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Surface tension of molten stainless steels under plasma conditions

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The surface tension and the density of 304 stainless steels with the sulfur contents of 10, 100 and 250 ppm were measured under low pressure Ar plasma conditions in the temperature range of 1823–2073 K. The measurements were carried out by the sessile drop method and a $(La_{0.9}Ca_{0.1})CrO_3$ substrate was used. No significant influence of the plasma was observed on the surface tension and its temperature coefficient. The surface tension and density of 304 stainless steel are expressed using the following equations:

$$\gamma = -0.12 \times T + 1980\ \text{(mN/m)} \quad \text{(10 ppm Sulfur)}$$

$$\gamma = 0.29 \times T + 1030\ \text{(mN/m)} \quad \text{(110 ppm Sulfur)}$$

$$\gamma = 0.49 \times T + 520\ \text{(mN/m)} \quad \text{(250 ppm Sulfur)}$$

$$\rho = -0.616 \times T + 8.11 \times 10^{+3}\ \text{(kg/m}^3\text{)}$$

1. Introduction

The Marangoni flow has a large effect on the weld shape [1, 2], because the shape depends on the convection inside the weld pool. Although the convection depends on the balance between several forces, namely the Marangoni force, the electromagnetic force, the air drag force and the buoyancy, the Marangoni flow can often be the main factor. For example, when welding is conducted for stainless steels, the depth of the weld pool is smaller for a low sulfur content, but it is larger for a high sulfur content [3–5]. It is considered that the change in the direction of the Marangoni flow on the pool surface causes this phenomenon.

In order to calculate the shape of the weld pool using a numerical simulation, all of the above mentioned forces are included and suitable physical properties are necessary [4, 6]. During the welding process, the surface of the weld pool is covered with the plasma, and the effect of the plasma on the surface tension should be considered. However, the values measured in Ar gas [7] or in a mixed gas of Ar, He, and H_2 [5, 8, 9] or the values calculated using thermodynamics [10, 11] are used in the simulation of the welding process. Although the surface tension measurements under plasma conditions have been carried out by Wen *et al.* [12] and Sahoo *et al.* [13], the accuracy of the measurements was not validated, as discussed in Section 4.1.

In this study, the effect of the plasma on the surface tension of the stainless steel was investigated. The sessile drop method was adopted, and the symmetry of the drop was confirmed by observing it in two directions. The surface tension and density were precisely measured for three kinds of stainless steel with the sulfur contents of 10, 110, and 280 ppm under Ar plasma conditions.

2. Experiments

A schematic diagram of the equipment used for the surface tension measurements is shown in Fig. 1. A couple of tungsten electrodes is positioned in the center of the equipment. The upper electrode has a ring shape and the lower electrode has a disk shape. A $(La_{0.9}Ca_{0.1})CrO_3$ substrate, which has a high electric conductivity at high temperature [14, 15], was positioned on the lower electrode and a sample droplet is formed on the substrate. In this setup, the droplet is a part of the electrode.

The chamber is equipped with four viewing ports to confirm the symmetry of the droplet by observing it in right-angled two directions. Two He-Ne lasers are used as the backlight, and two band-pass filters are placed in front of the two digital cameras. These band-pass filters pass only the light with the wavelength of 632 nm, and cut out the disturbing light from the sample itself and the bright heaters. Consequently, a clear profile of the droplet with a high contrast is realized in the obtained image.

In order to prevent the droplet from reacting with the substrate or atmospheric gas, a solid sample was kept at the cool end of the dropping tube at room temperature while the temperature was raised [16, 17]. After the requisite temperature of the substrate was reached, the sample was moved to the hot end of the Al_2O_3 dropping tube, and melted in 90 s. The molten sample is then

