

Thermal Conductivities of Platinum Alloys at High Temperatures

OBSERVATIONS COMPLIANT WITH THE WIEDEMANN-FRANZ RELATION

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The thermal conductivity of platinum alloys with a f.c.c. single phase was comprehensively surveyed by the laser flash method. Thermal conductivity is predominantly determined by alloy composition and temperature and is little affected by work hardening. An addition of solute clearly decreases the thermal conductivity of Pt, and the conductivity-composition relationship is characterised by a sharp maximum at pure Pt. The Wiedemann-Franz relationship that holds for Pt alloys suggests that the electron is the dominant carrier of thermal conduction. An empirical rule is proposed that the thermal conductivity of a Pt alloy decreases significantly as the position in the Periodic Table of the solute element becomes horizontally more distant from Pt (for the B-subgroup). The thermal conductivity of Pt alloys increases with increasing temperature in the range 300 to 1100 K. The temperature coefficient of thermal conductivity was found to be inversely correlated with the thermal conductivity.

The advantage of using platinum (Pt) in industrial applications is due to its unique properties, such as its catalytic activity, high melting point (1), ductility (2, 3) and chemical inertness over a wide range of temperatures (4, 5). Platinum has been used for biomedical components, specialty chemicals, fuel cells and for pollution control catalysts, such as in automobile exhausts, as well as for jewellery, thermocouples and the cathodic protection of ships' hulls (3).

One typical application of platinum is in electronics devices, with thick film conductors being among the major products (6). Alloying elements, selected from the platinum group metals and noble metals, are usually employed to help develop higher strength or to protect a surface against deleterious service conditions (3). However, the addition of an alloying element may degrade the conductivity. Until now, the data available on the conduction properties of platinum alloys have been limited (7–12).

This present investigation will survey the para-

meters of thermal conductivity in various platinum alloys at high temperatures. First, the composition dependence of thermal conductivity will be investigated and the results will be ordered according to the Periodic Table; second, the effect of work hardening will be investigated; and third, the temperature dependence of thermal conductivity will be surveyed.

Dependence of Thermal Conductivity on Composition

The thermal conductivities at 300 K for Pt alloys as a function of solute concentration, is shown in Figure 1, together with data for pure Pt (1, 13, 14). Vanadium (V) and nickel (Ni) were selected as solutes. Nickel belongs to the same column as Pt in the Periodic Table (Pt-Ni is an isoelectronic system) while V is positioned horizontally far distant from Pt (Pt-V is a non-isoelectronic system). All the alloys used in this investigation have a face centred cubic (f.c.c.) single phase; whereas in the Pt-V system, the

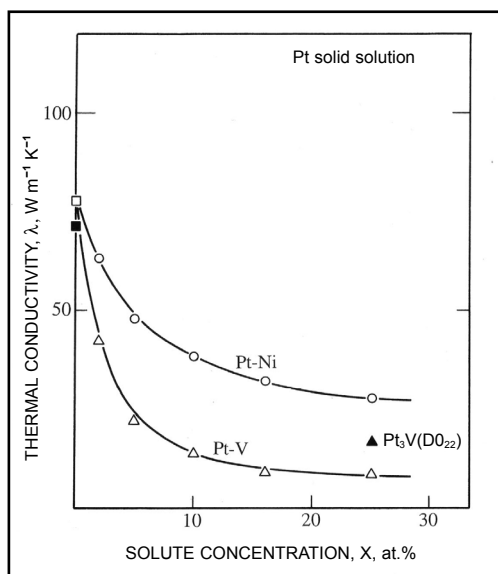


Fig. 1 Composition dependence of thermal conductivity at 300 K in Pt-Ni and Pt-V alloys. Data for pure Pt are represented by the solid square on the axis (1, 13, 14). The recommended values for pure Pt in these data sources are similar. The solid triangle is data for Pt₃V with the D0₂₂ ordered structure (15)

order-disorder transformation occurs at a stoichiometry of 3:1. The data for Pt₃V with a f.c.c. disordered structure and a D0₂₂ ordered structure are from earlier work (15). Note that the heat treatment at 1573 K for 1 hour was undertaken to achieve the disordered state in Pt₃V, while ageing at 1020 K for 168 hours was employed for the ordering reaction.

