-frame models of the step-plate geometries processed by HP-DC and GSC. The regions of interest for both the microstructural investigations and the hysteresis measurements are marked by the black rectangulars in figure 1b) and 1d). The magnetic hysteresis curves were determined using rectangular specimens with dimensions of 5 mm x 5 mm x 2 mm prepared by wire electric discharge machining (wire EDM). The magnetic hysteresis measurements were performed using a vibrating sample magnetometer (VSM) made by Princeton Applied Research.

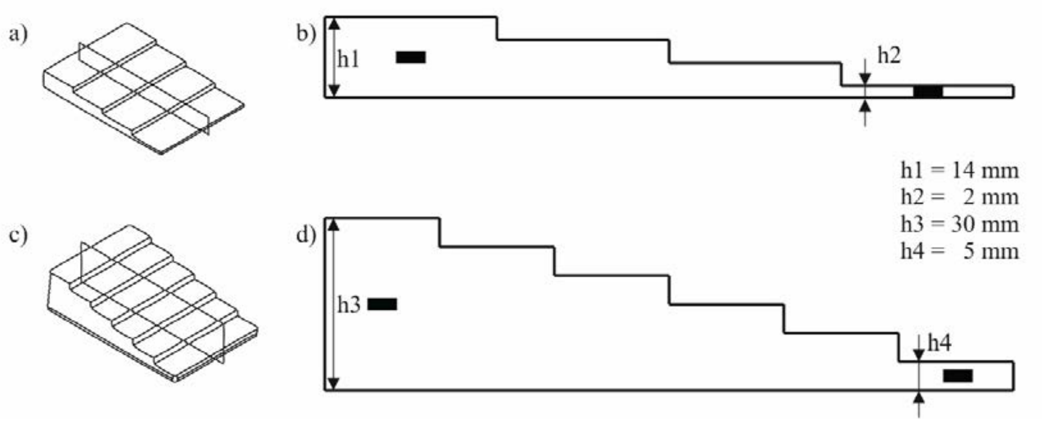

Figure 1: Step-plate casting geometries for a), b) HP-DC and c), d) GSC; the black rectangles mark the areas of interest

The investigated ternary magnetic magnesium alloy consisted of pure magnesium (99.95%, Magnesium Elektron) alloyed with cobalt and zinc. The nominal concentrations of the alloying elements were 4 wt.% cobalt (99.9%) and 1 wt.% zinc (99.8%). For the preparation of the magnetic Mg alloy, an alloying process using extruded Mg-Co powder rods was employed in order to facilitate the dispensation of the ferromagnetic powder in the Mg melt. The rods consisted of a blend of 60 wt.% of pure magnesium and 40 wt.% of pure cobalt powder. The details of the manufacturing process are given in previous publications [8, 10]. During the subsequent casting experiments, the magnesium melt was inoculated with the extruded Mg-Co rods.

The magnetic magnesium alloy was manufactured by means of a die casting method using a resistance-heated Nabertherm K4/10 furnace with a shielding-gas atmosphere (N_2 + 0.3% SF_6) and by employing a boron nitride coated, unalloyed steel crucible. The basic material was melted and held at a temperature of 730 °C. At the beginning of the mechanical stirring process (45 min. at 300 revolutions/minute), the extruded Mg-Co powder rods were introduced into the melt. For the characterization of the material in the GDC condition, the melt was cast into boron nitride-coated steel molds (geometry: Ø 22 mm x length 250 mm) with horizontal feeders, which were preheated to 350 °C. Subsequently, threaded cylindrical tensile specimens with a nominal diameter in the gauge section of 6 mm were machined from the GDC bars.

The step-plate geometry manufactured by gravity sand casting is shown in figure 1c). The sand mold was made from rutile sand. The binder system consisted of 3 wt.% Carbophen (Hüttenes Albertus) and CO_2 gas. To minimize oxidation of the melt during the casting processes, the cavity of the cured sand mold was filled with shielding gas. The cooling rate in the sand casting process was very low as compared to the die casting process. A low cooling rate generally leads to a slow solidification process and therefore to a microstructure with a large grain size. By contrast, the rapid solidification rate in the die casting process leads to a substantially smaller grain size, which was expected to affect both the mechanical and the magnetic properties.

