Control of Electrical and Thermal Properties by 8 vol% Al_2O_3 Distribution States in Zn–50Sn for AC-Low Voltage Fuses

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The addition of 8 vol% Al_2O_3 in Zn–50 mass%Sn, was carried out for the control of electrical and thermal properties, for Pb-free fuse elements used in electric power line. The distribution-control of Al_2O_3 particles in Zn–50Sn was carried out by the varying process parameters such as the temperature and period for Al_2O_3 -addition and -stir in its melt or semi-solid. Homogeneous and heterogeneous Al_2O_3 -distributions were achieved in microstructure consisting of primary Zn and eutectic, which meant the location of Al_2O_3 in both regions and only eutectic in constituent phases, respectively. The temperature dependence of specific resistivity, thermal conductivity, specific heat and density was measured for electrical and thermal calculations to obtain the temperature distribution in fuses. The values on their properties were determined depending on Al_2O_3 distributed states in alloys. Both the melt and un-melt down performance for AC-low voltage fuse elements could be satisfied on both Zn–50Sn alloys with different distribution of Al_2O_3 , and the superior performance was shown in the homogeneously Al_2O_3 distributed alloy.
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1. Introduction

Lead and its alloys or compounds are considered environmental hazards because of lead's toxicity therefore many countries are going to ban their use.^{1,2)} The practical Pb–Sn alloys used as solders in electrical and electronic industries are classified into two groups (Pb–5 mass%Sn and Pb–60 mass%Sn) by their melting temperatures. The Sn–40Pb system alloys have been also used as AC-low voltage fuse elements in electric power line.^{3,4)} Due to the world-wide legislative requirements,^{5,6)} it is important to develop viable alternative Pb-free alloys for AC-fuse elements used in electric power line. The main requirements for alternative fusible alloys are:

- (1) Low melting point: The melting points should be comparable to practical Sn–Pb system alloys.
- (2) Availability: There should be adequate supplies or reserves available of candidate metals.
- (3) Ability of manufacture: The production of raw materials should not be difficult.

The Sn–9Zn alloy has been investigated in our previous study as a Pb-free alloy for low-voltage fuse elements, except for the points of its performance in a break at high value (3000 A) in electric current, weather proof and wettability on copper.^{3,4,7)} In contrast, since an eutectic point (471 K) of Sn–Zn system alloys is similar to that (456 K) of the practically used Sn–40Pb, it has been also considered by other investigators as a candidate alloy system for a lead-free solder material.^{8,9)} The Sn–Zn eutectic system which is basically classified as an anomalous eutectic alloy has a broken-lamellar type eutectic structure.¹⁰⁾ The faceting lamellas are Zn and the non-faceting phase is the Sn solid solution. Under rapid cooling conditions, the lamellar Zn becomes fibrous,^{10,11)} which means the sensitivity to solidifying conditions. It is considered that electrical and thermal conductivity of Sn–Zn eutectic system alloys are difficult to

be estimated using Maxwell¹²⁾ and Landauer¹³⁾ models, because those properties are directly influenced by morphology of each phase in them as described in Fan's model.¹⁴⁾ Also in our proposed estimations,¹⁵⁾ not only volume fraction of pure Zn and Sn-solid solution containing Zn of less than 1 mass%¹⁶⁾ but morphologies of both phases were considered in Sn–Zn alloys, which led to excellent estimation for their electrical and thermal properties as the function of the composition and temperature.¹⁵⁾ For instance, both primary Zn and eutectic were observed as the continuous phases in Sn–50Zn alloy,¹⁵⁾ which led to the same microstructural consideration between both Sn–50Zn and Zn–50Sn alloys with same continuous phases and their amount, according to the compositional ranges classified from the standpoint of continuity or non-continuity of constituent phases.

The dependence of solidifying conditions on microstructural morphologies such as eutectic structures are greater as the eutectic amount increases in Sn–Zn system alloys. It is considered that Zn-rich Sn–Zn alloys show a little of change in solidified microstructures because of the small amount of eutectic, compared with a eutectic composition of Sn–9Zn which has variously solidified ones due to high sensitivity to manufacturing conditions.

