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Thermal analytical investigations of the magnesium alloys AM 60 and AZ 91 including the melting range

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Abstract

The following thermophysical properties were determined for the magnesium alloys AZ 91 and AM 60: The density in the temperature range 30–500 °C, the specific heat capacity including the melting range, the melting point temperature, and the melting enthalpy. The following devices were used: NETZSCH DSC 404C Pegasus, NETZSCH DIL 402C as well as SETARAM TGDTA92 for thermogravimetric investigations within the melting range. The difficulties which arose, in particular, as a result of the reactivity of magnesium during the investigations are presented in addition to the results.

Keywords: DSC; Magnesium alloy; Heat capacity; Enthalpy of melting; Density

1. Introduction

Over the last few years, increasingly higher demands have been placed on cast pieces for engine construction. The cast pieces are continually becoming more and more complicated in terms of geometry. Lower masses of the components as well as improved material properties are required which leads to thinner walls or to the intensified use of light metal alloys. The external dimensions of the engines remain the same but the performance rises. This leads to constantly increasing stresses placed on the materials whose strength potential nearly approaches their limiting values [1–3].

The use of Mg-alloy becomes significant due to a one-third lower density of magnesium compared with aluminum, improved damping ability, a higher resistance to corrosion, and better mechanical properties [4].

From the view of product engineering, the technological parameters of the casting process need to be optimized to remove possible weak points as well as to provide the most favorable production conditions [5–7]. To accomplish this task, the design of the process is simulated. In order to optimize results from the simulated technical investigations reliable values for a set of thermophysical inputs are required which are often not available with the desired accuracy. Therefore, measurements are necessary.

DSC measurements for the determination of the specific heat capacity require a high measuring accuracy and good reproducibility. In [8], the possibilities for improving the signal-to-noise ratio were discussed

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Table 1
Measuring parameters for the determination of the thermal physical properties

	Measuring device	
	DIL 402C	DSC 404C Pegasus
Heating rate	5 K/min	20 K/min
Temperature range	30–500 °C	30 °C to melt
Inert gas	Argon, flow rate: 75 ml/min	
Crucible material	–	Graphite
Dimension of sample $(d/h)_{cyl}$	5 mm/25 mm	5 mm/0.3–0.5 mm
Calibration tests	Al_2O_3-standard	Sensitivity, temperature

and in [9], a model for the description of the heat transfer at a DSC plate transducer is presented. The latter can be used for planning the experiments.

The following thermophysical properties were determined for the magnesium alloys AZ 91 and AM 60:

- density $\rho(T)$ in the temperature range 30–500 °C;
- specific heat capacity $c_p(T)$ including the melting range;
- melting point temperature T_m;
- enthalpy of melting Δh_m.

In addition to the results, the difficulties which arose as a consequence of the reactivity of magnesium during the investigations are presented.

2. Measuring device

The measurements were carried out with a DSC 404C Pegasus (dynamic difference calorimeter) and a DIL 402C (push-rod dilatometer) manufactured by NETZSCH. The devices operate in the temperature ranges 20–1650 and 20–1550 °C, respectively, and with a static or dynamic atmosphere or with a vacuum. Both devices are connected to a turbomolecular pump which pulls a vacuum of 10^{-5} mbar. The measuring parameters used are represented in Table 1.

3. Experimental

The influence of the samples on the crucible and on the thermocouple materials were tested in preliminary investigations. The samples proved to be highly reactive with platinum and also affected the internal alumina crucibles. In addition, the highly sensitive Mg-alloys oxidize easily in solid state (burn with a bright flame). Melting phase, starting below 600 °C, is accompanied by a noticeable mass loss. Fig. 1 shows the DTA signal as well as the mass signal from a thermogravimetric investigation (protected DTA plate transducer) of the Mg-alloy AM 60. In order to avoid alloying of the evaporating magnesium with the platinum plate transducer, the retention time in the liquid phase must be minimized during the measurements. Further research must be carried out without the use of the platinum crucible with an internal alumina crucible, which is not favorable in terms of base-line stability and signal-to-noise ratio [9]. In order to prevent damages by magnesium vapors, insensitive graphite crucibles are used. In addition, the sample masses must be reduced to a minimum. Due to the high reactivity of the samples with oxygen, a highly pure inert gas atmosphere is necessary both with the DIL and in the DSC equipment. Multiple evacuating followed by rinses with inert gas are absolutely required. In this way oxidation can be avoided. Oxidations during the measurements lead to smaller $c_p(T)$-values.

