

Physical, Thermal, Mechanical Properties, and Microstructural Characterization of Sn-9Zn-XGa Alloys



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The microstructural features, physicochemical, thermal, and mechanical properties of eutectic SnZn alloys with varying Ga contents were examined in this study. In the microstructure study using scanning electron microscope and X-ray diffraction analysis, intermetallic phases were not observed. The results indicated that the primary effect of Ga was increased mechanical properties. The physicochemical properties of liquid alloys, density, viscosity, and surface tension were measured using the free flow method. The addition of Ga to eutectic SnZn alloy generally reduced density, surface tension, viscosity, and melting point, and increased the coefficient of thermal expansion and electrical resistivity.

DOI: 10.1007/s11661-015-3235-3

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I. INTRODUCTION

REDUCING the melting temperature is one of the objectives in finding a replacement for lead-free solders. The melting temperature of eutectic SnPb is 456 K (183 °C), which compares to alternatives as follows: SnZn 471 K (198 °C), Sn-Cu-Ag 490 K (217 °C), SnAg 494 K (221 °C), and Sn-Cu 500 K (227 °C), as presented by Zhang and Tu.^[1] As shown in the preliminary study performed by Reference 2, the melting point is reduced with the addition of Ga to SnZn alloys. In the same study, the authors showed an increase of the wetting rate and a reduction of wetting angle with increasing addition of Ga. Chen *et al.*^[3] obtained similar data for the wetting test on Cu substrate using SnZn alloys with Ga, observing an increasing spreading area, but only to 0.5 Ga. For 1.0, 2.0, and 3.0 Ga the spreading area values were the same. In the soldering process, the thickness of intermetallic phases (IMPs) at the interface of the solder and Cu substrate with the addition of Ga to alloys increased. Song *et al.*^[4] studied the microstructure, thermal, and tensile properties of SnZn-Ga alloys to 1.8 wt pct Ga content. Reducing melting temperature and increasing tensile strength with increasing addition of Ga to eutectic SnZn were shown.^[4] Xue *et al.*^[5] investigated the influence of Pr addition to SnZn (0.5 Ga), and the obtained IMPs layer thickness for an SnZn (0.5Ga) alloy on Cu substrate was similar to that found by previous authors.^[3] The addition of Ga, which dissolves in eutectic SnZn alloys as observed in Reference 4, caused increasing tensile strength, and similar effect was obtained for the addition

of Na to SnZn alloys. However, in the latter case, increasing tensile strength was indicated for precipitates of IMPs Na-Sn and Na-Zn.

The aim of this study is to identify the characteristics of SnZn eutectic alloys with Ga additions (0.1, 0.2, 0.5, 1.0, and 3.0 wt pct). The density, viscosity, and surface tension were obtained using the free flow method. Differential scanning calorimetry (DSC) measurements were taken to determine the melting point, then the specified linear expansion was determined by dilatometry and resistivity measurements, using the four-point probe method. The characteristic microstructures of the obtained cast alloys were also observed by SEM and analysis of the occurring phase using X-ray diffraction (XRD) analysis, and a mechanical test was carried out to show the positive effect of Ga addition to eutectic SnZn alloys.

II. EXPERIMENTAL

High purity metals Sn, Zn, and Ga (99.999 pct), were used for the preparation of the alloys. Samples were melted in a furnace placed in a glove box with high purity argon, to provide the best possible protective atmosphere during the experiment. The level of O₂ and H₂O was below 1 ppm as measured by solid-state analyzers for oxygen and moisture, and the N₂ content was lowered (although it was not monitored), owing to Ar gas circulating through the high temperature purification system filled with Ti shavings heated to 1123 K (850 °C). In order to prepare samples for electrical resistivity measurements, the liquid alloys were sucked into quartz capillaries of 2 mm uniform inner diameter, in which they solidified rapidly.^[6] The equipment and experimental procedure for DSC, thermo-mechanical analysis (TMA), electrical resistivity, and mechanical tests were described.^[6] To measure the physicochemical properties of SnZnGa alloys, the discharge crucible

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Manuscript submitted April 4, 2015.

Article published online November 16, 2015

method (DC)^[7] was used. The free outflow of molten metal occurred through an orifice of specified diameter in the bottom of a crucible, and from a measurement of the mass of molten metal flowing out of the crucible as a function of time, the surface tension, density, and viscosity could be calculated simultaneously, from one experiment. Calibration involved the use of a crucible with a hole, and the parameters specifying the experiment were obtained for pure metals Sb, Sn, and Zn.^[8] The liquid metal temperature was controlled with a thermocouple placed inside the crucible and connected to a temperature controller. The equipment for the DC method was constructed and placed in a glove box with high purity argon, to provide the best possible protective atmosphere during the experiment. The microstructure characteristics and elemental analysis were analyzed using scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS), and XRD to improve the occurring phases. Mechanical tests were conducted on an INSTRON 6025 testing machine modernised by Zwick/Roell. The conditions of testing were in accordance with EN ISO 6892-1:2009, with a strain rate of 0.00025 (1/s) at room temperature. The tensile and compressive tests were performed for each of the SnZn alloys with Ga additions, and three successful measurements were taken. The samples for tensile tests were cast to graphite molds (Ø8 × 100 mm) with the base measuring 5 mm diameter and 40 mm length.

