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Viscosity, Thermal Conductivity, and Surface Tension of High-Temperature Melts[1]

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High-temperature melts are substances which are solids at room temperature and liquids at high temperatures. They include liquid metals, molten salts, and other melts such as molten semiconductor materials. Although they show scientifically interesting behavior and have industrially important characteristics, the thermophysical properties of these substances at high temperature are not sufficiently known due to experimental difficulties. Many melts show strong chemical activity and therefore are corrosive to materials of container and sensors. Applicable sensors are limited also because of the high temperature and the electrical conductivity of melts. In this paper the present status of available data for the viscosity, the thermal conductivity, and the surface tension of high-temperature melts is reviewed. Limited experimental information is available and these properties are difficult to predict theoretically. The transport properties are important for predicting heat transfer and flow patterns. For the prediction of the behavior of melts under microgravity condition, the temperature dependence of the surface tension plays a major role.

KEY WORDS: high-temperature melts; liquid metals; liquid semiconductors; molten salts; surface tension; thermal conductivity; viscosity.

1. INTRODUCTION

High-temperature melts are substances which are solids at room temperature and liquids at the temperature of interest, namely, at high temperatures. They include liquid metals, molten salts, and recently also molten semiconductor materials. Typical melts are listed in Table I. The category includes many other substances, such as volcanic lava, molten

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Table I. Typical High-Temperature Melts

Category	Examples of substances	Applications
Liquid metals	Na, Na–K	FBR coolant
	Li	Coolant/fuel of fusion reactor
	Fe, Al	Metallurgy
	Slugs	Metallurgy
	Molten structural materials	Safety (accident)
Molten salts	Nitrates	Heat carrier thermal energy storage
	Carbonates	Fuel cell
	Fluorides	Higher-temperature thermal energy storage
Others	Si, GaAs, Ge	Semiconductor
	Molten nuclear fuels	Production, safety
	Glass	Production
	Lava	Geophysics

glasses, molten nuclear materials, etc. Information on the thermophysical properties of these substances is needed not only because of their scientifically interesting behavior but also because of rising interest in modern industrial applications [1]. Data are needed on salts for high-temperature fuel cells and thermal-energy storage units, on lithium for fusion reactors, on oxides and semiconductor materials for the production of new materials in microgravity conditions, etc. In Japan, the Iron and Steel Institute of Japan has continually made an effort to survey thermophysical property data on slags and molten metals and has published reports from time to time [2]. A committee of the Japan Society for the Promotion of Science has made a survey of references on slag properties [3]. The Society of Molten-Salts Thermal Technology has collected data and completed reports on several particular salts [4, 5]. In the Japan Society of Mechanical Engineers, a committee is actively working on the numerical analysis and on simulation techniques of applied thermofluid dynamics including high-temperature melts. Since 1987, a research group has been working on the thermophysical properties of high-temperature melts under a grant-in-aid from the Japanese Ministry of Education.

In research and development processes of large-scale industrial applications, the possibilities for experimental research are quite limited because of financial reason and therefore simulation studies are important. Figure 1 shows an example of a flow pattern in the case of single-crystal formation from melt by the Czochralski method. Simulation studies are needed to control convection. This kind of simulation requires precise numerical information on the thermophysical properties over a wide range of temperatures.

The viscosity, the thermal conductivity, and the surface tension of high-temperature melts are the most needed and the most poorly established properties. Viscosity is used in flow simulation calculations. Thermal conductivity is needed in heat-transfer calculations. Surface tension is needed in the study of droplet or surface behavior and in the prediction of Marangoni convection. The experimental measurements of these properties are extremely difficult at high temperatures, especially for high-temperature melts. The difficulties are due to strong reactivity of the sample with con-