The thermal conductivity of pure Pt found in the present experiment was 77.8 W m⁻¹ K⁻¹, which is slightly higher than values in the literature (1, 13, 14). It decreased monotonically with increasing solute concentration for both alloys. In the composition ranges used, the conductivity-composition plots are characterised by a sharp maximum at pure Pt in each case. The composition dependence is more pronounced in the Pt-V alloy, with the addition of only two atomic percent V reducing the thermal conductivity of Pt by one half. The rate of reduction in thermal conductivity becomes smaller at higher V concentrations, typically above ten atomic percent.

Figure 1 shows that the thermal conductivity increases on formation of the D0₂₂ ordered phase

at composition Pt₃V. This increase in conductivity by ordering seems to be a general feature which is also demonstrated by Pt₃Cr with the L1₂ structure, and in Ni₃V(D0₂₂), Ni₃Mn(L1₂) and Ni₃Fe(L1₂) (15). Thermal conductivity is usually degraded by the scattering of carriers in the crystal lattice. Topological and configurational disorder, such as impurities, vacancies and lattice defects, impede the flow of heat carriers. Hence, well-ordered intermetallic compounds should have higher conductivity than their disordered alloys, assuming that the carrier concentrations do not change in both phases (16).

The essential question then to be answered is what is responsible for thermal conduction in Pt alloys. The thermal conductivity of metallic materials is generally composed of an electronic component and a phonon component. The Wiedemann-Franz relation is a criterion for identifying the carrier of thermal conduction. The Wiedemann-Franz law states that at high temperatures the ratio of thermal to electrical conductivity (the reciprocal of the resistivity) for all metals is proportional to absolute temperature. When the electronic component is the dominant contributor to the total thermal conductivity, λ , the Wiedemann-Franz relation should hold (17–19), as in Equation (i):

$$\lambda = L T \sigma \quad (i)$$

where L is the Lorentz number, T is the absolute temperature and σ is the electrical conductivity. A universality constant of λ/σ was found to be equal to $7.5 \times 10^{-6} \Omega \text{ K}^{-1}$ at 300 K for pure metals (17).

The Wiedemann-Franz relation was examined for the Pt alloys under investigation here. Figure 2 shows the electrical conductivity (the inverse of electrical resistivity) plotted against the thermal conductivity for Pt-Ni and Pt-V alloys. The straight line indicates the Wiedemann-Franz relation given by Equation (i) at 300 K. All the plots for the Pt alloys, including pure Pt, fall close to the line. This indicates that Pt alloys satisfy the Wiedemann-Franz relation at 300 K, even highly concentrated alloys.

The dominant carrier of thermal conduction in Pt alloys is, therefore, ascribed to an electron