Optimization of fuse elements is carried out by both methods of their alloy- and shape-design. In the shape-design, temperature distributions in the fuse element-connector-electric wire system, have to be exactly known in some conditions evaluating the main requirements (period showing melt or un-melt down and temperature increment at fixed current flow conditions) for AC-low voltage fuse elements.⁷⁾ The period for melt down of fuse elements increased on Zn-rich alloys, or the melt down could not be achieved less than the control period, because of small amount of heat generation due to small value of the specific resistivity (Sn–9Zn: 12.1, Zn–50Sn: 9.7, Sn–37Pb: 17.0 $\mu\Omega\text{cm}$).¹⁵⁾ The values of thermal diffusivity are

Fig. 1 Schematic drawing of (a) the handling for different Al_2O_3 distribution in constituent phases and (b) the split-die made of carbon steel used in this study, showing initial position of Al_2O_3 particles for their heterogeneous distribution. Units are given in millimeters in (b).

4.3×10^{-5} , 4.4×10^{-5} and $2.6 \times 10^{-5} \text{ m}^2/\text{s}$ in Sn–9Zn, Zn–50Sn and Sn–37Pb, respectively, which means almost its same value in both Sn–Zn alloys. In contrast, the control period for un-melt down becomes to be sufficient in Zn-rich alloys, compared with Sn–9Zn. Therefore, there is the reciprocal relation between melt and un-melt down performance for the fuse elements, and both electrical and thermal properties must be controlled for the practical application. It is reported that the microstructural, electrical and thermal properties of Sn–50Zn were controlled by addition of 8 vol% Al_2O_3 with high melting point, high and low values in specific resistivity and thermal diffusivity, respectively.¹⁷⁾ Microstructural characteristics of Sn–50Zn as the metal matrix were same to those of Zn–50Sn alloy, as described above. In this alloy, the Al_2O_3 particles were located only in the eutectic region with low melting point. Their properties might be controlled by the variation of location of Al_2O_3 particles in the Zn–50Sn–8 vol% Al_2O_3 microstructure.

This study aimed to measure the temperature dependence of electrical and thermal properties on Zn–50Sn alloys with different Al_2O_3 distribution states, in order to control their properties for the development of lead-free fuse elements used in electric power line.

2. Experimental Procedures

2.1 Preparation of samples

Pure Zn with the purity of 99.9% and pure Sn with the purity of 99.9% were weighed according to the nominal compositions of Zn–50 mass%Sn alloy as master ingots. The costs were 2922 and 180 yen/kg in Sn and Zn, respectively, in May 2013 in Japan. They were melted in a graphite crucible in air. Molten metals were held for 1.2 ks at temperatures which were 100 K higher than the liquidus temperature, as shown ① in Fig. 1. Zn–50Sn microstructure shows the continuity for constituent phases of both primary Zn and eutectic,¹⁵⁾ as described in section 3.1. It was tried for the achievement of homogeneous or heterogeneous distribu-

tions of Al_2O_3 in alloys, that its particles were located in both regions of primary Zn and eutectic, or only eutectic in their microstructures, respectively. The homogeneously Al_2O_3 distributed alloy was prepared as follows: (1) The stir of Al_2O_3 with the 50 μm diameter in Zn–50Sn melt in graphite crucible at or above the liquidus temperature, for heterogeneous nucleation of primary Zn on Al_2O_3 surfaces, shown ② in Fig. 1. (2) After pouring the melt with Al_2O_3 and primary Zn nucleuses in the cylindrical mold kept at 603 K, the stir of Al_2O_3 in semi-solid of primary Zn for 40 s below the liquidus temperature, for the presence of Al_2O_3 in the eutectic region by trap of its particles among primary Zn crystals, shown ③ and ④ in Fig. 1. In contrast, the heterogeneously Al_2O_3 distributed alloy was prepared as follows: (1) After ① in Fig. 1, the pouring of Zn–50Sn melt without Al_2O_3 and with primary Zn nucleuses in the mold, for nucleation and growth of primary Zn below liquidus temperature. 8 vol% Al_2O_3 particles were set at the bottom part in the hot mold with the inner diameter of 22 mm and height of 121 mm, as shown in Fig. 1(b), shown ③ in Fig. 1. (2) The stir of Al_2O_3 in semi-solid state of primary Zn for 40 s after the pouring the melt, for the presence of Al_2O_3 just in the eutectic region by trap of its particles among primary Zn crystals, shown ④ in Fig. 1. The used spherical Al_2O_3 particles with 50 μm diameter were supplied by Showa Denko K.K., which characteristics were CB-A50, ZCD and 4000 yen/kg in the grade, Lot number and cost in September 2013, respectively. Further, the mold for Sn–9Zn reference and Zn–50Sn master ingots had the inner diameter of 15 mm and height of 116 mm, which lead to the faster cooling rate of their ingots, compared with that of Zn–50Sn–8 vol% Al_2O_3 . Their microstructural observation was carried out using an optical microscope and scanning electron microscope.

