J. Min. Metall. Sect. B-Metall. 53 (3) B (2017) 279 - 284

Journal of Mining and Metallurgy, Section B: Metallurgy

THERMOPHYSICAL PROPERTIES OF SOME LIQUID BINARY Mg-BASED ALLOYS

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(Received 22 June 2017; accepted 17 August 2017)

Abstract

In this study, some structure-sensitive thermophysical properties, namely, electrical conductivity, thermal conductivity and thermoelectric power of liquid binary alloys $Al_{33.3}Mg_{66.7}$, $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.3}Zn_{66.7}$ (all in wt.%), as the most promising cast alloys to fabricate components for cars, aircraft and other complex engineering products, were investigated. The electrical conductivity and thermoelectric power were measured in a wide temperature range by the four-point contact method. The thermal conductivity was measured by the steady-state concentric cylinder method. The obtained results are compared with literature experimental and calculated data.

Keywords: *Magnesium alloys; Mg–Al; Mg–Zn; Electrical conductivity; Thermal conductivity; Thermoelectric power.*

1. Introduction

Light magnesium alloys are of scientific and practical interests, because of such physical and mechanical properties as good damping, specific strength and electromagnetic shielding. Most of them are environmental friendly. Besides, the potential use of magnesium alloys in the field of electronic packaging, such as heat dissipation for light entropy dioxides (LEDs), has drawn new research interest, resulting from their excellent electrical and thermal transport properties.

Magnesium based alloys are widely used as cast alloys for many cars components as well as in some high-performance vehicles [1–5]. These alloys have been also intensively studied as appropriate biodegradable materials in a number of biomedical applications [6]. The binary Mg–Al, Mg–Zn alloys are under intense consideration as favourable cast alloys for using in automotive and aircraft industry and other high-strength applications [7]. Mechanical characteristics of Mg–Al alloys are quite good at ambient temperature. Nevertheless, a low melting temperature of the $Al_{12}Mg_{17}$ phase deteriorates their creep resistance at higher temperature even under low loads.

In order to solve this problem and improve the properties of Mg–Al based alloys at higher temperatures, the new phases should be formed and an influence of the $Al_{12}Mg_{17}$ phase should be reduced. Development of new Mg–Zn–Al alloys with higher creep resistance allowed to expand the areas of their use in the automotive industry.

Another problem that limits the widespread use of magnesium alloys in the industry is the slow heat dissipation, which is the result of an increase in the operating speed of parts and units of vehicles. Since reliability, performance, and durability of devices are very temperature dependent, these parameters may deteriorate rapidly over time according to the exponential law. Therefore, new magnesium alloys should have high thermal conductivity.

The development of light Mg alloys requires a detailed information about their structure and phase transformations, which can be obtained from thermophysical data. The importance of simulating technological processes requires the most accurate values of the physical characteristics of the alloys used. But physical properties and structure of a solid alloy strongly depend on solidification peculiarities of a melt. Thus, production of new materials with predicted properties requires information about their physical properties in the molten state as well as in the melting-solidification range.

Dedicated to the memory of Professor Dragana Živković

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DOI:10.2298/JMMB170622029P

At this point, behaviour of electrical conductivity and thermoelectric power at temperature changes can give detailed information about phase transformations and structure of the liquid alloy. The development of Mg-based alloys with high elevated thermal conductivity will help to solve numerous problems, connected with their practical applications at elevated temperature.

This work is devoted to investigations of the thermophysical properties (electrical and thermal conductivity and thermoelectric power) of liquid binary Mg-based alloys Mg–Al and Mg–Zn, namely, $Al_{33.3}Mg_{66.7}$, $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.3}Zn_{66.7}$ (all in wt.%), as the most promising cast alloys to fabricate components for various complex engineering products. These manufacturing processes are related to reflow procedure, while the solid-liquid transition of multi-component system is connected with significant changes in the microstructure and physico-chemical properties. The measurements were carried out in a wide temperature range between the melting temperatures of the samples and 1200 K.