III. RESULTS AND DISCUSSIONS

The DSC curves of SnZn alloys with Ga addition are presented in Figure 1. With increasing Ga addition to eutectic SnZn, the melting temperature reduced and the

same results were obtained.^[2,4] Song *et al.*^[4] recorded a melting point of 468 K (195 °C) for 1.8 Ga, compared to 472K (199 °C) for 2 (wt pct) Ga obtained by Reference 2. But Zhang *et al.*,^[2] for alloys with higher Ga content, recorded a greater decrease of the melting point [468 K, 461 K, 447 K, and 428 K (195 °C, 188 °C, 174 °C, and 155 °C) for 3, 4, 6, and 8 (wt pct) Ga, respectively]. According to the phase diagram of Ga-Sn-Zn,^[2] which is built from the binary eutectic components, of E1 Sn8.8Zn [471.5 K (198.5 °C)], E2 Ga15Zn (292.0 K (19 °C)), and E3 Ga4Sn (298 K (25 °C)). In this ternary system, the eutectic points formed a triangle that can be described as a pseudo-binary eutectic Ga-Sn8.8Zn section, and the calculated eutectic point of the ternary system is 283 K (10 °C).^[2] For the samples with 3.0 (wt pct) addition of Ga, the regions of high Ga concentration with Sn or Zn start to dissolve from 323 K (50 °C), and this reaction reaches its maximum at 392 K (119 °C). The same behavior was observed in thermal expansion coefficient (CTE) and electrical resistivity measurements.

Physical data on density, viscosity, and surface tension were obtained from the DC method.^[7] The method consists of allowing the free flow of the liquid alloy through a hole in the bottom of the crucible, to a second crucible which is on a set of scales. The changes of mass vs time data obtained from the experiment, and use of the numerical method, allow Eq. [1] to be solved and give all three properties.^[7,8]

$$h = \frac{1}{2g} \left(\frac{Q}{\left(a_4 \left(\frac{2\rho Q}{\pi r_0 \eta} \right)^3 + a_3 \left(\frac{2\rho Q}{\pi r_0 \eta} \right)^2 + a_2 \left(\frac{2\rho Q}{\pi r_0 \eta} \right) + a_1 \right) \pi r_0^2} \right) + \frac{\sigma}{\rho g r_0} \quad [1]$$

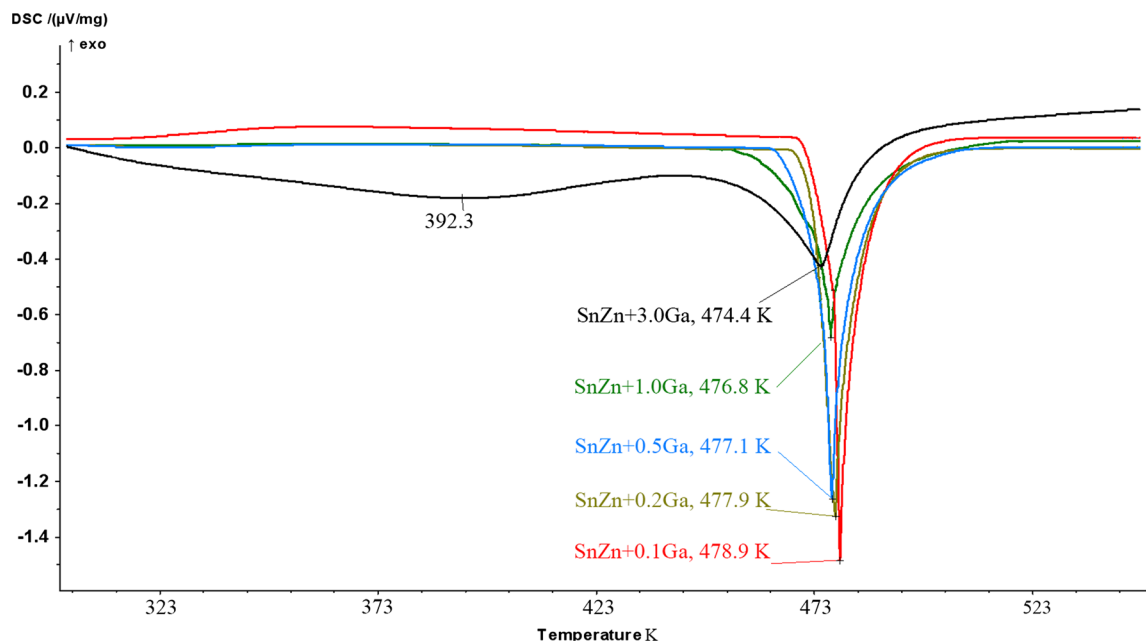


Fig. 1—DSC measurements of SnZn alloys with Ga (Color figure online).