2.2 Measurement of physical properties

The specific resistivity (ρ_e) was simultaneously measured from 293 K to about 470 K by the standard four probe DC-method in air using a computer-controlled equipment. The

Fig. 2 (a) The construction of a fuse box. (b) The schematic illustrations showing the size of the copper wire, copper connector and Sn–Zn–Al₂O₃ fuse element in the fuse element-connector-electric wire system for simulation. Units are given in millimeters.

size of samples was 1 mm × 1 mm × 17 mm. The temperature gradient along the length (17 mm) of samples for the measurement of ρ_e was about 5 K. The thermal conductivity (λ) was measured from 293 to 460 K using samples with the diameter of 11 mm and length of 50 mm, under the steady-state condition in air. The construction of a Zn–Sn sample, copper heating rod with a cartridge heater and cooling plate and detail procedure were early reported for measurement of the heat conduction.¹⁵⁾ The specific heat (c_p) was measured from 293 K to about 470 K at the rate of 2 K/min, using samples with the diameter of 5 mm and thickness of 2 mm in a nitrogen stream, by the differential scanning calorimetry. Density (ρ) measurement using a high density liquid was performed at various temperatures in the range of 293–360 K by Archimedes' method.

2.3 Model for electrical and thermal calculations

The schematic illustration showing the assembly of some parts in a practically used fuse box⁴⁾ is shown in Fig. 2(a). The fuse box consisted of a fuse element, copper connector, copper sleeve, cover, case and vinyl coated electric copper wire with a diameter of 3.2 mm.^{4,7)} For AC-low voltage fuses used in electric power line, both main requirements are the melt down of a fuse element to the period less than 600 s at 99 A, and its un-melt down for 3 s at 210 A after current discharge of 72 A.^{3,4)} The values of 72 and 99 A correspond to 130 and 180% of a rated current, respectively. The assembly of the Zn–50Sn–8 vol%Al₂O₃ fuse element, copper connector and electric copper wire, and the size of each

object used in this calculation are shown in Fig. 2(b). A three-dimensional Cartesian coordinate system was used in the fuse element-connector-electric wire system. The governing equations are based on Ohm's and Fourier's laws for electrical and thermal analyses, which can be written as following eqs. (1) and (2), respectively,

$$\rho_e c_e \frac{\partial E}{\partial t} = \frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + \frac{\partial^2 E}{\partial z^2} = 0 \quad (1)$$

where ρ_e , c_e , E and t represented the specific resistivity, capacitance, voltage and time, respectively,

$$\rho c_p \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + Q \quad (2)$$

where T and Q represented the temperature and amount of heat generation per 1 s, respectively. Q and the governing equation for boundary mesh points such as the fuse element/connector, were described in the early report.¹⁵⁾ The finite difference method, FDM, was used to solve the above equations for voltage and temperature as a function of time and position.

3. Results and Discussion

3.1 Microstructures

The λ and ρ_e have been estimated with good accuracy, in application of the compositional ranges classified from the standpoint of continuity or non-continuity of constituent phases such as the primary Zn, Sn-solid solution and eutectic in microstructures of Sn–1 to 100Zn alloys.¹⁵⁾ Different size of each phase among proposed and reference alloys was shown by the different cooling rates depending on the mold-size as described in section 2.1. It is considered that the effect of the phase-sizes on microstructures on the λ and ρ_e is small at same condition for the continuity and volume fraction of constituent phases.

The microstructures of as-cast state on the homogeneously and heterogeneously Al₂O₃ distributed Zn–50Sn alloys and reference alloys are shown in Fig. 3. The master ingot of Zn–50Sn showed a microstructure consisting of two grains which were a primary Zn and eutectic of both Sn-solid solution and pure Zn, as shown in Fig. 3(c). Both the eutectic and primary Zn were continuously present in the master ingot. In contrast, the metal matrix of both different Al₂O₃ distributed Zn–50Sn alloys, showed the microstructure as well as the Zn–50Sn master ingot, although their grains were coarser than the master ingot because of long holding at the handling temperature and the slower cooling rate, as shown in Figs. 3(a) to 3(c). For the heterogeneously Al₂O₃ distributed alloy, Al₂O₃ particles were randomly dispersed in the interdendrite regions consisting of eutectic by a trap of Al₂O₃ particles among primary Zn. In contrast, for the homogeneously Al₂O₃ distributed alloy, Al₂O₃ particles were randomly dispersed in both primary Zn and eutectic, because Al₂O₃ particles acted as sites of nucleation of primary Zn and were also trapped among primary crystals, respectively. Both homogeneously and heterogeneously Al₂O₃ distribution in Zn–50Sn alloys were achieved by the selection of the temperatures and period of Al₂O₃-addition and -stir in the melt or semi-solid of Zn–50Sn, as shown in Fig. 1.

