

## Chapter 2

# Requirements of Thermal Management Materials

**Abstract** In this chapter, we will present the requirements of thermal management materials from a physics point of view. First, the mechanism of a metal electron and the mechanism of a metal lattice on thermal conductivity are discussed in detail. Next, the effects of atomic structure, chemical composition, porosity, and temperature on thermal conductivity are presented. In the following section, we will introduce methods to measure thermal conductivity, the coefficient of thermal expansion, and hermeticity. Finally, the emergence of quality requirements for thermal management materials are discussed.

To fulfill the functions of mechanical support, electric connection, heat transfer, and protection of microchips, thermal management materials must meet the requirements described in the following sections.

### 2.1 Thermal Conductivity Requirements of Thermal Management Materials

The main purpose of thermal management materials in electronic components is the timely transfer of heat generated by microchips through external heat-spreading channels. The pros and cons of thermal management materials play a very important role in the life span and reliability of electronic components. Metallic materials like copper, silver, and aluminum have good thermal conductivity. Copper has a thermal conductivity of up to 400 W/mK. Good thermal conducting oxides and ceramic materials include beryllium oxide, silicon carbide, and aluminum nitride. Aluminum oxide is one of the most widely used materials; unfortunately, its thermal conductivity is not good enough. 96%  $\text{Al}_2\text{O}_3$  has a thermal conductivity of 20 W/mK at 25°C. The thermal properties of common thermal management materials are listed in Table 2.1.

**Table 2.1** Thermal conductivity of thermal management materials

Material	Thermal conductivity (W/mK)	Material	Thermal conductivity (W/mK)
Si	150	W	174
Ge	77	Mo	140
SiC	270	Invar	11
GaAs	45	Kovar	17
SiGe	150	Al	230
InP	97	Cu	400
GaP	133	Au96.85%-Si	27
GaN	13–33	Au80%-Sn	57
InAs	35	Au88%-Ge	44
InSb	19	W85-Cu	200
96%Al <sub>2</sub> O <sub>3</sub>	20	Mo85-Cu	170
AlN	270	CMC1:1:1	280
BeO	210	CPC1:1:1	300
Epoxy	1.7	SiC70%-Al	160
CVD Diamond	1,300–2,000	Si75%-Al	150
C <sub>r</sub> /Al	350	C <sub>r</sub> /Cu	415
Diamond/Al	500	Diamond/Cu	600

### 2.1.1 Heat-Conducting Mechanism

When two pieces of metal or two objects with different temperatures contact each other, heat energy shall transfer from the high-temperature piece to the low-temperature piece. This is the thermal conducting phenomenon. The process of heat conduction is a process of energy transport. In a solid, energy may be carried by free electrons, lattice vibration waves (phonons), and electromagnetic radiation (photons). Therefore, solid-state thermal conducting can be accomplished by electrons, phonons, and photons. For insulators, the phonon is the main carrier; for pure metals, the electron is the main carrier; for alloys, lattice wave plays some role in addition to electrons. As a result, for the materials discussed previously, metals have the highest thermal conductivity, alloys are next, and semiconductors have the lowest thermal conductivity.

Another commonly used engineering parameter related to thermal conductivity is thermal diffusivity. It is defined as

$$\alpha = \frac{\lambda}{dc}, \quad (2.1)$$

where  $\alpha$  is the thermal diffusivity,  $d$  the density,  $c$  the specific heat capacity, and  $\lambda$  the thermal conductivity.

The physical meaning of thermal diffusivity is linked to a transient heat conduction process. Transient heat conduction is a process involving both temperature change and heat transfer. Thermal diffusivity is the physical link between the two. It marks the rate of temperature change. Under identical heating and cooling

conditions, the greater the thermal diffusivity, the smaller the temperature difference throughout the object. For example, in a quenching process, the outside steel temperature is outside, while the internal temperature is high. If the thermal conductivity is high, the temperature gradient will be small and the sample temperature uniform; on the other hand, the temperature difference between samples will be large. Because the density and the specific heat capacity of steels are quite similar, it is generally accepted that the higher the thermal diffusivity, the higher the thermal conductivity.

Thermal conductivity is an engineering parameter used to judge the utility of insulation or heat exchange materials. It is also an important parameter for calculating the holding time of material heat treatments. Thermal conducting is a complex problem that can be affected by many factors. Generally speaking, it is a nonequilibrium problem. Here we make only a preliminary introduction.

### 2.1.1.1 Mechanism of Metal Electron Thermal Conductivity

According to the electron theory of metals, a large number of free electrons in metals can be regarded as free-electron gas. It is a reasonable approximation to borrow the ideal gas equation to describe the thermal conductivity of the thermal conductivity of free electrons. The expression for ideal gas thermal conductivity is

$$k = \frac{1}{3} cvl \quad (2.2)$$

where  $c$  is the gas heat capacity per unit volume,  $l$  the mean free path of the particle, and  $v$  the average particle velocity.