where ρ density of liquid (kg/m^3), g gravitational acceleration (m/s^2), r_0 orifice radius in the bottom of crucible (m), σ surface tension (mN/m), Q free flow (m^3/s), η viscosity (mPa s), a_1 , a_2 , and a_3 are constants in the polynomial describing C_d vs Re , C_d discharge coefficient determined for a given crucible based on the free flow of liquids with known density, Re Reynolds number.

Density, viscosity, and surface tension are presented in Figure 2. The properties of pure Ga at 623 K (350°C) (density 5.921 g/cm^3 , surface tension 696.0 mN/m , and viscosity 0.942 mPa s) were taken from Reference 9. Compared to eutectic SnZn 6.900 g/cm^3 , 546.1 mN/m , 1.652 mPa s ,^[10] the addition of Ga to SnZn, caused a reduction of surface tension, density, and viscosity. As expected, the density and viscosity of SnZnGa alloys are lower than those of eutectic SnZn,^[10] whereas a decrease of surface tension [about 2 pct in the case of alloy containing of 3 (wt pct) of Ga] is not uncommon, because of the similar effect of a small addition of high surface tension component, as observed earlier in the case of Ga-Sn.^[11] In the Ga-Sn and Ga-Zn system,^[11] negative deviations from the ideal solutions were observed. In the SnZn with Ga doped to 3.0 (wt pct), surface tension slightly reduced with Ga addition, as shown in Figure 2(b). Reduction of density (Figure 2(a)) and viscosity (Figure 2(c)) for SnZn with Ga, are caused by dissolved Ga in eutectic SnZn, which shows on the microstructure of the cast alloys (Figure 3), and is also indicated in phase diagrams of Ga-Sn, Ga-Zn^[14] and Ga-Sn-Zn.^[2] In the case of the SnZn + Na system, viscosity increased with the addition of Na, caused by the creation of IMPs precipitates. The obtained density, surface tension, and viscosity for SnZn + Ga were lower compared to the literature data for eutectic PbSn 8.127 g cm^{-3} , 495 mN m^{-1} ,^[12] and 1.864 mPa s ^[13] respectively, at a temperature of 623 K (350°C). Temperature dependencies of density, surface tension, and viscosity are presented in Table I. The values obtained were described by the linear and Arrhenius equations, and the parameters of the equation presented in the table, along with the density, surface tension, and viscosity values, are calculated for a temperature of 623 K (350°C).

The microstructure of the casting alloys are presented in Figure 3 for (a) 0.1, (b) 0.2, (c) 0.5, (d) 1.0, and (e) 3.0 (wt pct) content Ga in SnZnGa alloys. For 3.0 (wt pct) Ga, the secondary electron micrographs and EDS elemental maps for Ga, Sn, and Zn were done. On the EDS maps, the dispersion of Ga in the entire volume of the sample is shown. In Table II, the EDS analysis obtained for SnZn with 1.0 (wt pct) Ga, presenting Ga occurrence in the Sn and Zn region, is shown. The XRD analyses are shown in Figure 4. EDS analysis revealed the dissolution of Ga in Sn and Zn, which is in agreement with the phase diagram of Ga-Sn and Ga-Zn.^[14] Comparing the obtained microstructure with the literature, such as Song *et al.*^[4] and Chen *et al.*,^[15] the Ga content to 3.0 pct does not change the structure of the eutectic SnZn.

Electrical resistivity is presented in Figure 5, for (a) temperature dependences of SnZn alloys doped with Ga,