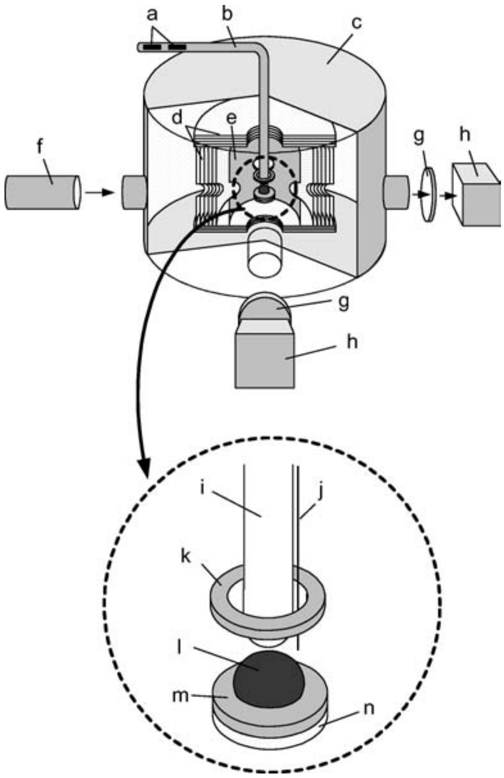

Figure 1 Schematic diagram of the measurement equipment. (a) solid samples, (b) dropping tube, (c) chamber, (d) reflectors, (e) Ta heater, (f) He-Ne laser, (g) band-pass filter, (h) digital camera, (i) dropping tube, (j) W-Re thermocouple, (k) electrode, (l) molten sample, (m) $LaCrO_3$ substrate, and (n) electrode.

dropped onto the substrate using a small difference in the pressure between the chamber and the inside of the drop tube.

The stainless steel sample weighed about 1.7 g piece. The sample and the substrate were polished and cleaned in acetone using an ultrasonic cleaner, and then the substrate was placed at the center of the equipment. The furnace was evacuated using a rotary pump and a turbomolecular pump. When the vacuum level reached to approximately 10^{-5} Pa, the heating was started. In order to remove any impurity adsorbed on the inside of the chamber, the temperature was first raised 30 K higher than the experimental temperature, and then lowered to 1473 K to introduce the Ar gas. When the temperature was raised to the experimental temperature again under the Ar gas atmosphere, the pressure was reduced to approximately 100 Pa and the sample is moved to the hot end of the dropping tube. After 90 s, the sample was dropped onto the substrate. The plasma was generated in a low pressure Ar gas by applying a DC voltage between electrodes. The current density used was 64 mA/cm^2. Although this current density is not very high, it is considered to be high enough to have an influence on the surface tension because the surface tension determined by the characteristics of several atomic layers on the surface. As soon as the sample formed a sessile drop shape, the first photo was taken. After taking the photos, the sample was then immediately cooled to a temperature below the melting point. After the experiments, the sulfur and oxygen contents of the sample were measured by the combustion infrared absorption method and the non-dispersible infrared absorption method, respectively.

Using the obtained photographs, the coordinates of 99 points on the profile of the droplet were decided. The surface tension was calculated by fitting these points to the Laplace equation using a computer program. The density was also measured simultaneously.

3. Results

Fig. 2 shows the change in the surface tension before and after the plasma is generated. The plasma was generated 60 s after the sample was dropped on the substrate. No significant effect by the plasma is observed.

Fig. 3 shows the temperature dependence of the surface tension for three types of stainless steels in the temperature range of 1723–2073 K. Only when the difference between the values in two directions were less than 3%, were the results adopted. The sulfur contents of the 10 and 110 ppmS samples did not change during the experiments. However, the 280 ppmS changed to 250 ppm after the experiments. The sulfur content of this sample is defined as 250 ppm because the surface tension was calculated using the data generated during the last 60 s of the experiments. The oxygen contents of

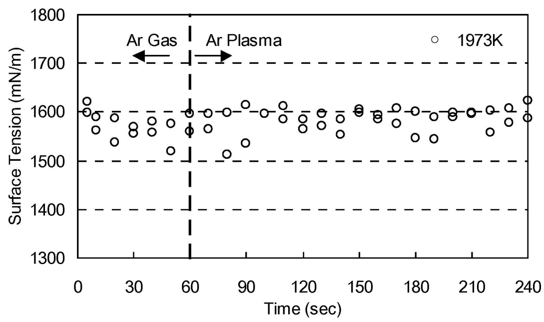

Figure 2 Effect of Ar plasma on surface tension of 304 stainless steels.

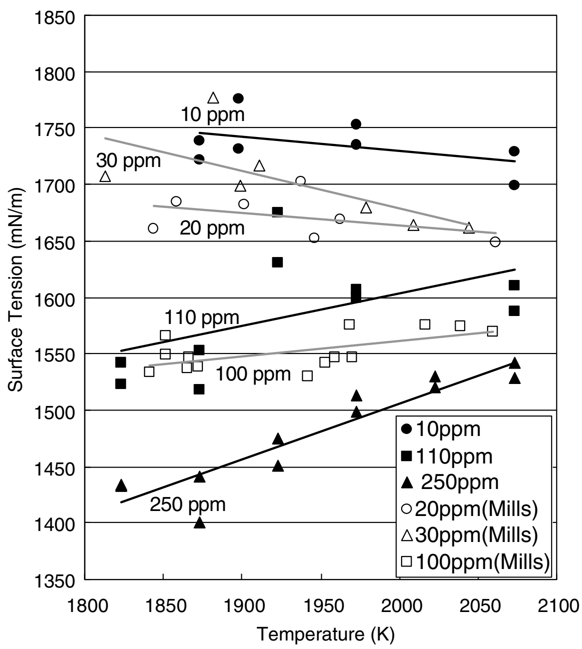

Figure 3 Surface tension of 304 stainless steels with various sulfur contents.

