JOURNAL OF MATERIALS SCIENCE **40** (2005) 2161 – 2166

A new method for simultaneous measurement of surface tension and viscosity

H. FUJII*, T. MATSUMOTO, T. UEDA, K. NOGI
Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
E-mail: fujii@jwri.osaka-u.ac.jp

A new method for the simultaneous mesurement of the surface tension and viscosity of a liquid was developed by combining the principle of the oscillating drop method with a microgravity environment. This new method can be used in an ordinary laboratory. A droplet falls for 1.5 m in approximately 0.55 s. During this short period, the surface oscillation of the droplet is recorded by two high speed line sensors equipped with a laser backlight and cylindrical lenses. The recording speed and resolution of the line sensors are 84000 line/s and 2048 pixels, respectively. The laser backlight forms a shadow of the droplet, and each of the cylindrical lenses makes the shadow into be a line, allowing the maximum diameter to be precisely measured by a line sensor. Before focusing the laser column to a line, it was split into two columns and each of them is forcused into a different line in order to determine the changes in the diameters in two right-angled directions. The measured oscillations show only a single peak for the $n = 2$ mode in the Fourier spectrum. This fact guarantees that the surface oscillation is almost ideal, and the simple equations for a spherical droplet can be used without any corrections.

1. Introduction
The oscillating drop method is one of the best methods for the measurement of the thermophysical properties of high temperature melts, because it can be performed under contamination-free conditions without a crucible or substrate. In addition, the thermophysical properties can be measured over a much wider temperature range because an undercooled state is easily achieved, and the sample does not react with any refractory materials even at high temperatures. Although the oscillating drop method can be used under terrestrial conditions when assisted by an external force such as an electromagnetic force, the droplet is not spherical, thus complicating surface oscillation [1–3].

In order to redress this problem, a microgravity environment has been used, and consequently, the potential superiority of the oscillating drop method under microgravity conditions was proved [4–7]. However, the microgravity facilities such as a space station cannot be commonly used because of its extremely high cost. Accordingly, in this study, a new, inexpensive and convenient oscillating drop method was developed to simultaneously measure the surface tension, density and viscosity with high accuracy.

This method enables us to measure the thermophysical properties of many unknown samples over a short time period. In order to significantly reduce the effect of the emissivity variation for unknown samples, an ultraviolet pyrometer was developed.

2. Free-fall oscillating drop method
The principle of the oscillating drop method is used in the new method for the simultaneous measurement of the surface tension, density and viscosity of a liquid. However, apart from an ordinary oscillating drop method, the sample is dropped for 1.5 m in approximately 0.55 s in order to achieve a microgravity condition. Because it was thought that such a short microgravity condition restricts the accuracy of the measurement, a new system shown in Fig. 1 has been devised.

First, the droplet size was decreased to increase its oscillation frequency. In this study, a 1 μl water droplet was used. For example, when the frequency is 1000 Hz, 550 oscillations can be obtained during the 1.5 m drop. This number of oscillations is high enough to obtain accurate values of the thermophysical properties. In addition, in order to minimize the size of the system, only the droplet, not the entire device, was free-falling in this method.

The system includes two high-speed line sensors, a laser backlight, and two cylindrical lenses. The high-speed line sensors record the surface oscillation of the

*Author to whom all correspondence should be addressed.