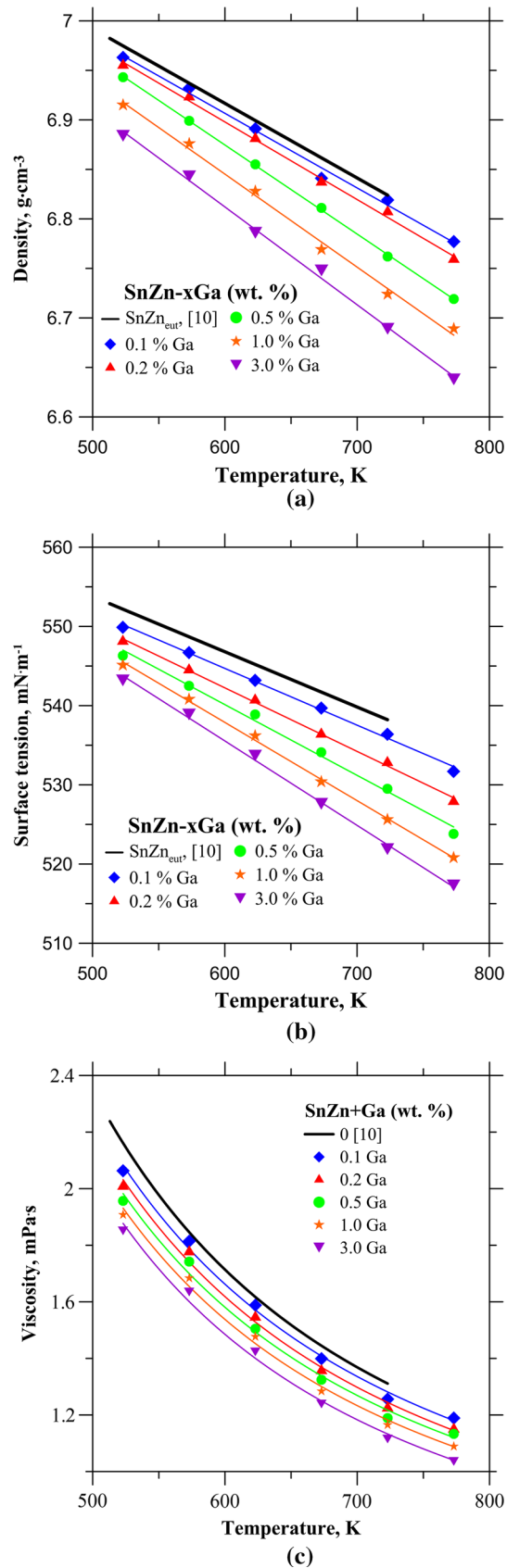


Fig. 2—Physicochemical properties of SnZn with Ga, (a) density, (b) surface tension, and (c) viscosity (Color figure online).

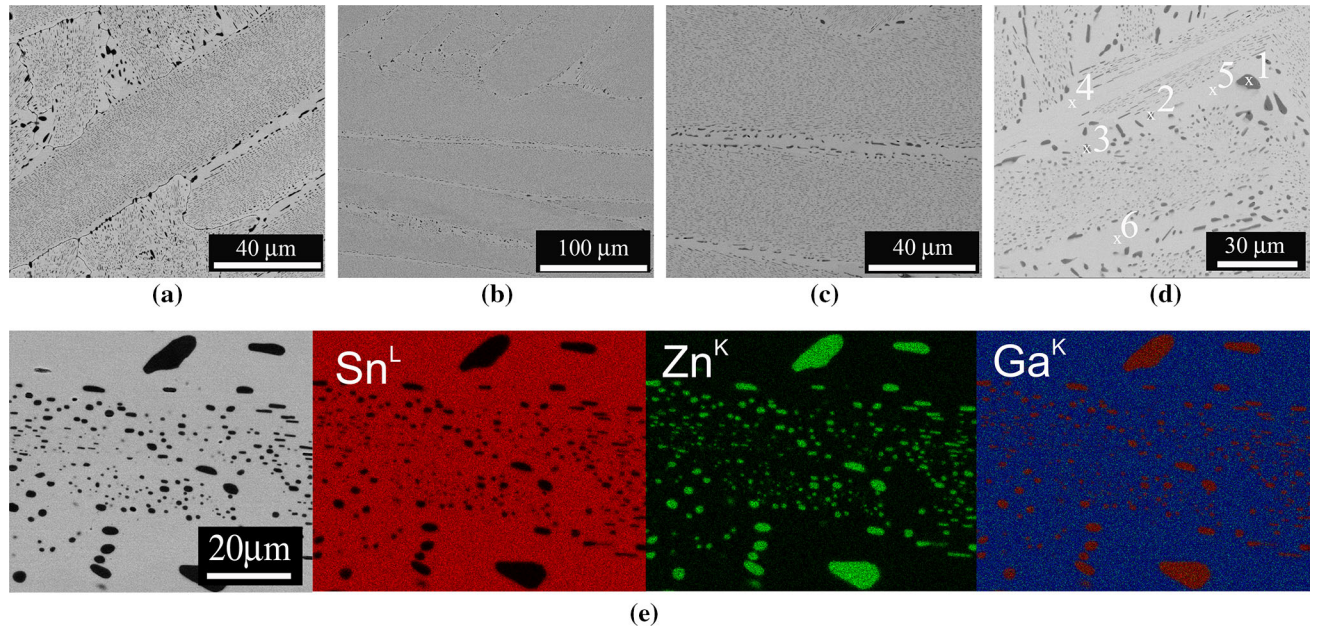


Fig. 3—Microstructure of cast alloys SnZn with Ga, (a) 0.1, (b) 0.2, (c) 0.5, and (d) 1.0 with marked points of EDS analysis and (e) 3.0 (wt pct) and EDS maps.

