Acta Materialia 126 (2017) 272–279

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

A general model for thermal and electrical conductivity of binary metallic systems

Changdong Wei, Nikolas Antolin, Oscar D. Restrepo, Wolfgang Windl*, Ji-Cheng Zhao**

Department of Materials Science and Engineering, The Ohio State University, Columbus, OH, 43210, United States

ARTICLE INFO

Article history:
Received 7 September 2016
Received in revised form
10 December 2016
Accepted 18 December 2016
Available online 9 January 2017

Keywords:
Thermal conductivity
Electrical conductivity
Mott^{+} two-band conductivity model
CALPHAD
First-principles
Density of states

ABSTRACT

We extended and updated Mott's two-band model for the composition-dependence of thermal and electrical conductivity in binary metal alloys based on high-throughput time-domain thermoreflectance (TDTR) measurements on diffusion multiples and scatterer-density calculations from first principles. Examining Au-Cu, Au-Ag, Pd-Ag, Pd-Cu, Pd-Pt, Pt-Rh, and Ni-Rh binary alloys, we found that the nature of the two dominant scatterer-bands considered in the Mott model changes with the alloys, and should be interpreted as a combination of the dominant element-specific *s*- and/or *d*-orbitals. Using orbital and element-resolved density-of-states values calculated with density functional theory as input, we determined the correct orbital mix that dominates electron scattering for all examined alloys and found excellent agreement between fitted models and experimental results. This general model of the composition dependence of the thermal and electrical resistivity can be readily implemented into the CALPHAD framework.

1. Introduction

Thermal conductivity is one of the most important thermophysical properties in engineering and scientific research, with applications in areas such as microelectronics [1], gas turbine engines [2], and thermoelectric devices [3]. For instance, high thermal conductivity materials are needed in microelectronics to dissipate the accumulated heat generated by electronic components, while low thermal conductivity materials such as thermal barrier coatings (TBC) [4] are required in jet engines to limit the exposure of key structural components to high temperatures. Thus, thermal conductivity data are critically needed in engineering product design and computational modeling of system performance [5].

In metals and alloys, free electrons are the main carriers for both thermal and electrical conduction, which make the thermal and electrical conductivities proportionally related by the Wiedemann-Franz relation. There, phonon-induced lattice thermal conductivity only contributes less than 5% to the total thermal conductivity [6]. In alloys, solute atoms result in lattice perturbation and change the electron distribution, and thus significantly alter the electrical conduction behavior of the host materials. As a consequence, residual resistivity (which is the resistivity caused by electron interaction with the defects in the material) is mainly a function of alloy and defect concentration, and is therefore nearly independent of temperature.

Based on these observations, conductivity models have been proposed that model the composition dependence of resistivity in metal alloys based on simple model assumptions, most notably by Nordheim [7] and Mott [8,9]. However, as we will show, the model assumptions underlying these models do not generally hold for all alloy systems, and not all systems can be described to a satisfactory degree. Also, for model calibration, there is a significant lack of experimental data for a fine enough mesh of compositions for many alloys. While the by now ubiquitous high-throughput computations have provided data for many alloy properties, this is not true for metal-alloy conductivity since the electronic nature of heat transport there requires explicit treatment of electron scattering in alloys, which is to date mostly unexplored. The vast majority of predictive modeling of thermal conductivity has been performed for non-metals such as simple oxides and elemental semiconductors, where the thermal transport is dominated by lattice vibrations, which can be treated in a more straightforward way using molecular dynamics [10], perturbation theory [11–13] and Monte-Carlo calculations [14].

This lack of computational calibration data makes experimental

* Corresponding author.
** Corresponding author.
E-mail addresses: windl.1@osu.edu (W. Windl), zhao.199@osu.edu (J.-C. Zhao).

http://dx.doi.org/10.1016/j.actamat.2016.12.047
1359-6454/

data indispensible, which due to the high cost and low efficiency of traditional measurement techniques, were previously scarce [15], resulting in an inability to develop and calibrate thermal conductivity models on the CALPHAD level. However, this situation has been changed through the recently proposed coupling of diffusion multiples with well-developed micron-scale spatial resolution properties microscopy tools (such as TDTR) [16,17]. Diffusion multiples are blocks of three or more pure metal elements or alloys with a pre-designed geometry and intimate interfacial contacts to contain many diffusion couples and triples within one sample. After diffusion annealing at an elevated temperature, complete libraries of solid-solution phases and intermetallic compounds, with wide ranges of compositions, are formed. While the diffusion-multiple approach has long been used to determine phase diagrams and materials kinetics such as diffusion coefficients [18–20], gathering of high-throughput property data and building composition-structure-property relationship of alloys is a rather recent approach [21]. This combinatorial approach, compared to the conventional properties measurements using individually made single-composition alloys, has orders of magnitude higher efficiency for studying the composition-dependent properties, which we exploit here to develop for the first time a physical CALPHAD-level description of thermal conductivity in binary systems, accompanied by a full calibration for a series of binary noble- and transition metal alloys, specifically Au-Cu, Au-Ag, Pd-Ag, Pd-Cu, Pd-Pt, Pt-Rh, and Ni-Rh.