Taking into account various mechanisms, the thermal conductivity of the solid  $\lambda$  is expressed as

$$\lambda = \frac{1}{3} \sum_j^n c_j v_j l_j, \quad (2.3)$$

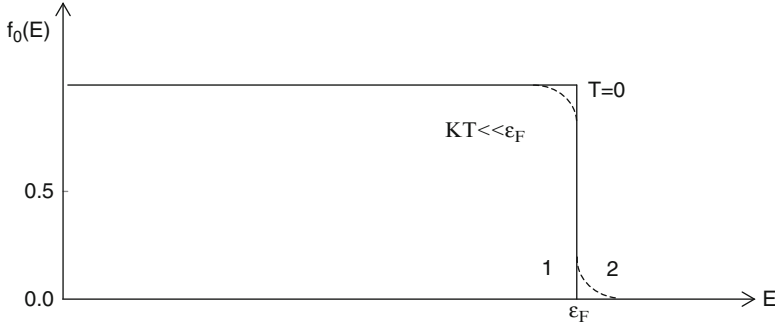
where the subscript  $j$  represents the type of heat carrier,  $c_j$  and  $l_j$  represent various heat carriers' heat capacity per unit volume and the mean free path, and  $v_j$  is the carrier fluid velocity. If the heat carrier is a lattice wave, then  $v_j$  is the corresponding group velocity of the lattice wave.

A thermal conducting carrier in a metal is mainly free electrons; the lattice wave also plays a role. As a result, total thermal conductivity can be written as

$$\lambda = \lambda_e + \lambda_a \quad (2.4)$$

where  $\lambda_e$  is the electron thermal conductivity and  $\lambda_a$  is the lattice thermal conductivity. For pure metals, the thermal conductivity is determined mainly by free electrons; for alloys, the phonon thermal conductivity contribution needs to be considered.

For electronic thermal conductivity, the electron mean free path  $L$  is determined entirely by scattering of electrons in metals. If the metal lattice is complete, then



**Fig. 2.1** Fermi distribution function. 1: distribution function at absolute zero. 2: distribution function at low temperature

movement of electrons will not be hindered and  $L$  is infinite. Electronic thermal conductivity could be infinitely large. In fact, the periodic lattice of metals is not complete. This is due to the thermal motion of atoms on the grid resulting from displacement from the equilibrium position, elastic distortion of the lattice caused by foreign atom, lattice dislocation, and fracture caused by grain boundaries. Therefore, electronic thermal conductivity is controlled by the scattering process and could not be infinitely large.

For lattice thermal conductivity, many factors, such as the nonresonance of the lattice wave, lattice defects, and the presence of impurity atoms, can impact the scattering mechanism. Therefore, the lattice thermal conducting process is a very complicated one. Because a heat carrier can only have a limited mean free path and the mean free path is in turn limited by various scattering mechanisms, for each heat carrier, its mean free path takes the following overlapping form:

$$\frac{1}{l} = \sum_{\alpha} \frac{1}{l_{\alpha}}, \quad (2.5)$$

where  $\alpha$  represents various scattering mechanisms.

In metals, the electron density is very high. At absolute zero, the energy of all electrons is below the Fermi energy level. As the temperature increases, the probability that an electron occupies an electronic state with the energy  $\varepsilon$  can be expressed as a Fermi distribution function curve (Fig. 2.1) and  $f_0$  can be calculated using the following formula:

$$f_0 = \frac{1}{e^{\frac{\varepsilon - \varepsilon_F}{KT}} + 1}, \quad (2.6)$$

where  $K$  is the Boltzmann constant.

It can be proved that at a normal temperature, or when  $KT < \epsilon_F$ , the electron energy distribution in metals is similar to that at absolute zero. In other words, electrons are highly degenerate oriented. Therefore, the thermal conductivity characteristics of metals depend on the electron characteristics within an energy range of  $\epsilon_F \pm 0(KT)$ . The main factors that affect the states of electrons are point defect electron scattering and electron–electron scattering.