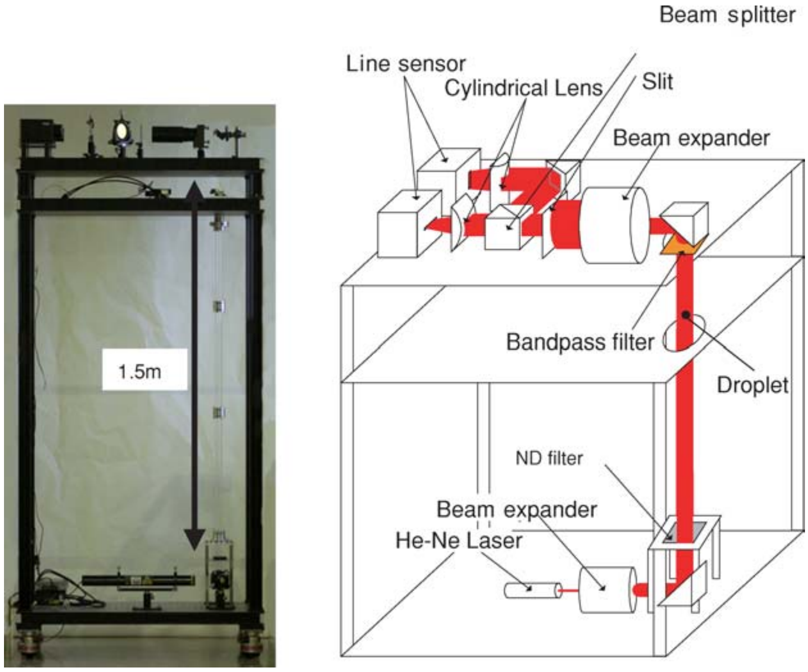

Figure 1 Developed system of free-fall oscillating drop method.

droplet with high resolution. In order to make the measurement error less than 0.1%, the droplet must be placed on more than 1000 dots of the line sensor. In addition, when the error due to the oscillation phase is less than ±2.5 deg, the measument error in the diameter can be less than 0.1%. To get a smaller phase error less than ±2.5 deg, the observation rate should be 71 times higher than the osicllation frequency. Namely, if the frequency of the surface oscillation is 1000 Hz, the observation rate should be greater than 71,000 frame/s. In order to satisfy these requirements, line sensors with the recording speed of 84,000 lines/s and resolution of 2048 pixels were used in this study.

The droplet falls inside the laser beam column. The laser backlight system minimizes any complicated focusing problems. It is generally difficult to observe a moving object while keeping it in focus. Even when an autofocusing mechanism is used, the observed size of the object changes as it moves. Because the laser is a parallel beam, on the other hand, the size of the shadow is constant at any place inside the laser column. Each of the cylindrical lenses makes the shadow into a line. The shadow of the droplet can be observed as a dark line on the sensor, allowing the maximum diameter to be precisely measured by a line sensor for any position of the droplet. Before focusing the laser column to a line, it was split into two columns and each of them is focused as a different line in order to determine the changes in the diameters in two right-angled directions. The data obtained by the line sensors are converted into a real length using a calibrated scale, which was determined using five steel ball bearing spheres of different sizes.

3. Principle of the oscillating drop method

When the equilibrium shape is spherical, the oscillation frequency is determined by the surface tension, γ, and the mass, M, of the droplet, as shown by the following equation [8]:

$$\omega_{\mathrm{l}}^2 = \frac{4}{3}\pi l(l-1)(l+2)\frac{\gamma}{M} \tag{1}$$

where ω is the angular frequency of the surface oscillation, and l denotes the oscillation modes. The frequency of $l = 2$ is called the Rayleigh frequency. Thus, when only the frequency of the surface oscillation and the droplet mass are known, the surface tension can be calculated using

$$\nu_{\mathrm{R}}^2 = \frac{8}{3\pi}\frac{\gamma}{M} \tag{2}$$

where $\omega = 2\pi\nu_{\mathrm{R}}$. One of the main advantages of this method is that only the mass of the sample is necessary rather than the density, a value that often includes an approximately 5% error.

In the conventional oscillating drop method, the equilibrium shape is not spherical and, therefore, a frequency spectrum with several peaks is obtained. For such cases, some correction formulas have been proposed by Cummings and Blackburn [2] and Suryanarayana and Bayazitoglu [3] to calculate the Rayleigh frequency. Cummings and Blackburn proposed the following equation:

$$\omega_{\mathrm{R}}^2 = \frac{1}{5}\left(\omega_{\mathrm{l=2,m=0}}^2 + 2\omega_{\mathrm{l=2,m=1}}^2 + 2\omega_{\mathrm{l=2,m=2}}^2\right) - \omega_{\mathrm{tr}}^2\left\{1.90 + 1.20\left(\frac{z_0}{a}\right)^2\right\} \tag{3}$$

$$z_0 = \frac{g}{2\omega_{\mathrm{tr}}^2}$$

where ω_{tr} is the mean translation frequency of the drop's center of mass, g is the gravitational acceleration, and

a is the radius of the droplet, while l and m are the labels for the oscillation. Unfortunately, the reliability of Equation 3 has not yet been confirmed [5].

For a spherical droplet, on the other hand, the surface tension, γ, density, ρ, and viscosity, ηs can easily be calculated from the oscillation using the following equations.

$$\gamma = \frac{3}{8}\pi M \nu^2 \tag{4}$$

$$\rho = \frac{M}{V} \tag{5}$$

$$\eta = \frac{3}{20\pi}\frac{1}{\tau}\frac{M}{R} \tag{6}$$

where M is the droplet mass, ν is the frequency of the oscillation, V is the droplet volume, τ is the damping constant, and R is the radius of the spherical droplet.

