Flow curves of Sn and Sn-3.5Ag obtained by rotational viscometry using a stainless steel cone

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Abstract. Corrosion of stainless steel in a flow soldering bath by a lead-free solder was investigated using a cone-plate-type rotational viscometer. The rotational torque of the stainless-steel cone in contact with a molten solder was measured at various shear rates. The delicate measured torque was related to the change of the viscosity of the solder owing to dissolution of materials originating from the cone. The estimated viscosity coefficient was ten times greater than the values which have been reported. The result was attributed to the tin content of the solder combined with oxygen from the passive state oxide film on the cone surface. The increase of the viscosity of the silver-containing solder was much greater than in case of pure Sn.

1. Introduction
Alternative Pb-solders, which contain Sn in high concentration ratios, lead to erosion and corrosion damage of stainless steel due to metal flow occurring in the soldering bath. A Sn-Ag solder system is used in flow soldering. The viscosity coefficient of the Sn-3Ag-0.5Cu solder at 523 K was 37 mPa·s, calculated from the data reported by M Jeyakumar et al. [1]. This value was greater than the value of 2.42 mPa·s for Sn-2Cu solder at 533 K by N Zhao et al. [2]. There are three types of rotating bob devices: a parallel-plate rotational device, a cone/plate-type rotational device and a double concentric cylindrical rotational device [3]. The cone/plate-type viscometer creates constant shear stress within the molten metal and on the surface of the cone/plate. Using a rotational cone-plate-type viscometer, the delicate rotational torque change related to erosion and corrosion of the stainless-steel cone was investigated for the Sn-3.5Ag solder.

2. Experimental
Sn-3.5 mass% Ag solder alloys were produced by a mixture of Sn (99.97% purity) drops and Ag (99.99% purity) wire at their eutectic composition. The weight of the mixture was approximately 5.5 mg. The diameter of the cone made from stainless steel 304 with a taper \( \theta \) of 3° was 21 mm. Additionally, Sn (99.97% purity) melts were also prepared for a comparison of the viscosity changes caused by oxidation of the fluid in contact with the oxide film on top of stainless steel. The viscosity was measured using a graphite cone.

Figure 1 schematically shows the cone/plate viscosity tester used in this experiment. The viscometer was composed of a motor, a shaft, a vortex spring and a pointer that indicated the distortion after
rotation. The cone plate was rotated by means of a lever fixed to the spring end. The vortex spring was made of a bimetal serving as a thermometer from 270 to 670 K to calibrate the thermal distortion of the spring at the measurement temperature of 523 K, and its spring constant was 1.117 mN/rad. When the temperature of the graphite crucible reached 623 K, the solder in the crucible was entirely molten. The crucible was then slowly cooled until it reached 523 K. During this time, the heated cone made of stainless steel 304, also kept at 523 K, was placed into the molten solder.

The cone/plate-type viscometer creates a constant shear velocity \( D \) on the cone surface, which is related to a constant angular speed \( \omega \). \( D \) is expressed in equation (1), where \( V \) is the speed of the cone surface and \( y \) is the separation distance between the cone and the plate, and is inversely proportional to the cone-plate separation in the fluid. The shear rate \( \dot{\gamma} \), in the fluid is expressed by \( \dot{\gamma} = \dot{\theta}u / \dot{\theta}y \), where \( u \) is the velocity in the fluid, as shown in Figure 2.

\[
D = \frac{V}{y} \tag{1}
\]

The shear rate does not yield the radius \( r \) from the rotational axis, according to equation (2).

\[
D = \frac{r\omega}{r \tan \theta} = \frac{\omega}{\tan \theta} \tag{2}
\]

This rotational viscometer can provide various fluid shear rates by changing the rotational speed. The shear stress \( \tau \) is assumed to be proportional to \( \dot{\gamma} \) by \( \tau = \mu \dot{\theta}u / \dot{\theta}y \), where \( \mu \) is the dynamic viscosity of a Newtonian fluid. However, the used cone/plate viscometer creates constant \( \tau \) across the local cone surface according to equation (3).

\[
\tau = \mu D \tag{3}
\]

The overall torque \( T_{\text{all}} \), as measured by the viscometer, is the integral of the shear stresses on the cone surface.

\[
T_{\text{all}} = \int_{0}^{R} r \tau 2\pi \cos \theta dl = \frac{2}{3} \tau \pi R^3 \frac{1}{\cos \theta} \approx \frac{2}{3} \tau \pi R^3 \tag{4}
\]

In equation (4), \( \cos \theta \approx 1 \), and the viscosity is finally derived from equation (5).

\[
\mu = \frac{3T_{\text{all}}}{2\pi R^3 D} \tag{5}
\]

Based on equation (5), the viscosity of fluid can be estimated from the slope of the curve of shear stress \( \tau \) versus shear velocity \( D \).