2. Experimental

The samples were prepared from Al (99.99% metallic purity), Mg (99.95% metallic purity) and Zn (99.994% metallic purity, all metals from Alfa Aesar, Karlsruhe, Germany) according to the designated composition. Temperature dependence of the electrical conductivity and thermoelectric power was measured by the four-point contact method. Cylindrical boron nitride (BN) crucibles were used for the molten samples. The samples were produced from pure elements, which had been melted and evacuated inside the sealed quartz ampoules. The composition of the sample was accurate within 0.02 wt. %. In order to keep a constant chemical composition of the melt the measurements were carried out in neutral atmosphere of argon under pressure of about 10 MPa. In order to avoid a direct contact between melt and thermocouples, the intermediate graphite electrodes for potential and current measurements were inserted into a wall of the crucible. Each electrode was connected with a WRe-5/20 thermocouple for temperature measurements, while one of two dissimilar conductors of the thermocouple was used for the measurement of electrical conductivity. The electrical conductivity and thermoelectric power were determined with an uncertainty of about ±2% and ±5%, respectively. The experimental facility and details of this method were reported in [8].

Thermal conductivity was measured by the steady-state concentric cylinder method. The facility consists of two coaxial BN cylinders separated by a gap, filled with the investigated melt [9]. A heater of Mo wire located inside the inner cylinder, provides the needed temperature gradient in the studied layer of the melt. The outer heaters allow regulation of the temperature gradient over the height of the sample. The temperature is controled by WR5/20 thermocouples. The thermocouples located in the inner cylinder allow to control temperature distribution over the radius of the furnace. The coefficient of thermal conductivity is found from the following equation:

$$\lambda = \frac{Q \ln(d_2 / d_1)}{2\pi l (T_1 - T_2)} \quad (1)$$

where Q is the quantity of heat liberated by the heater per unit time, $l = 1/3\ L$, where L is the length of the measuring cell, d_1 is the external diameter of the inner cylinder and d_2 is the internal diameter of the outer cylinder [9]. The design of the apparatus assures a maximum reduction of the heat leakage and of convection. The resultant uncertainty of thermal conductivity measurements does not exceed ±7 %.

3. Results and discussion.

In Fig. 1 we present temperature dependence of the electrical conductivity, $\sigma(T)$, of the liquid $Al_{33.3}Mg_{66.7}$ alloy measured between the melting temperature T_L = 710 K and 1200 K, together with experimental results for liquid Al and Mg. The alloys were heated and cooled several times with different rates. It was found that velocity of heating or cooling had practically no influence on behaviour of electrical conductivity. The heating and cooling curves almost overlapped with the same slope.

Electrical conductivity of pure Al and Mg is compared with available literature data. Electrical resistivity of Al was studied many times, but a range of reported electrical resistivity data is very large [10–12]. The present electrical conductivity values taken from our previous work [13] are very close to the values reported in [14] (converted from resistivity) and agree generally with [14] within a total experimental uncertainty ±2 %.

The temperature dependence of electrical conductivity $\sigma(T)$ for pure Al is well described by a linear equation:

$$\sigma = \sigma_0 + \frac{d\sigma}{dT} \times (T - T_L) \quad (2)$$

where σ_0 = 41400 $\Omega^{-1}\cdot cm^{-1}$ is the conductivity at the melting temperature; $d\sigma/dT$ = –19.36 $\Omega^{-1}\cdot cm^{-1}\cdot K^{-1}$ is the temperature coefficient of the electrical conductivity.

Even less research has been devoted to the electrical conductivity of liquid magnesium, and the reported data [15–17] are quite contradictory. Both positive and negative values of the temperature coefficient of resistivity were reported (see Fig. 1).

Studies of Al–Mg alloys in the solid state were

carried out previously [18, 19]. Several studies were dedicated to theoretical calculations of resistivity in the liquid state, but only one of them was devoted to the experimental investigation of this system [20].

It should be noted that the remarkable properties of binaries with strong non-ideal mixing tendency are of permanent interest and useful in different fields (see [21]). Especially investigation of the Al–Mg system is of importance for geology, metallurgical chemistry and astrophysics which involves the study of interior of planets (the core of the earth and interior of planets are made up in part of a liquid mixture). Usually theoretical and computational investigations were carried out to determine the partial structure factor and electrical resistivity of the liquid Al-Mg alloy by using model potential. The Ziman formalism [22] allows studying the concentration dependence of electrical resistivity through an electron-ion potential.