It is obvious that thermal vibration and electron scattering are proportional to  $\langle \epsilon^2 \rangle$ . Taking advantage of this point, the magnitude of *point defect electron scattering* can be estimated by the magnitude of thermal vibration at room temperature. In most solids, at room temperature  $\langle \epsilon^2 \rangle$  is approximately 0.01. The value of  $\langle \epsilon^2 \rangle$  is determined by atomic volume and elastic constants, but the difference is not large. Electrical resistivity and thermal resistivity at room temperature can be found to be

$$\rho_0 \approx (\rho_i)_{RT} c, W_0 T \approx (W_i)_{RT} c T_{RT}, \quad (2.7)$$

where  $(\rho_i)_{RT}$  and  $(W_i)_{RT}$  are the intrinsic room temperature resistivity and thermal resistivity, respectively;  $c$  is the concentration of point defects (expressed as a percentage) and is about 300K.

*Electron–electron scattering* plays a fairly important role in determining the resistivity and thermal resistivity of metals with very high density such as transition metals. In this case, the electrical resistivity and the thermal resistivity have the following form:

$$\rho_{ee} = BT^2, W_{ee} = DT. \quad (2.8)$$

In general, the electron–electron scattering effect at the low temperature limit (not a very low temperature) is important because for very pure samples,  $\rho_0$  and  $w_0$  do not play a major role. This is due to the relationship

$$\rho_i \propto T^5, W_i \propto T^2. \quad (2.9)$$

In comparison,  $\rho_{ee}$  and  $w_{ee}$  could play more important roles than  $\rho_0$  and  $w_0$ . Therefore, for the transition metals, in many cases  $\rho_{ee}$  and  $w_{ee}$  or the impact of the electron–electron scattering effect must be considered.

### 2.1.1.2 Mechanism of Metal Lattice Thermal Conductivity

The thermal motion of solid atoms in a crystal lattice contributes to thermal conductivity. In an insulator, the lattice thermal conductivity is almost the only mechanism and only at very high temperatures will thermal photons be of any significance. In metals, the main thermal conducting carriers are free electrons; in alloys, they are lattice thermal waves; and in semimetals and semiconductors, the magnitude of thermal conducting is often the same as that of electrons. Because the lattice vibration energy is quantized, the energy of a quantized lattice is called a quantum phonon with energy of  $\omega$ , and  $\omega$  is the angular frequency of the lattice wave.

We can see from the expression of thermal conductivity that lattice thermal conductivity is related to heat capacity, the average speed of lattice waves, and the mean free path of phonons.

The law of metal lattice thermal conductivity differs from that of insulators. In addition, electron–phonon scattering constitutes a difference in metal lattice thermal conductivity and insulator lattice thermal conductivity. For a complete crystal structure, a lattice wave has a frequency range, that is, from a low to a high frequency  $\omega_m$ .  $\omega_m$  is typically  $10^{13}$  Hz. At low frequency, lattice waves can be regarded as elastic waves; at high frequency, due to the dispersion effect, their wavelength is similar to atomic spacing.

The interacting force between structural defects and atoms does not completely obey the law of elasticity (or Hooke's law). In fact, crystal lattice waves exchange energy with each other continuously, so each lattice wave has a finite mean free path  $l$ . Also, it is generally a function of frequency. Therefore, the lattice thermal conductivity can be expressed as

$$\lambda_g = \frac{1}{3} \int_0^{\omega_m} c(\omega) v_g l(\omega) d\omega, \quad (2.10)$$

where  $\omega_g$  is the lattice wave group speed and  $c(\omega)$  the specific heat. Because  $c(\omega)$  is proportional to  $T^3$  at very low temperatures and is independent of  $T$  at high temperatures, the lattice thermal conductivity  $\lambda_g$  depends mainly on the phonon mean free path. In what follows, we will discuss the law of metal lattice thermal conductivity from points of phonon–phonon scattering: from phonon–phonon scattering, electron–phonon scattering, and defect-phonon scattering.

- Phonon scattering on a phonon

At high temperatures, the under thermal strain, adjacent atoms are almost independent of one another and scattering is proportional to  $\langle \varepsilon^2 \rangle$ . That is, it is proportional to temperature. Therefore, the intrinsic mean free path is similar to the electron mean free path, namely:

$$l_i \propto \frac{1}{T}. \quad (2.11)$$

Since a lattice wave has a continuous spectrum range, every vibrating atomic position can be considered as a separate scattering source and its scattering effect is weak on a long wavelength lattice wave. And  $l_\omega$  increases sharply with a decrease in  $\omega$ . At low frequencies,  $l_i$  is proportional to  $1/\omega^4$  and  $c(\omega)$  is proportional to  $\omega^2$ . As a result, at low temperatures, the lattice thermal conductivity ( $\lambda_g$ ) integral diverges. Peierls made a rough estimate of the intrinsic thermal resistivity:

$$W_U = U \left( \frac{h}{K} \right)^3 \cdot \frac{\gamma^3}{Ma} \frac{T}{\Theta_D^3}, \quad (2.12)$$

where  $M$  is the atomic mass and  $a^3$  the atomic volume; the coefficient  $U$  depends on the crystal structure with a typical value of  $1/3$ ;  $\gamma$  is a nonharmonic-vibration-related parameter, and  $\Theta_D$  is the Debye temperature.