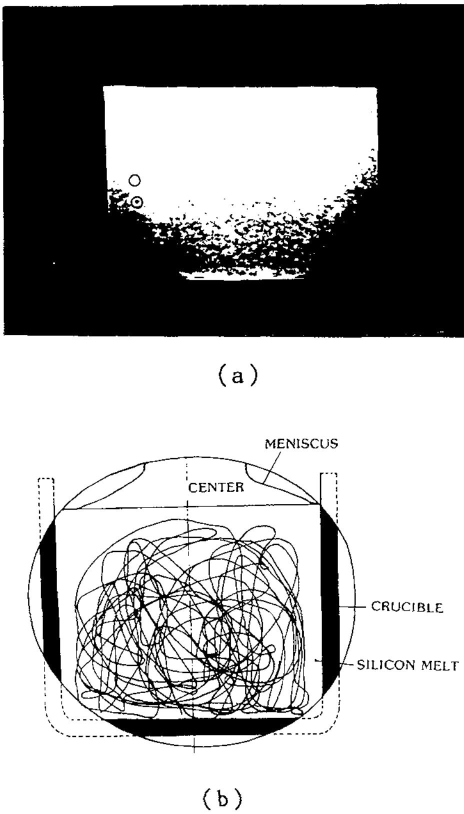

Fig. 1. Convection of silicon melt in a crucible. (a) X-ray photo showing the melt with tungsten tracers (in circles). (b) Traces of a tungsten particle moving with silicon convection. (Courtesy of Dr. K. Kamimoto, Mr. M. Eguchi, Mr. H. Watanabe, and Dr. T. Hibiya, NEC Corporation.)

tainer walls, rapid degradation of the samples, effect of electrical conductivity on sensors, sensitive impurity effects, and occurrence of supercooling and non-Newtonian behavior near the melting temperature.

The present paper reviews the availability and the quality of experimental data for the viscosity, the thermal conductivity, and the surface tension, discusses the present status of experimental techniques, and proposes future tasks. Since review papers are already available for specific melts, the intention is more on clarifying the problems common to high-temperature melts in general.

2. PRESENT STATUS OF EXPERIMENTAL DATA: AVAILABILITY AND QUALITY

2.1. Viscosity

Viscosity is a key property to study the structure of liquids and also is the most important transport property in industrial applications.

The most systematically studied substances among high-temperature melts are molten salts. Extensive compilations are available [6]. This is the fruit of a well-organized effort for many years by Janz at the Rensselaer Polytechnic Institute and of collaborating or coordinating researchers including Ejima and Yamamura of Tohoku University in Japan. They collected available data, evaluated them critically, performed round-robbin tests by distributing standard samples to experts in the world, and established calibration-quality reference data sets.

Although their efforts were beyond other people's reach, still future research is needed. There are two salts, namely, potassium nitrate and sodium chloride, for which the recommended viscosity data of calibration quality are available. Figure 2 shows the temperature dependences of the viscosity of NaCl based on recent measurements. Some of them were used as the bases for the 1983 recommendation by the Molten Salts Data Center. The shift of the 1968 recommendation to the new 1983 recommendation was up to about 30% and it suggested the importance of year-by-year check of recommended data. Smaller but still appreciable differences were found for data sets by the groups of Oye and of the present author. Oye and co-worker claimed as the cause of this discrepancy the so-called meniscus effect in the oscillating-cup viscometer. The recent redetermination by the present author's group yielded values a little lower than those obtained originally, but the change was due to a temperature correction and not to meniscus effect. For other salts, there are no well-established recommendation and systematic efforts are still needed.

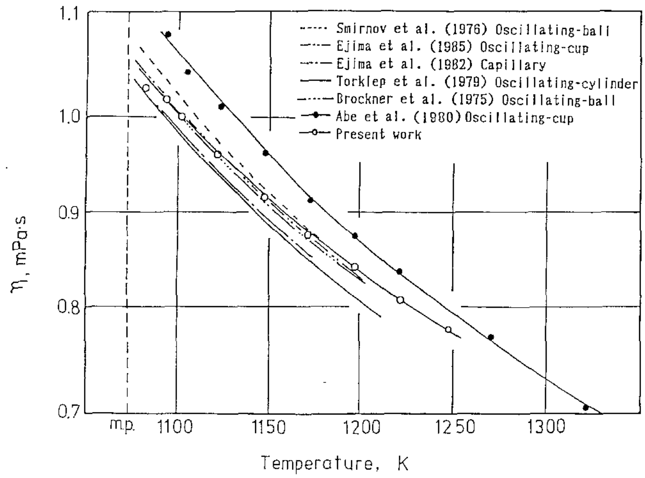

Fig. 2. Viscosity of sodium chloride.