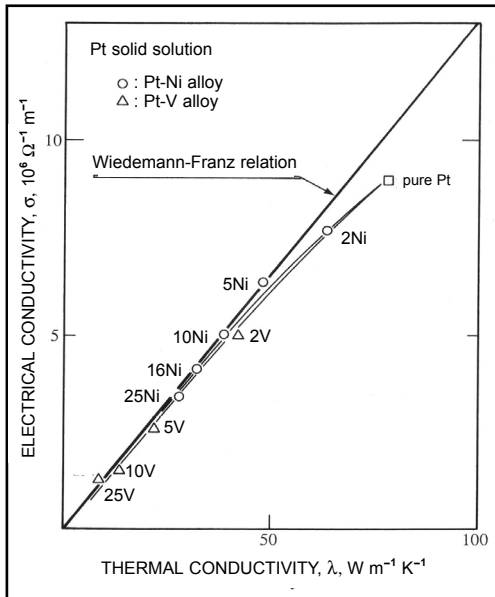
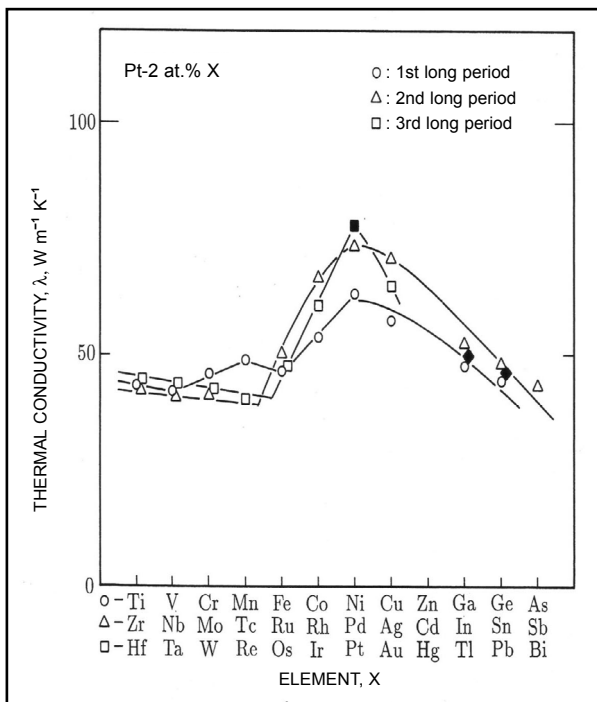


Fig. 2 Wiedemann-Franz relation for Pt-Ni and Pt-V alloys at 300 K. Alloy compositions are in atomic percent

rather than to a phonon: more specifically, the 6s electrons are considered to be responsible for the thermal conduction.



Dependence on the Constituents

Figure 1, the dependence of thermal conductivity on composition in Pt alloys, shows that there is a drastic decrease in thermal conductivity at low concentrations of solute, up to 2 atomic percent, from the value for pure Pt. It is well known that Pt has a wide solid solubility range for most alloying elements (20). In this section, we focus on the thermal conductivities of various Pt-2 at.% X alloys to identify the effect of solute, X, on the thermal conductivity of Pt.

Figure 3 summarises the thermal conductivities of Pt-2 at.% X alloys at 300 K. Solute X is arranged in Periodic Table order. It can be clearly observed that the addition of a solute element decreases the thermal conductivity of Pt. When solute X belongs to B-subgroup (Cu, Ga, Ge) in the first long period, the thermal conductivity decreases monotonically as the horizontal distance of X from the solvent Pt increases. This trend also holds for the solute X in the second long period. It is worth noting that Al and Si, which are located above Ga and Ge, respectively, also fall on the same line.

This trend was reported for electrical resistivity and is known as the Norbury rule (21). Norbury studied the change in electrical resistivity by the addition of solutes to Fe, Ni, Cu, Ag, Au and Mg and the molten states of Na and K. An

Fig. 3 The thermal conductivity at 300 K of Pt-2 at.% X alloys as a function of the atomic number of solute X.

The solid black square shows the thermal conductivity for pure Pt.

Data for Pt-2 at.% Al and Pt-2 at.% Si are the solid diamond-shaped symbols.

As, Pb and Bi are not soluble in Pt (20).

There are no data for Tc because the alloy is unstable.

There are no data for Zn, Cd, Hg and Tl as their lower boiling temperatures prevent the alloy ingots being prepared by arc melting

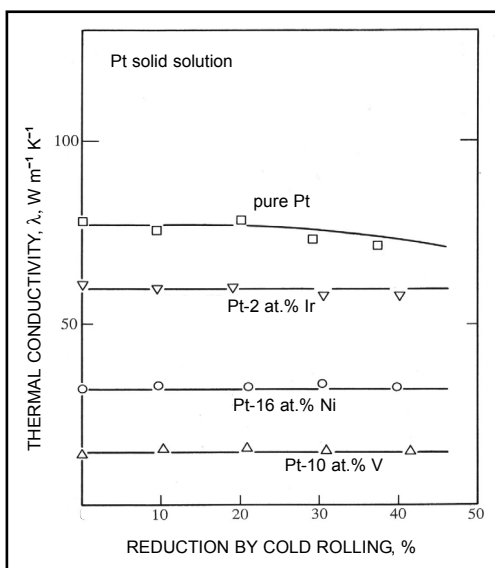


Fig. 4 Thermal conductivity of pure Pt and Pt alloys as a function of reduction by cold rolling. The values of the thermal conductivities were measured at 300 K