Table I. Linear and Arrhenius Dependence for SnZn with Ga Addition for Density (ρ), Surface Tension (σ), and Viscosity (η), with Errors and Parameters, Determined for a Temperature of 623 K (350 °C)

Alloys (Weight Percent)	A	δA	B	δB	ρ , g cm ⁻³ 623 K (350 °C)	$\delta\rho$
SnZn + 0.1Ga	7.36	0.02	0.00075	0.00003	6.626	0.265
SnZn + 0.2Ga	7.37	0.01	0.00078	0.00002	6.606	0.275
SnZn + 0.5Ga	7.41	0.01	0.00090	0.00001	6.539	0.316
SnZn + 1.0Ga	7.41	0.02	0.00094	0.00003	6.495	0.333
SnZn + 3.0Ga	7.41	0.02	0.00099	0.00003	6.443	0.343
Alloys (Weight Percent)	A	δA	B	δB	σ , mN m ⁻¹ 623 K (350 °C)	$\delta\sigma$
SnZn + 0.1Ga	587.7	1.4	-0.072	0.002	517.98	25.22
SnZn + 0.2Ga	590.4	1.2	-0.080	0.002	512.33	28.37
SnZn + 0.5Ga	593.7	2.4	-0.089	0.004	506.82	32.08
SnZn + 1.0Ga	597.2	1.3	-0.099	0.002	501.04	35.16
SnZn + 3.0Ga	599.5	1.7	-0.107	0.003	495.78	37.92
Alloys (Weight Percent)	A	δA	E	δE	η , mPa s 623 K (350 °C)	$\delta\eta$
SnZn + 0.1Ga	0.360	0.006	7633.1	22.8	1.571	0.017
SnZn + 0.2Ga	0.349	0.008	7649.1	31.5	1.527	0.018
SnZn + 0.5Ga	0.340	0.005	7671.1	37.8	1.494	0.011
SnZn + 1.0Ga	0.328	0.006	7713.2	25.8	1.453	0.024
SnZn + 3.0Ga	0.302	0.005	7938.8	30.2	1.400	0.023

Parameters of the straight line $A + BT$, with errors δA , δB for density and surface tension. The parameters of the Arrhenius equation $Ae^{E/(RT)}$, with errors δA , δE for viscosity.

Table II. EDS Analysis of SnZn1.0Ga Marked in Fig. 3(d), at Weight Percent

Element/Marked Point	1	2	3	4	5	6
Sn ^L	8.85	9.58	14.45	97.98	97.91	97.63
Zn ^K	89.90	89.25	84.68	0.62	0.63	0.82
Ga ^K	1.25	1.17	0.87	1.40	1.46	1.55