Fig. 3 The microstructures of as-cast ingots for (a) heterogeneously, (b) homogeneously Al_2O_3 distributed Sn-50Zn, (c) Sn-50Zn and (d) Sn-9Zn alloys. Where, the upper right corner in (a) shows the high magnification of eutectic consisting of Zn and Sn.

In contrast, the microstructure of the Sn-9Zn reference alloy showed a typical Sn-Zn eutectic structure with the light contrast Sn-solid solution and the dark contrast Zn phases which were formed alternately. Sn-9Zn was also considered to be a two phase material consisting of pure Zn and Sn-solid solution with Zn of less than 1 mass%, and Sn-solid solution phase was continuous one in this alloy.

3.2 Specific resistivity

The ρ_e of Al_2O_3 -distribution controlled Zn-Sn-8 vol% Al_2O_3 , Zn-50Sn and Sn-9Zn alloys was measured at various temperatures in the range of 293–470 K. Figure 4 shows the temperature, Al_2O_3 distribution and compositional dependence of the ρ_e . In this figure, 4 straight lines approximated by a least squares method using experimental values of ρ_e for each alloy mean the qualitative tendency of its change. As can be seen in the figure, the ρ_e increased monotonously with increasing temperature, regardless of Al_2O_3 distribution states and Zn content in alloys. The values of ρ_e also 4–6% increased even at same temperatures on the homogeneously Al_2O_3 distributed alloy, compared with heterogeneously one. Below the eutectic point (471 K) for homogeneously and heterogeneously Al_2O_3 distributed alloys, the ρ_e is roughly represented as the functions of the temperature using eqs. (3) and (4), respectively,

$$\rho_{e\text{-homo}} = 5.90 \times 10^{-2} \text{ Temp.} - 3.02 \quad (3)$$

$$\rho_{e\text{-hetero}} = 5.82 \times 10^{-2} \text{ Temp.} - 3.57 \quad (4)$$

where, Temp. represents the temperature.

Fig. 4 Specific resistivity measured in this study for the heterogeneously and homogeneously Al_2O_3 distributed Sn-50Zn, Sn-50Zn and Sn-9Zn alloys.

In contrast, eq. (5) is presented for Zn-50Sn without Al_2O_3 addition.

$$\rho_e = 3.80 \times 10^{-2} \text{ Temp.} - 1.40 \quad (5)$$

The temperature dependence of the ρ_e was increased by the Al_2O_3 addition in alloys.

In previous report,¹⁵⁾ ρ_e and λ could be estimated exactly in the standpoint of continuity or non-continuity of constituent phases in microstructures of alloys. Both the eutectic and primary Zn were continuously present in Zn-50Sn alloy as shown in Fig. 3. Therefore, it is considered that the electric

Fig. 5 Thermal conductivity measured in this study for the heterogeneously and homogeneously Al₂O₃ distributed Sn–50Zn, Sn–50Zn and Sn–9Zn alloys.

current flows via only one phase having higher electric conductivity, if the other phase is an insulator. In the heterogeneously Al₂O₃ distributed alloy, the electric current flows fast via the primary Zn phase without Al₂O₃ particles showing the low value in the ρ_e , compared with the eutectic region with Al₂O₃ showing higher one. It is found that the heterogeneously Al₂O₃ distributed alloy having the primary Zn-region without Al₂O₃ particles, showed lower ρ_e , compared with the homogeneously one having both Al₂O₃ distributed regions.

3.3 Thermal conductivity

The λ of Al₂O₃-distribution controlled Zn–Sn–8 vol% Al₂O₃, Zn–50Sn and Sn–9Zn alloys was measured at various temperatures in the range of 293–460 K. Figure 5 shows the temperature dependence of the λ , and the tendency of its change using 4 lines in the same manner with Fig. 4. As can be seen in this figure, the λ decreased monotonously with increasing temperature, regardless of Al₂O₃ distribution state and Zn content in alloys. The values of λ also approximately 4%-decreased even at same temperatures on the homogeneously Al₂O₃ distributed alloy, compared with heterogeneously one in the same manner with the ρ_e . Below the eutectic point (471 K) for homogeneously and heterogeneously Al₂O₃ distributed alloys, the λ is roughly represented as the functions of the temperature using eqs. (6) and (7), respectively,

$$\lambda_{\text{homo}} = -9.00 \times 10^{-2} \text{ Temp.} + 110.71 \quad (6)$$

$$\lambda_{\text{hetero}} = -8.62 \times 10^{-2} \text{ Temp.} + 111.51 \quad (7)$$

The change of the λ can be explained in the same reason with that of the ρ_e , between both different Al₂O₃ distributed alloys.