4. Experimental procedure

Fig. 2 shows the sample dropping device for a liquid such as water. It is consists of two tungsten needles facing each other. First, a droplet is placed between two needles, and it is then dropped by pulling the two needles away from each other very quickly. The geometry of the needle is one of the important factors. The tip of the needle was sharpened like a circular cone. When the needle with this geometry is pulled out from the droplet, the total interfacial free energy between the needles and the droplet gradually decreases. This gradual decrease in the free energy gives a smaller force to the droplet in the vertical direction and enables the needles to be smoothly pulled out of the droplet. When needles with a flat tip are used, the interfacial free energy suddenly decreases at the tip and a strong force is given to the needles.

The wettablity of the needles by the droplet is also an important factor for the stable dropping of the sample. The better the wettablity, the stronger the force that generated in the vertical direction. In this case, it seems better to use a material with a poor wettablity. However, when a poor-wetting material is used for the needles, the droplet cannot surround the needle, and consequently it adheres to only a part of the needle. When the needles are pulled away under these conditions, the droplet is pulled toward the other side of the adhering position. When a material with a good wettability is used for the two needles, the wettablity of the two needles must be exactly equal. A slight difference in the wettablity generates unbalanced wetting of the two needles. Based on these considerations, good-wetting needles partially covered with a poor-wetting Teflon film have been adopted. The areas of the good-wetting surface of the two needles can be controlled to be same by the film. Using these types of needles, the initial speed is controlled to almost zero.

The geometry and motion of the needles are adjusted so that the droplet can fall straight down. In this study, pure distilled water was first used as the sample material. The droplet mass was immediately measured after falling. The droplet mass was varied from 1 μl to 7 μl. The surface tension and the viscosity of the droplet were calculated using the measured frequency and damping constant of the surface oscillation.

5. Calculation of thermophysical properties

Fig. 3 shows the change in the maximum length of the droplet observed using a line sensor. The surface oscillation occurs with the fundamental frequency, and it is also damping. The obtained data were analyzed by a fast Fourier transformation (FFT), as shown in Fig. 4. The measured oscillations show only a single peak for the $n = 2$ mode in the Fourier spectrum. This fact guarantees that the surface oscillation is almost theoretical, and Equations 4–6 can be used without any corrections. Table I shows the surface tension value calculated using the single peak. The scatter for these results come from the resolution of the Fourier spectrums and depends on the oscillation frequency, namely the droplet mass.

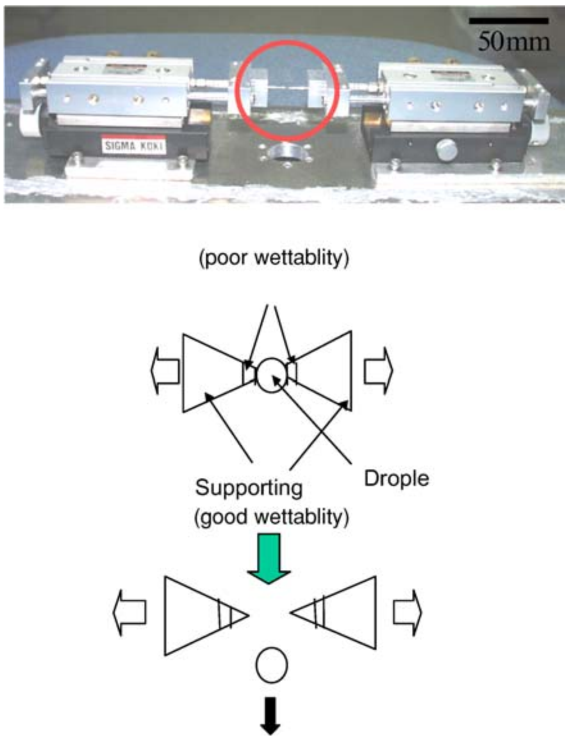

Figure 2 Sample dropping device.