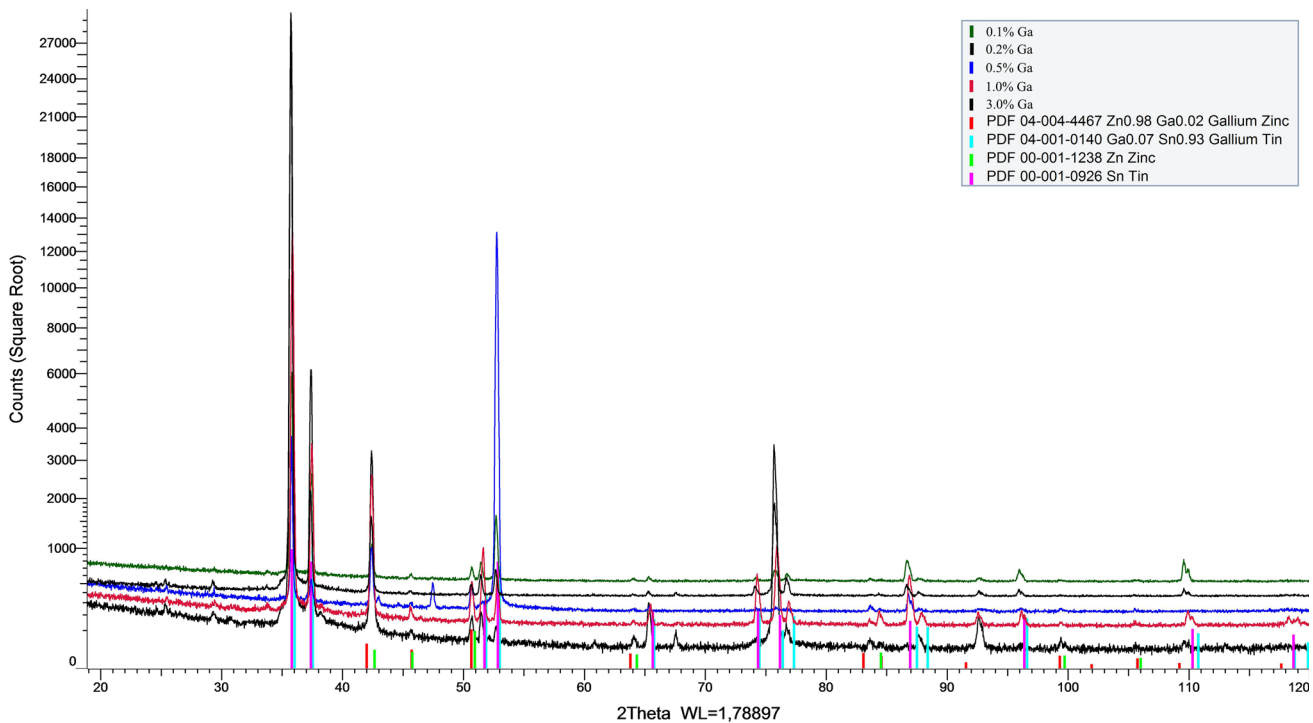
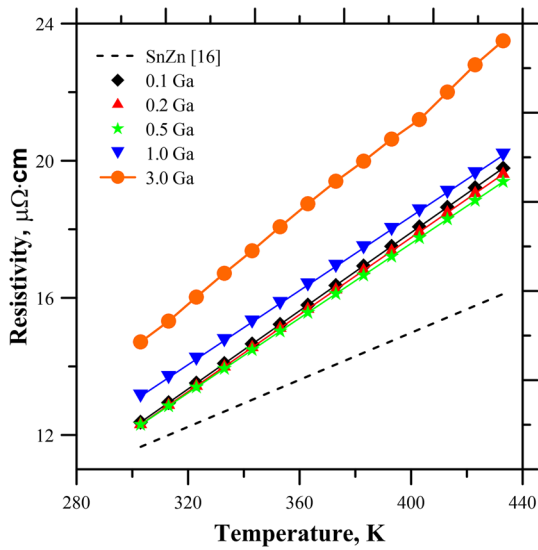


Fig. 4—XRD analyses of SnZn alloys with Ga (Color figure online).

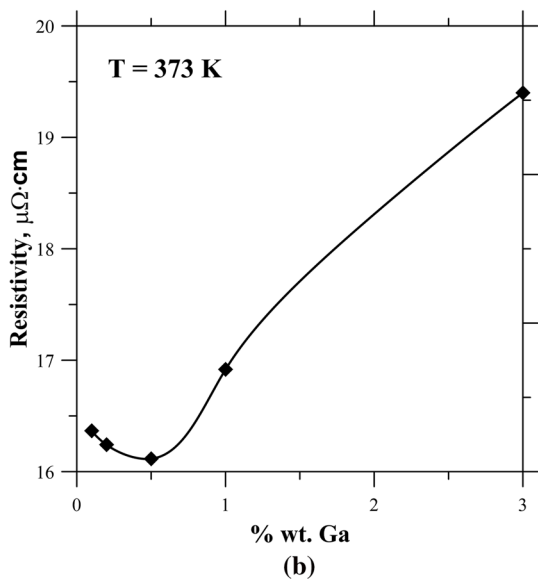
and (b) the influence of the addition of Ga to SnZn alloys at 373 K (100 °C) for electrical resistivity. The influence of Ga on SnZn alloys means that a small addition of Ga reduces electrical resistivity [up to 0.5 (wt pct) Ga], and after that point increases it. The reducing of electrical resistivity is related to the solubility limit of Ga in Sn and Zn according to phase diagrams of Ga-Sn and Ga-Zn.^[14] Beyond this limit, the electrical resistivity increases with increasing Ga content in alloys. In the case of SnZn with In,^[16] the electrical resistivity increases with the addition of In to alloys. All received data for SnZn + Ga alloys show that electrical resistivity is higher compared to eutectic SnZn,^[16] but lower compared to eutectic Sn37Pb.^[16] For the addition of 3.0 (wt pct) Ga, three temperature ranges in the slope of the electrical resistivity line were observed. Changes of the same character were observed for linear expansion for SnZn + 3Ga (wt pct). The electrical resistivity of eutectic Sn37Pb (wt pct) alloy is 14.50 ($\mu\Omega$ cm), which is very high compared to eutectic SnZn alloy 11.70 ($\mu\Omega$ cm) and SnZn with Ga from 12.09, 12.03, 12.02, 12.86, and 14.41 ($\mu\Omega$ cm) at 298 K (25 °C). This lower value leads to reduced loss of energy and increased efficiency, thus expanding the possibility of the application of SnZn with Ga in industry.