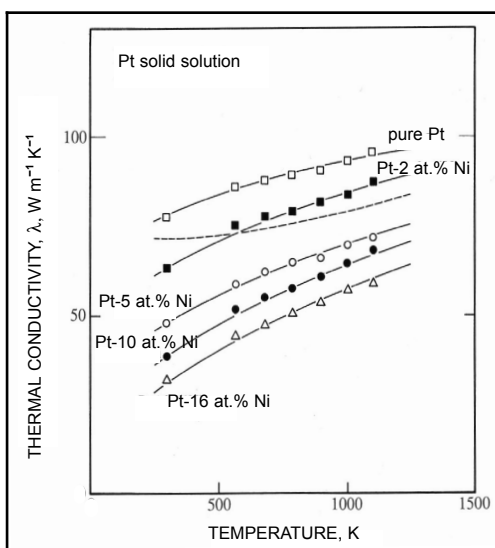


Fig. 5 Thermal conductivity versus temperature for the Pt-Ni alloys. Data for pure Pt recommended in the data sources are shown by the dotted line (13, 14). The values from the data sources are similar

empirical rule was found that the electrical resistivity of binary alloys increases as the position in the Periodic Table of the solute element becomes horizontally distant from that of the host component. The current results imply that the Norbury rule generally holds for transport phenomena driven by

electrons. Unlike the case of B-subgroup elements, however, the behaviour is more complicated when the solute belongs to the remaining transition elements. For the first long period, the thermal conductivity decreases monotonically as the distance of X from Pt increases. This breaks down at Mn. The breakdown occurs at elements distant from Pt when solute X belongs to the third long period. It is notable that Re most significantly decreases the thermal conductivity of Pt. Also noteworthy is the fact that the thermal conductivities are quite similar to one another for solutes belonging to the same column, typically demonstrated in the columns IVA, VA and VIII (Fe, Ru, Os). The data in Figure 3 also suggest that the thermal conductivity is more dependent on the column of solute X and is less dependent on the period.

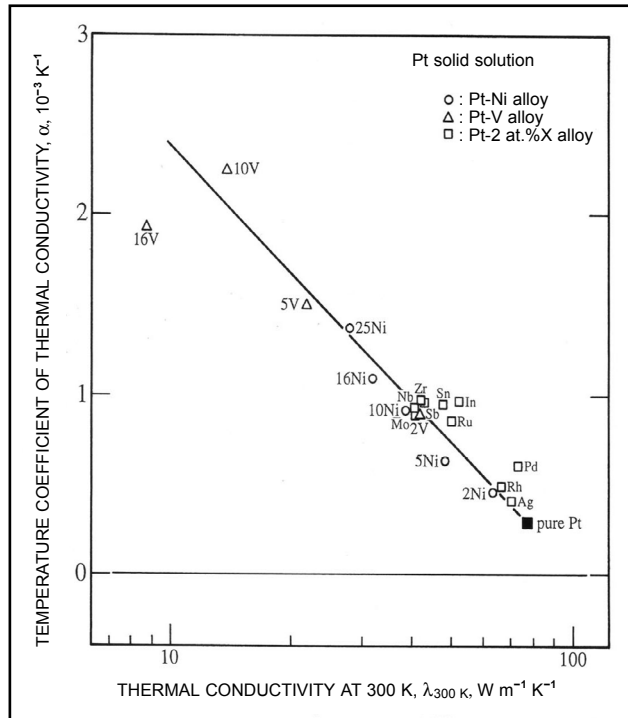
Dependence on Work Hardening

In order to study the sensitivity to fabrication conditions, thermal conductivity was investigated as a function of reduction by cold rolling for some Pt alloys. Figure 4 shows results for pure Pt and for three Pt alloys. A slight decrease in thermal conductivity was observed in pure Pt, typically at above 30% of reduction by cold rolling, while a fairly constant value is maintained for high concentrated alloys with lower conductivities. The results imply that the thermal conductivity of these alloys is chiefly determined by the initial composition and hardly by the defect structure developed during fabrication.