From the preceding formula it can be seen that the intrinsic thermal resistance is mainly determined by the Debye temperature. In general, the higher the Debye temperature, the higher the phonon thermal conductivity. According to Peierls's theory, the phonon process is divided into a forward process and a reverse process. At high temperatures, most of the phonon collisions are entail the reverse process. As in the previous analysis, the thermal resistance rate is proportional to the temperature, and the thermal conductivity is inversely proportional to the temperature.

At low temperatures, phonons reaching the reverse process change according to  $e^{-\Theta_D/T}$ . Therefore, thermal resistivity changes exponentially, that is,  $WU$  is proportional to  $e^{-\Theta_D/T}$ , where  $b$  is a constant related to the crystal structure. The variation agrees well with the experimental data.

- Electron–phonon scattering

In metals, electron–phonon scattering usually plays a major role at low temperatures. The effect of electron–phonon scattering is similar to the effect of lattice–electron scattering. These interactions limit the phonon mean free path. It is found that

$$\frac{1}{l_{pe}(\omega)} \propto \omega, \quad (2.13)$$

where  $\omega$  is the angular frequency of the lattice wave.

When  $\lambda_g$  is calculated according to Eq. 2.10, the effect of electron–phonon scattering must be taken into account for calculation of the mean free path. This scattering mechanism causes  $\lambda_g$  of metals to be smaller than  $\lambda_g$  of insulators with elastic properties. For the latter case,  $\lambda_g$  is proportional to  $T^2$ . As in the previous analysis, the high-temperature resistance of a nonharmonic vibration is dominant; that is,  $\lambda_g$  is proportional to  $1/T_g$ . Therefore, there is a maximum value of  $\lambda_g$  as the temperature changes from low to high. Usually, the maximum  $\lambda_g$  value of metals is smaller than that of insulators.

Equation 2.13 is based on the assumption that an electron has a long mean free path  $l'$ , and it is longer than the wavelength of a lattice wave. That is,  $l' > \lambda$ . In this situation, phonons can interact with a single electron. In alloys,  $l'$  is limited. In the typical case,  $l'$  is about  $100a$  ( $a^3$  is the volume of atoms). If the concentration of impurity elements is 1%, then the wavelength of the lattice wave is

$$\lambda \approx \frac{1}{3}a \left( \frac{\Theta_D}{T} \right).$$

This condition of  $l' > \lambda$  can still be satisfied. If the content of alloying elements increases, then there will be a situation where  $l' < \lambda$ . In this situation, phonons will no longer interact with single electrons; instead, the phonons behave as a whole electron gas. The scattering effect becomes

$$\frac{1}{l_{\text{pe}}} \propto \omega^2, \lambda_{\text{g}} \propto T. \quad (2.14)$$

In another case, even if the alloy composition is not high, at very low temperatures the lattice wave wavelength increases rapidly, and the effect of electron–phonon scattering is still obvious.

- Phonon scattering

There is a general rule about the effect of defect–phonon scattering. The main contribution to thermal resistance at low temperatures comes from a large area defects; the main contribution to thermal resistance at middle temperatures comes from point defects.

At very low temperatures, dislocation is usually the most important phonon scattering factor, the thermal resistance can be expressed as

$$\frac{1}{\lambda_{\text{g}}} = W_{\text{g}} = W_{\text{ge}} + W_{\text{gd}} \propto T^2, \quad (2.15)$$

where  $W_{\text{ge}}$  is the lattice thermal resistivity caused by electrons and  $W_{\text{gd}}$  is the lattice thermal resistance caused by dislocation.

When the density of dislocation reaches  $10^{10}/\text{cm}^2$ , then the value of  $W_{\text{ge}}$ , and  $W_{\text{gd}}$  are similar. Therefore, the lattice thermal conductivity of alloys is closely related to cold processing conditions, while the effect of cold processing upon electrical resistivity is not large. At low temperatures, the relationship between the phonon mean free path and frequency reflects the relationship between the lattice thermal conductivity and temperature. If there is the relationship

$$l(\omega) \propto \omega^{-n} \propto T^{-n} \chi^{-n},$$

then there is the relationship

$$\lambda_{\text{g}} \propto T^{3-n}, \quad (2.16)$$

where  $n$  denotes the form of the relevant defects; for point defects,  $n=4$ ; for line defects,  $n=3$ ; for sheet defects,  $n=2$ ; for dislocation,  $n=1$ .

