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ABSTRACT

Several investigators have found that the resistance to heat transfer at certain metal-metal interfaces is dependent upon the direction of heat flow across these interfaces. This paper shows that such a phenomenon can be explained by application of the theory of heat conduction in the solid state.

Nomenclature

A	numerical constant, $\frac{4\pi mk^2}{h^3} = 0.75 \times 10^{21} \quad \frac{1}{cm^2 sec\,°K^2}$
E	energy of an electron
$\bar{E}$	average energy
E_o	height of potential barrier
E_ψ	work function
E_m	Fermi level
h	Planck's constant, 6.624×10^{-34} joule-sec
$\bar{h}$	heat conductivity chu/ft^2 hr°K
k	Boltzmann constant, 1.381×10^{23} joule/°K
ℓ	thickness of potential barrier
m	mass of an electron, 9.107×10^{-31} Kg
N	number of electrons transferred from one metal to the other
Q	heat transferred from one metal to the other
r	$\frac{\text{true contact area}}{\text{nominal contact area}}$
T	temperature, °K
$\bar{T}$	transmissivity
v	velocity
π	constant, 3.1416

Subscripts:

1	metal 1
2	metal 2
12	direction from metal 1 to metal 2
21	direction from metal 2 to metal 1
e	associated with electrons
p	associated with phonons

s   oxide film

t   total

x   x-direction, direction of heat flow

y   y-direction

z   z-direction

Introduction

In 1936, Starr [1] conducted experiments with a copper-copper oxide rectifier which seemed to indicate that thermal conductivity at the interface between the two materials depended upon the direction of heat flow across the interface. These results were later described in a standard text on rectifiers [2]. However, in 1951 Horn [3] criticized Starr's experiments on the basis that Thomson emf caused by the temperature gradient across the rectifier led to spurious results, since Starr used uninsulated thermocouples with a common lead. In 1955, Barzelay et.al. [4] found in the course of determining thermal conductivity of aircraft joints that the conductivity across the aluminum-stainless steel joints depended on the direction of heat flow. Since their experiments were not specifically designed to test for the presence of this effect, they proposed further experimentation in the field.

Finally, Rogers and his group at the University of Bristol carefully designed experimental apparatus to determine whether the asymmetric heat conduction effect really existed. Their results are described in a previous work [5]. Rogers found a definite directional heat transfer effect in the systems he studied, but he offered no theoretical explanation for this phenomenon.

Theory

The directional heat transfer phenomenon at the interface of dissimilar metals in a metal-metal contact can be predicted by application of the theory of heat conduction in the solid state.

When two metals are placed in physical contact with one another, heat transfer across the metal-metal interface may take place by several mechanisms. Those are

1) Electronic heat conduction

2) Phonon heat conduction

3) Radiative heat transfer (where metals are not in complete surface to surface contact)

4) Conduction across fluid film at interface

5) Convection across fluid film at interface

In his experiments, Rogers eliminated the last two modes of heat transfer by carefully cleaning surfaces and placing the entire system under a vacuum. Since heat transfer by radiation is negligible at the temperature of Rogers' experiments, only the first two mechanisms of heat transfer need be considered in a theoretical analysis of his data.

When many metals are exposed to air, they rapidly become coated with a thin film of oxide. For example, aluminum, one of the heat transfer metals used in Rogers' work is rapidly coated with an oxide film greater than 20 Å thick upon exposure to air. In heat transfer across an interface formed by a metal-oxide-metal contact, the oxide layer or layers can be considered a low conductivity barrier layer at the surface of contact between two metals of different conductivity. After the physical contact which forms the interface, electrons may be thought of as "flowing" over the top of the insulating barrier until a double layer of charge is built up, bringing the Fermi energy levels of the metals to values such that the number of electrons "transferred" from metal 1 to metal 2 is equal to the number of electrons "transferred" in the opposite direction; i.e., we are at the thermal steady state.