3.4 Specific heat

The c_p of Al₂O₃-distribution controlled Zn–Sn–8 vol% Al₂O₃, Zn–50Sn and Sn–9Zn alloys was measured at various temperatures in the range of 293–460 K. Figure 6 shows the temperature dependence of the c_p , and the tendency of its change using 3 lines in the same manner with Fig. 4. As can be seen in this figure, the c_p increased monotonously with increasing temperature, regardless of Al₂O₃ distribution state

Fig. 6 Specific heat measured in this study for the heterogeneously and homogeneously Al₂O₃ distributed Sn–50Zn, Sn–50Zn and Sn–9Zn alloys.

Fig. 7 Density measured in this study for the heterogeneously and homogeneously Al₂O₃ distributed Sn–50Zn, Sn–50Zn and Sn–9Zn alloys.

and Zn content in alloys. The c_p also decreased and increased even at same temperatures as the Sn and Al₂O₃ contents increased in alloys, respectively. Below the eutectic point (471 K) for both homogeneously and heterogeneously Al₂O₃ distributed alloys, the c_p is roughly represented as the functions of the temperature using same eq. (8),

$$c_{p-\text{Al}_2\text{O}_3} = 2.00 \times 10^{-4} \text{ Temp.} + 0.26 \quad (8)$$

There is same temperature-dependence of the c_p between both alloys with different Al₂O₃ distribution, because the microstructure dependability of c_p is low due to non-conductivity of heat, compared with the ρ_e , and λ showing the conductivity of electricity and heat.

3.5 Density

The ρ of Al₂O₃-distribution controlled Zn–Sn–8 vol% Al₂O₃, Zn–50Sn and Sn–9Zn alloys was measured at various temperatures in the range of 293–360 K, according to Archimedes' principle. Figure 7 shows the temperature dependence of the ρ , and the tendency of its change using 3 lines in the same manner with Fig. 4. As can be seen in this figure, the ρ on all alloys decreased somewhat in this temperature range, regardless of Al₂O₃ distribution state and Zn content in alloys. The ρ also increased and decreased even at same temperatures as the Sn and Al₂O₃ contents increased

Table 1 Some properties at 293 and 470 K of the heterogeneously and homogeneously Al₂O₃ distributed Zn–50Sn and Zn–50Sn alloys.

Alloys		Homogeneously located Al ₂ O ₃ in Zn–50Sn	Heterogeneously located Al ₂ O ₃ in Zn–50Sn	Zn–50Sn
ρ_e ($\mu\Omega\cdot\text{cm}$)	293 K	14.27	13.48	9.73
	470 K	24.89	23.96	16.57
λ ($\text{W m}^{-1}\text{K}^{-1}$)	293 K	83.2	86.25	96.18
	470 K	67.69	70.74	80.72
c_p ($\text{kJ kg}^{-1}\text{K}^{-1}$)	293 K	0.3192	0.3192	0.3042
	470 K	0.3552	0.3552	0.3409
ρ (g cm^{-3})	293 K	6.81	6.81	7.19
	470 K	6.70	6.70	7.11
$\alpha \times 10^{-6}$ (m^2s^{-1})	293 K	38.28	39.68	43.98
	470 K	28.45	29.73	33.28

in alloys, respectively. Below the eutectic point (471 K) for both homogeneously and heterogeneously Al₂O₃ distributed alloys, the ρ is roughly represented as the functions of the temperature using same eq. (9),

$$\rho_{\text{Al}_2\text{O}_3} = -6.17 \times 10^{-4} \text{ Temp.} + 6.99 \quad (9)$$

Same temperature dependency of the ρ between both different Al₂O₃ distributed alloys showed due to the same reason with that of the c_p .