When the temperature is high and the concentration of point defects is high, strictly speaking, when  $n=4$ , Eq. 1.10 diverges. Therefore, the thermal resistance caused by point defects is often estimated using another method. That is, at low temperature, it is associated with electron scattering; at high temperatures, it is associated with nonharmonic vibrations. As the temperature is gradually increased from low to high, the Eq. 2.15 relationship will deviate more and more. Point defects will lower the maximum value of  $\lambda_{\text{g}}$  and broaden the temperature range of the maximum  $\lambda_{\text{g}}$ . At high temperatures, due to the presence of point defects,  $\lambda_{\text{g}}$  changes more



slowly with  $T^{-1}$ . When the temperature and the concentration of point defects are high, the relationship between  $\lambda_g$  and the temperature will be

$$\lambda_g \propto [c(1-c)]^{-1/2} T^{-1/2}, \quad (2.17)$$

where  $c$  is the concentration of point defects.

### 2.1.1.3 Other Thermal Conducting Mechanisms

In addition to the two major heat transfer mechanisms—electronic and phonon thermal conducting mechanisms—there are a photon thermal conducting mechanism and a magnetic thermal conducting mechanism. If the thermal conducting medium is transparent at a particular wavelength range, then the thermal radiation can get through the media, hence the emergence of photon thermal conduction.

A magnon is a quantized unit of spin wave energy, defined in analogy with the phonon as a quantized lattice vibration. Interaction between magnons and spin waves develops into a new thermal conducting mechanism; it also becomes a thermal resistance mechanism in electronic and phonon thermal conduction. Various magnetic effects occur in rare earth materials. They have become a very important class of magnetic material. The magnetic effect of ferromagnetic and nearly ferromagnetic transition metals is also very important. The thermal conductivity of these materials is under continued research. No complete theory about their thermal conductivity has been developed yet.

The thermal conductivity of superconductors has unique characteristics. Below the superconducting transition temperature, some of the conduction electrons separated from the normal state are condensed into a state of zero entropy. They become so-called superfluid electrons and conduct current without resistance. The superfluid electrons do not conduct heat or scatter phonons. Under normal magnetic field constraints, thermal conductivity measurements can be performed under a normal state and a superconducting state.

### 2.1.2 Factors Affecting Thermal Conductivity

The thermal conductivity of materials is closely related to their material structure, density, temperature, and pressure. In general, to determine the precise thermal conductivity of a material, it must be measured by experimental apparatus. The factors that affect the thermal conductivity of materials still represent a very important topic. On the one hand, thermal conductivity can be used to identify the reliability of measured data; on the other hand, it can be used to make predictions about the properties of thermal conductivity of some materials. We will discuss four factors that can influence metal thermal conductivity.

### 1. Effect of atomic structure on thermal conductivity of metals

Because free electrons play important roles in metal thermal conductivity, it is natural to link the thermal conductivity of metals with their atomic structure and with the periodic table of elements. If a suitable thermal conductivity unit is chosen, some regularity can be found. It has been found that, both in long periods and short periods, metals with one valence electron, such as the alkali metals, copper, silver, and gold, have the best conductivity. In the same period, thermal conductivity decreases from metals with one valence electron to metals with two valence electrons, such as from sodium to magnesium, or from copper to zinc. Some elements have only partially metallic characteristics, such as silicon, and their conductivity is low. In addition, some elements have a complex atomic structure, such as zirconium and titanium, and their conductivity is low.

### 2. Effect of chemical composition and structure on thermal conductivity of metals

- The effect on thermal conductivity of adding a small amount of impurities  
The addition of impurities will cause the residual resistivity of the sample to increase, lowering the thermal conductivity. Studying the effect of impurities on the thermal conductivity of iron, it can be seen that the addition of foreign atoms will lower the thermal conductivity initially; as the amount of impurities increases, the proportion of thermal conductivity reduction decreases. In addition, if the atomic structure of the impurities is similar to that of the parent phase, the thermal conductivity will decrease less; an example is the case of adding cobalt and nickel. If the impurities' atomic structure and the structure of the parent phase are very different, then the thermal conductivity will decrease more; an example is the case of adding manganese and aluminum. The addition of the metalloid element silicon changes iron's thermal conductivity the most. When a variety of impurity atoms is added, the contributions to thermal resistance will be complex.

There is another point to be made: the higher the thermal conductivity of the solvent (mother metal) element, the greater the impact of the impurity on the thermal conductivity of the parent metal.

- Impact of orderliness  
Slow cooling in an alloy or annealing at very low temperature may generate ordered alloys. In a typical body-centered cubic structure of an Fe–Co alloy, the iron atom percentage is 50%. Iron atoms are located in the center of a cube of cobalt atoms, whereas cobalt atoms are located in the center of a cube of iron atoms, forming an ordered alloy. This causes the mean free path of the conduction electrons to increase and their thermal conductivity is much greater than that of the disordered state.