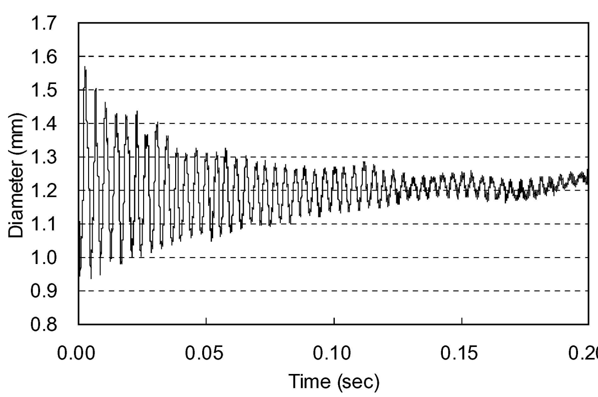

Figure 3 Change in the maximum length of droplet observed using a line sensor. (Distilled water).

TABLE I Surface tension of distilled water

		Surface tension (mN/m)	
Droplet volume (μl)	Temperature (C)	This study	Ref.[10]
1	23	72.3 ± 2.7	72.1
	27	73.2 ± 2.8	71.6
	27	72.8 ± 2.7	71.6
3	26	73.9 ± 2.4	71.8
	27	70.3 ± 4.9	71.6
	27	72.9 ± 4.9	71.6
7	28	71.5 ± 3.5	71.5
	28	73.1 ± 3.8	71.5
	28	70.9 ± 3.7	71.5

TABLE II Viscosity of distilled water

	Viscosity(mPa·s)	
Temperature (C)	This study	Ref.[11]
23	0.88	0.935
27	0.88	0.853
27	0.98	0.853

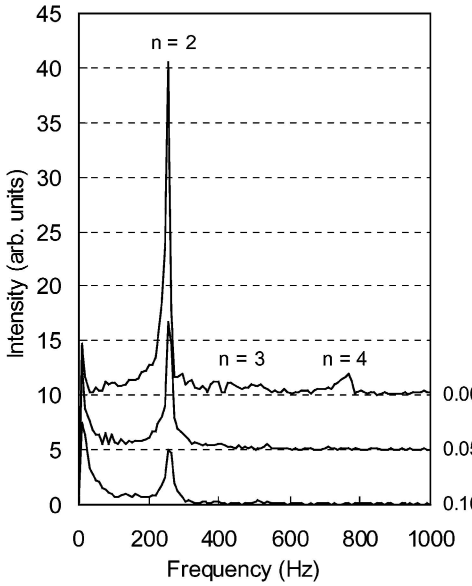

Figure 4 Fourier spectrum of surface oscillation. (Distilled water).

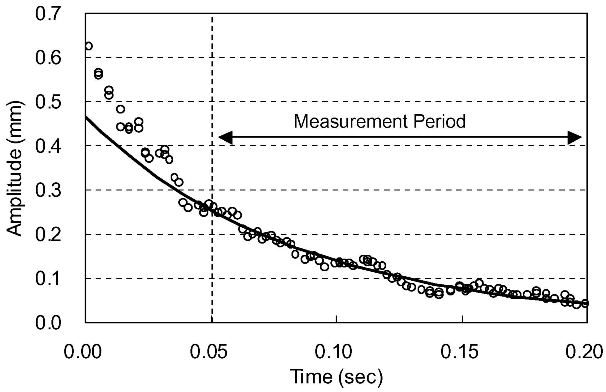

Figure 5 Damping of surface oscillation of water droplet.

The calculated thermophysical properties of pure water show good agreement with the previously reported values [10], and are independent of the droplet volume. These results prove the accuracy of this method. A higher resolution can be obtained using the smaller droplet.

During the initial period, the oscillation of the $n = 4$ mode as well as that of the $n = 2$ mode are recognized. However, oscillation of a higher n mode is generally damped very quickly. In this case, the oscillation of the $n = 4$ mode is also damped within 0.05 s. Accordingly, only the data after 0.05s are used to calculate τ for the viscosity. Fig. 5 shows the change in the amplitude and the damping curve fit to the data after 0.05 s. The damping rate before 0.05 s is faster than that after 0.05 s because the non-fundamental oscillations damp very quickly in this period. The viscosity value was calculated using Equation 6 and the results are shown in Table II, and compared with the reported values. The droplet size was 1 μl in this case. These values are in good agreement with the reported values [11].

6. Measurement of thermophysical properties of molten metals

Using this new method, the thermophysical properties of molten metals such as tin and copper were also precisely measured. In this case, an electromagnetic levitation method was used to levitate, heat and melt the sample during the initial stage, as shown in Fig. 6. When the electricity is switched off, the droplet starts to fall and the measurement is started. The initial oscillation can be obtained in the levitation stage by the electromagnetic force.