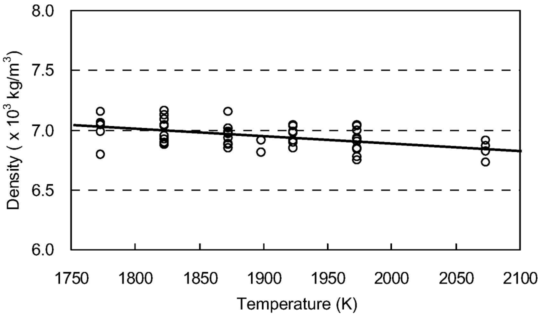

Figure 4 Density of 304 stainless plotted against the temperature.

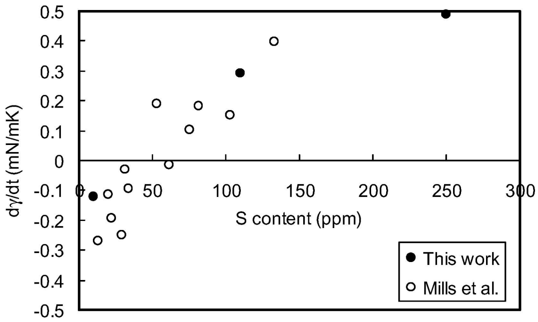

Figure 5 Temperature coefficient of surface tension of 304 stainless steels against sulfur content.

all the samples were less than 40 ppm. The surface tensions of the 304 stainless steel can be expressed using the following equations.

$$\gamma = -0.12 \times T + 1980\,(\mathrm{mN/m}) \quad (10\,\mathrm{ppm\ Sulfur})$$

$$\gamma = 0.29 \times T + 1030\,(\mathrm{mN/m}) \quad (110\,\mathrm{ppm\ Sulfur})$$

$$\gamma = 0.49 \times T + 520\,(\mathrm{mN/m}) \quad (250\,\mathrm{ppm\ Sulfur})$$

Fig. 4 shows the temperature dependence of the density of the 304 stainless steels. Because the low sulfur contents do not affect the density, the obtained results for the three types of stainless steels are plotted on the same graph. The density in the temperature range of 1723–2073 K is given by the following equation:

$$\rho = -0.616 \times T + 8.11 \times 10^{+3}\,(\mathrm{kg/m^3})$$

4. Discussion

4.1. Effect of plasma

Based on our result, no effect of the plasma on the surface tension of the 304 stainless steels in wide temperature range of 1823 to 2073 K was observed. The surface tension under plasma conditions was previously measured by Wen *et al.* and Sahoo *et al.* Wen *et al.* measured the surface tension of the 304 stainless steel using the drop weight method, and the value of 1169 mN/m was obtained. An arc plasma was generated to heat the sample using a welding torch. In this case, the surface of the sample was exposed to the strong arc plasma and the measured surface tension value seems to be affected by some forces such as an electromagnetic force. In addition, the sample temperature was not reported. They compared their result with Ahmad's value of 1172 mN/m at 1748 K obtained without plasma [18], and they concluded that the plasma does not affect the surface tension. Even though their conclusion is the same as ours, their conclusion is not reasonable because Ahmad's value is too small in comparison with our new results or other researcher's recent results [5]. Sahoo *et al.* used a sessile drop method, but they adopted an rf induction furnace to heat the sample and to generate the plasma. They used a horizontal vicor tube as the furnace and an rf coil was positioned around it. In their setup, the shape is possibly distorted in one direction by an electromagnetic force, but the symmetry of the droplet shape was not confirmed because the droplet shape was observed in only one direction. They concluded that the plasma lowered the surface tension of pure Fe, however, it is not clear that the change was actually caused by the plasma or was affected by other forces. In this study, the absence of any other forces was confirmed in two ways. One was to compare the shapes and the surface tension values between before and after generating the plasma. The other was to confirm the symmetry of the droplet. Accordingly, precise surface tension values were obtained by these processes.

