Thermal Conductivity of Molten Al, Si and Ni Measured under Microgravity

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ABSTRACT

The thermal conductivities of molten Si, Ni, Al and their alloys have been measured by means of the non-stationary hot wire method under 1 G and microgravity of 10^{-5} G. A Mo wire was used as the heating wire and coated with alumina by the electrophoretic deposition to prevent an electric current leakage through the melts. Natural convection in the melts was suppressed by measuring the thermal conductivity under the microgravity of 10^{-5} G using the drop shaft facility of the Japan Microgravity Center. Moreover, the free surface of the melts was covered with a ceramics plate to prevent Marangoni flow. The thermal conductivity of molten Si is about 10 $Wm^{-1}K^{-1}$, and that of molten Al is 47 $Wm^{-1}K^{-1}$ at 1260 K. The thermal conductivity of molten Al-30 mass% Si alloy is about 30 $Wm^{-1}K^{-1}$, and that of molten Ni is 5 $Wm^{-1}K^{-1}$ at 1773 K. The thermal conductivities of some molten metals are discussed on the deviation from the Wiedemann-Franz law.

1. INTRODUCTION

Many structural and functional materials such as iron, steel, and single crystalline silicon are produced through their liquid states during the manufacturing processes. The thermal conductivities of high-temperature melts are one of the most important thermophysical properties as well as heat capacity, density, viscosity and surface tension for the improvement of process control and process simulation. The measurement of thermal conductivity of molten metals involves the experimental difficulties caused by natural convection, Marangoni flow and contamination from contact materials. Because of the experimental difficulties, the thermal conductivities of molten metals have been estimated from the electrical conductivity using the Wiedemann-Franz law. The law is derived from the free electron theory for pure solid metals. The estimated thermal conductivities of pure solid metals almost agree with the measured values; however, those of alloys and molten metals do not always agree with the measured values.

In previous papers /1/, some efforts have been made to measure the thermal conductivity of molten metals using steady state methods and non-steady state methods such as cyclic heating method, laser pulse method and hot wire method. Some methods give just the thermal diffusivity. The thermal conductivity is calculated additionally using heat capacity and density. In the previous measurements of thermal conductivity, the suppression of the convection in the melts caused by buoyant force and Marangoni force were scarcely taken into account. Usually the temperature of top of a sample is kept higher than that of the bottom to minimize the effect of natural convection. However, this results in insufficient suppression of convective heat transfer in the melts.

Recently, Hibiya *et al.* measured the thermal conductivity of molten InSb under microgravity using the TEXUS-24 rocket in 1989 /2/ and the drop shaft facility (microgravity of 10^{-5} G for 10 s), JAMIC (Japan Microgravity Center) in 1991 /3, 4/. They diminished the free surface using a piston type vessel to prevent Marangoni flow. They used a platinum line source printed on an alumina substrate covered by a thin alumina layer. The thermal conductivities of InSb melts are slightly smaller than the values estimated by the Wiedemann-Franz law. Nagai *et al.* measured the thermal conductivity of molten Hg and Si under the microgravity of 10^{-3} G for 1.2 s using the short-duration drop tower facility of HNIRI (Hokkaido National Industrial Research Institute), Japan /5, 6/. They used the hot-disc thermal constant analyzer (Hot Disc Inc., Sweden). They obtained smaller values by 3 to 5 % than that measured on the ground.

The aim of the present paper is to develop a method to measure the precise thermal conductivity of molten metals at elevated temperatures without the effect of convection under the microgravity of 10^{5} G using the drop shaft facility of the Japan Microgravity Center, JAMIC. Based on the obtained results, the deviation from the estimated values by the Wiedemann-Franz law is discussed.