For liquid metals, the situation is poorer. An example is shown in Fig. 3 for molten lithium, which is one of the well-studied metals. Available data show very poor agreement. The recent study by the present author has explained the origins of the discrepancies [7]. The main causes appeared to be the use of an inadequate working equation and of chemical degradation of the sample in some of studies. Figure 4 shows the situation for the viscosity of sodium. Thermophysical properties of alkali metals are reviewed in an IUPAC volume edited by Ohse [8]. For molten semiconductor materials, recently Kakimoto and Hibiya [9] performed measurements on GaAs with an oscillating-cup viscometer. Their data show a very steep rise of the viscosity near the melting point. Similar devia-

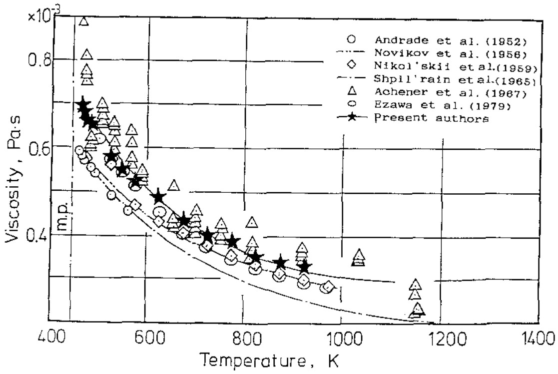

Fig. 3. Viscosity of lithium.

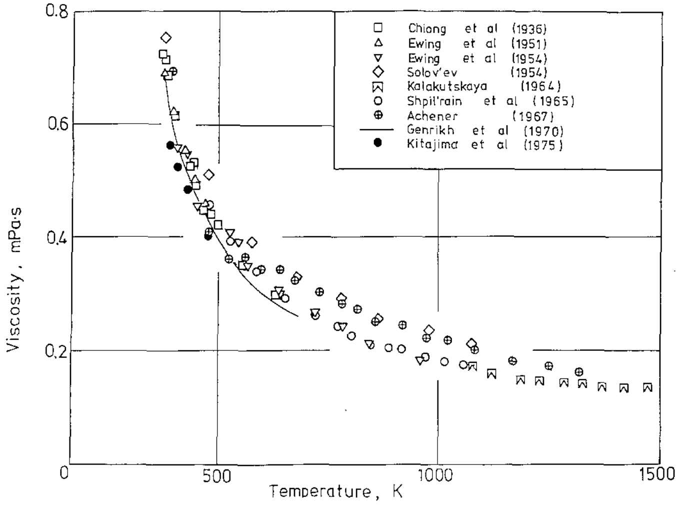

Fig. 4. Viscosity of sodium.

tions from the Arrhenius equation were reported for other semiconductors [10]. For materials production in a microgravity environment, a magnetic force might be a good means to prevent the Marangoni convection and Ozawa and others studied the effect of a magnetic field on the viscosity [11].

For slags, an extensive survey of references and of data was prepared by a committee of the Japan Society for the Promotion of Sciences in 1982 [3].

Table II shows the major techniques to measure the viscosity of high-temperature melts. The principle of the method should be based on physically well-defined flow condition. The techniques listed in Table II are reliable in this sense if designed and used properly. There are no commercially available instruments for high-temperature melts. Oscillating viscometers are suitable for precision measurements but require com-

Table II. Recommended Techniques to Measure the Viscosity of High-Temperature Melts

Technique	Difficulties
Oscillating cup	Meniscus effect
Oscillating cylinder (sphere)	Difficult for high-vapor pressure fluids
Capillary flow	Limited capillary materials
Falling ball	Difficult for non-transparent fluids

plicated computation of an implicit series which is the solution of the equation of motion. Researchers are tempted to use a simplified approximated equation and this has often led to serious errors, just as those described earlier for the viscosity of lithium. Another usual difficulty is ignorance of laminar flow conditions at high temperatures, where the liquid viscosity become smaller and the Reynolds number tends to be larger. The falling-ball method is difficult to use for nontransparent liquids. The viscosity of normal liquids shows typically an exponential decrease with temperature as seen in Figs. 3 and 4. This means that the viscosity near the melting temperature is very sensitive to errors in the temperature measurement. Especially at high temperatures, radiation is dominant and temperature error tends to be the largest error source.

2.2. Thermal Conductivity

As far as the thermal conductivity is concerned, the situation for high-temperature melts is surprisingly poor in comparison with other fluids.