4.2. Effect of sulfur content

A few researchers measured the surface tension of 304 stainless steels, and the most reliable results were obtained by Mills *et al.* [5, 8, 9]. They measured the surface tension by the oscillating drop method using electromagnetic levitation. However, because earlier results obtained by the oscillating drop method were not corrected using Cummings' equation [19], care should be take of referring their results. Their collected values [5] are also displayed in Fig. 3 using the open symbols. The values of the 30 ppmS sample are larger than that of the 20 ppmS sample, and their values of the 100 ppmS sample are larger than our values of the 110 ppmS sample. This seems to be strange because the surface tension is usually lower for the higher contents of the surface active elements. The obtained temperature coefficients are shown in Fig. 5 with Mills' results. The value for the sulfur content of 110 ppm shows good agreement, however, the result for the 10 ppm is slightly different. Ogino *et al.* measured the surface tension of the Fe-S-O system [20] and Hajra and Divakar calculated the surface tension and the temperature coefficient of the Fe-S-O system [21, 22]. They showed that these properties are affected by both the sulfur and oxygen contents. It is a reasonable assumption that the surface tension and its temperature coefficient of stainless steel are also affected by both the sulfur and oxygen contents. The oxygen content in this study was less than 40 ppm, though the oxygen content in Mills' experiment was 70–90 ppm.

5. Conclusions

The surface tension and the density of 304 stainless steels with sulfur contents of 10, 100 and 250 ppm were measured under Ar plasma conditions. No significant effect of the plasma on the surface tension was observed. The surface tension of the 304 stainless steel is expressed using the following equations.

$$\gamma = -0.12 \times T + 1980 \text{ (mN/m)} \quad \text{(10 ppm Sulfur)}$$

$$\gamma = 0.29 \times T + 1030 \text{ (mN/m)} \quad \text{(110 ppm Sulfur)}$$

$$\gamma = 0.49 \times T + 520 \text{ (mN/m)} \quad \text{(250 ppm Sulfur)}$$

The density of the 304 stainless steel is expressed using the following equation.

$$\rho = -0.616 \times T + 8.11 \times 10^{+3} \text{ (kg/m}^3\text{)}$$

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References
1. S. KOU and D. K. SUN, *Metallurg. Trans.* **A16** (1985) 203.
2. C. R. HEIPLE and J. R. ROPER, *Weld. J.* **61** (1982) 97s.
3. C. R. HEIPLE, J. R. ROPER, R. T. STAGNER and R. J. ADEN, *ibid.* **62** (1983) 72s.
4. T. ZACHARIA, S. A. DAVID, J. M. VITEK and T. DEBROY, *ibid.* **68** (1989) 510s.
5. P. R. SCHELLER, R. F. BROOKS and K. C. MILLS, *ibid.* **74** (1995) 69s.
6. M. TANAKA, H. TERASAKI, M. USHIO and J. J. LOWKE, *Plasma Chem. Plasma Process.* **23** (2003) 585.
7. R. E. SUNDELL, H. D. SOLOMON, and S. M. CORREA, "Advances in Welding Science and Technology" (ASM International, Metals Park, Ohio, 1987) p. 53.
8. B. J. KEENE, K. C. MILLS, J. W. BRYANT and E. D. HONDROS, *Canadian Metallurg. Quart.* **21** (1982) 393.
9. R. F. BROOKS and K. C. MILLS, *High Temperat.-High Press.* **25** (1993) 657.
10. T. ZACHARIA, S. A. DAVID, J. M. VITEK and T. DEBROY, *Weld. J.* **68** (1989) 499s.
11. M. J. MCNALLAN and T. DEBROY, *Metallurg. Trans.* **22B** (1991) 557.
12. J. WEN and C. D. LUNDIN, *Weld. J.* **65** (1986) 138s.
13. P. SAHOO and T. DEBROY, *Metallurg. Trans.* **18B** (1987) 597.
14. T. BRYLENSKI, K. PRZYBYLSKI and J. MORGIEL, *Mater. Chem. Phys.* **81** (2003) 434.
15. D.-H. PECK, M. MILLER and K. HILPERT, *Solid State Ion.* **143** (2001) 391.
16. K. NOGI and K. OGINO, *Can. Inst. Mine. Metall.* **22** (1983) 19.
17. H. FUJII, H. NAKAE and K. OKADA, *Acta Metallurg.* **41** (1993) 2963.
18. U. M. AHMAD and L. E. MURR, *J. Mater. Sci.* **11** (1976) 224.
19. D. CUMMINGS and D. BLACKBURN, *J. Fluid Mechan.* **224** (1991) 395.
20. K. OGINO, K. NOGI and C. HOSOI, *Testu to Hagane* **69** (1983) 47.
21. J. P. HAJRA and M. DIVAKAR, *Metallurg. and Mater. Trans. B* **27B** (1996) 241.
22. M. DIVAKAR and J. P. HAJRA, *Steel Res.* **68** (1997) 417.

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