If metal 1 has a greater work function than metal 2, the electrons will flow from metal 2 to metal 1 since the electrons in the conduction band of metal 2 are nearer to the top of the potential barrier than those in metal 1.

The number of electrons penetrating the potential barrier (tunneling effect) is negligible, according to quantum mechanics and in addition, not all the electrons in one metal which have a greater energy than the height of the potential barrier will transfer into the other metal. Thus, it is necessary to use quantum mechanics to calculate the transmission of electrons across such a potential barrier, and this will be done later in this paper.

Then,

$$Q_t = Q_e + Q_p \tag{1}$$

Considering only electronic heat transfer, and using a simple energy balance

$$Q_{e_{12}} = N_{12}\,\bar{E}_{12} - N_{21}\,\bar{E}_{21} \tag{2}$$

At the thermal steady state,

$$N_{12} = N_{21} \tag{3}$$

Then, we can write

$$Q_{e_{12}} = N_{12}\,(\bar{E}_{12} - \bar{E}_{21}) \tag{4}$$

N_{12} is calculated by use of the random current density model for electrons passing over a potential barrier, as developed by Richardson [6] for quantitatively describing thermionic emission. For the model developed in this paper,

$$N_{12} = r_{12}\,\bar{f}_{12}\,\frac{2m^3}{h^3}\int_{v_x}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{1}{1+\exp\left(\frac{E-E_{m_1}}{kT_1}\right)}\,v_x\,dv_x\,dv_y\,dv_z \tag{5}$$

where $v_x = \left(\frac{2E_o}{m}\right)^{1/2}$

Since $\frac{E-E_{m1}}{kT_1} \gg 1$, we can neglect the term unity in the denominator of the integrand. Integrating, we obtain

$$N_{12} = r_{12}\,\bar{T}_{12} \cdot \frac{4\pi m k^2}{h^3} \exp -\left[\left(\frac{E_{w_1} - E_{w_s}}{kT_1}\right)\right] \tag{6}$$

The average energy carried by an electron is given by the relationship

$$\bar{E} = \frac{\text{total energy carried by electrons}}{\text{number of electrons transferred}} \tag{7}$$

Using the random current approach as before,

$$\bar{E}_{12} = \frac{\bar{T}_{12}\int_{v_x}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2\right) dN}{\bar{T}_{12}\int_{v_x}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dN} \tag{8}$$

$$\text{where } dN = \frac{2m^3}{h^3} \; \frac{1}{1 + \exp\left(\frac{E-E_{m_1}}{kT_1}\right)} \; v_x\, dv_x\, dv_y\, dv_z \tag{9}$$

Since $\exp\left(\frac{E-E_{m_1}}{kT_1}\right) >> 1$, the term unity in equation (9) is negligible, and equation (8) is integrated, yielding

$$\bar{E}_{12} = E_o + 2kT_1 \tag{10}$$

and

$$\bar{E}_{21} = E_o + 2kT_2 \tag{11}$$

Substituting equations (6), (10) and (11) into equation (4), we obtain the final expression for heat transfer,

$$Q_{e_{12}} = r_{12}\,\bar{T}_{12}\,AT_1^{\,2} \exp\left[\frac{-\left(E_{w_1} - E_{v_s}\right)}{kT_1}\right] \; 2\,k\,(T_1 - T_2) \tag{12}$$

According to quantum theory, a fraction of the electrons which have sufficient energy to pass over a potential barrier will be reflected. This fraction is given by $\bar{T}_{12}$, the transmissivity in equation (12). When the shape of the potential is assumed to be square, the transmissivity is given by a solution of the Schrodinger equation in one dimension.

$$\bar{T}_{12} = \left[1 + \frac{E_o^2 \sin \ell\sqrt{k(\bar{E} - E_o)}}{4\,\bar{E}\,(\bar{E} - E_o)} \right]^{-1} \tag{13}$$