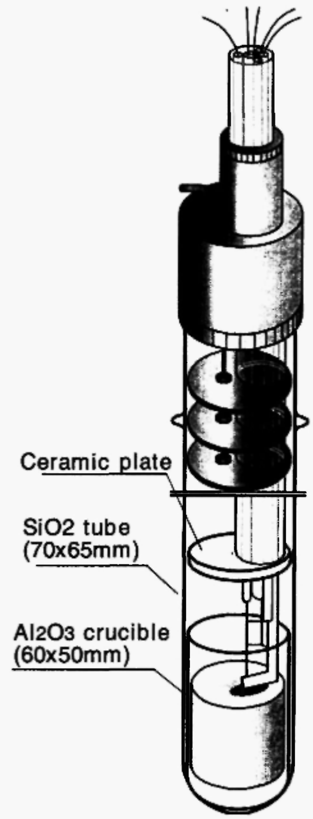


Fig. 1: Schematic diagram of the experimental apparatus for thermal conductivity measurements of molten metals.

2. EXPERIMENTAL

In the non-stationary hot wire method /7, 8/, a constant electric current is supplied to a thin metal wire of 150 μm diameter and 30 to 40 mm length placed in the molten metals, which serves as a heating element (hot wire) as shown in Fig. 1. The thin metal wire is Mo or Pt. When the thermal conductivity of molten metal is small, the temperature of the heating element rises rapidly, and vice versa. The temperature of the heating element can be measured as its electric resistance change by means of the 4-terminal method. The heating wire is coated with an alumina or silica film in order to prevent an electrical current leakage through molten metals. The present authors tried to coat the heating wire with silica slurry by a dipping method. The dipped wire was dried and sintered at elevated temperature. This coated wire was used as the hot wire for the measurement of molten silicon, but the coating layer was thick, porous and easy to break as shown in Fig. 2(a). The method was also time-consuming. The present authors have alternatively developed a new technique, termed electrophoretic deposition. The fine powder of alumina, silica or zirconia is suspended in a solution, and electric field is applied between a metal wire and Al plate. The fine particle has a charge and migrates and deposits on a metal wire as shown in Fig. 2 (b). This method has the advantages of easy manufacturing, uniform thickness, dense layer without pores, availability of various ceramics as coating materials and rapid coating.

The thermal conductivity,. , of molten metals is obtained from Eq. (1).

$$\lambda = \frac{Q}{4\pi} \Big/ \frac{d\Delta T}{d\ln t} \qquad (1)$$

where Q is the heat generation rate per unit length of the heating element and t is the time during passing a direct current through the heating element. The appropriate currents were pre-experimentally determined to be 2.0

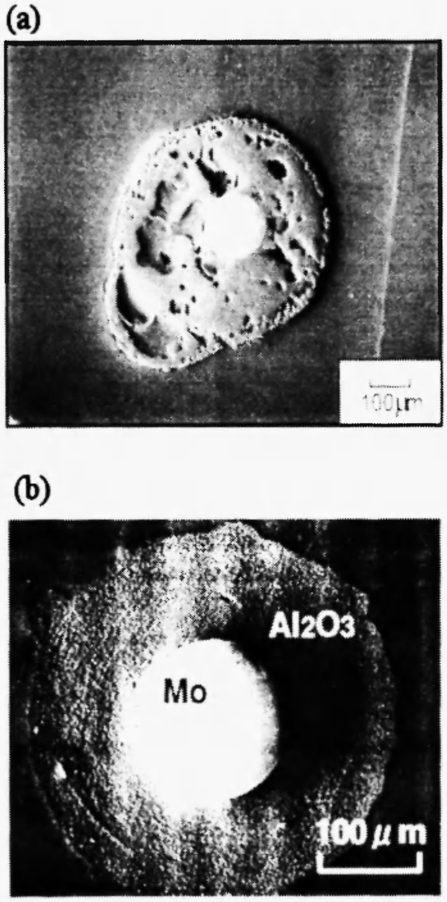


Fig. 2: Cross-sections of heating element coated with a thin layer using (a) silica slurry and (b) alumina-electrophoretic deposition.