3.6 Comparison in thermal diffusivity and electric resistivity

The values of ρ_e , λ , c_p and ρ can be generally represented on homogeneously and heterogeneously Al₂O₃ distributed Zn–50Sn alloys, using the eqs. (3), (4), (6), (7), (8), (9) as the function of the temperature. The ρ_e , λ , c_p and ρ measured at 293 and 470 K for both Zn–50Sn–8 vol%Al₂O₃ alloys, are listed in Table 1. Their values of Zn–50Sn alloy¹⁷⁾ are also listed in this table, as reference. Thermal diffusivity (α) determined by eq. (10), was obtained using values of the λ , c_p and ρ , for evaluation of heat-conduction as one requirement for fuse elements.

$$\alpha = \lambda / (\rho \cdot c_p) \quad (10)$$

The values of the thermal diffusivity at 293 and 470 K for the homogeneously Al₂O₃ distributed Zn–50Sn alloy are 3.7–4.5% smaller than those of the heterogeneously one, which leads to the reject for the requirement of un-melt down more than 3 s at 210 A and the satisfaction for the requirement of melt-down less than 600 s at 99 A, due to the lower speed for the achievement to the thermally equilibrium state. In contrast, the values in ρ_e at 293 and 470 K for the homogeneously Al₂O₃ distributed Zn–50Sn alloy are 3.9–5.9% higher, compared with those of the heterogeneously one, which leads to the satisfaction and reject for both requirement of the melt down and un-melt down, respectively, due to larger amount of Joule's heat generation. The temperature-increment per unit time at the center of the fuse element, is decided by the balance between the heat generation and heat conduction amount throughout the fuse element-connector-electric wire system, under 3 dimensionally heterogeneous heat release in air. Therefore, it can be

confirmed by electrical and thermal calculations as mentioned below section 3.7, that both critical periods more than 3 s and less than 600 s for the un-melt and melt down performance at 210 and 99 A, respectively, are satisfied or not on both Zn–50Sn–8 vol%Al₂O₃ alloys.

3.7 Temperature simulation under the constant current discharge of both 99 and 210 A

3.7.1 The constant current discharge of 99 A for the performance of melt down

For AC-low voltage fuses used in electric power line, the fuse element with the diameter of 2.5 mm and length of 10 mm in the smaller diameter part has been designed for the fuse element-connector-electric wire system, as shown in Fig. 2.⁴⁾ Figures 4–7 also shows the parameters as the function of temperature, used for the electrical and thermal calculations. The voltage and temperature were calculated using eqs. (1) and (2), respectively. The electric current of 99 A was discharged from the edge surface of the copper electric wire to another one, as shown in Fig. 2. The current density on the edge surface of the electric wire was 12.3 A/mm² at room temperature. For instance, the measured value in the total electrical resistance was 706 $\mu\Omega$ throughout the fuse element-connector-electric wire system. The time step was 0.0001 s in temperature calculations. The largest heat source or the maximum value of the temperatures throughout the used system was shown at the center in the smaller diameter part of fuse elements.⁷⁾

The change in calculated temperature at the center of fuse elements with the diameter of 2.5 mm and length of 10 mm in their smaller diameter parts, is shown in Fig. 8, for three Zn–50Sn system alloys with and without Al₂O₃ additions. The result obtained from the practical used Sn–38Pb alloy is also shown in this figure. The temperature rose to the eutectic ones as the time increased, for fuse elements made of three alloys, except for Zn–50Sn. The temperature in fuse elements made of the homogeneously and heterogeneously Al₂O₃ distributed alloys increased to the eutectic temperature for the periods of 250 and 525 s, respectively. This result can be easily explained on the basis of the different values between thermal diffusivity and specific resistivity for both alloys, as listed in Table 1. In this paper, for convenience, it is assumed

Fig. 8 The relation between the temperature and time obtained from the calculations under the constant current flow of 99 A at the center in fuse elements made of the heterogeneously and homogeneously Al_2O_3 distributed Sn-50Zn, Sn-50Zn and Sn-38Pb alloys. Sample has the diameter (d) of 2.5 mm and length (l) of 10 mm in the smaller diameter part.

that the melt down of fuse elements was caused at their eutectic temperatures. The melt down on the fuse elements after both periods (250 and 525 s) led to the satisfaction of the time limit (less than 600 s) at the melt down examination at 99 A. In contrast, the rate of increase in the temperature decreased with increasing the period in current flow, and the saturated value of the temperature under this condition was shown below the melting temperature, as the current discharge time increased even to 600 s for the Zn-50Sn element under this condition. It is clear that the performance of melt down was satisfied on the both Al_2O_3 distributed samples with practically used fuse size⁴⁾ as shown in Fig. 2, although the temperature distribution through fuse elements can be varied even by change in their sizes.

