International Journal of Thermal Sciences 100 (2016) 1–9

Contents lists available at ScienceDirect

International Journal of Thermal Sciences

journal homepage: www.elsevier.com/locate/ijts

The measurements of electrical and thermal conductivity variations with temperature and phonon component of the thermal conductivity in Sn–Cd–Sb, Sn–In–Cu, Sn–Ag–Bi and Sn–Bi–Zn alloys

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ARTICLE INFO

Article history:
Received 29 April 2015
Received in revised form
2 September 2015
Accepted 4 September 2015
Available online 5 November 2015

Keywords:
Metals and alloys
Phonons
Thermoelectric
thermal analysis

ABSTRACT

The electrical and thermal conductivity variations with temperature for lead-free ternary solders, namely Sn-41.39 at.% Cd-6.69 at.% Sb, Sn-49 at.% In-1 at.% Cu, Sn-50 at.% Ag-10 at.% Bi and Sn-32 at.% Bi-3 at.% Zn alloys, were measured by the d.c. four-point probe method and radial heat flow apparatus, respectively. The contributions of electrons and phonons to the thermal conductivity were separately determined by using the measured values of the thermal and electrical conductivities obtained by the Wiedemann–Franz law in the lead-free ternary solders. The percentages of the phonon component of thermal conductivity were found to be in the range of 46–55%, 46–50%, 38–47% and 69–73% for Sn-41.39 at.% Cd-6.69 at.% Sb, Sn-49 at.% In-1 at.% Cu, Sn-50 at.% Ag-10 at.% Bi and Sn-32 at.% Bi-3 at.% Zn alloys at the ranges of 318–443 K temperature, respectively. The temperature coefficients (α) of electrical conductivity for the lead-free ternary solders were found to be 2.47×10^{-3}, 4.97×10^{-3}, 1.14×10^{-3} and 1.00×10^{-3} K^{-1}, respectively. The thermal conductivities of the solid phases at their melting temperature and the thermal temperature coefficients for the lead-free ternary solders were also found to be 47.72 ± 2.38, 68.57 ± 3.42, 73.52 ± 3.67, 37.53 ± 1.87 W/Km and 1.47×10^{-3}, 1.48×10^{-3}, 1.85×10^{-3} and 2.21×10^{-3} K^{-1}, respectively.

1. Introduction

Investigations of the thermal and electrical properties of alloys are important for many technological applications. In order to characterize and to test the performance and the stability of metallic alloys, electrical and thermal conductivities are essential physical quantities. In the literature, there is not much knowledge about the thermal and electrical properties of lead-free ternary solders. Thus, determining the thermal and electrical properties for lead-free ternary solders could be of great use to researchers and engineers [1].

Heat is carried by electrons, phonons, magnetic excitations, and sometimes photons in solids. The total thermal conductivity is the sum of the thermal conductivities of all energy carriers in a solid. The thermal conductivity of energy carriers can be shown as

$$K_{thermal} = \frac{1}{3}\sum_{j} C_j\, v_j\, l_j \quad (1)$$

where the subscript j demonstrates the kind of carriers. C_j is the the specific heat per unit volume, v_j is the velocity of the carrier and l_j is a mean free path.

Since the electrons and phonons in conductors are the main carriers of heat, the total thermal conductivity of the metal can be expressed as the sum of electron and phonon contributions.

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http://dx.doi.org/10.1016/j.ijthermalsci.2015.09.004
1290-0729/

$$K_{thermal} = K_e + K_{ph} \quad (2)$$

where K_e and K_{ph} are the contribution of electrons and phonons to the thermal conductivity, respectively [1].

In metals, which energy carriers transmit the most heat? The contribution of electrons is greater than that of phonons at all temperatures in pure metals. However in disordered alloys or in impure metals, the phonon contribution approaches the electronic contribution owing to the reducing of the electron mean free path [2]. The ratio of the electronic contribution of the thermal conductivity (K_e) to the electrical conductivity (σ) of a metal is expressed as the Wiedemann–Franz law, and this value is proportional to the temperature (T).

$$\frac{K_e}{\sigma} = LT \quad (3)$$

Theoretically, the proportionality constant L, known as the Lorenz number [2], is equal to

$$L = \frac{K}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.44 \times 10^{-8} W\Omega K^{-2} \quad (4)$$

As can be seen from Eqs. (2) and (3), the contribution of the electron or phonon components to the thermal conductivity can be individually determined from Eqs. (2) and (3) if the electrical conductivity and thermal conductivity of the materials are measured or known at a given temperature.