The CALPHAD (CALculation of PHAse Diagram) approach [22–27] was initially established as a tool for treatment of the composition- and temperature-dependent thermodynamic functions and phase equilibria from experimentally measured phase diagrams and thermochemical data. The merit of this approach is its ability to extrapolate from binary and ternary systems to multi-component systems to enable thermodynamic predictions of multicomponent phase diagrams and thermochemical properties for computational design of materials. The CALPHAD approach is also suitable for modeling phase-based properties using experimental data and physics-based models. This method has been successfully applied to diffusion coefficients in multicomponent systems [28,29] and forms the basis for diffusion process simulations. A successful description of properties in CALPHAD requires both a solid physical model framework that allows interpolation and expansion to multi-component alloys, as well as sufficient composition-dependent validation and calibration data. Recent successful additions of alloy properties include molar volume, coefficient of thermal expansion (CTE) [30] and elastic constants [31]. With the resulting ability to predict the desired properties of multicomponent materials, the CALPHAD approach has been successfully used to design a number of new materials [32,33]. Among the design-crucial properties that are currently not yet well included in the CALPHAD framework, thermal conductivity is arguably one of the leaders. Although semi-empirical models of thermal conductivity of insulators in which thermal conduction is dominated by phonons have been proposed by Gheribi and Chartrand [34], for metals and alloys in which the thermal transport is dominated by electrons, there are currently no reliable models available in the CALPHAD framework, which the current work will provide.

2. Theory

2.1. Nordheim rule

For a completely soluble binary materials system (A-B solid-solution with x_A mole fraction of A and x_B mole fraction of B), the Nordheim rule [7] proposes that the residual resistivity can be described by

$$\rho(x_B) = Cx_Ax_B \tag{1}$$

where ρ is the residual resistivity and C is a constant for all compositions.

The Nordheim rule assumes random distributions of solute atoms in single phase solid solutions, without any phase mixtures. In addition, it is assumed that there is no significant change in crystal structure, atomic volume, and number of free electrons during alloying. The Nordheim rule has been successfully applied to a number of binary systems to describe the concentration-dependent thermal conductivity or electrical resistivity, such as phonon dominated thermal conductivity of Si-Ge alloy [35] and *s-s* electron scattering dominated electrical resistivity of noble metal alloys [36]. For alloys or systems containing transition metal elements, the Nordheim rule inadequately describes the electronic interactions, as detailed below.

2.2. Mott's two-band conductivity model

The localization of electronic states determines the nature of the associated electrons as itinerant, where they can travel through the crystal and carry charge or heat, or localized, where they are mostly immobile. The band structure, defined in reciprocal space and thus "reciprocal" to real-space extent of the electronic states, gives a measure of the degree of localization: itinerant electrons have wide bands, while narrow bands indicate localized electrons. For alloys containing transition metal elements, the wide *s*-valence bands house the conduction electrons traveling around, while the narrow *d*-bands indicate localized electrons, which only scatter the *s*-electrons, but contribute to conduction to a negligible degree.

This division into itinerant and localized electrons was first proposed by Mott in the 1930's as a basis for resistivity modeling in alloys [8,9]. While this model assumption is generally accepted and was used as a basis for the present discussion, we point out that positron-annihilation experiments have shown that *d*-electrons can also be itinerant in a number of metals [37], suggesting a straightforward potential future expansion of our model where needed for such metals.

According to Mott's model, electrical resistivity is controlled by scattering of the itinerant *s* electrons on impurities/solutes (or more exactly, their electrons) and phonons into vacant *s*- and *d*-states. Thus, the scattering rate is proportional to the density of states (DOS) of these vacant states at the Fermi level [8]. He proposed to use Fermi's Golden Rule for the scattering probability $P(kk')$ per unit time for electrons transitioning from state k to state k',

$$P(kk') = \langle\psi_{k'}|\Delta V|\psi_k\rangle^2 g[E(k')] \tag{2}$$

where ψ_k and $\psi_{k'}$ are the wave functions of the itinerant electrons before and after transition, ΔV is the scattering potential introduced by the lattice distortion from alloying, and $g[E(k')]$ is the DOS of the final state k'.

Mott carefully studied the Pd-Ag system as an example. He argued that in pure Ag, only *s*-states were available at the Fermi level, and thus these dominated the DOS in Eq. (2). When Pd was added into Ag, excessive *s*-electrons from Ag filled the open *d*-states of Pd up to about 40 at% Pd composition. After that, there were insufficient *s*-electrons from Ag to fill all of the vacant states in the *d*-band of Pd, and *d*-states became available as final scattering states. That was the reason that the electrical resistivity versus Pd concentration curve exhibited a sharp increase at that point. From this, Mott concluded that the total resistivity could be taken as the