The HP-DC trials were conducted on a cold chamber die casting machine of the type Frech DAK 350-40. Here, two different die cast tools were used; (i) a special tool for the production of tensile specimens (Ø 6 mm) and (ii) a step-plate geometry for the microstructure investigations (cf. figures 2 and 3). In preparation for these experiments, the Mg-Co-Zn alloy was divided into smaller portions matching the shot weight of the casting tools. A standard AZ91D alloy provided by Magnesium Elektron was also cast as a reference condition. The temperature of the dies was set always to 160 °C.

GDC and HP-DC tensile specimens were used for the determination of the mechanical strength values in standard tensile tests. Further samples of the Mg-Co-Zn alloy were subjected to cyclic loading tests using stepwise increasing loads from 200 to 1400 N in order to test whether correlations can be established between the stresses applied to the specimens and their magnetic properties. During these experiments the magnetic properties were measured by the harmonic analysis of eddy-current signals as described in [8]. For the evaluation of the magnetoelastic behavior, the 3rd harmonic is most appropriate.

Sections of the Mg-Co-Zn castings were metallographically prepared by grinding using SiC abrasive papers down to a P2500 grit size. Afterwards, the specimens were polished to 1 µm using diamond paste and rinsed with ethanol. The Mg-Co-Zn alloys' microstructures were investigated employing the compositional contrast mode (back-scatter electron imaging; BSE) of a Zeiss LEO 1455VP scanning electron microscope (SEM). [11]

3. Results and Discussion

The different mold geometries in conjunction with the technical casting processes used in the present study, i.e. gravity sand casting (GSC), gravity die casting (GDC) and high-pressure die casting (HP-DC), enabled processing of the magnetic magnesium alloy with substantially different cooling conditions. As demonstrated in the following, the cooling rate is a key parameter for both the microstructure as well as the mechanical and the magnetic properties of the Mg-Co-Zn alloy.

Microstructure of the Mg-Co-Zn alloy processed by GSC and HP-DC

As reported in a related study [8], the element cobalt usually precipitates in a eutectic structure. This is also apparent from the SEM images shown in figure 2. In BSE mode, the material with a high density appears bright and light materials are gray.

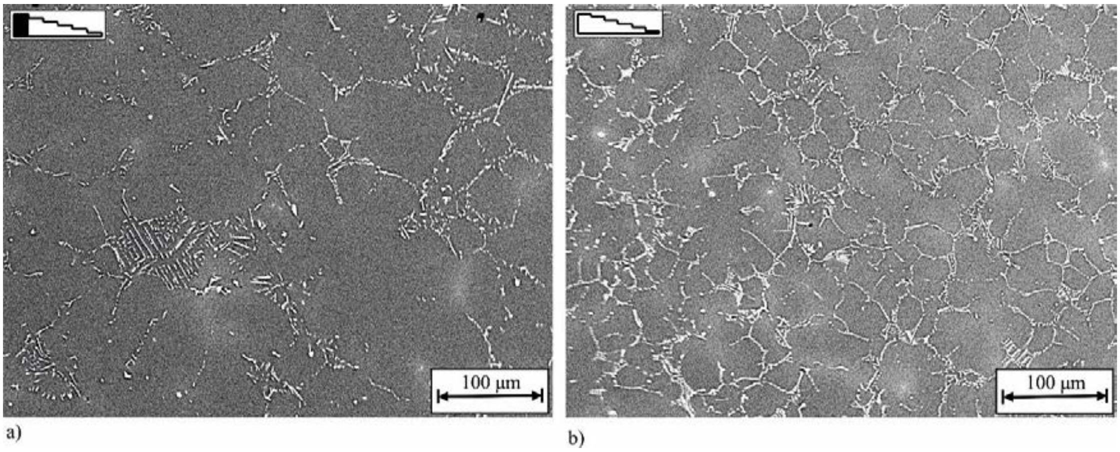

Figure 2: Comparison of the microstructures in different sections of the GSC step-plate casting (SEM image, BSE mode) [11]