![Figure 1. Schematic illustration of the used cone/plate-type rotational viscometer.](image)
3. Results

3.1. Flow curves of Sn using graphite and stainless steel cones

Rotational torque data for molten Sn at 573 K using a graphite cone were stably obtained at various rotation speeds of 102, 148, 184, 216, 248, 289, 330, 369, 402, 435 and 468 rpm (204, 296, 368, 432, 498, 577, 659, 737, 803, 869 and 935 s⁻¹ in shear velocity), as shown in Figure 3. The torque values were obtained avoiding oxidation of molten Sn by the use of excess flux. The viscosity coefficient was estimated to be 3 mPa·s from the linear relationship between shear stress $\tau$ and shear velocity $D$ as in a Newtonian fluid (Figure 2). At the rotation speeds listed above, the flow of the molten solder was lamellar with a shear rate of below 800 s⁻¹. The derived viscosity value is almost identical to the reported value of 1.56 mPa·s⁴ employing this simple measurement method.

![Figure 2](image_url)  
**Figure 2.** Illustration of the calculation of rotational torque at a constant shear rate.

![Figure 3](image_url)  
**Figure 3.** Flow curve of pure Sn, obtained using a graphite cone at 573 K.

Rotational torque data for molten Sn at 573 K using a stainless steel cone were reliably obtained at various rotation speeds of 184, 216, 248, 289, 330, 369 and 402 rpm. The viscosity coefficient was
estimated to be 100 mPa·s from the linear relationship between τ and D as in a Newtonian fluid (Figure 4). At these rotation speeds, the flow of the molten solder was lamellar and was maintained below a shear rate of 800 s⁻¹. This viscosity coefficient was greater than the previously reported value [4] due to the presence of oxygen.

Figure 4. Flow curve of Sn, obtained using a stainless-steel cone at 523 K.

3.2. Flow curve for Sn-3.5Ag
Rotational torque data for Sn-3.5Ag solder at 523 K were stably obtained at various rotation speeds of 184, 216, 248, 289, 330, 369 and 402 rpm. High shear stresses were observed at low rotational speeds of 184 and 216 rpm. The viscosity coefficient was estimated to be 256 mPa·s from the slope of the flow curve shown by the broken line between 500 and 800 s⁻¹ (Figure 5). At these rotation speeds, the flow of the molten solder was lamellar and was maintained below a shear velocity of less than 800 s⁻¹. At the slow rotational speeds of 184 and 216 rpm, large values of shear stress were obtained, similar to those previously reported [1,5].

Figure 5. Flow curve of Sn-3.5Ag obtained using a stainless-steel cone at 523 K.
We attempted to measure speeds for accelerated life testing for erosion and corrosion tests at higher shear stress at the entire local cone surface in lamellar flow. The selected speed was 500 s\(^{-1}\) (250 rpm) because stable rotation could be achieved.

3.3. Change in rotating torque with time

The measurements of the rotational torque could be started one minute after immersion of the stainless steel cone into the solder. Measurements were taken every 30 min with a resolution of \(2 \times 10^{-5}\) N\(\cdot\)m. Once an increase in the torque was observed, the cone was removed from the graphite crucible. The cones and solder alloys were then cooled under ambient conditions. Figure 6 shows the measured rotational torque deduced from the shear resistance of the molten solder with respect to time at 523 K at the velocity of 250 rpm. The initial torque was 0.11 mN\(\cdot\)m when the cone was immersed in the solder, and an increase in the rotational torque was observed for approximately 500 min after immersion. Then, the torque quickly reached 0.15mN\(\cdot\)m.

![Figure 6. Measured rotational torque deduced from the shear resistance of the molten Sn-3.5Ag solder with respect to time at 523 K.](image)

3.4. Observation of cone plate after rotating torque change test

Cone plates were cross-sectioned after erosion and corrosion tests to observe if any solder alloy had adhered to the stainless steel. A scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX) analysis examined the surface of the stainless-steel cone that had been in contact with the solder. The optical image (a) and SEM image (b) of Figure 7 show the surface damage to the apex of the cone. The line analysis for (c) Ag, (d) Cr, (e) Ni, (f) Sn and (g) Fe in Figure 7(b) were performed from the apex at point A to point B, corresponding to approximately 40 \(\mu\)m. Figure 7(f) shows the adhesion of Sn at about 5 \(\mu\)m from A and around B. The dark area in Figure 7(b) is considered to be related to the distribution of (c) Ag in the length from 10 to 20 \(\mu\)m.