Figure 5 shows thermal-conductivity data for KCl, one of the standard

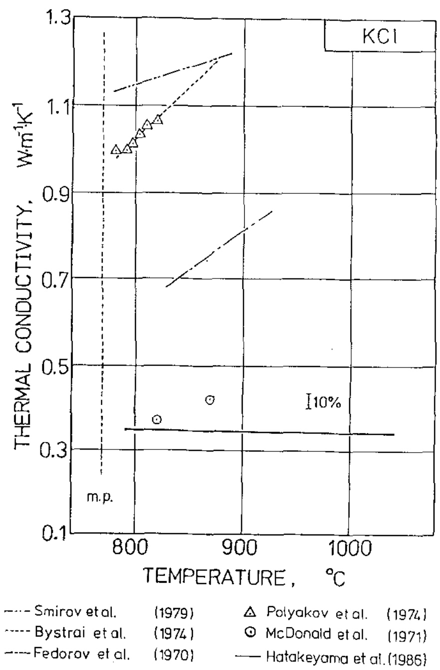

Fig. 5. Thermal conductivity of potassium chloride.

salts. The latest data from the present author's group [12] gave values completely different from the earlier values obtained by Russian groups [13–15] both in magnitude and in temperature dependence. The agreement with the work of McDonald and Davis [16] was better. The total deviation is of the order of 300–400%. Measurements by the present author's group were made with the so-called forced Rayleigh-scattering method. In order to confirm the reliability of the method, measurements were performed with water, toluene, KCl, and other liquids and compared with measurements with other established methods [17]. The estimated error is about 10% and there is little possibility of reaching even as large as 300%. All other data listed in Fig. 5 show a strong positive dependence on temperature. Since the temperature dependence of the thermal conductivity of most of other liquids including salts is zero or has a weak negative value, the strong positive temperature dependence is rare. Even at moderate temperatures, the situation is not much better. Figure 6 shows the composition dependence of the thermal conductivity of a mixture of $NaNO_3$ and KNO_3. Earlier data obtained by Bloom et al. [18] showed a very large change, in conflict with the linear dependence on temperature found by McDonald and Davis [19]. More recent data obtained by the present author's group with the modified transient hot-wire method [20] confirmed the linear dependence and yielded values about 10% smaller than those obtained by McDonald and Davis. Figure 7 shows the temperature dependences of available experimental data for HTS (high-temperature salt). Some of the data show strong negative temperature dependence while others show positive temperature dependence [21].

These three examples show how serious the situation is for the thermal conductivity. This is not only the case for molten salts but also for other

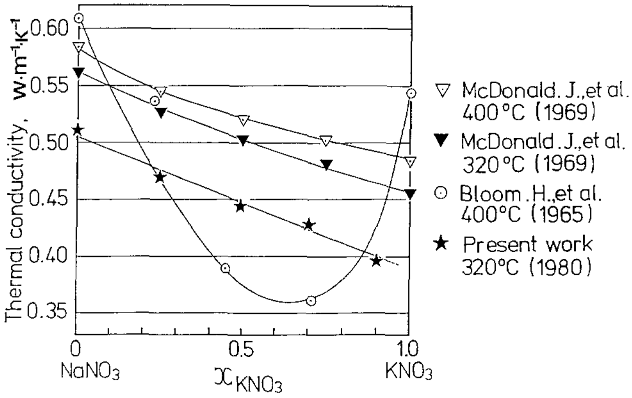

Fig. 6. Thermal conductivity of a mixture of $NaNO_3$ and KNO_3.

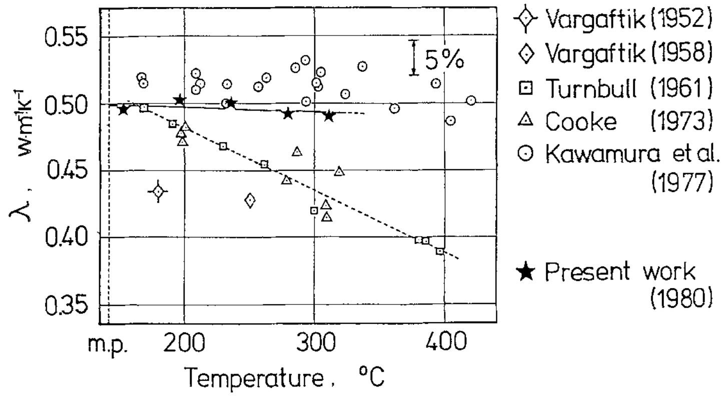

Fig. 7. Thermal conductivity of HTM (high-temperature melt).

high-temperature melts. In the case of many other substances, this kind of large discrepancy is not observed, simply because there are not enough data available.