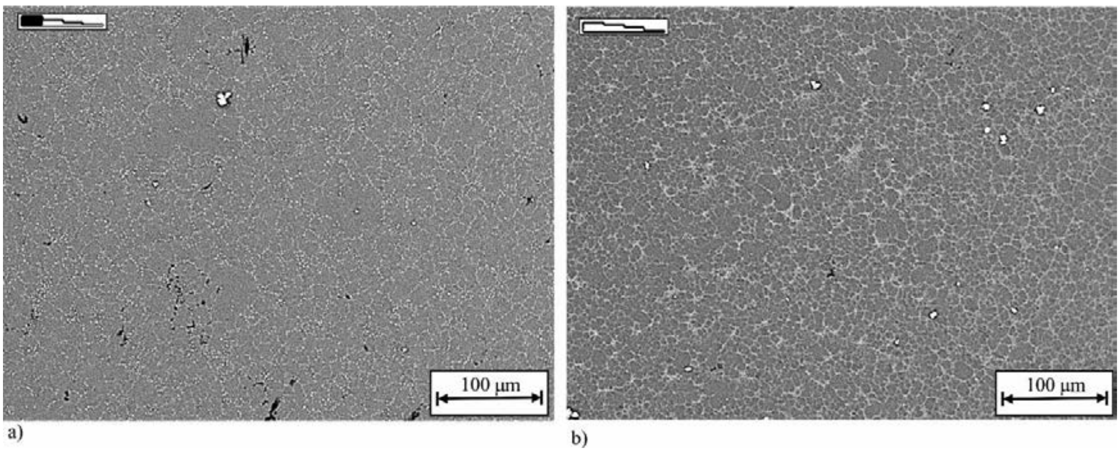

Figure 3: Comparison of the microstructures in different sections of the HP-DC step-plate casting (SEM image, BSE mode) [11]

Figure 2 shows the microstructure of the GSC specimens. In general, the narrow end of the step-plate geometry features smaller grains, which are surrounded by Co-rich precipitations (figure 2b). The GSC process leads to acicular Co-rich precipitations and large eutectic structures at the grain boundaries. Furthermore, the grain size decreases with increasing cooling rate.

In figure 3 the microstructure of the HP-DC specimens is illustrated. Different from the GSC process shown in figure 2, the Co-rich precipitations in the area of the grain boundaries are now fine grained and the structure is globular instead of acicular. The cooling rate, which is given in table 1, affects the grain size like in the GSC process. The listed values were calculated using Magma5 by thermocouples placed at the marked areas in figure 1. The cooling rate describes the temperature drop during solidification processes between liquidus and solidus.

Table 1. Casting simulation results for the cooling rates in both casting processes.

Casting process	Position	Cooling rate in °C/s
GSC	Narrow end	26
	Wide end	2
HP-DC	Narrow end	1296
	Wide end	29

Comparison with literature with respect to the microstructure and properties of Mg-Co based alloys are difficult because cobalt is not often used as an alloying element in magnesium. Nevertheless, the formation of a cobalt-rich eutectic precipitations structure is also reported in earlier publications. In [6] it is noted that, due to the tendency of agglomeration, a completely eutectic microstructure can only be achieved by rapid cooling. This is confirmed in the present study (cf. figure 3b).

Magnetic Properties of GDC and HP-DC Specimens

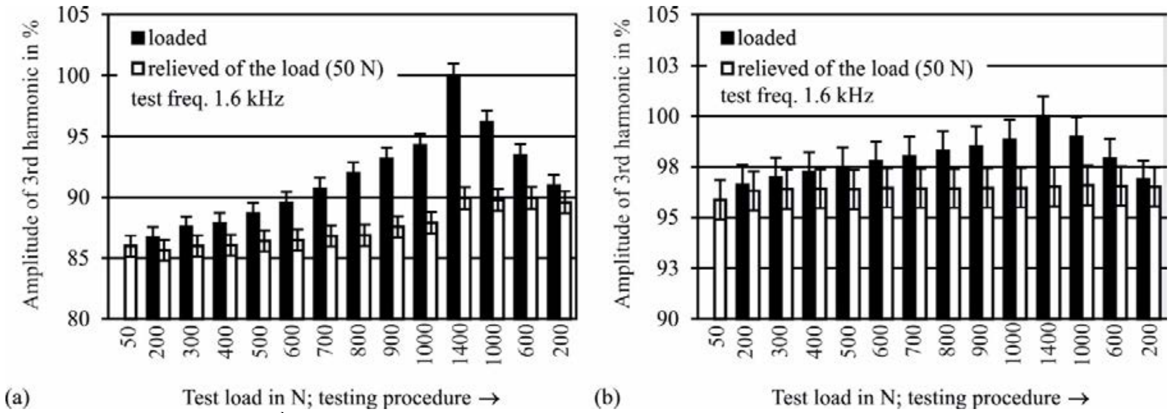

Figure 4: Amplitudes of the 3rd harmonic measured in cyclic loading tests on the Mg-Co-Zn alloy; (a) gravity die cast condition, (b) high-pressure die cast condition [11]