The main aim of the present work was to determine the phonon component of the thermal conductivity in ternary alloys. To do this, the variations of electrical and thermal conductivities with temperature in the lead-free ternary solders were measured by the four-point probe method and the radial heat flow method, respectively. By using the measured electrical conductivity (σ) value of the alloy, the electronic component of the thermal conductivity (K_e) can be calculated from the Wiedemann–Franz law for a given temperature. Then the phonon component of the thermal conductivity (K_{ph}) can be obtained from Eq. (2) by using the values of calculated K_e and measured $K_{thermal}$.

In the present study, Sn–Cd–Sb, Sn–In–Cu, Sn–Ag–Bi and Sn–Bi–Zn ternary alloys were chosen for measuring the electrical and thermal conductivities. What was the reason for choosing these ternary alloy systems? Since lead and lead-containing materials are very toxic and hazardous for the human body and the environment, the EU Directives on Waste Electrical and Electronic Equipment (WEEE) have forbidden the use of lead in selected electronic devices sold in the European market [3]. Consequently investigation of the properties of lead-free solders is crucial. A number of studies have also been focused on Sn based multicomponent alloys because tin is a reasonably cheap material compared to other alloying elements.

Sn–Sb solder, which contains a low amount of antimony, has good mechanical properties such as creep resistance and mechanical strength [4,5]. Cd has several unique and remarkable characteristics such as excellent resistance to corrosion, good electrical conductance, low melting point, and resistance to chemicals [6]. Therefore the Sn–Cd–Sb ternary alloy can be used in electronic applications because of its low cost, low melting temperature and wettability.

In general, materials which form solder alloys should have lower melting temperatures. Since indium has a low melting temperature it is usually preferred in solder applications. Thus the Sn–In–Cu ternary alloy system is a suitable candidate for lead–tin solders [7].

The Sn–Zn eutectic alloy is a good alternative for a lead-free solder alloy due to its low melting temperature (198 °C), perfect mechanical properties, low cost [8,9] and being harmless to human health and the environment. The Sn–Zn alloy can be used in electronic packaging but it is sensitive to oxidation and corrosion [10–12]. Sn–Bi–Zn and Sn–Bi–Ag which both contain Bi, are good candidates for lead-free solder alloys because these alloys have a low melting temperature and good wettability [13–17].

Thus, the first step of this work is to experimentally measure the variations of electrical and thermal conductivities with the temperature by the four-point probe and radial heat flow methods, respectively in Sn–Cd–Sb, Sn–In–Cu, Sn–Ag–Bi and Sn–Bi–Zn lead-free solders. The second step of the present work is to determine the phonon component of thermal conductivity for the same alloys.

2. Experimental procedure

2.1. Sample production

Sn-41.39 at.% Cd-6.69 at.% Sb, Sn-49 at.% In-1 at.% Cu, Sn-50 at.% Ag-10 at.% Bi and Sn-32 at.% Bi-3 at.% Zn were melted in a vacuum furnace. The purity of all the metals used in the preparation of alloys in the present work was more than 99.9%. After stirring, the molten metal was poured into a graphite crucible in a hot filling furnace. Two different graphite crucibles were used for the experimental measurement of electrical and thermal conductivity. For electrical conductivity measurements, the crucibles were prepared from graphite and were 20 mm in length and 4 mm in diameter. For thermal conductivity measurement, the crucibles were prepared from graphite and were approximately 100 mm in length and 30 mm in diameter. The molten material in the graphite crucible was then directionally solidified from the bottom to the top. More details of the apparatus and experimental procedures are given in Refs. [18,19].

2.2. Measurement of electrical conductivity variation with temperature

Electrical conductivity is an imperative physical property. Impurities deform the lattice in metals and can affect the properties of electrical conductivity/resistivity. The value of electrical conductivity is also affected by grain size, plastic deformation, heat treatment, and some other factors, but to a smaller extent compared to the effect of temperature and chemical composition [20].

Atoms vibrate at all temperatures in the balance positions and the amplitude of the vibrations increases by increasing the temperature of the sample. When the atoms leave from their lattice, vacancies occur in the crystal structure [21]. If the dislocation density increases in the crystal lattice, the possibility of deviation in the electron waves increases, phonon–phonon, electron–electron and phonon–electron inelastic collisions increase, the mean free path decreases, resistance increases and electrical conductivity decreases. These defects may be dislocations, in the corners of the blank lattice, grain boundaries, and substituted atoms [22]. These mechanisms, which depend on composition and temperature, can decrease the electrical conductivity. In metals, electrical conductivity decreases with increasing temperature. The temperature dependency of electrical conductivity can be expressed as

$$\sigma(T) = \sigma_0[1 + \alpha(T - T_0)] \quad (5)$$

where, α is the temperature coefficient of electrical conductivity, T_0 is a fixed reference temperature (usually room temperature), and σ_0 is the conductivity at temperature T_0. Then we can obtain the temperature coefficient of electrical conductivity α from Eq. (5).