Figure 8 shows the EPMA maps corresponding to the cross-section of Figure 7(a) at a ring radius of \(l = 9\) mm where the surface lost luster. In other areas of the cone, adherent materials were not observed. Adherent Sn could not form an Fe-Sn alloy because iron was not detected. Elemental Sn was found inside the stainless-steel cone. The composition of the damaged surface was 73.41 mass\% of Fe, 19.76 mass\% of Cr, 6.10 mass\% of Ni and 0.75 mass\% of Sn. Cr atoms remained at the surface and Sn atoms diffused in the cone, according to the detection of 0.03 mass\% of Sn inside the cone. The compositional change of the surface was attributed to the loss of oxygen dissolved into the solder. This phenomenon was caused by the adhesion of Sn atoms, but also by the dissolution of Fe and Ni atoms from stainless steel into the solder, based on a decrease of the Ni concentration from 8 mass\% to 5-6 mass\%. The elution of Ni was considered to be promoted by a high shear velocity and friction.
**Figure 7.** Energy-dispersive X-ray spectroanalysis of the conical surface after the erosion and corrosion test. (a) Optical and (b) SEM images of sectioned cone after the test. Line analyses of (c) Ag, (d) Cr, (e) Ni, (f) Sn and (g) Fe were performed from the apex at point A of the cone to point B, covering a distance of approximately 40 μm.

**Figure 8.** EDX analysis of Fe, Cr, Ni, Sn, and Ag and back-scattering electron images of the sectioned cone after testing.
Table 1. EDX analysis of Fe, Cr, Ni, Sn and Ag at the points 1 and 2 indicated in Figure 8.

|       | Fe mass% | Cr mass% | Ni mass% | Sn mass% | Ag mass% |
|-------|----------|----------|----------|----------|----------|
| 1     | 70.97    | 18.12    | 10.18    | 0.03     | Not detected |
| 2     | 73.41    | 19.76    | 6.10     | 0.75     | Not detected |

3.5. Differential thermal analysis (DTA)

A difference between the DTA curves of the solders after 360 and 840 min of the erosion and corrosion tests was verified by a rise in the liquidus line of the solder by approximately 3 K (Figure 9). The DTA-plot was obtained using a heating rate of 10 K per minute under an argon atmosphere. The eutectic point was detected at 220.48 °C (493.63 K) according to the DTA curves recorded after 360 and 840 min testing time. The DTA-plot revealed that the liquidus line rose with time and reached 228 °C (501 K) after 840 min. It was considered that this rise is due to the elution of nickel to the solder, according to the Ni-Sn binary phase diagram.

![Figure 9. DTA analyses of the solders after erosion and corrosion testing.](image)

4. Discussion

In the case of the inert graphite cone, molten Sn dissolved oxygen adsorbed at the cone surface and the viscosity increased beyond than that of pure Sn. In the case of the stainless steel cone, adhesion of Sn atoms first occurred at the passive oxide film on top of the cone surface but, subsequently, Sn-Ag solder then dissolved oxygen atoms gradually for a while. Therefore, the viscosity of the Sn-Ag solder containing oxygen increased. The large value of 256 mPa·s using stainless steel cone was attributed to the silver content combined with the presence of oxygen around the conical apex area at low shear velocities. The flow curve of molten Sn-3.5Ag solder was not linear at low shear rates, while the viscosity of molten pure Sn was linear [1,5]. Adhesion of Sn after erosion and corrosion tests was observed at the apex of the cone where the shear velocity was low. The sudden increase in torque during the tests for the Sn-3.5Ag molten solder was attributed to the fracture of the passive oxide film by shear stress. When the cone was immersed in molten Sn-3.5Ag alloy, oxygen atoms were unable to penetrate into the cone and to recover from the passive layer because the concentration of dissolved...
oxygen atom in the molten solder was less than that in the stainless steel [6-10]. As for the elution of stainless steel into the molten solder, the concentration of dissolved oxygen in the oxide layer at 523 K has an effect on the elution speed. As a result, Ni atoms eluted into the Sn-Ag solder, and Sn atoms diffused into the cone after testing for 840 min. Local corrosion caused damage to stainless steel after the protective oxide film disappeared from the cone at a 9 mm radius where the shear rate was higher.

5. Conclusions

The viscosity of solders was investigated using the change in torque during rotating rheometry tests with the cones of stainless steel 304. An increase in the rotational torque was observed approximately 500 min after dipping the cone into the molten solder. In terms of the elution of stainless steel, the effect of the consistency of dissolved oxygen due to the high viscosity coefficient of 256 mPa·s for Sn-3.5Ag solder containing oxygen was examined.

Adhesion of Sn atoms occurred at the passive oxide film on top of the cone surface. Sn-Ag solder then dissolved oxygen, and the viscosity of the Sn-Ag solder containing oxygen increased. The increase in torque during the erosion and corrosion test for Sn-3.5Ag molten solder was attributed to the damage of the cone surface. Stainless steel is prone to erosion because its passivity is not recovered under the conditions present in a molten metal.

Ni atoms eluted into the Sn-Ag solder, and Sn atoms diffused into the cone. Local corrosion causes damage to stainless steel after the oxide film disappeared from the cone at about 9 mm in radius.

Acknowledgments

The authors wish to acknowledge assistance and technical support from the Center for Advanced Materials Analysis, Tokyo Institute of Technology.

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