The Mg-Co-Zn alloy's load-sensor abilities were investigated for the different casting processes by means of cyclic loading experiments. The results are summarized in figure 4. The magnetic properties of all tested samples, which were measured by an eddy-current sensor, were sufficient to distinguish the values of the 3rd harmonic between the loaded and the unloaded condition. Moreover, an obvious correlation existed between the applied mechanical loads and the measured amplitude values. Following the test sequence in figures 4a) and 4b) from left to right, every value is the average result of three consecutive measurements at the same force standardized to the highest measured value. While a force of 200 N led to a slightly greater amplitude than in the initial state, the highest load in this experiment (1,400 N) caused the 3rd harmonic to increase significantly. In case of the GDC specimens (figure 4a), there was a gradual increase of the amplitudes in the unloaded condition until they reached a constant value after the application of the maximum load. The load-sensitive properties though remained throughout the whole measurement even after the onset of local plastic deformation. Compared with the GDC condition, the HP-DC specimens generally exhibited a much higher amplitude of the 3rd harmonic (figure 4b), i.e. the magnetic properties are much more pronounced in this material. Basically, higher amplitudes are favorable because the actual signal can be differentiated easier from the background noise during measurements. In addition, the HP-DC alloy showed an almost ideal linear correlation between the measured amplitude and the actual load on the tensile specimen. Apart from the greater absolute values, the difference between the amplitudes under a load of 1,400 N and 50 N seems to be virtually independent of the cooling conditions.

In addition to the analysis of the alloy's sensory properties as a function of the cooling conditions, the ferromagnetic properties have been characterized by magnetic hysteresis curves measured with a vibrating sample magnetometer (VSM). For details see [13].

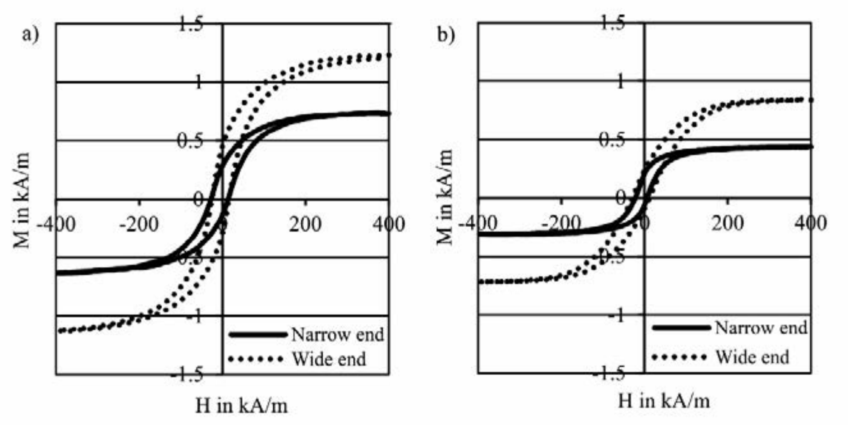

Figure 5: Hysteresis (M(H)) curves of GSC (a) and HP-DC (b) specimens

Figure 5 shows the results of the VSM measurements. The specimens' nominal ferromagnetic content was 4 wt.%. Thus, the measured magnetic characteristics are very low as compared to literature values for bulk material.

In general, the specimens produced by the GSC process showed a larger saturation magnetization than the HP-DC specimens. Furthermore, the wide ends of both step-plate geometries exhibited larger values for saturation and remanence magnetization than the narrow ends (cf. table 2), and the saturation magnetization increases with a decreasing cooling rate of the specimens.

Table 2. Magnetic characteristics of the specimens in both casting processes.