To determine the specific heat capacity, at least three measurements are necessary. The reproducibility of the individual measurements was confirmed by repetition.

For the determination of the melting enthalpy, zinc and aluminum were used as calibration substances, since their melting point temperatures are similar to Mg-alloys. During the calibration experiments it was made certain that the geometrical dimensions and surface quality of the samples (flat plate with polished surface) approximately corresponded to those of the magnesium alloys. The mass of the calibration

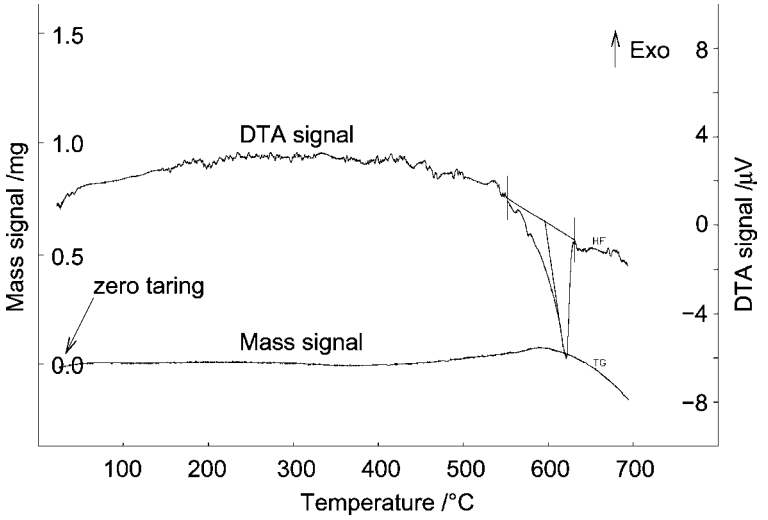

Fig. 1. DTA and thermogravimetric investigation of the Mg-alloy AM 60; increased mass loss within the melting range; mass: 34 mg, heating rate: 10 K/min, atmosphere: He.

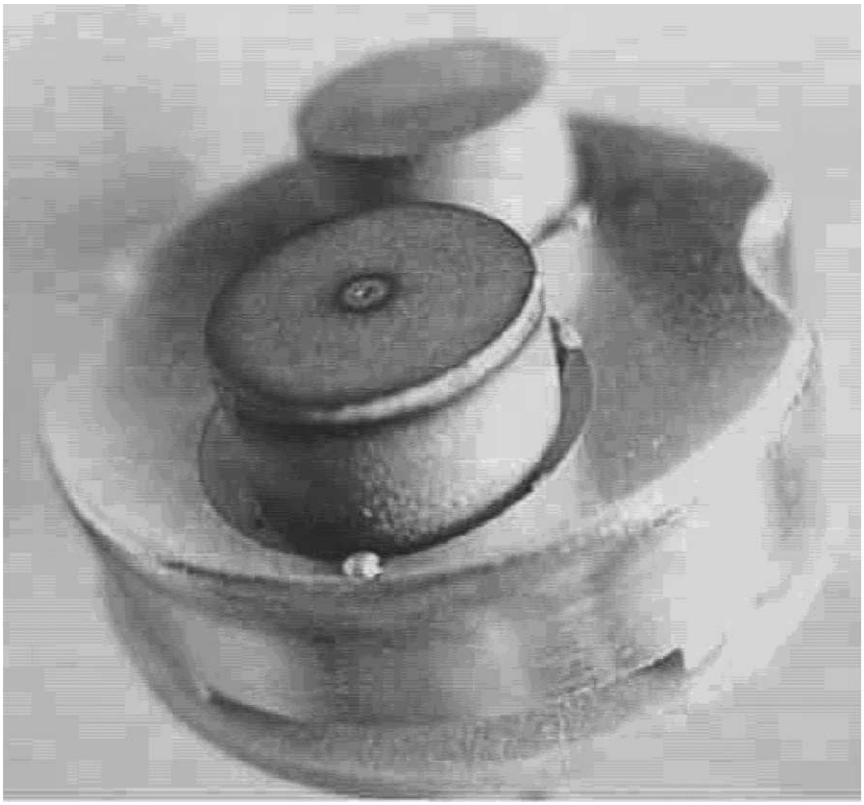

Fig. 2. Appearance of the DSC plate transducer with graphite crucible after the measurements.

substances was selected in such a way that the sizes of the melting peaks resulted in the same order of magnitude as those of the magnesium alloys.