Experimental difficulties in thermal-conductivity measurements are diverse and serious compared with those of the measurements of other properties. The major methods to measure the thermal conductivity are listed in Table III. Sensitive temperature sensors can not be used because of high corrosiveness. Metals and slags are not transparent and therefore the optical method is not applicable. Conventional methods are difficult to apply due to the very high value of the thermal conductivity of high-temperature melts, so that the temperature gradient in the specimen is very small. The greatest care should be taken to exclude convection errors, which are often the most serious error source even at room temperatures.

In addition to experimental difficulties, the observed behavior is confusing. For example, lithium and sodium, both in the alkali metal family, show a contrary dependence on temperature as shows in Fig. 8 [22]. As

Table III. Recommended Techniques to Measure the Thermal Conductivity of High-Temperature Melts

Technique	Difficulties
Concentric cylinder	Convection, difficult filling (void)
Parallel plates	Convection
Transient hot wire	Electrical insulation needed
Kohlrausch	Convection
Optical	Transparent fluids only

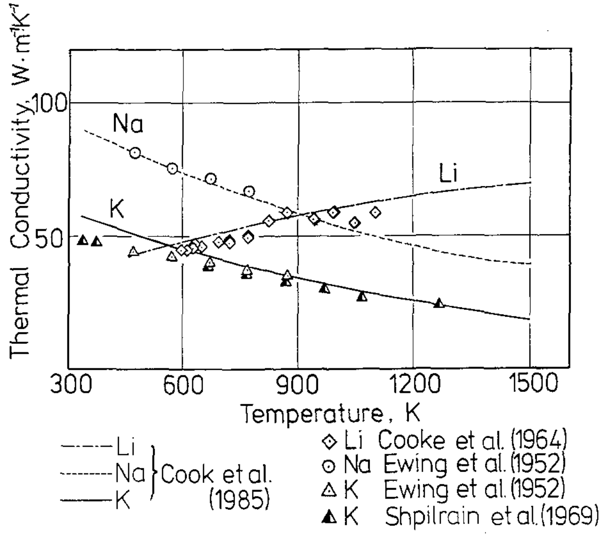

Fig. 8. Temperature dependence of the thermal conductivity of alkali metals.

for the pressure dependence of the thermal conductivity of molten metals, even the sign had not been confirmed for many years [23]. Thermal conductivity of molten semiconductor materials is poorly studied and reviews are given in, for example, Refs. 22 and 24. For slags, available data and references are surveyed in Refs. 2 and 3. Among the proposed techniques for slag, Takeuchi and co-workers [25] used a transient hot-wire apparatus with a noninsulation wire.

2.3. Surface Tension

Surface tension is very sensitive to physical and chemical interactions, and therefore, its measurement is difficult, especially at high temperatures. In addition to the importance in science, surface tension has significant importance in recent engineering applications. In the production of new materials in a microgravity environment in space, the analysis of Marangoni flow, the flow due to the temperature gradient of the surface tension, is essential. Control of surface behavior is the key to obtain high-quality single crystals of silicon from the melt. A study of direct contact heat transfer requires surface tension data in order to predict the behavior of droplets or bubbles. This is also the case in developments of high-temperature fuel cells, the study of loss-of-coolant accidents, and reflooding of nuclear reactors.

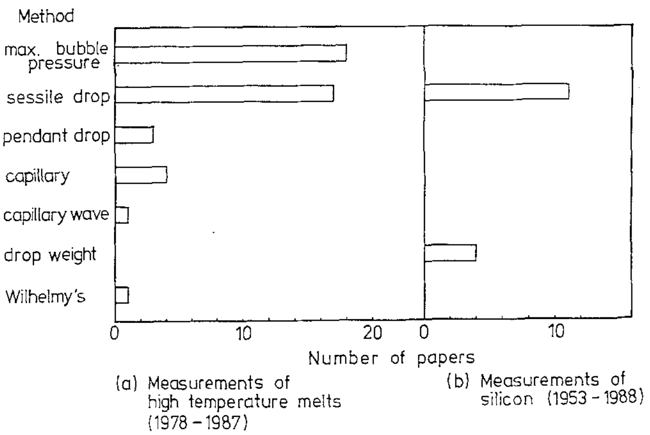

Fig. 9. Measuring methods for the surface tension of high-temperature melts.