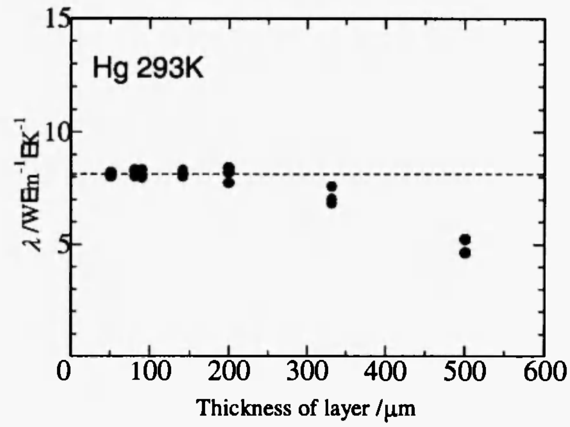


Fig. 3: Influence of thickness of coating layer on heating element on the thermal conductivity of Hg.

to 3.5 A depending on the sample. The thickness of the coating layer is 50 to 100 μm and the coating layer has no influence on the thermal conductivity of mercury as shown in Fig. 3.

A metal sample was contained in an alumina crucible and it is set in a one-end closed silica tube closed with a stainless steel cap. An argon gas of 99.999 % was filled in the silica tube and kept at 1 atm. The metal sample was heated in the resistance furnace, melted and kept at the desired temperature for 15 to 30 min. Subsequently, the probe for the thermal conductivity measurements was vertically immersed in the melt at the rate of 60 mm/min through the stainless steel cap by means of a stepping motor. After the sample temperature became stable within ±1K, the capsule was dropped. At 2 or 3 s after start of the drop, the electric current was supplied to the heating element for 7 or 8 s. The temperature was measured at the upper part of the melt by means of an R-type thermocouple of Pt-Pt·13%Rh.

The excellent quality of microgravity can be obtained in the drop capsule of the JAMIC, which falls 490 m. During the fall, the microgravity of 10^{-5} G is attained for 10 s. The drop capsule consists of inner and outer capsules. The experimental set-up for the thermal conductivity measurement was mounted in the inner capsule. The inner capsule was in the evacuated outer capsule. During the fall, the inner capsule was isolated in the evacuated outer capsule. The outer capsule falls in air while compensating for the air resistance using a gas thruster, which allows the inner capsule to fall freely.

The temperature increase in the heating element, ΔT, is recorded as the voltage difference between 2 terminals of the heating element, ΔV, using a data logger with 14 bit and the sampling interval of 1 ms. The linear relationship between ΔV and the logarithms of t could be obtained in case of no convection in molten metals and no reflection of heat from vessel wall. Fig. 4 shows the relation between ΔV and log t for Al-30%Si molten alloy under 1 G and 10^{-5} G conditions. Under 1 G, thermal convection in the melt appeared during the measurement. Under 10^{-5} G, there is no convection but a little reflection of heat from the vessel wall after 2 s.