Now, consider an experiment such as Rogers'. Suppose that we hold the metal 1 side of the interface at a certain temperature, T_A, and the metal 2 side of the interface at a certain lower temperature, T_B. Then, for this situation, equation (12) becomes

$$Q_{e_{12}} = r_{12}\,\bar{T}_{12}\,A\,T_A^2 \exp\left[\frac{-\left(E_{w_1} - E_{w_s}\right)}{kT_A} \right] 2\,k\,(T_A - T_B) \tag{14}$$

Now suppose we reverse the interface temperatures. Heat will now flow from metal 2 to metal 1.

$$Q_{e_{21}} = r_{21}\,\bar{T}_{21}\,A\,T_B^2 \exp\left[\frac{-\left(E_{w_1} - E_{w_s}\right)}{kT_B} \right] 2\,k\,(T_A - T_B) \tag{15}$$

The ratio of these quantities is given by the expression,

$$\frac{Q_{e_{12}}}{Q_{e_{21}}} = \frac{r_{12}}{r_{21}}\;\frac{\bar{T}_{12}}{\bar{T}_{21}}\;\frac{T_A^2}{T_B^2} \exp\left[\frac{E_{w_1} - E_{w_s}}{k}\;\frac{T_A - T_B}{T_A\,T_B} \right] \tag{16}$$

A consideration of the order of magnitude of terms in equation (16) clearly shows the presence of directional heat transfer. The ratio $\frac{\bar{T}_{12}}{\bar{T}_{21}}$ is approximately one. The term $T_A^2 \,/\, T_B^2$ is greater than unity, and since $E_{w_1} > E_{w_s}$, the exponential term will be greater than one. The term $\frac{r_{12}}{r_{21}}$ is usually close to unity, but may vary between $\frac{1}{2}$ and 2, depending upon the hardness of the metals in contact. In any event, the exponential factor is controlling, and may be as great as ten, dominating the contribution of the ration $\frac{r_{12}}{r_{21}}$.

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Discussion

This paper gives a qualitative explanation of asymmetric heat flow at the interface between dissimilar metals. Exact quantitative calculations of this effect cannot be made until we know more about the nature of the potential barriers existing between different metals at their surface of contact. If we assume a value of $E_{v_1} - E_{v_s} = 0.3$ ev, and set $T_A = 350^{\circ}K$, $T_B = 300^{\circ}K$ as in Rogers' work, with $r_{12} = r_{21} = \frac{1}{155}$, we obtain a value for $\bar{h}e_{12} - \bar{h}e_{21}$ of 150 chu/ft^2 °C which compares favorably with Rogers' value of approximately 100 chu/ft^2 hr °C.

In order to investigate the effect on asymmetric heat flow of using specimen metals with widely different thermoelectric potentials, Rogers conducted a series of experiments with the specimen pair T1 alloy (chromel) - T2 alloy (alumel). He found no directional effect with this pair. Since the widely different thermoelectric potentials produce a high potential barrier which virtually eliminates the electronic contribution to heat transfer, the only significant heat transfer mechanism remaining is the phonon contribution. Thus, it can be concluded that the phonon heat transfer mechanism is non-directional. Insertion of a mica shim between the stainless steel-aluminum pair produced the same effect, eliminating asymmetric heat flow.

Williams [7] pointed out that the contact configuration of two metals might change with the direction of heat flow. As pointed out previously, this mechanism is not considered significant, but is taken into account in equation (16) by the factor r_{12}/r_{21}.

Conclusions

Additional experimental results are needed to test the theory developed in this paper. For instalnce, experiments could be performed over various temperatures and temperature differences, and values of $E_{v_1} - E_{v_s}$ could be back-calculated to test consistency, since this quantity varies only slightly with temperature. However, although solid state theory qualitatively explains directional heat transfer, solid state physicists will have to obtain accurate values of work functions of various metals and their oxide films before this effect can be predicted quantitatively.

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