### 3. Impact of porosity on thermal conductivity

There are two types of metal materials that can be impacted by porosity: metal powder material (the metal is surrounded by air or gas) and pressed and sintered porous metal materials (where voids exist inside the solid metal). Their thermal conductivity can be estimated by Maxwell's equations. For powder material that

is not sintered, if the powder is in a dispersed phase, then the thermal conductivity of the air is negligible relative to that of the powder and its conductivity can be obtained by

$$\lambda_p = \frac{\lambda_A (1 + 2\phi)}{1 - \phi}, \quad (2.18)$$

where  $\lambda_p$  is the thermal conductivity of the powder,  $\lambda_A$  is the thermal conductivity of the air, and  $\phi$  is the volume percentage of the metal powder.  $\phi_A = (1 - \phi)$  is the volume percentage of the air. Then, the preceding equation can be written as

$$\lambda_p = \lambda_A \left( \frac{3}{\phi_A} - 2 \right). \quad (2.19)$$

This equation does not contain the thermal conductivity of a metal powder; the thermal conductivity of powder materials is directly proportional to the thermal conductivity of the surrounding air.

#### 4. Effect of temperature on thermal conductivity

Whether the thermal conductivity of a metal increases, decreases, or remains the same depends, with increasing temperature, on the temperature effect on the mean free path. In general, for pure metals, as the temperature increases, the mean free path decreases. The thermal conductivity change due to a temperature-induced mean free path reduction is more important than the direct effect of temperature on the thermal conductivity. Therefore, the thermal conductivity of pure metals generally decreases with increasing temperature. For alloys, because of the presence of foreign atoms, the effect of a change in the mean free path due to temperature is relatively small, and temperature plays a major role in the thermal conductivity of alloys; the thermal conductivity of alloys increases as the temperature increases.

### 2.1.3 Methods of Measuring Thermal Conductivity

Presently, there are two methods to determine thermal conductivity: steady-state and dynamic methods. The steady-state method is a classical method for determining the thermal conductivity of thermal insulation materials. It is still widely used and is based on the principle that the heat transfer rate is equal to the cooling rate at steady state. According to the Fourier one-dimensional steady-state heat conduction model, thermal conductivity is calculated by measuring the heat flux through a sample, the temperature difference at both ends of the sample, and the thickness of the sample.



**Fig. 2.2** Flash method equipment for measuring thermal conductivity

The principle is simple and clear. This method has high accuracy, but the measurement time is long and it has strict requirements with respect to the environmental conditions. The steady-state method is divided into a heat flow meter method and a guarded hot plate method. The steady-state method is suitable for measurements of thermal conductivity at moderate temperatures. The guarded hot plate method has the highest accuracy, but measurements take a long time and the measurement process is complicated and expensive. The heat flow meter method is fast and accurate, but the measurement range is narrow. A dynamic method has been developed in recent decades. It is suitable for high-thermal-conductivity materials or in high-temperature conditions. The dynamic method requires a fixed-power heat source and records of sample temperature variations with respect to time. Thermal conductivity, thermal diffusivity, and heat capacity can be found from the sample temperature changes with respect time. The dynamic method is divided into a hot-wire method and a laser flash method. The measurement speed is high, but the accuracy is not (5%). The dynamic method is suitable for high-thermal-conductivity materials or in high-temperature conditions. A laser flash is generally used to measure the thermal conductivity of thermal management materials.

The laser flash method for thermal diffusivity measurement is based on the flash method first proposed by W.J. Parker in the United States in 1960. At that time, the sample was heated with a Xenon flash, and Xenon lights were later replaced by lasers. Seventy-five percent of the thermal diffusivity data is obtained from this measurement. The measuring principle is based on the assumptions that the circular sheet sample insulated from its surroundings is heated by a uniformly distributed instantaneous laser pulse, the temperature on the backside of the samples will rise, and the heat transfer is one-dimensional. Thermal diffusivity is calculated according to the theoretical model of thermal diffusivity. A set of measuring equipment is shown below (Fig. 2.2).