Figure 9 shows the calculated isothermal contours in the y - z section obtained from the smaller diameter part of fuse. The temperature distribution of three Zn-50Sn system alloys with and without Al_2O_3 additions, showed symmetry with respect to y or z axes, regardless of kinds of fuse elements. The temperature distribution was almost unchanged in the y -direction. The largest heat source or the maximum value of the calculated temperature was shown at the center in the smaller diameter part of fuse elements, and the shape of its distribution was unchanged depending on kinds of alloys. The heterogeneously in temperature or a little deviation from the constant distribution in the y -direction was developed by the two step cylindrical shape of fuse elements. The heat flow was mainly caused from the center to the both edges in the fuse elements. The Zn-50Sn alloy showed maximum temperature of 408 K (65 K-lower than eutectic point, 473 K) and temperature difference of 4 K throughout the smaller diameter parts in fuses, which corresponded to the steady state in temperature curve, as shown in Fig. 8. This meant the achievement of heat balance by the saturation between three dimensional heat-generation and -release depending on the small and large values in specific resistivity and thermal diffusivity at 99 A discharge in air, as listed in Table 1. In contrast, the temperature showing eutectic point was achieved even at unsteady state in temperature curves on the

Fig. 9 Calculated isothermal contours in the y - z plane after the current flow periods ((a) 600, (b) 525, (c) 250 s) showing temperatures near eutectic point at the center of the fuse element made of (a) Sn-50Zn, (b) heterogeneously and (c) homogeneously Al_2O_3 distributed alloys under the current discharge of 99 A. Units in temperatures are given in Kelvins.

homogeneously Al_2O_3 distributed Zn-50Sn alloy, because of larger and smaller values in the specific resistivity and thermal diffusivity, compared with other both Zn-50Sn system alloys. This alloy showed the faster arrival to eutectic point for 250 s and smaller temperature difference via fuse of 33 K, compared with those for 525 s and of 41 K on the heterogeneously one showing roughly steady state in the temperature curve. This difference between both Al_2O_3 containing alloys, was caused by the different values in their thermal diffusivity and specific resistivity between both alloys, as listed in Table 1. These thermal and electrical properties could be controlled by the decision of distribution state of spherical Al_2O_3 particles in both constituent phases in Zn-50Sn, on the basis of the suitable selection in the temperature and period of Al_2O_3 -addition and -stir in the melt or semi-solid of Zn-50Sn.

3.7.2 The constant current flow of 210 A after discharge of 72 A for the performance of un-melt down

The electric current of 72 A was firstly discharged from the edge surface of the copper electric wire to another one, according to performance examination for the un-melt down. The current density on the edge surface of the electric wire was 8.95 and 29.4 A/mm² at 72 and 210 A, respectively, at room temperature.

The change in calculated temperature at the center of fuse elements with respect to current discharge time at a constant current discharge of 72 and 210 A is shown in Fig. 10 for the Zn-50Sn system alloys with and without Al_2O_3 . The saturated values in the temperature were also shown after the current discharge for 360–700 s at 72 A in the calculation,⁷⁾ although the constant current of 72 A was discharged via fuse elements for 1 ks in the practical experiments.⁴⁾ The constant current of 210 A was discharged via the fuse element-connector-electric wire system after the current discharge of 72 A for 700 s, in the potential and thermal calculations. The temperature at the center of fuse elements made of the homogeneously and heterogeneously Al_2O_3 distributed alloys, reached to the eutectic temperature after the current discharge times for 3.1 and 4 s, respectively, at 210 A. However, it is considered in section 3.6 that the achievement

Fig. 10 The relation between the time and temperature at the center of fuse elements of the heterogeneously and homogeneously Al_2O_3 distributed Sn-50Zn and Sn-50Zn alloys, obtained from the calculations under the constant current flow of 72 and 210 A, for obtaining arrival periods to eutectic points at 210 A.

Fig. 11 Calculated isothermal contours in the y - z plane after the current flow periods (a) 4.0 s, (b) 3.1 s showing the eutectic point at the center of the fuse elements made of (a) heterogeneity and (b) homogeneously 8 vol% Al_2O_3 distributed alloys, under the current discharge of 210 A after the discharge of 72 A for 700 s. Units in temperatures are given in Kelvins.

of the un-melt down performance becomes to be difficult on the homogeneously Al_2O_3 distributed alloy because of the larger amount of heat generation due to higher value in ρ_e , compared with heterogeneously one, as shown in Fig. 4. The period more than 3 s for the un-melt down requirement at 210 A could be satisfied even on the homogeneously Al_2O_3 distributed alloy. Figure 11 shows the calculated isothermal contours in the y - z section obtained from the smaller diameter part of fuse. The both Al_2O_3 doped alloys showed the unsteady state in temperature curves under 210 A discharge, as shown in Fig. 10. The homogeneously Al_2O_3 distributed Zn-50Sn alloy showed the faster arrival to eutectic point for 3.1 s and smaller temperature difference via fuse of 12 K, compared with those for 4 s and of 31 K on the heterogeneously one, because of the smaller and larger values in the thermal diffusivity and specific resistivity. The effects of their values were larger on the temperature distribution under the

higher current of 210 A, than those under 99 A discharge, as shown in Figs. 9 and 11.