Casting process	Position	Coercive field strength in kA/m H_c (M = 0)	Remanence magnetization in kA/m M_r (H = 0)	Saturation magnetization in kA/m
GSC	Narrow end	20.292	0.220	0.730
	Wide end	20.292	0.391	1.230
HP-DC	Narrow end	20.193	0.144	0.438
	Wide end	20.292	0.176	0.836

Mechanical properties of the HP-DC Mg-Co-Zn alloy

The mechanical strength and ductility were determined in standard tensile tests. In order to classify the mechanical properties of the experimental Mg-Co-Zn alloy, tensile specimens made out of AZ91 were produced with identical HP-DC parameters. Additionally literature values of high-strength magnesium alloys like AM50, ZK60 and WE43 were compared with the measured values in table 1. The results demonstrate that, compared to the binary Mg-Co alloys, which were investigated in previous work [8], the yield strength is clearly improved by the addition of Zn. According to the Hall-Petch relationship, further increases in both strength and ductility are achieved through a refined microstructure which can be produced by, for instance, HP-DC. Here, the yield strength of the Mg-Co-Zn alloy was found to be 84% higher than in the GDC condition.
Compared with the commercial alloy AZ91, the HP-DC magnetic magnesium alloy showed a lower but still acceptable yield strength. Compared to high-strength alloys like AM50, ZK61 or WE43 the magnetic magnesium alloys showed low yield strength and especially a low elongation. Interestingly, the tensile strength of the experimental alloy was almost identical to AZ91 and the elongation at fracture was even better (table 3). It should be noted that the ultimate tensile strength and the ultimate elongation of the AZ91 samples tested in this study were considerably lower than the standard values issued by the alloy's producer [12]. This can be attributed to the specific cooling conditions during the casting experiments which were not identical to other HP-DC experiments with different casting geometries.

Table 3: Mechanical properties (mean values) of the experimental Mg-Co-Zn alloy and the reference alloy AZ91 (YS: yield strength; UTS: ultimate tensile strength; UE: ultimate elongation) [11]

Alloy	Mg-Co-Zn		AZ91	AM50 [14]	ZK61 [15]	WE43 [15]
Condition	GDC	HP-DC	HP-DC	HP-DC	T6	T6
YS in MPa	70.3	129.6	152.8	110-140	180	165
UTS in MPa	135.7	187.1	187.2	180-220	310	250
UE in %	3.5	5.9	1.5	5-9	10	2

Conclusions and Outlook

In the present study, the influence of the casting conditions on the magnetic properties of magnesium-cobalt based alloys was analyzed by means of eddy-current measurements. In particular, different cooling conditions were applied through the use of different casting geometries (cylindrical test bar Ø 22 mm, tensile specimens Ø 6 mm) in conjunction with gravity die casting (GDC) and high-pressure die casting (HP-DC). Furthermore a step-plate shaped casting geometry was manufactured with gravity sand casting (GSC) and high-pressure die casting (HP-DC) to investigate the effect of the different cooling conditions on the magnetic properties of the magnesium alloys. The results can be summarized as follows:

- Structure and distribution of Co-rich magnetic phases in the alloys varied substantially depending on the cooling conditions.
- A relationship between the applied test load and the measured amplitude of the 3rd harmonic of the eddy-current signal could be established for the Mg-Co-Zn alloy in GDC and HP-DC condition.
- The measured amplitudes of the 3rd harmonic of the eddy-current signal were greater in the specimens produced by HP-DC, i.e. their magnetic properties were more pronounced.
- The measured hysteresis curves showed different remanence and saturation magnetizations depending on the cooling conditions applied. Despite the low content of only 4 wt.-% of ferromagnetic material in the specimens, the change in ferromagnetic properties upon an increase in mechanical stress can be clearly detected.
- The measured yield strength of the HP-DC Mg-Co-Zn alloy was slightly lower than that of HP-DC AZ91, but the ultimate tensile strength was almost identical. The elongation to fracture of the magnetic magnesium alloy was higher than for AZ91. Compared to high-strength alloys the mechanical properties are low

Magnetic magnesium alloys were already employed in the production of load-sensitive lightweight components in the wheel suspension of a formula-student race car [5, 8]. The load-sensitive magnesium components, such as wheel carriers and pushrods, were equipped with eddy-current sensors and could be used successfully in order to measure the applied loads qualitatively during test drives. Further investigations will be done in order to establish a quantitative correlation between the measured eddy-current signal and the loads during test drives. Although the initial series of components was manufactured by sand casting, this study suggests that better load-sensitive properties and mechanical strength are achieved through the use of HP-DC components. However, higher magnetic remanence was observed with increasing grain size which should be taken into account for component-inherent data storage applications.