During the falling of the molten metal droplet, the temperature of the droplet may be decreased although the falling period of 0.55 s is very short. Accordingly, a furnace was located around the dropping tube. Before the droplet is introduced between the coils using the sample introduction device and levitated by the electromagnetic force, the furnace is heated to the experimental temperature. The droplet was then levitated, melted and heated to the experimental temperature, which was adjusted by the input of the electromagnetic force and the flow rate and mixing ratio of the Ar and He gases. When 0.4 s passed after the start of the free-fall, an electrical signal is input for moving the sample catching device to below the droplet. The sample mass is easily obtained by measuring the total weight of the sample and the edge part of the catching device. Fig. 7 shows the measured surface tension of copper together with previously reported values.

In principle, one experiment can be performed within several minutes which includes heating of the sample in this method. This is very effective when many samples are handled, for example, when the optimal composition is determined for lead-free solders or cast alloys. However, when unknown alloys are used, the temperature measurement is generally difficult, because the emissivity is dependent on the kind of materials. Accordingly, in this study, an ultraviolet pyrometer was developed, as shown in Fig. 8. While an infrared wavelength is used for an ordinary pyrometer, the wavelength of 350 nm is used in this system. Because the thermal radiation is weak for this short wavelength, it

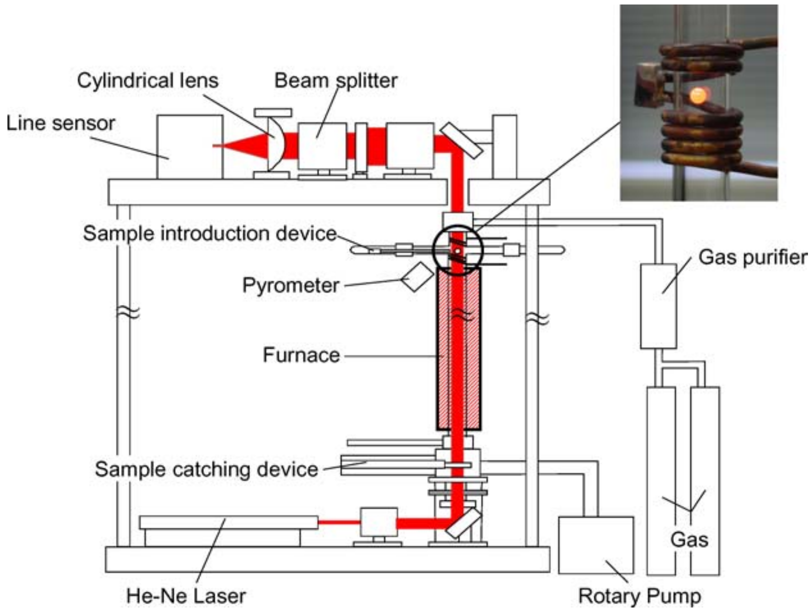

Figure 6 Free-fall oscillating drop method equipment for molten metals.

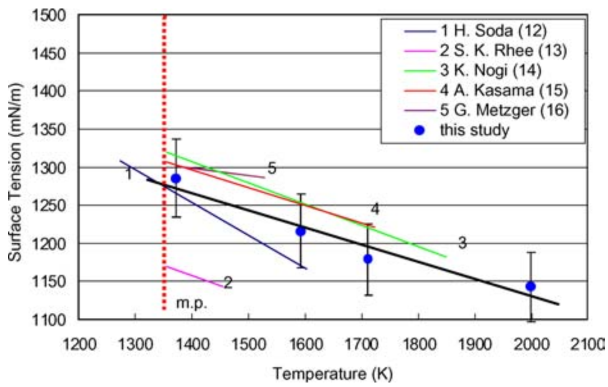

Figure 7 Surface tension of pure copper.

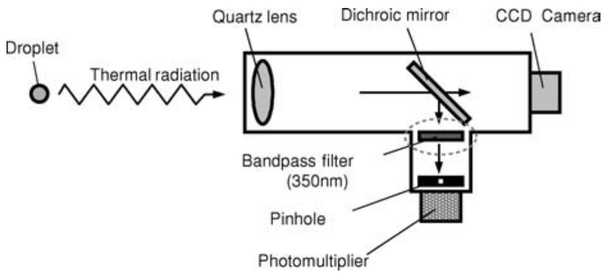

Figure 8 Ultraviolet pyrometer.