Linear expansion for SnZn alloys with Ga is presented in Figure 6, and the CTE in Table III. The different trends obtained for SnZn + Ga is compared to SnZn + In.^[16] In the literature, linear expansion data increase with the addition of In. For CTE, this expansion increases up to 1.0 (wt pct) Ga, and reduces for 3.0 (wt pct) Ga. The solubility limit of Ga in Sn and Zn has an influence on linear expansion, as shown on the phase diagram.^[2] The 3 (wt pct) of Ga is very close to the chemical content in SnZnGa, when observed as a liquid at room temperature. The linear thermal expansion vs temperature for SnZn + 3.0Ga (wt pct) alloy show changes to the slope, which has an impact on the value of CTE. The same changes were observed in electrical resistivity and DSC measurement, indicating that surplus Ga leads to changes of these properties.

The effect of Ga addition to eutectic SnZn on mechanical properties can be seen from the strain–stress curves shown in Figure 7. The ultimate tensile strength and elongation values are summarised in Table IV. The $R_{p0.2}$ (plastic strain of 0.2 pct), R_m (tensile strength), and $A_{5.65}$ (percentage elongation after fracture) were obtained from tensile testing. The Ga additions caused increasing tensile strength, but at the same time elongation was reduced. The tensile strength of the Sn-37Pb,



(a)



(b)

Fig. 5—Electrical resistivity for SnZn with Ga, (a) temperature dependence, and (b) with changes of Ga content at a temperature of 373 K (100 °C) (Color figure online).

Sn-9Zn, Sn-9Zn-0.5Ag, Sn-9Zn-0.5Al, and Sn-9Zn-0.5Ga (wt pct) were 55, 78, 62, 73, and 78 MPa, respectively, according to data obtained by Chen *et al.*^[15] Comparing

the literature data^[15] with the results obtained from the experiment, the tensile strength for 1.0 and 3.0 (wt pct) Ga are higher. All of the SnZnGa alloys showed higher values of tensile strength than Sn-37Pb.^[15] The addition of Ga to SnZn reduced the elongation very quickly. For 0.5 (wt pct) Ga this was 16.8 pct, while the literature data on elongation for Sn-37Pb, Sn-9Zn, Sn-9Zn-0.5Ag, Sn-9Zn-0.5Al, and Sn-9Zn-0.5Ga were 38, 41, 37, 38, and 41 pct, respectively.^[15] Although the obtained data and^[15] value of tensile strength for SnZn with 0.5 Ga are almost the same, the elongation value is a factor of the two smaller. Song *et al.*^[4] obtained elongation of more than 50 pct for SnZn alloys with Ga addition to 1.0 (wt pct), and recorded reduced elongation to ~30 pct for 1.8 Ga, but the tensile strength was similar to that presented in this work. The various results obtained for elongation could be due to different preparations of alloys, even for similar morphologies, which were obtained by References 4 and 15. Osorio *et al.*^[17] show the influence of preparation of samples for obtained stress and elongation for eutectic SnAg, SnBi, SnZn, SnPb alloys. The most sensitive was eutectic SnZn, for which the obtained stress value ranged from ~41 to ~59 (MPa), and strain from 50 to 26 pct. This study and Reference 4 confirm the occurring trend of increasing tensile strength with the addition of Ga to SnZn. From the viewpoint of SnZnGa alloys as a replacement for lead solders, increasing the stress will raise the strength of soldered connections.

IV. SUMMARY

The addition of Ga to a eutectic SnZn alloy generally reduced density, surface tension, viscosity, and melting point, and increased the coefficient of thermal expansion and electrical resistivity. The obtained density, surface tension, and viscosity for SnZn + Ga were lower compared to the literature data for eutectic PbSn.^[12,13] Increasing addition of Ga to eutectic SnZn alloys caused increasing tensile strength but reduced elongation values. The DSC measurement for the alloy SnZn + 3.0Ga (wt pct) shows dissolution, which starts around 323 K (50 °C), which is also apparent in regard to thermal expansion and electrical resistivity, and which is in line with the phase diagram of Ga-Sn-Zn.^[2] The microstructures of SnZn + Ga are similar to eutectic SnZn and the same as obtained in References 4 and 15.

