Available online at www.sciencedirect.com

SciVerse ScienceDirect

Acta Materialia 61 (2013) 1525–1536

Acta MATERIALIA

www.elsevier.com/locate/actamat

The Wiedemann–Franz–Lorenz relation for lead-free solder and intermetallic materials

Yao Yao [a,*], Jared Fry [b], Morris E. Fine [b], Leon M. Keer [c]

[a] *School of Mechanics, Civil Engineering and Architecture, Northwestern Polytechnical University, Xi'an 710072, People's Republic of China*
[b] *Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive, Evanston, IL 60208, USA*
[c] *Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208, USA*

Received 26 June 2012; received in revised form 18 November 2012; accepted 18 November 2012
Available online 19 December 2012

Abstract

Lead-free solders are replacing lead-rich solders in the electronics industry. Due to the limitation of available experimental data for thermal conductivity of lead-free solder and intermetallic compound (IMC) materials, the Wiedemann–Franz–Lorenz (WFL) relation is presented in this paper as a possible solution to predict thermal conductivity with known electrical conductivity. The method is based upon the fact that heat and electrical transport both involve free electrons. The thermal and electrical conductivities of Cu, Ni, Sn and different Sn-rich lead-free solder and IMC materials are studied by employing the WFL relation. Generally, analysis of the experimental data shows that the WFL relation is obeyed in both solder alloy and IMC materials, especially matching close to the relation for Sn, with a positive deviation from the theoretical Lorenz number. Thus, with the available electrical conductivity data, the thermal conductivity of solder and IMC materials can be obtained based on the proper WFL relation, and vice versa. A coupled thermal–electrical three-dimensional finite element analysis is performed to study the behavior of lead-free solder/IMC interconnects. Solder and IMC material properties predicted using the WFL relation are adopted in the computational model. By applying the WFL relation, the number of experiments required to determine the material properties for different lead-free solder/IMC interconnects can be significantly reduced, which can lead to pronounced savings of time and cost.

Keywords: Wiedemann–Franz–Lorenz; Lead-free solder; Intermetallic; Thermal conductivity; Electrical conductivity

1. Introduction

Solder used in interconnects between chip carriers and printed circuit boards used to be composed of eutectic Pb–Sn. Due to concerns regarding the toxicity of Pb, which can threaten the environment, the electrical and mechanical properties of lead-free solders and corresponding intermetallic compounds (IMCs) have been explored widely in the past decade [1–9]. With various options to replace the common Pb–Sn solder, two alternatives, made of near eutectic ternary Sn–Ag–Cu alloys, are studied experimentally in the paper. These solders, when used on circuit boards, form intermetallic compounds with the metallizations on the Cu conducting paths or with the Cu paths themselves; these greatly influence the properties of the interconnects. The intermetallic layers may grow when interconnects are exposed to higher temperatures [10]. The layer of IMC creates an interface between the solder and the surface of the substrate, and has markedly different properties than the bulk solder [11]. Knowledge of thermal conductivity characteristics is essential to understanding thermal management of the electronic component due to Joule heating, which increases temperature when the device is turned on.

In Pb-free solders, Sn-base IMCs play an important role since Sn is the major component of the solder. They are important to study since properties of the entire joint are affected. One property of particular interest is the thermal conductivity, which is of utmost importance since many applications involving solders will require the solder to

* Corresponding author. Tel.: +86 18691457660.
E-mail addresses: yaooay@gmail.com, yaoy@nwpu.edu.cn (Y. Yao).

1359-6454/$36.00 © 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.actamat.2012.11.030

operate at high temperatures. Proper dissipation of the heat ensures that the part attached to the circuit board is unlikely to overheat, giving the assembly a longer lifetime. It is a common practice to dissipate the heat through the solder, making thermal conductivity data a crucial property to understand. Thermal conductivity is difficult and time-consuming to measure. However, the thermal conductivity of a material can be approximated by knowing the material's electrical conductivity. The electrical conductivity is one physical property of materials that can be used to measure the material's ability to conduct an electric current. The relationship between the thermal conductivity and the electrical conductivity is established by the classic Wiedemann–Franz–Lorenz (WFL) relation [12,13], which is based upon the fact that heat and electrical transport both involve free electrons. According to the WFL relation, the ratio of the thermal conductivity to the product of electrical conductivity and absolute temperature is known as the Lorentz number, which varies with each material.