In the range between the liquidus and eutectic temperature, the presence of both the solid and liquid leads to satisfy the performance of un-melt down under the higher fixed value (210 A) of electric current as one of main requirements for fuse elements,^{3,4)} compared with the Sn-9Zn and Sn-38Pb alloys of eutectic compositions, even in the point of the post-reach of temperature in fuse elements to eutectic one. This is supported by the microstructural characteristic of Zn-50Sn-8 vol% Al_2O_3 which means the presence of the primary Zn phase having the large amount and coarse size, as shown in Figs. 3(a) and 3(b). The melting point of the primary Zn phase is higher than one in the eutectic consisting of fine Zn and Sn solid solution phases.

3.8 Effects of microstructural control by Al_2O_3 in solidification process

The control of electrical and thermal properties was successfully carried out by the decision of distribution states of Al_2O_3 particles in constituent phases on the Zn-50Sn alloy, for lead-free fuse elements used in electric power line, which led to the control of their properties in wide range by compositional and distributional variations of metal matrix and Al_2O_3 for some applications as practical fuses.

It was reported that Sn-9Zn alloy showed the 4%-increase and 4%-decrease in λ and ρ_e , respectively, at the temperatures below the eutectic point, compared with those of Sn-20Zn alloy.¹⁵⁾ In other words, the effect of the 4%-increase and 4%-decrease in λ and ρ_e , respectively, for Sn-20Zn alloy, was caused by the 11%-increase of Sn content in the Sn-9Zn alloy. In contrast, same effect showing their 4%-variations was caused by the control of Al_2O_3 -distributed positions in the Zn-50Sn-8 vol% Al_2O_3 alloy, as described for comparison of their values in Figs. 4 and 5. The 11 mass% and 8 vol% (= 4.14 mass%) increase in Sn and Al_2O_3 contents in Sn-9Zn and Sn-50Zn alloys, leads to the high cost of approximately 415 and 184 yen per 1 kg, respectively, according to their costs described in section 2.1, which leads to the establishment of the strategic method for suppressing utilization of rare metals by the use of Al_2O_3 particles and their microstructural control in solidification process.

Further, it has been reported in the previous study¹⁸⁾ that the stability for performance of fuse elements in long time is kept even on specimens having the microstructural change at interface Sn-9Zn/Cu wire which was caused by diffusion under the condition of accelerated heat treatment at 443 K near the eutectic temperature for 7.2 ks. In contrast, long time stability must be evaluated in detail on the Al_2O_3 distribution controlled Zn-50Sn alloys.

4. Conclusions

- (1) For the metal matrix composite of the Zn-50Sn alloy and Al_2O_3 particles having the different densities and melting points, the control of Al_2O_3 distribution in its microstructure, could be successfully carried out by the selection of the suitable temperatures and periods of Al_2O_3 -addition and -stir in the melt or semi-solid of Zn-50Sn.

- (2) Specific resistivity and thermal conductivity increased and decreased in the temperature range to the eutectic temperature on the homogeneously Al₂O₃ distributed Zn–50Sn alloy, compared with heterogeneously one. This resulted from the low conductivity of electricity and heat due to presence of Al₂O₃ particles on both continuous phases for the homogeneously Al₂O₃ distributed alloy.
- (3) Specific heat and density showed the same values at temperatures to the eutectic point, on both alloys with different Al₂O₃ distributed states, because their properties were independent of microstructures due to non-conductivity of physical quantities such as the heat.
- (4) On the basis of electrical and thermal calculations, the temperature at the center of fuse elements made of the homogeneously and heterogeneously Al₂O₃ distributed Zn–50Sn alloys, reached to the melting temperature after the current discharge time of 3.1 and 4 s, respectively, at 210 A, after the current discharge of 72 A for 700 s. This result meant the satisfaction for the un-melt down performance of one requirement for AC-low voltage fuses used in electric power line. In contrast, the melt down of fuse element made of the homogeneously and heterogeneously Al₂O₃ distributed Zn–50Sn alloys, was caused after the current discharge time of 250 and 525 s, respectively, which meant the satisfaction of the time limit less than 600 s at 99 A, for its melt down performance.
- (5) The control of electrical and thermal properties could be successfully carried out by the control of distribution states of Al₂O₃ particles in constituent phases on the Zn–50Sn alloy, for lead-free fuse elements used in electric power line.

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