The DIL measurements were based on the comparison with the well-known thermal expansion of a standard material. Both curves also reflected the signal of the thermal expansion of the sample holder, therefore a corrected thermal expansion of the sample was calculated. Using the corrected thermal expansion of the samples, the software calculates the density of the samples using a default reference value. The reference values of the density for the magnesium alloys were determined by means of pycnometer:

AM 60: $\rho_{30°C} = 1.765\,g/cm^3$,

AZ 91: $\rho_{30°C} = 1.792\,g/cm^3$.

4. Results

4.1. Specific heat capacity

Despite the high reactivity of magnesium vapors, the plate transducer showed only traces of a yellowish coloring on the surface. In Fig. 2, the plate transducer and the graphite crucible are shown. Traces at the lid of the sample crucible, which could easily be removed, are clearly visible.

Fig. 3 shows exemplarily the DSC signal curves (without smoothing) of the reference measurements with the sapphire standard and the sample measurements. The curves reveal good signal stability as well as a good signal-to-noise ratio. Despite the small sample masses of only about 20 mg (plate thickness 0.3 mm) and the graphite crucible which is not optimum for $c_p(T)$ measurements, the maximum deviation of the DSC signals of several repetition measurements amounts to under 5%. Comparative measurements with platinum crucibles and internal crucibles of alumina using a larger sample mass resulted likewise in deviations of <5% in the $c_p(T)$-values. A further comparison of the $c_p(T)$ function for the magnesium alloy AZ 91 with a calculated curve with the use of simple equation

$$c_p(T) = \sum c_{p,i}(T)x_i$$

is presented in Fig. 4. The values for the specific heat capacity of the pure components $c_{p,i}$ with the mass ratio x_i were taken from [10]. This comparison like-

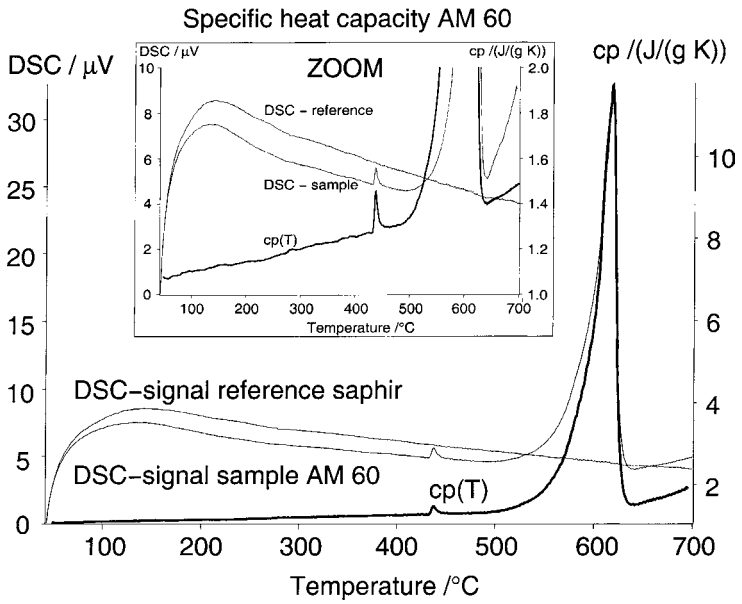

Fig. 3. Specific heat capacity of the magnesium alloy AM 60 including the DSC signal curves of the experiments with sample and reference (without smoothing the curves).