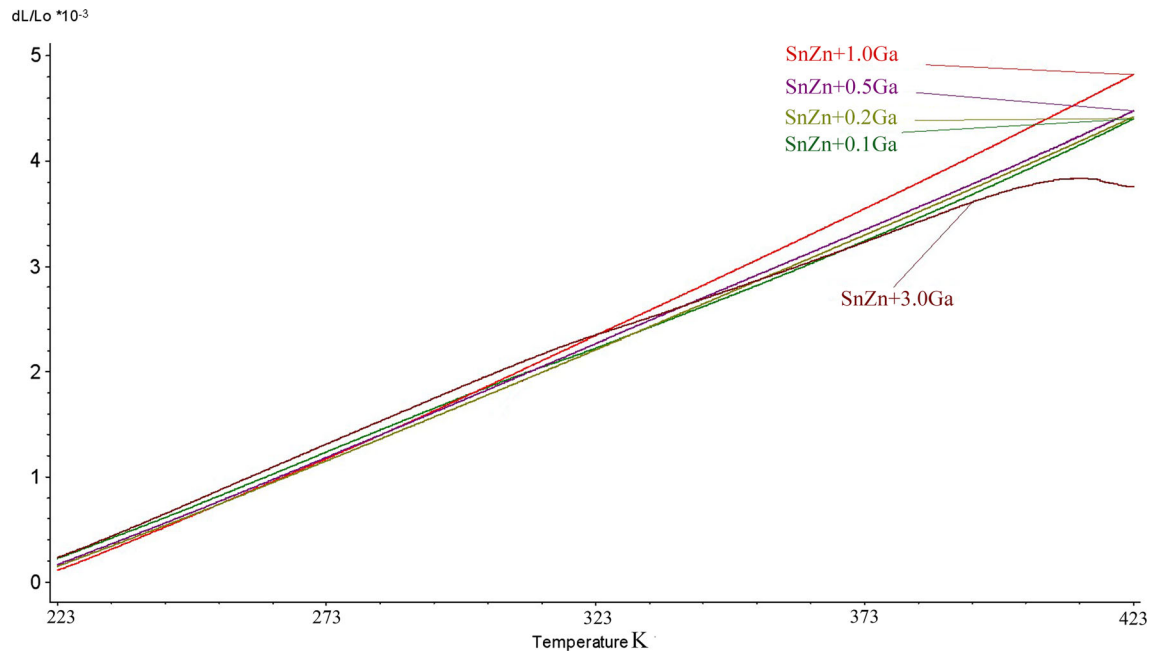


Fig. 6—The linear expansion for SnZn alloys with Ga (Color figure online).

Table III. CTE Parameters of SnZn with Ga Alloys

Composition	Temperature Range [K (°C)]	CTE, 10^{-6} K^{-1}
SnZn _E ^[16]	223 K to 473 K (−50 °C to 200 °C)	20.88
SnZn + 0.1Ga	223 K to 473 K (−50 °C to 200 °C)	20.88
SnZn + 0.2Ga	223 K to 473 K (−50 °C to 200 °C)	20.90
SnZn + 0.5Ga	223 K to 473 K (−50 °C to 200 °C)	21.55
SnZn + 1.0Ga	223 K to 473 K (−50 °C to 200 °C)	23.55
SnZn + 3.0Ga	223 K to 323 K (−50 °C to 200 °C)	21.43

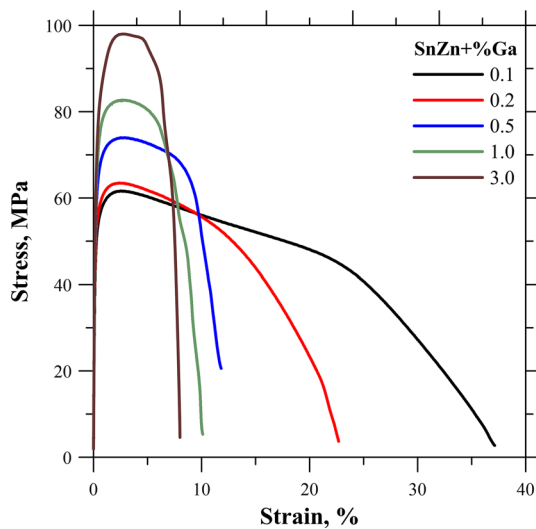


Fig. 7—Mechanical properties of SnZn with Ga addition for the strain–stress curves (Color figure online).

Table IV. The Tensile Strength and Elongation Values of SnZn with (Weight Percent) Ga

Alloys	$R_{p0.2}$ (MPa)	R_m (MPa)	$A_{5,65}$ (Pct)
SnZn0.1Ga	51.9	60.8	37.5
SnZn0.2Ga	55.6	65.4	27.8
SnZn0.5Ga	56.9	73.9	16.8
SnZn1.0Ga	68.4	82.4	11.9
SnZn3.0Ga	74.7	98.5	9.8

ACKNOWLEDGMENT

This work was financed by the National Science Centre Poland grant 2013/09/D/ST8/03991 “Physico-chemical properties of SnZn + X (X = Ga, Na) alloys” in the year 2014 to 2017.

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