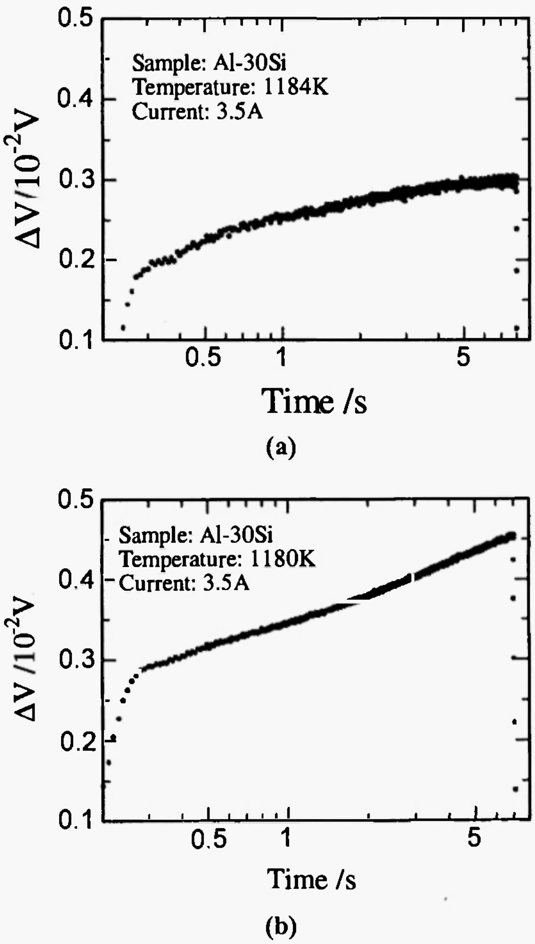


Fig. 4: Relation between the temperature increase of heating element and the logarithm of t for Al-30%Si molten alloy under (a) 1 G and (b) 10^{-5} G.

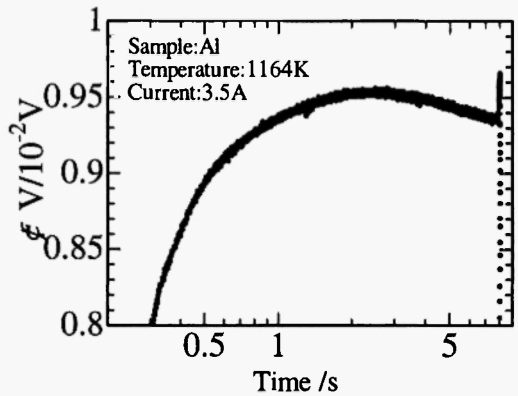


Fig. 5: Influence of Marangoni flow on the relation between the temperature increase of heating element and the logarithm of t for molten Al.

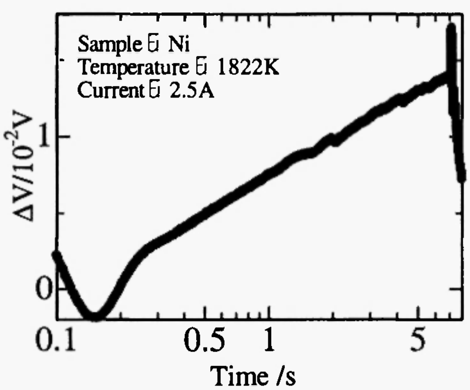


Fig. 6: Relation between the temperature increase of heating element and the logarithm of t for molten Ni under 10^{-5} G.

Even under 10^{5} G, free surface of molten metals causes Marangoni flow. Then, a ceramic plate is put on the surface of molten metal as shown in Figure 1. Fig. 5 shows the influence of Marangoni flow on the relation between ΔV and log t for molten Al without a ceramic plate on the surface. It is realized that strong convection appears and it is impossible to obtain the thermal conductivity of molten Al without suppression of Marangoni flow.

Fig. 6 shows the result of molten Ni under 10^{-5} G. A linear relationship between ΔV and log t is successfully obtained, indicating that no convection occurred during the measurement. The linearity between ΔV and log t was much improved even under 1 G when the ceramic plate is set for preventing Marangoni flow and temperature in molten metal is carefully controlled to be higher at the top of molten metal than the bottom for preventing thermal convection.

3. RESULTS

Fig. 7 shows the thermal conductivity of molten Al and Al-30%Si alloy. Si addition to Al decreases the thermal conductivity. The thermal conductivity of molten Al is much smaller than the values estimated from the electrical conductivity /9/ by the Wiedemann-Franz law. The previous values reported by Touloukian *et al.* /1/, Powell *et al.* /10/ and Bidwell /11/ were all