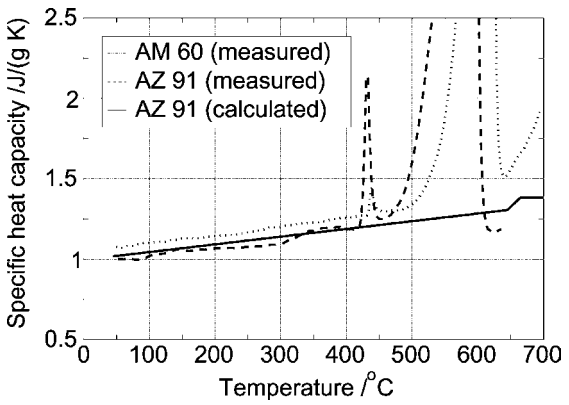

Fig. 4. Comparison of the measured and calculated $c_p(T)$ curves using the equation $c_p(T) = \sum c_{p,i}(T)x_i$.

wise shows small deviations which are appropriately below 4% with the exception of the phase change ranges.

In Tables 2 and 3, the regression coefficients of the functions are listed, which describe the course of the $c_p(T)$ curves with an accuracy of approximately ±2% in the total temperature range. The range of phase change of the sample AM 60 (433–445 °C) was linearized. The maximum deviation at the peak amounts to 14%.

4.2. Density

The dilatometer measurements proved to be unproblematic. The sample holder from alumina as well as the platinum thermocouple were not damaged by the magnesium sample. A slight surface oxidation occurred at the cylindrical sample. The thermal expansion of the two magnesium alloys is represented in Fig. 5. The effects of the phase change are clearly shown at 420 and 429 °C, which are also reflected in the DSC measurements (see Figs. 6 and 7). Outside the phase change ranges, almost linear processes of the thermal expansion and the density are recognizable. The density can be well described as a function of the temperature by the following equations:

$$\rho_{\mathrm{AM\,60}}(T)(\mathrm{g/cm^3}) = 1.784 - 7.972 \times 10^{-5}T,$$
$$30^{\circ}\mathrm{C} \leq T \leq 429^{\circ}\mathrm{C},$$
$$\rho_{\mathrm{AZ\,91}}(T)(\mathrm{g/cm^3}) = 1.815 - 8.010 \times 10^{-5}T,$$
$$30^{\circ}\mathrm{C} \leq T \leq 420^{\circ}\mathrm{C}.$$

4.3. Melting parameters

Figs. 6 and 7 show the DSC curves with integration of the phase change peaks. All typical values for the

Table 2
Regression coefficients for the $c_p(T)$ function of the magnesium alloy AM 60[a]

Temperature (°C)	A_0	A_1	A_2	A_3	A_4
50–500	1.03412	5.77E−04	0	0	0
501–618	16085.3	−119.724	0.33419	−4.140E−04	1.9297E−07
619–638	589851	−2784.06	4.38015	−2.297E−03	0
639–700	−3.64944	8.004E−03	0	0	0

[a] $c_p(T)\,(\mathrm{J/g\,K}) = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^4$.

Table 3
Regression coefficients for the $c_p(T)$ function of the magnesium alloy AZ 91[a]

Temperature (°C)	A_0	A_1	A_2	A_3	A_4
50–421	0.95684	5.647E−04	0	0	0
422–432	−40.8937	0.099746	0	0	0
433–445	28.983	−0.062394	0	0	0
446–595	2171.45	−17.3124	0.051825	−6.906E−05	3.46E−08
596–613	2.55E+06	−16184.9	38.5616	−0.040799	1.6173E−05
614–640	1.31904	−2.294E−04	0	0	0

[a] $c_p(T)\,(\mathrm{J/g\,K}) = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^4$.