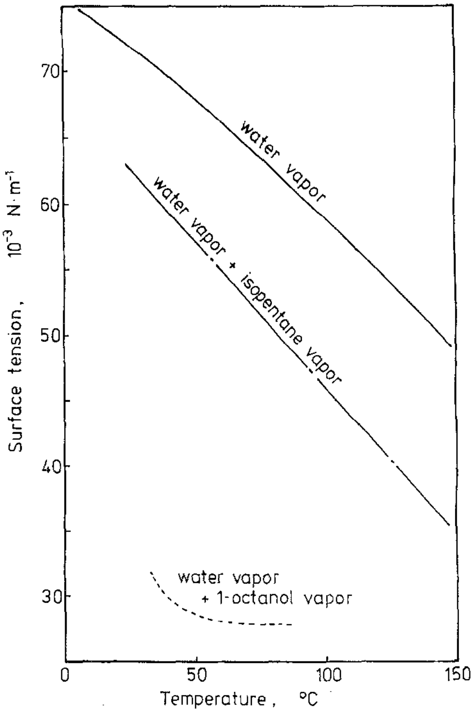

Fig. 10. Effect of contacting vapor on the surface tension of water.

As far as the experimental methods are concerned; Fig. 9 shows the frequency of various methods used in studies on high-temperature melts in the last 10 years (Fig. 9a) and also in studies on Si (Fig. 9b). Many researchers used the maximum-bubble pressure method and the sessile-drop method. Although these methods require a precise knowledge of the effect of the contacting gas, systematic studies are not yet available for many high-temperature melts. Only limited studies are available for some melts such as chloride [26], metals [27, 28], semiconductor materials [29], etc. In the case of other ordinary liquids such as water [30], the significant effect of contacting vapor is known as shown in Fig. 10.

For molten salts, systematic efforts to evaluate available data and to establish standard data sets have been performed by Janz and collaborators [6]. Calibration-quality data sets were established for two standard salts, KNO_3 (temperature range, 620–760 K) and NaCl (1080–1240 K).

Silicon is one of the most repeatedly studied substance and available data are shown in Fig. 11. These data seem to form two groups. Although most studies agreed with a lower value, Keene [31] suggested that lower values might be due to oxygen contamination. The effect of oxygen was studied by Hardy [29] and he noted a decrease in the surface tension with

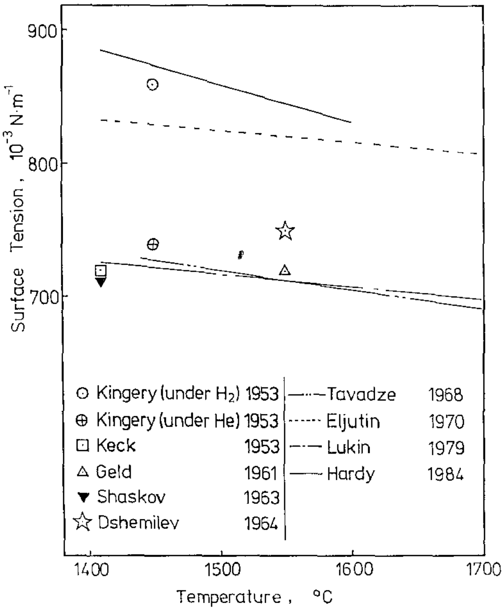

Fig. 11. Available surface-tension data for silicon.

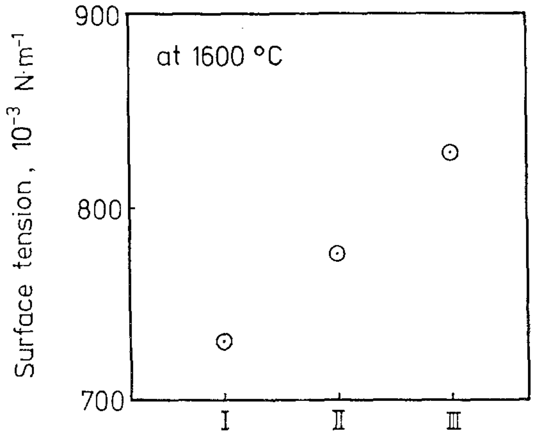

Fig. 12. An example of the effect of contacting gas to the surface tension of solicon.