## 2.2 Coefficient of Thermal Expansion Requirement of Thermal Management Materials

In general, material will expand when the temperature increases and shrink when it cools. At the same temperature, different materials undergo different amounts of material expansion and contraction. Therefore, when two different materials are welded together, material expansion and contraction are restrained, resulting in thermal stress at the interface between the two materials. After a period of time and after repeated temperature cycling, thermal stress will cause material to bend, deform, or even crack. In the field of thermal management materials, die and package materials include Si, GaAs, InP, and  $\text{Al}_2\text{O}_3$  or BeO and other semiconductor materials and ceramics. They are brittle materials. When they are welded together with a heat sink material, the difference between the CTEs is too large. After repeated temperature cycling, the chip or ceramic will warp and the welding joint could fail. Serious and complete failure or the cracking of ceramic materials and microchips could happen, affecting the life span and reliability of the components. In general, thermal management materials are required to have a CTE of less than  $7 \times 10^{-6} \text{K}^{-1}$  and to have an optimal match of the CTE between thermal management materials and die materials to reduce interfacial thermal stress. The CTE match requirements of thermal management materials places limits on many good-thermal-conductivity materials with wide applications. For example, copper has good thermal conductivity, but unfortunately its CTE is up to  $16.5 \times 10^{-6} \text{K}^{-1}$ . The large CTE difference in dies and ceramics will cause the welding to deform and crack. Therefore, to meet the demands of high-power components, many researchers have developed functional composite thermal management materials, such as the second generation of the W–Cu and SiC–Al composites and the third generation of thermal management materials Diomand/Cu and  $\text{C}_f/\text{Cu}$ . These advanced materials have a low CTE and high thermal conductivity and their CTEs match those of the die materials. They represent the research and development direction for the future. Table 2.2 lists the CTEs of the second- and third-generation thermal management materials.

### 2.2.1 Definition of Coefficient of Thermal Expansion

The CTE is divided into the linear CTE and volume CTE. The linear CTE is defined as the average coefficient of linear expansion: when the temperature changes from  $t_1$  to  $t_2$ , the length of the correspondingly the length changes from  $L_1$  to  $L_2$ ,

$$\bar{\alpha} = \frac{L_2 - L_1}{L_1(t_2 - t_1)} = \frac{\Delta L}{L_1 \Delta t}.$$

**Table 2.2** Coefficients of thermal expansion of thermal management materials

CTE (10 <sup>-6</sup> K <sup>-1</sup> )		CTE (10 <sup>-6</sup> K <sup>-1</sup> )	
Material	20°C	Material	
Si	4.1	W	4.6
Ge	5.5	Mo	5.4
SiC	4.0	Invar	0.4
GaAs	7.5	Kovar	4.2
InP	28	Al	22
96%Al <sub>2</sub> O <sub>3</sub>	6.3	Cu	17
AlN	4.2	Au96.85%-Si	12.3
BeO	6.4	Au80%-Sn	15.9
Epoxy	5.4	Au88%-Ge	13.4
		W85-Cu	6.9
		Mo85-Cu	6.7
		CMC1:1:1	8.9
		CPC1:4:1	7.8
		SiC70%-Al	7.0
		Si75%-Al	6.5
		C <sub>f</sub> /Cu	6.5
		Diamond/Cu	

As  $\Delta t$  approaches zero, the preceding limit (in the case of constant pressure  $P$ ) is defined as the differential linear expansion coefficient:

$$\alpha_t = \frac{1}{L} \left( \frac{\partial L}{\partial t} \right)_P.$$

Corresponding to this, when the temperature changes from  $t_1$  to  $t_2$ , the volume of material changes from  $V_1$  to  $V_2$ , and the average coefficient of volume expansion becomes

$$\bar{\beta} = \frac{V_2 - V_1}{V_1(t_2 - t_1)} = \frac{\Delta V}{V_1 \Delta t}.$$

Similarly, when  $\Delta t$  approaches zero, the preceding limit (in the case of constant pressure  $P$ ) is defined as the differential volume expansion coefficient:

$$\beta_t = \frac{1}{V} \left( \frac{\partial V}{\partial t} \right)_P.$$

The differential coefficient of expansion is the expansion coefficient at a given point and at a certain temperature. For engineering applications, the average expansion coefficients are used most often.

### **2.2.2 *Methods for Measuring the Coefficient of Thermal Expansion***

Traditional methods for measuring the CTE of solid materials include push-rod dilatometer, optical lever dilatometer, the direct observation method, optical interferometry, X-ray method, the capacitance method, and others. Many of these methods were developed under certain conditions for specific research purposes; they cannot be used indiscriminately. Methods for measuring the CTE of composite materials can be divided into relative and absolute groups. The former group includes a volume method and a differential method; the latter group includes a telescope direct observation method and an interferometry method. The most recently developed laser method may be used more for measurements of composite materials.

The volume method is suitable for testing the composite volume expansion coefficient. The working principle is as follows. After the specimen is put into the liquid bath, the liquid height change is recorded along with the temperature change. The volume change and the volume CTE of the sample can be found after the effect of the liquid volume change itself due to the temperature change is eliminated.