The experimental work [20] also reports only concentration dependence of electrical resistivity, measured at 500 °C (773 K). Our study is focused on the temperature dependence of electrical conductivity. It is seen in Fig. 1 that electrical conductivity of liquid $Al_{33.3}Zn_{66.7}$ alloy decreases gradually with heating.

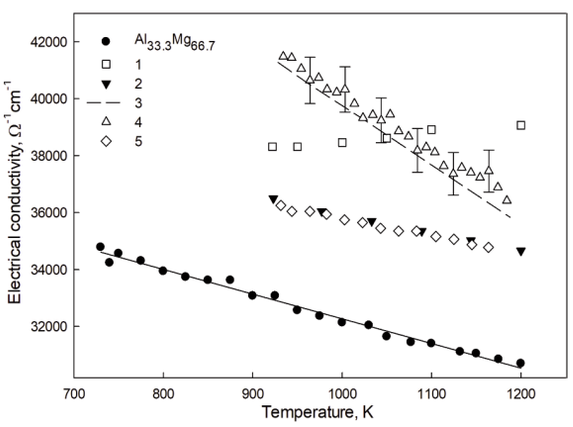

Figure 1. *Electrical conductivity vs. temperature for liquid Al, Mg, $Al_{33.3}Mg_{66.7}$ alloys, compared to literature data: 1 – Mg [15]; 2 – Mg [16]; 3 – Al [14]; 4 – Al [13]; 5 – Mg [17]. A fitting curve (marked as solid line) and error bars are shown for clarity at selected points only in one plot*

The temperature dependence of electrical conductivity can be well described by the linear equation (2), where $\sigma_0 = 34800\ \Omega^{-1}cm^{-1}$ is the conductivity value at the melting point, $d\sigma/dT = -8.67\ \Omega^{-1}\cdot cm^{-1}\cdot K^{-1}$ is a temperature coefficient of electrical conductivity.

The absolute electrical conductivity values of liquid $Al_{33.3}Zn_{66.7}$ alloy are lower than those of pure elements, which is typical for the alloy of the eutectic composition. At the same time, a rough comparison of our data with results reported in [20], which are based on the values obtained in both studies at 773 K, revealed that the present values are significantly higher. At this point, further studies are needed.

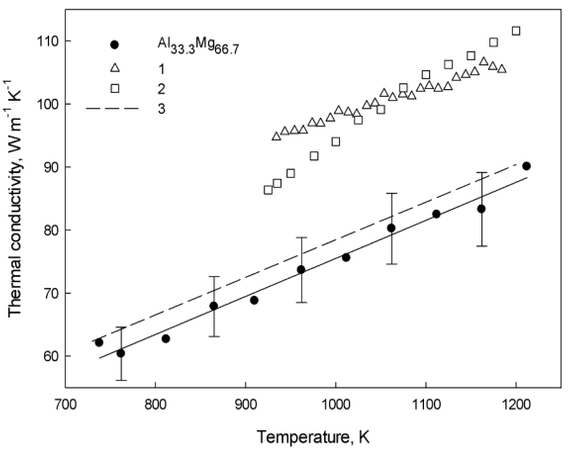

Figure 2. *Thermal conductivity vs. temperature for liquid $Al_{33.3}Mg_{66.7}$ alloys, compared to literature data: 1 – Al [13]; 2 – Mg [23]; 3 – – – – $Al_{33.3}Mg_{66.7}$ calculated from WFL. A fitting curve (marked as solid line) and error bars are shown for clarity at selected points only in one plot*

Thermal conductivity λ(T) was measured in a temperature interval beginning from the melting temperature 710 K up to 1200 K (Fig. 2). The λ(T) dependence is described by:

$$\lambda = \lambda_0 + \frac{d\lambda}{dT} \times (T - T_L) \tag{3}$$

where λ_0(T) = 58 $W\cdot m^{-1}\cdot K^{-1}$ is thermal conductivity at the melting point and $d\lambda/dT = 0.06\ W\cdot m^{-1}\cdot K^{-2}$ is the temperature coefficient of the conductivity.