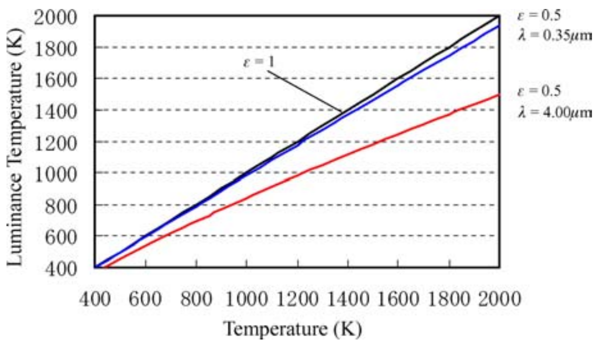

Figure 9 Effect of emissivity on luminance temperature.

must be amplified and therefore, this wavelength has not been used. However, as shown in Fig. 9, the effect of emissivity on the luminance temperature is very small, compared with a typical infrared ray, because the dependence of the temperature is much higher for that of the infrared wavelength. Accordingly, using this developed equipment, the thermophysical properties of many unknown materials can be precisely measured in a very short time.

7. Conclusions

1. A new method for the simultaneous measurement of the surface tension, density and viscosity of a liquid was developed by combining the oscillating drop method with a microgravity environment.
2. The system includes two high-speed line sensors, a laser backlight and cylindrical lenses. The laser backlight forms a shadow of the droplet, and each of the cylindrical lenses converts the shadow into be a line, allowing the maximum diameter to be precisely measured by a line sensor.
3. Before focusing the laser column to a line, it was split into two columns and each of them is focused as a different line in order to determine the changes in the diameters in two right-angled directions.
4. The measured oscillations show only a single peak for the $L = 2$ mode in the Fourier spectrum. This fact guarantees that the surface oscillation is ideal, and the equations can be used without any corrections.
5. Using this method, the thermophysical properties of molten metals can also be measured. This system enables us to measure the thermophysical properties of many unknown samples over a short period of time. An ultraviolet pyrometer was developed in order to significantly reduce the effect of the change in emissivity for unknown samples.

Acknowledgements

This study was supported by the Industrial Technology Research Grant Program from New Energy and

Industrial Technology Development Organization (NEDO) of Japan and the "Ground Research Announcement for Space Utilization" promoted by the Japan Space Forum.

References

1. D. L. CUMMINGS and D. A. BLACKBURN, *J. Fluid Mech.* **224** (1991) 395.
2. P. V. R. SURYANARAYANA and Y. BAYAZITOGLE, *Phys. Fluids* **A3** (1991) 967.
3. K. ECKLER, I. EGRY and D. M. HERLACH, *Mater. Sci. Eng.* **A133** (1991) 718.
4. I. EGRY, G. LOHOEFER and G. JACOBS, *Phys. Rev. Lett.* **75** (1995) 4043.
5. H. FUJII, T. MATSUMOTO, N. HATA, T. NAKANO, M. KOHNO and K. NOGI, *Metall. Mater. Trans.* **A31** (2000) 1585.
6. H. FUJII, T. MATSUMOTO and K. NOGI, *Acta Mater.* **48** (2000) 2933.
7. T. MATSUMOTO, T. NAKANO, H. FUJII, M. KAMAI and K. NOGI, *Phys. Rev.* **E65** (2002) 031201.
8. LOAD RAYLEIGH, *Proc. R. Soc. London* **29** (1879) 71.
9. H. LAMB, "Hydrodinamics," 6th ed. (Cambridge University Press, Cambridge, 1932).
10. A. G. GAONKAR and R. D. NEUMAN, *Colloids and Surface* **27** (1987) 1.
11. J. KESTIN and M. SOKOLOV, *Phys. Chem. Ref. Data* **7** (1978) 941.
12. H. SODA, A. MCLEAN and W. MIKKER, *Trans. JIM* **18** (1977) 445.
13. S. K. RHEE, *J. Amer. Ceram. Soc.* **53** (1970) 639.
14. K. NOGI, K. OISHI and K. OGINO, *Mat. Trans. JIM* **30** (1989) 137.
15. A. KASAMA, T. IIDA and Z. MORITA, *J. Jpn Inst. Metals.* **40** (1976) 1030.
16. G. METZGER, *Z. Phys. Chem.* **211** (1959) 1.

Received 31 March
and accepted 20 October 2004