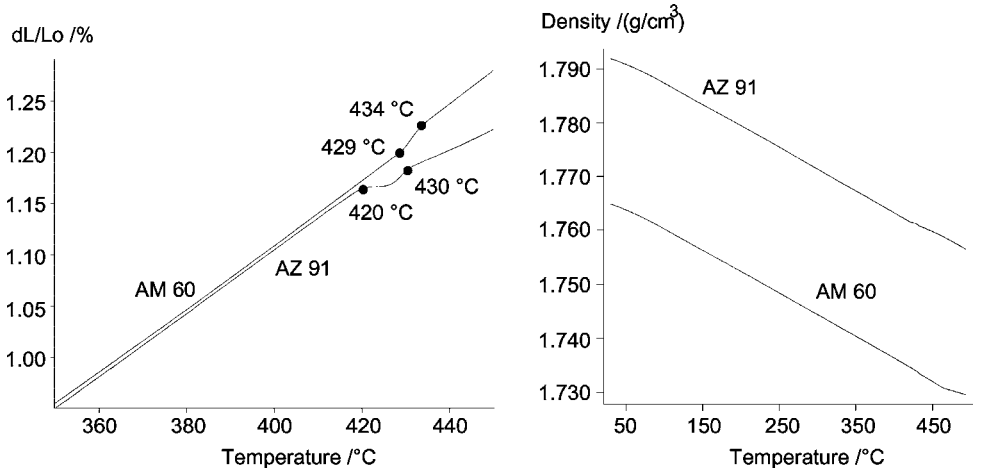

Fig. 5. Thermal expansion and density of the magnesium alloys AM 60 and AZ 91.

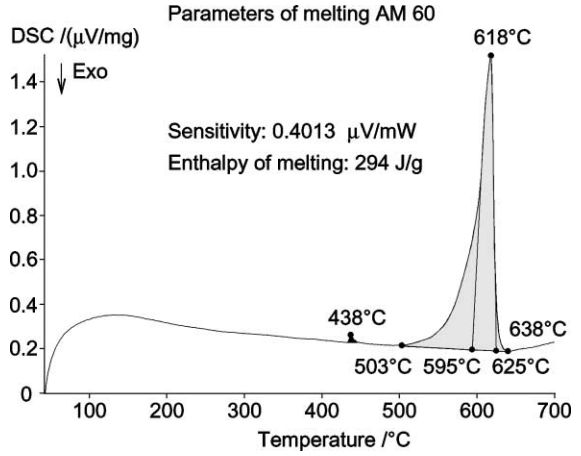

Fig. 6. DSC curve of the magnesium alloy AM 60 with integration of the phase change peak; melting enthalpy, onset temperature, peak temperature, beginning and end of the melting range.

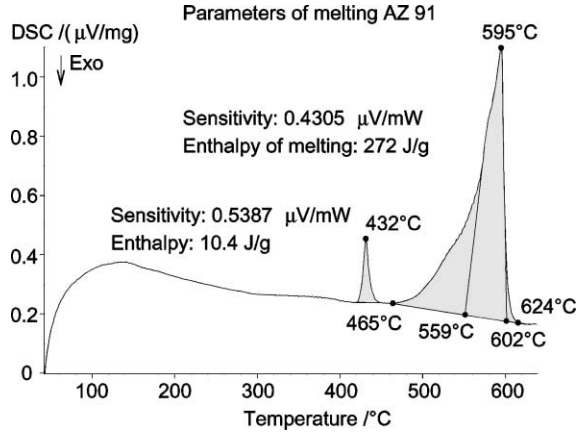

Fig. 7. DSC curve of the magnesium alloy AZ 91 with integration of the phase change peaks; melting enthalpy, onset temperature, peak temperature, beginning and end of the melting range.

melting enthalpy, onset temperature, peak temperature, and beginning and end of the melting range were registered. A comparison of Fig. 6 with the preliminary experiment represented in Fig. 1 with TG–DTA equipment shows a very good agreement of the onset temperature determined from different devices. In both units an onset temperature of 595 °C was determined for the magnesium alloy AM 60.

5. Conclusion

During the DIL investigations, optimum conditions for the measurement were used. The reproducibility of the measured curves was very good. A typical error of ±1% was observed. The correct determination of the density by means of the thermal expansion presupposes an accurate reference value. The uncertainty

of the reference value of 30 °C, determined by means of the pycnometer, is ±0.3%.

The DSC measurements were carried out in the lower temperature range of the DSC 404 Pegasus (below 1000 °C). In addition, optimal conditions for the measurement were not achieved due to the use of graphite crucibles and the application of relatively thin sample plates. Both affected the signal curves through a comparatively larger noise. Thus an uncertainty of ±5% was associated with the c_p values outside the phase change ranges.

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