An increase of thermal conductivity during heating was found for all investigated liquid alloys, according to Eq. (3). The λ(T) data for liquid Al were calculated from σ(T) according to the Wiedemann-Franz-Lorenz law, the λ(T) data for liquid Mg were taken from [23]. The thermal conductivity values and a temperature dependence of thermal conductivity indicate a predominance of the electron heat transfer and demonstrate strong gas degeneracy [22]. For similar alloys the Wiedemann-Franz-Lorenz (WFL) law is valid and consequently, it is possible to determine the Lorenz number. Based on the results obtained, it was revealed that the Lorenz number did not change with temperature and is almost coincide with a theoretical value of $2.445\cdot10^{-8}\ W\Omega K^{-2}$. As seen in Fig. 2, the experimental data of thermal conductivity (solid points) are in agreement with data determined from electrical conductivity (dashed line) within the limits of the experimental uncertainty ±7 %.

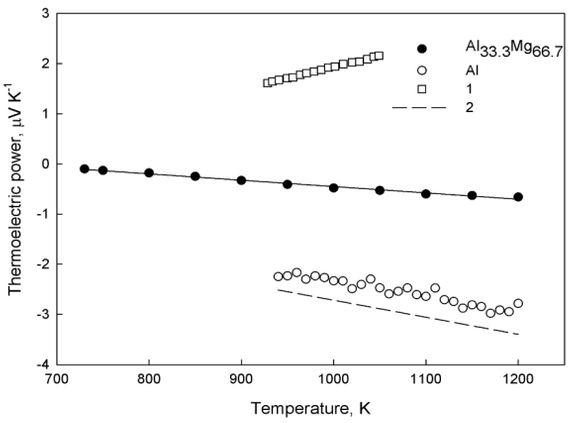

Figure 3. *Thermoelectric power vs. temperature for liquid Al and $Al_{33.3}Mg_{66.7}$ alloy, compared to literature data: 1 – Mg [25]; 2 – Al [24]*

Temperature dependences of the thermoelectric power S(T) of the liquid $Al_{33.3}Zn_{66.7}$ alloy together with liquid Al and Mg as well as some literature data are presented in Fig. 3. The S(T) dependence is described by equation:

$$S = S_0 + \frac{dS}{dT} \times (T - T_L) \quad (4)$$

where S_0(T) = –0.0837 μV·K^{-1} is the thermoelectric power at the melting point and dS/dT = – 0.0013 μV·K^{-2} is the temperature coefficient of the thermoelectric power.

The thermoelectric power of the dense packed Al in the liquid state has negative values [24], while the S(T) values of Mg are positive [25]. In both elements the thermoelectric power increases by absolute values upon heating. Thermoelectric power of the liquid $Al_{33.3}Zn_{66.7}$ alloy corresponding to the eutectic composition is small but still negative. Its temperature dependence is negligible. It is suggested that the alloy structure has a quasi-eutectic distribution of atoms, and in this case the minima of the electrical conductivity and thermoelectric power can be expected.

Temperature dependence of the electrical conductivity, thermal conductivity and thermoelectric power of the liquid $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.3}Zn_{66.7}$ alloys is shown in Figs. 4–6.

The experimental electrical conductivities of the liquid $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.3}Zn_{66.7}$ alloys as well as liquid Mg and Zn, measured between the melting temperatures and 1200 K, are presented in Fig. 4 together with literature data. All samples were heated and cooled several times with different rates, which had no influence on electrical conductivity behaviour. A good agreement between the heating and cooling curves was revealed.

Several studies of the electrical resistivity (conductivity) of liquid Zn have been reported [17, 26, 27]. As in the case of liquid Mg, a noticeable inconsistency between the $\sigma(T)$ curves is observed. The present electrical conductivity values are taken from our previous work [28].