Metals and alloys arrange themselves with respect to thermal conductivity in approximately the same order as for electrical conductivity. This is to be expected since in each case the free electrons are primarily responsible for the conduction. There is no such parallelism in the temperature coefficients of conductivity since the amount of electrical energy carried by the electrons depends upon the electron charge while the amount of thermal energy carried by the electrons depends upon the absolute temperature. Thus the temperature coefficient of electrical conductivity is usually negative for metallic materials with a few exceptions in low conductivity materials, and for thermal conductivity both positive and negative coefficients are found. In metals the WFL relation between thermal and electrical conductivities is written as [14,15]:

$$\kappa = L_0 \sigma T \tag{1}$$

where κ represents the thermal conductivity (in W m^{-1} K^{-1}), σ represents the electrical conductivity (in S m^{-1}) and T is the absolute temperature. For metal and alloy materials, the thermal conductivity mainly consists of two parts [16,17]:

$$\kappa = \kappa_e + \kappa_l \tag{2}$$

where κ_e is the electronic conductivity and the intercept κ_l corresponds to the lattice conductivity, which typically has a small value. The electrical and thermal conductivities are related by:

$$\kappa = L_e \sigma T + \kappa_l \tag{3}$$

where L_e is the Lorenz factor.

The WFL relation is known to show deviations at temperatures below the material's Debye temperature. Below the Debye temperature, conduction electrons no longer follow the ideal free-electron model, which explains the variations from the WFL relation. The purpose of the experimental work is to show that a plot of thermal conductivity (κ) vs. temperature times electrical conductivity (σT) for pure tin would give a straight line, with slope equal to the Lorenz constant for tin. The electrical conductivity of tin would be measured and this plot could be used to predict the thermal conductivities of two tin-based lead-free solders and IMCs, such as Cu_6Sn_5, Cu_3Sn and Ag_3Sn, at various temperatures.

2. Experimental analysis

The electrical conductivity was measured using two different methods in current research. The first method was a four-point approach which was used for wire-like samples. This used a Keithley 6220 precision current source to pass a constant current through the wire. Then the voltage drop

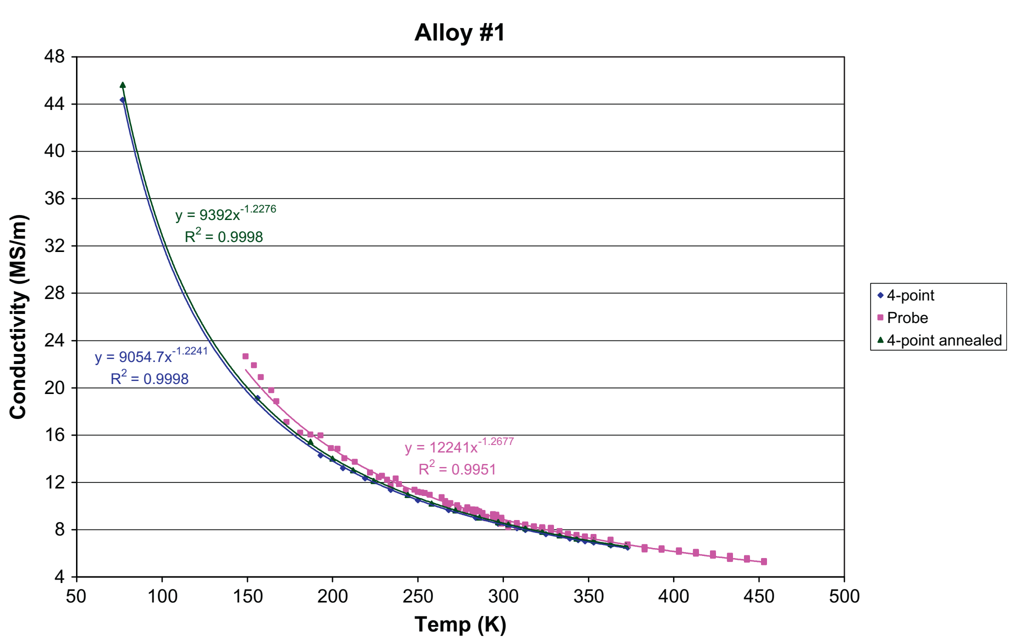

Fig. 1. Electrical conductivity vs. temperature for alloy #1.