an increase in oxygen as shown in Fig. 12. As seen from Fig. 13, the agreement between the data for germanium is slightly better, as the effect of oxygen contamination is less. The effect of the contacting solid wall materials in the measurement by the sessile-drop method is shown in Fig. 14 for germanium [32]. The temperature dependence is reasonably

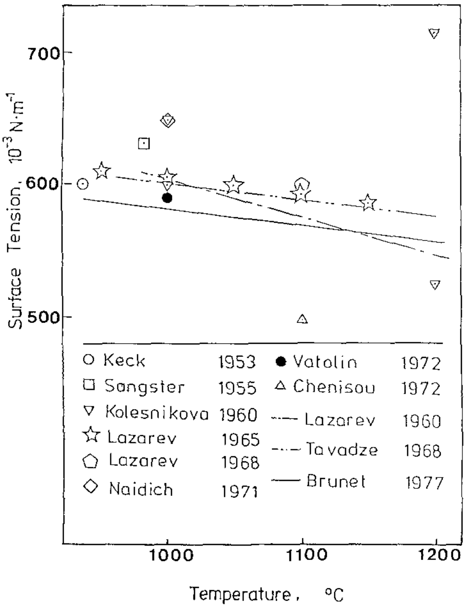

Fig. 13. Available surface-tension data for germanium.

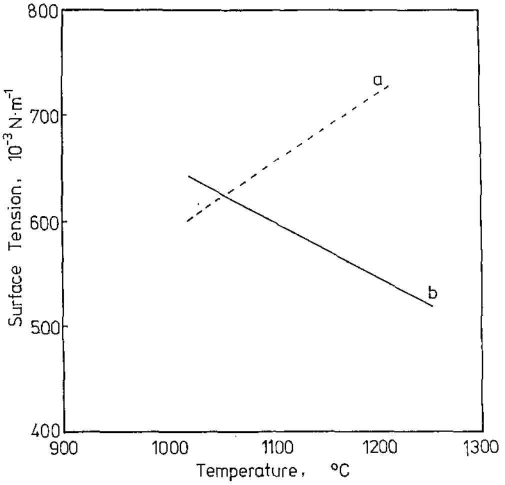

Fig. 14. Surface tension of germanium as measured by Kolesnikova [32] (sessile drop method): (a) on the graphite bed; (b) on the quartz bed.

known for silicon. It is poorly known for other semiconductor materials, since the number and the temperature range of available data are insufficient. The surface tension of mixtures of silicon and other substance was studied by Keene [31].

A review of the surface tension of alkali metals has been given by Allen [33]. A number of data sets are available for sodium and potassium. Although these data show larger deviations, the temperature dependences are in reasonably good agreement except for that of one study. Data on liquid metals are reviewed in Ref. 34.

The surface tension literature for slags is surveyed in Ref. [2].

3. FUTURE TASKS: CHALLENGES TO NEW TECHNIQUES

The most urgent task at the present time is to develop new measurement techniques which are capable of measurements above 1500°C. For many substances, experimental data are available up to 1000°C with reasonably good accuracy and up to 1300–1500°C often with unknown accuracy. It may be possible to reach 1500°C with presently available techniques. However, above 1500°C, we need new breakthroughs in the measurement techniques as summarized below.

(1) Transient method: subsecond or, hopefully, submillisecond measurements.

(2) Noncontact method: optical measurements coupled with levitation techniques.

(3) Methods applicable to highly corrosive or high-vapor pressure fluids.

Tasks specifically on each property are as follows.

(1) For viscosity, recalculation or reevaluation should be done of older data which have been obtained by oscillating methods and calculated with equations other than Kestin-Newell theory.

(2) For thermal conductivity, an urgent task is to establish calibration-quality standard reference data, at least for one substance, preferably for each category of substances.

(3) For surface tension, systematic research is needed to find the effects of trace impurities, of contaminating gas, and of contacting solid material.

Further tasks, in general, are critical evaluations of available data and establishing theoretical or semitheoretical prediction methods especially for mixtures or solutions. We have to manage a well-balanced and a harmonious trio of experimental measurement, theoretical prediction, and critical evaluation of data.