The temperature dependence of the electrical conductivity of liquid $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.3}Zn_{66.7}$ alloys can be described by the nonlinear polynomials:

$$\sigma = 16900 + 16.26T - 0.008T^2 \quad (\text{for } Mg_{47.6}Zn_{52.4},\ 615 < T < 1200) \quad (5)$$

$$\sigma = 17516 + 12{,}1T - 0.0056T^2 \quad (\text{for } Mg_{33.3}Zn_{66.7},\ 745 < T < 1200) \quad (6)$$

The absolute electrical conductivity values of the liquid $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.3}Zn_{66.7}$ alloys are lower than those of pure elements Mg and Zn. The electrical conductivity of liquid $Mg_{47.6}Zn_{52.4}$ alloy is very close to that of pure Zn, while the $\sigma(T)$ curve for liquid $Mg_{33.3}Zn_{66.7}$ is located lower. The both curves are nonlinear and similar to the convex $\sigma(T)$ curve of liquid Zn. The data obtained generally agree with theoretical calculations reported in [29]. Based on the Faber-Ziman theory, the authors of this fundamental study used different methods and parameters for estimation of the concentration dependence of electrical resistivity of Mg–Zn alloys. At the same time, the temperature dependence of electrical conductivity of these alloys in the liquid state was measured for the first time, to our knowledge.

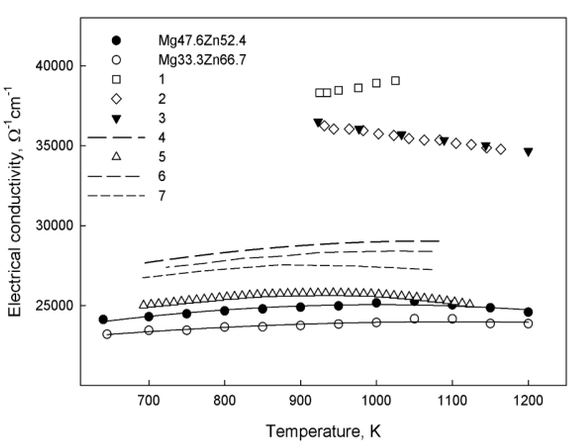

Figure 4. *Electrical conductivity vs. temperature for liquid Mg, Zn, $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.3}Zn_{66.7}$ alloys, compared to literature data: 1 – Mg [15]; 2 – Mg [17]; 3 – Mg [16]; 4 – Zn [26]; 5 – Zn [28]; 6 – Zn [27]; 7 – Zn [17]. Solid lines denote the fitting curves*

Dependence of thermal conductivity on temperature, λ(T), was measured in the temperature range from the melting temperature up to 1200 K (Fig. 5). The λ(T) data for liquid Mg were taken from [23]. Experimental thermal conductivity values of liquid Zn are in agreement with data calculated from

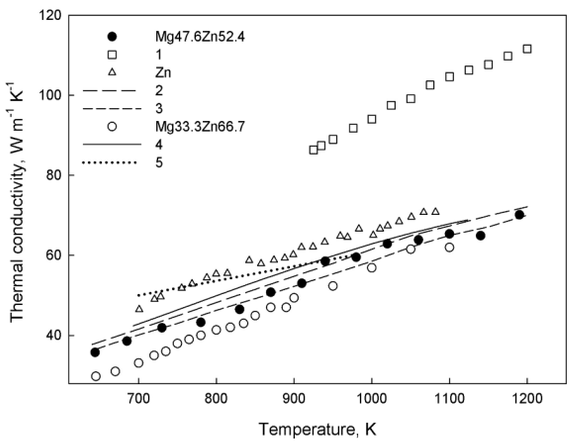

Figure 5. *Thermal conductivity vs. temperature for liquid Mg, Zn, $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.3}Zn_{66.7}$ alloys, compared to literature data: 1 – Mg [23] ; 2 – $Mg_{47.6}Zn_{52.4}$, calculated from WFL; 3 – $Mg_{33.3}Zn_{66.7}$, calculated from WFL; 4 – Zn, calculated from WFL; 5 – Zn [23].*

σ(T) according to the WFL law as well as with data reported in [23].