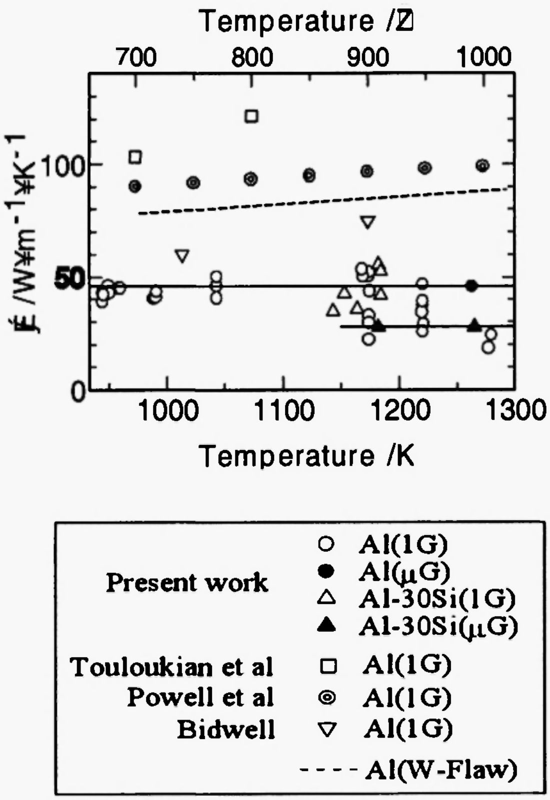


Fig. 7: Thermal conductivity of molten Al and Al-30%Si molten alloy.

measured by steady-state methods.

Fig. 8 shows the thermal conductivity of molten Ni and Ni-base alloy, TMS 75 (60Ni-12Co-6Al-3Cr). The values under 1 G and 10^{-5} G agree with each other within the experimental errors and are about one tenth of those estimated by the Wiedemann-Franz law. On the other hand, the data reported by Ostrovskii *et al.* /12, 13/ and Zinovyev *et al.* /12, 14/ are larger than the estimated values.

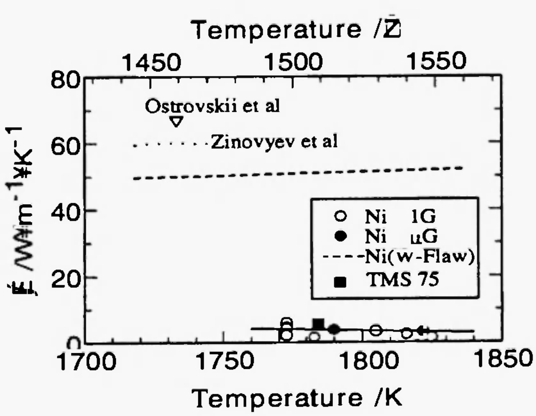
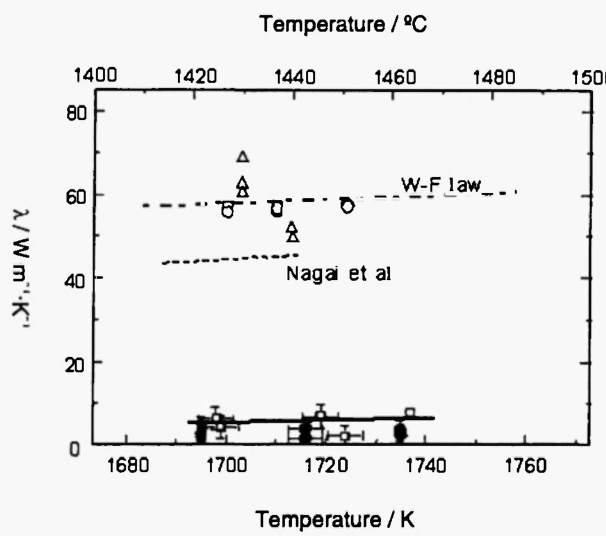


Fig. 8: Thermal conductivities of molten Ni and molten TMS 75 (60Ni-12Co-6Al-3Cr).