Temperature Dependence

Thermal conductivities in Pt-Ni alloys as a function of temperature are shown in Figure 5 together with values for pure Pt from data sources represented by the broken line (13, 14). The thermal conductivity of pure Pt, measured in the present study, increases monotonically with increasing temperature and reaches approximately $95 \text{ W m}^{-1} \text{ K}^{-1}$ at 1100 K. The monotonic increase is also confirmed for the reference data, though the magnitude is systematically lower. Adding Ni does not alter the general trend of monotonic increase and only results in shifting the entire data to lower values. Furthermore, close observation

Fig. 6 Correlation at 300 K, between the thermal conductivity and the temperature coefficient for Pt-Ni and Pt-V alloys. Each value has an alloy composition. Ten values for Pt-2 at.% X alloys are plotted. Elements X are from the second long period



reveals that the temperature coefficient becomes larger with increasing nickel concentration and all the data seem to converge at higher temperatures.

The temperature coefficient, α , in the temperature range between 300 to 1100 K was initially estimated from Equation (ii):

$$\alpha = (1/\lambda_{300\text{ K}})(d\lambda/dT) \\ = (1/\lambda_{300\text{ K}})\{(\lambda_{1100\text{ K}} - \lambda_{300\text{ K}})/(1100 - 300)\} \quad (\text{ii})$$

where $\lambda_{300\text{ K}}$ and $\lambda_{1100\text{ K}}$ are the thermal conductivities at the indicated temperatures. In Figure 6, the temperature coefficients obtained for the Pt alloys are plotted against thermal conductivity at 300 K.

The pure Pt had a thermal conductivity of $77.8 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K with a positive temperature coefficient of $2.9 \times 10^{-4} \text{ K}^{-1}$. The thermal conductivity monotonically decreases with increasing Ni concentration, accompanied by the increase in the coefficient. Such an inverse correlation is more clearly seen in the semi-log plot, see Figure 6. Interestingly, most Pt-V alloys have the same correlation except for Pt-16V alloy. Moreover, various selected elements from the second long period shown by open squares also keep the same correlation, which implies the correlation may have a universal feature. The inverse correlation between α and $\lambda_{300\text{ K}}$ may be a general feature for metallic materials, and has been well documented

not only for binary solid solutions but also for multicomponent materials, such as steels and superalloys, and for intermetallic compounds (15, 22).

Conclusions

Thermal conductivity in Pt alloys was comprehensively surveyed as a function of solute concentration, work hardening and temperature. The results are as follows:

- [1] The thermal conductivity of Pt alloys is mainly determined by both alloy composition and temperature and is hardly influenced by work hardening.
- [2] Alloying decreases the thermal conductivity of Pt, and the conductivity-composition relationship is characterised by a sharp maximum at pure Pt. The Wiedemann-Franz relation held for Pt alloys indicates the dominant carriers of thermal conduction are electrons.
- [3] It is found that thermal conductivity decreases monotonically as the position of the solute element in the Periodic Table becomes horizontally more distant from that of Pt (but only for

B-subgroup elements). This is a counterpart of the Norbury rule originally proposed for electrical resistivity.

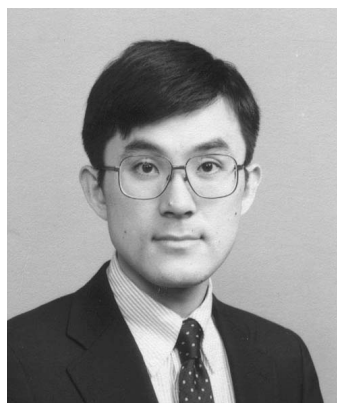
[4] A continuous increase in thermal conductivity

with temperature is observed for Pt alloys in the temperature range between 300 and 1100 K. The temperature coefficient and the thermal conductivity are inversely correlated.

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