Acknowledgements

This research was sponsored by the German Research Foundation (DFG) within the subproject E2 “Magnetic Magnesium Alloys” of the Collaborative Research Center 653 “Gentelligent Components in their Lifecycle”. The eddy current measurements were performed in cooperation with subproject S3 “Gentelligent Part Identification and Integrity Assessment”, and the VSM measurements in cooperation with subproject L3 “Writing & reading process of magnetic stored data”.

References

[1] R.C. O'Handley, “Modern Magnetic Materials. Principles and Applications”, New York, Wiley-VCH, 2000, 218-221.
[2] A. Bieńkowski, J. Kulikowski, “The magneto-elastic Villari effect in ferrites”, J. Magn. Magn. Mater. 19 (1980), 120-122.
[3] A. Bieńkowski, R. Szewczyk, J. Salach, “Industrial Application of Magnetoelastic Force and Torque Sensors” Acta Phys. Pol. A (118) (2010), 1008-1009.
[4] N.B. Ekreem, A.G. Olabi, T. Prescott, A. Rafferty, M.S.J. Hashmi, “An overview of magnetostriction, its use and methods to measure these properties”, J. Mater. Process. Tech. (191) (2007) 96-101.
[5] C. Klose, “Development of Magnetic Magnesium Alloys with Load-Sensitive Properties”, Hannover, Germany: PZH-Verlag, 2013, IV.
[6] A.A. Nayeb-Hashemi, J.B. Clark, “The Co-Mg (Cobalt-Magnesium) system”, Bulletin of Alloy Phase Diagrams 8 (4) (1984), 352-355.
[7] Z. Yang, J.P. Li, J.X. Zhang, G.W. Lorimer, J. Robson, “Review on Research and Development of Magnesium Alloys”, Acta Metallurgica Sinica (English Letters) 21 (5) (2008), 313-328.
[8] C. Klose, C. Demminger, G. Mroz, W. Reimche, F.-W. Bach, H.J. Maier, K. Kerber, “Influence of Cobalt on the Properties of Load-Sensitive Magnesium Alloys”, Sensors 13 (1) (2013), 106-118.
[9] L. Rafflenbeul, “Untersuchung von Magnesium-Gussknoten in der Großserienkarosserie”, Hannover, Germany: PZH-Verlag 2010, I.
[10] C. Klose, G. Mroz, G.L. Angrisani, K. Kerber, W. Reimche, F.-W. Bach, “Casting Process and Comparison of the Properties of Adapted Load-Sensitive Magnesium Alloys”, Production Engineering Research & Development 7 (1) (2013), 35-41.
[11] Klose, C.; Demminger, C.; Maier, H. J. (2015): Microstructure and Properties of Cobalt- and Zinc-Containing Magnetic Magnesium Alloys Processed by High-Pressure Die Casting, In: Manuel, M. V. et al. (Hg.): Magnesium Technology 2015. Proceedings of a symposium sponsored by Magnesium Committee of the Light Metals Division of The Minerals, Metals & Materials Society (TMS), 144th Annual Meeting & Exhibition, 15.-19.03.2015, Orlando, Florida. John Wiley & Sons, Inc., Hoboken, New Jersey, 2015; p. 451-454
[12] Magnesium Elektron Datasheet 440, “Magnesium Casting Alloys”, Magnesium Elektron, Manchester, UK (2006).
[13] B.D. Cullity, C.D. Graham, Introduction to magnetic materials. 2nd ed. Hoboken, N.J. Wiley; 2009.
[14] C. Kammer, “Magnesium Taschenbuch”, Düsseldorf, Aluminium-Zentrale e.V., 2000.
[15] H. E. Friedrich, B. L. Mordike, “Magnesium Technology – Metallurgy, Design Data, Applications”, Heidelberg, Springer, 2006.