As seen from Fig. 5, thermal conductivity increases with temperature rise in nonlinear manner, and the λ(T) dependence can be well described in the temperature ranges between T_L and 1200 K by the polynomial:

$$\lambda = \lambda_0 + aT + bT^2 \quad (7)$$

The parameters of Eq. (5) are summarised in Table 1.

Table 1. *Thermal conductivity vs. temperature for the studied melts: linear fits to the experimental data plotted in Fig. 2.*

Alloy composition	λ_0	A	B
Zn	–21.0242	0.1223	$-3.4677\cdot10^{-5}$
$Mg_{47.6}Zn_{52.4}$	–29.7592	0.1197	$-3.0236\cdot10^{-5}$
$Mg_{33.3}Zn_{66.7}$	–24.7128	0.0886	$-7.6811\cdot10^{-6}$

The absolute experimental λ values agree with data calculated from the WFL law. As in the case of electrical conductivity, thermal conductivities data of both binary alloys are slightly lower than thermal conductivities of pure Mg and Zn.

Temperature dependence of thermoelectric power, S(T), is shown in Fig. 6. Thermoelectric power for both components Mg and Zn are positive in the liquid state and can be described by linear expressions:

$$S = -0.3968 + 0.0026\ T \quad (\text{for } Mg_{47.6}Zn_{52.4},\ 615 < T < 1200) \quad (8)$$

$$S = -0.4645 + 0.0025\ T \quad (\text{for } Mg_{33.3}Zn_{66.7},\ 745 < T < 1200) \quad (9)$$

In both elements, thermoelectric power increases upon heating. The absolute S(T) values of $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.3}Zn_{66.7}$ are higher than the S(T) data of Mg and Zn.

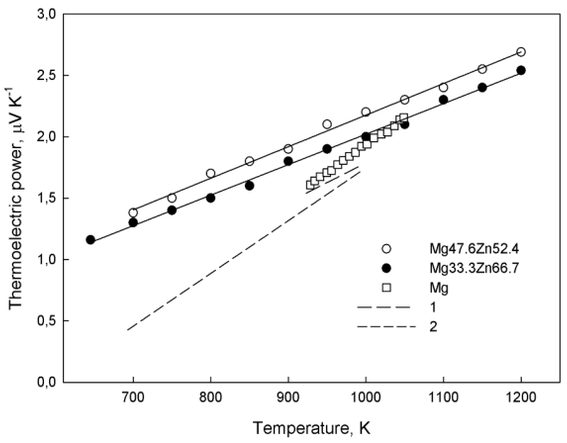

Figure 6. *Thermoelectric power vs. temperature for liquid Mg, $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.}3Zn_{66.7}$ alloys, compared to literature data: 1 – Zn [29]; 2 – Zn [30]*

4. Conclusions

Electrical conductivity, thermal conductivity and thermoelectric power of liquid binary Mg–Al and Mg–Zn alloys were measured in the wide temperature interval between the melting points and 1200 K, and the fit relations were proposed.

Temperature dependencies of electrical and thermal conductivity for liquid binary $Al_{33.3}Mg_{66.7}$ alloy obey a linear law, and their absolute values are lower than electrical and thermal conductivity of the pure elements Al and Mg. Thermoelectric power depends on negative S values of the dense packed Al and positive S values of Mg. Thermoelectric power of liquid $Al_{33.3}Zn_{66.7}$ alloy corresponding to the eutectic composition, is small but still negative. Its temperature dependence is negligible. A structure of $Al_{33.3}Zn_{66.7}$ has a quasi-eutectic distribution of atoms, which explains the minima of electrical conductivity and thermoelectric power. $Mg_{47.6}Zn_{52.4}$ and $Mg_{33.}3Zn_{66.7}$ liquid alloys are characterized by nonlinear behaviour of electrical conductivity and thermal conductivity, reflecting an influence of different conductivity behaviour in liquid Mg and Zn.

Acknowledgements

Financial support of this work by the Austrian agency for international mobility and cooperation in education, science and research (OeAD) and the Ministry of Education and Science of Ukraine (Project M/65–2017) is gratefully acknowledged.

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