REFERENCES

1. A. Nagashima, *Appl. Mech. Rev.* **41**:113 (1988).
2. Properties of Electroslag, A report (The Iron and Steel Institute of Japan, 1979) (in Japanese).
3. Survey of References on Physico-Chemical Properties of Molten Metals, Alloys, Slags and Molten Salts, A report of Committee 140 of the Japan Society for Promotion of Sciences (1982).
4. K. Furukawa and H. Ohno, *Data Books for Molten Materials. I. Molten LiF-BeF$_2$ System* (Japan Nuclear Energy Information Center, 1980).
5. *Data Books for Molten Materials. II. HTS* (Japan Nuclear Energy Information Center, 1988).
6. G. J. Janz, *Proc. 4th Jap. Symp. Thermophys. Prop., Yokohama,* (1983), p. 199; G. J. Janz, *High. Temp. Sci.* **19**:173 (1985). Other references are listed also in Ref. 1.
7. T. Ito, K. Minami, and A. Nagashima, Paper presented at 10th Symp. Thermophys. Prop., Gaithersburg, Md. (1988).
8. R. W. Ohse (ed.), *Handbook of Thermodynamic and Transport Properties of Alkali Metals* (Blackwell, Oxford, 1985).
9. K. Kamimoto and T. Hibiya, *Appl. Phys. Lett.* **50**:1249 (1987).
10. V. M. Glazov, S. N. Chizhevskaya, and N. N. Glagoleva, *Liquid Semiconductors* (Plenum, New York, 1988), 68.
11. S. Ozawa, M. Eguchi, T. Fujii, and T. Fukuda, *Appl. Phys. Lett.* **51**:197 (1987).

12. Y. Nagasaka and A. Nagashima, Paper presented at 10th Symp. Thermophys. Prop., Gaithersburg, Md. (1988).
13. V. I. Fedorov and V. I. Machuev, *Teplofiz. Vys. Temp.* **8**:912 (1970).
14. P. V. Polyakov and E. M. Gildebrandt, *Teplofiz. Vys. Temp.* **12**:892 (1974).
15. G. P. Bystrai, V. N. Desyatnik, and V. A. Zlokazov, *Atom. Energ.* **36**:517 (1974).
16. J. McDonald and H. T. Davis, *Phys. Chem. Liq.* **2**:119 (1971).
17. Y. Nagasaka and A. Nagashima, *Int. J. Thermophys.* (in press).
18. H. Bloom, A. Doroszkowski, and S. B. Tricklebank, *Aust. J. Chem.* **18**:1171 (1965).
19. J. McDonald and H. T. Davis, *J. Phys. Chem.* **74**:725 (1970).
20. T. Omotani, Y. Nagasaka, and A. Nagashima, *Int. J. Thermophys.* **3**:17 (1982).
21. T. Omotani and A. Nagashima, *J. Chem. Eng. Data* **29**:1 (1984).
22. A. R. Regel, I. A. Smirnov, and E. V. Shadrichev, *Phys. Stat. Sol.* **(a)5**:13 (1971).
23. B. Sundqvist and G. Backstrom, *Rev. Sci. Instrum.* **47**:177 (1976).
24. V. M. Glazov, S. N. Chizhevskaya, and N. N. Glagoleva, *Liquid Semiconductors* (Plenum, New York, 1988), p. 25.
25. M. Takeuchi et al., *Proc. 1983 ASME-JSME Therm. Eng. Joint Conf., Hawaii, Vol. 3* (1983), p. 341.
26. L. A. Pirog, *Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall.* **6**:109 (1986).
27. A. Passerone, R. Sangiorgi, and G. Caracciolo, *J. Chem. Thermodyn.* **15**:971 (1983).
28. L. Goumiri and J. C. Joud, *Acta Metall.* **30**:1397 (1982).
29. S. C. Hardy, *J. Crystal Growth* **69**:456 (1984).
30. M. Murase, H. Matsubara, Y. H. Mori, and A. Nagashima, *Trans. JSME* **51B**:2638 (1985).
31. B. J. Keene, *Surf. Interface Anal.* **10**:367 (1987).
32. T. P. Kolesnikova, *Izv. VUZ Chern. Metal.* **9**:14 (1960).
33. B. C. Allen, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, R. W. Ohse, ed. (Blackwell, Oxford, 1985), pp. 691–700.
34. T. Iida and R. L. Guthrie, *The Physical Properties of Liquid Metals* (Oxford, 1988), pp. 109–146.