The differential method is used based on the fact that a sample elongates as the temperature increases. The sample is connected to a micrometer and a gauge shows the total elongation amount of the specimen and the push rod. When the push-rod elongation amount is deducted, the specimen's amount of elongation is known. Thus, the linear expansion coefficient of the composite is obtained. This method is simple and reliable, and samples can be tested in a wide temperature range.

A high-sensitivity microtelescope direct observation method is used to observe the dimensional variation of test pieces due to temperature variation, resulting in a linear expansion coefficient. Its unique feature is that the upper temperature is high, currently up to 3,600°C. The working principle of an interferometer is introduced here. A change in specimen size will change the light optical path of one beam, so that the images rendered on a screen and the interference fringes will change. When enough fringe data are collected following the thermal expansion of the sample, the expansion length can be extrapolated using principles of physical optics. Thus, the linear CTE can be calculated. The greatest feature of this method is that even if the sample is thin, accurate results can be obtained; but the operation procedure is rather complicated and requires skilled specialists for testing. One piece of equipment for measuring the CTE is shown in Fig. 2.3.

## **2.3 Hermeticity Requirement of Thermal Management Materials**

To ensure a chip has a good working environment, thermal management materials with good hermeticity are often used for hermetic packages. In a hermetic package, the required hermeticity is less than  $1 \sim 5 \times 10^{-9}$  Pa.m<sup>3</sup>/s. Hermeticity reflects the



**Fig. 2.3** DL402PC thermal conductivity measurement equipment

density of the material inside. The airtightness performance of many dense metals such as Kovar is good, and no extra testing is required; but for composite thermal management materials such as the refractory metal series W (Mo)–Cu and the aluminum matrix composite series SiC (Si)/Al, which are prepared by powder metallurgy, achieving good air tightness is one of the key technical process challenges. If the process is not controlled properly, problems related to tightness quality could occur, causing the entire batch of products to be scrapped. Inspection of airtightness during the production process is required.

In general, the hermeticity of thermal management materials is tested at the gross leak level and fine leak level. There are three types of gross leak test, namely, the bubble test, the weight gain test, and the dye penetrant test. In the bubble test, the device is immersed in a bath of indicator fluid at a temperature above the boiling point of the tracer fluid. The device must first be pressurized with the tracer fluid at a given temperature and pressure, which are determined in a way similar to fine leakage tests. The weight gain test involves cleaning and weighing the package before pressurizing it in a fluorocarbon tracer. The tracer material should have low viscosity and a low vapor pressure. The device is then dried and reweighed. The dye penetrant test utilizes a dye as a tracer; hence it is mostly used on transparent packages. Again, the device is pressurized in the tracer. The next stage, after washing, is to visually inspect (using a UV light) the interior to find dye inside of the cavity.

For a helium leak test, the package is placed in a pressurization tank, which is pressurized with helium at a given temperature for a given amount of time. The package is then removed and placed into a mass spectrometer so that the amount of helium coming out of the case can be observed. The test parameters are based on the internal volume of the package.



## **2.4 Other Performance Requirements of Thermal Management Materials**

Electronic packaging materials must have high mechanical strength and good processing properties in order to be processed into a variety of complex-shape parts. In the aerospace field and in some portable electronic devices, electronic packaging materials must have lower density in order to minimize the weight of the devices. In addition, low cost is required for mass production.

## **2.5 Appearance Quality Requirements of Thermal Management Materials**

### ***2.5.1 Surface Layer of Nickel and Gold Plating Performance Requirements***

To improve the reliability and stability of electronic components, component surfaces need to be gold plated. Before they are gold plated, the surfaces need to be nickel plated. For certain devices, nickel plating can facilitate silver and copper soldering. Therefore, thermal management materials should have very high-quality nickel and gold plating. For a nickel plating layer, a thickness of between 100 and 300 micron. is required. When they are heated at a high temperature of 850°C for 5 min, there should be no visible air bubbles under a 10× microscope; for a gold plating layer, a thickness of between 50 and 100 micron. is required. When the materials are heated at a high temperature of 350°C, there should be no visible air bubbles under a 10× microscope.

### ***2.5.2 Quality Requirements of Surface Appearance***

1. Surface roughness must be less than 0.8  $\mu\text{m}$ , the lateral roughness less than 3.2  $\mu\text{m}$ , the surface parallelness less than 0.02 mm, and the surface flatness less than 0.02 to 0.05 mm.
2. The surface scratch depth must be less than 0.0125 mm, the pinhole depth less than 0.025 mm, and the diameter less than 0.0127 mm.
3. There must be no visible burr on the surface; the side burr depth must be less than 0.02 mm.
4. There must be no oil spots, rust spots, or cracks on surfaces.

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