Fig. 9 shows the thermal conductivity of molten Si. The values of molten Si without a ceramic plate on the surface under 1 G /8/ are ten times larger than those with a ceramic plate. These larger values seem to agree with those estimated by the Wiedemann-Franz law. However, taking account of occurrence of Marangoni flow, the smaller values are more reliable. Although Nagai *et al.* measured the thermal conductivity of molten Si under the microgravity of 10^{-3} G for 1.2 s using the short-duration drop tower facility of HNIRI (Hokkaido National Industrial Research Institute), Japan /6/, they did not experimentally suppress Marangoni flow.



Symbol	Gravity	Heating wire (diameter,μm)	Crucible	Prevention of Marangoni flow
□	μG	Mo (150)	silica	yes
•	1G	Mo (150)	sulica	yes
□	1G	Mo (150)	alumina	no
□	1G	Pt (150)	alumina	no

Fig. 9: Thermal conductivity of molten Si.

If SiO gas bubbles are formed by the reaction between the SiO_2-coating layer and molten Si at elevated temperatures, the hot wire might be covered with the SiO gas bubbles, which may result in lowering the thermal conductivity of molten Si. However, the partial pressure of SiO gas in equilibrium with Si and

SiO_2 is the order of 10^{-2} atm and no SiO gas bubble is formed under 1 atmosphere. The thermal conductivities of solid Si measured by the same method show an excellent agreement with the values measured by other methods /8/. It is concluded that the thin ceramic layer coated on the hot wire has no influence on the measured thermal conductivity of molten Si.

4. DISCUSSION

4.1 Influence of the thickness of the coating layer

The temperature increase in the hot wire coated with a ceramic layer can be calculated by the following equation /7, 8/,

$$\Delta T = \frac{Q}{4\pi\lambda}[\ln t + A + t^{-1}(B \ln t + C)] \tag{2}$$

where A, B and C are constant and calculated from the thermal conductivity and thermal diffusivity of the hot wire, ceramic coating layer and molten metal. The influence of SiO_2 coating layer of 200 µm on the hot wire on the thermal conductivity of liquid Hg is about 0.2 % after 1.5 s /7/. Figure 3 shows the effect of the thickness of the SiO_2 coating layer on the thermal conductivity of Hg at 293 K, supporting this evaluation. The layer is thinner and time is longer, the influence becomes smaller.

4.2. Deviation from the Wiedemann-Franz law

The Wiedemann-Franz law is derived from the free electron model on the assumption that the relaxation times are identical for electronic and thermal processes. The law states that the thermal conductivity is proportional to the product of the electrical conductivity, σ, and the absolute temperature as follows,

$$\lambda = L\sigma T. \tag{3}$$

where L is the Lorenz number (2.45×10^{-8} WΩ/K^2). Even in actual solid metals, this number calculated from the thermal conductivity and electric conductivity does not always agree with the theoretical value because the electron is not perfectly free but nearly free. The heat conduction in solid metals containing some amount of impurities and disordered alloys has the contribution of phonon as well as electron in the same magnitude /15/. The structure of molten metal could be highly disordered with a large number of lattice vacancies. The thermal conductivities of alkaline metals, Ag and Au follow the Wiedemann-Franz law. For the 12th group metals of Zn and Cd, the 13th group metals of Al, Ga and In and the 14th group of Si, Ge, Sn and Pb, the thermal conductivities, however, deviate to smaller values from those estimated by the Wiedemann-Franz law at higher temperatures /16/. From this consideration, it is expected that the heat conducted in molten metal will not always be contributed by free electron.

5. CONCLUSION

The thermal conductivities of Al, Ni, Si and Ni-base and Al-base alloys in molten state have been measured by means of the non-stationary hot wire method under 1 G and microgravity of 10^{-5} G. The thermal convection and Marangoni flow in molten metals can be suppressed by using microgravity condition and diminishing free surface of molten metals. The thermal conductivities of the melts are smaller than those estimated by the Wiedemann-Franz law.

ACKNOWLEDGEMENTS

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