Zirconium Surface Tension

Preliminary Recommendation

The preliminary recommendation for the surface tension of liquid zirconium, at its melting point is

$$1455 \pm 50 \text{ mN} \cdot \text{m}^{-1}$$

This is the mean of the melting point surface tensions obtained from measurements by Allen [1], Arkhipkin et al.[2], Vinet et al. [3] and Thiessen and Man [4]. No temperature dependence is available for the surface tension of liquid zirconium because measurements have been made only at the melting point.

Uncertainty

The 4% uncertainty is based on the uncertainty in the liquid density, which is used in the calculation of the surface tension from the measured parameters. This uncertainty is a factor of two higher than the 2% spread in the values that were used to obtain the recommendation. Although, the experimental uncertainty reported by Allen [1] is 2%, it does not include the uncertainty in the liquid density that Allen used in the data reduction. The greatest contribution to the surface tension uncertainty is in the value for the density of liquid zirconium at the melting point because no reliable data for the density of liquid zirconium have been published in the open literature. Estimated values for liquid densities were used in the reduction of the experimental data from early surface tension measurements. Their uncertainty was assumed to be about 10%. Liquid densities are now available for many transition metals and Vinet et al.[3] report that the densities they used in their data reduction are from recent measurements. Their density for liquid zirconium differs by 4% from the density used in the earlier measurements of Allen [1]. Because of this range in values for the density of liquid zirconium and the lack of experimental liquid density data**,** the larger uncertainty than that reported by Allen and that obtained from the deviation from the mean is warranted.

Discussion

Table 1 orders the available data on the surface tension of zirconium near the melting point according to year. Surface tension values are given in $mN \cdot m^{-1} = mJ \cdot m^{-2}$. The best value reported by each experimental group has been included in the table. Because Allen made measurements using two different methods, his best value for each method has been included in Table 1.

Table 1. Measurements of the Surface Tension of Zirconium near the Melting Point

Surface Tension, $mN \cdot m^{-1}$	Method	Experimenter	Year
1400	Drop weight	Peterson et al. [5]	1958
1411	Drop weight	Shunk and Burr [6]	1962
1480	Drop weight	Allen [1]	1963
1469 ± 4	Pendant drop		
1430	Detachment of a cylinder	Arkhipkin et al. [2]	1973
1435	Pendant drop	Vinet et al. [3]	1993
1463 ± 12	Quasi-containerless pendant drop	Thiessen and Man [4]	1995

The most recent review of data on the surface tension of zirconium was done by Keene [7] in 1993. At that time, only measurements by four experimental groups were available [1,2,5,6]. Keene recommended $1430\ mN \cdot m^{-1}$, which is the mean of the four highest values for the zirconium surface tension that were obtained by each of the experimental groups. In his review, Keene pointed out the scarcity in the data and the lack of any data on temperature dependence. Since the review by Keene [7], the surface tension of zirconium has been measured by Vinet et al. using the drop weight method [3] and by Thiessen and Man [4] using a quasi-containerless pendant drop method.

Prior to the 1990s, the definitive surface tension measurements on transition metals were those done by Allen [1]. Allen measured the surface tension of 18 transition metals using both dynamic drop-weight and static pendant-drop techniques on samples from the same material heated by electron bombardment in a high vacuum (10^{-5} to 10^{-7} Torr). The zirconium sample was from a high-purity crystalline bar. The surface tension given in Table 1 from the pendant drop measurements is the average of 30 photographs of drops. Allen [1] attributed the differences between his values for drop-weight measurements and those of earlier drop-weight measurements to differences in purity of the sample, outgassing in high vacuum prior to measurements, gas eruptions, the effect of rod diameter on oscillation of the drop prior to separation, and density differences. He commented that the largest uncertainty in the determination of surface tension comes from the uncertainty in the liquid density.

Vinet et al.[3] used the pendant-drop method in an ultrahigh vacuum (10^{-9} Torr) to determine the surface tension of rhenium, tungsten, niobium, iridium and zirconium. They used a range of wire diameters including very thin wire (0.3 mm in diameter) to study the process of detachment of the drop from the wire. During the growth of the drop, the refractory metal is purified. The drop falls when the surface tension can no longer balance the weight of the drop. They observed that poorly released drops have lower mass. From their measurements, they concluded that drops released from poorly outgassed wires or rods are statistically smaller and give an underestimation in the surface tension. Vinet et al. obtained a surface tension of 1435 $mN \cdot m^{-1}$ from ten measurements on zirconium wires with diameters equal to 1 mm and 0.76 mm.

In their data reduction, Vinet et al. used liquid densities from submillimetric resistive heating experiments, which are more accurate than calculated values used in earlier surface tension measurements. However, none of the references given by Vinet et al. are for measurements of the density of liquid zirconium. Thus, the source of the value they used for density of liquid zirconium is not clear. The density of liquid zirconium that was used by Vinet et al. is 6.05 $g \cdot cm^{-3}$, which is 4% higher than the estimated density, 5.8 $g \cdot cm^{-3}$, used by Allen [1]. If the surface tensions obtained by Allen in his drop-weight and pendant-drop measurements are adjusted for this higher density, Allen's zirconium surface tensions would be respectively, 1540 $mN \cdot m^{-1}$ and 1530 $mN \cdot m^{-1}$. These values are significantly higher than the value obtained by Vinet et al. Vinet et al. could not explain this disagreement. For W, Nb, Ta, and Re, the surface tension values determined by Vinet et al. showed good agreement with the values determined from measurements by Allen after these values were corrected for the liquid densities obtained from resistive heating experiments.

Consistent with the observation of Vinet et al., Thiessen and Man [4] found that measurements done over a four hour period showed an increase in surface tension with time as contaminants were gradually removed from the drop's surface by evaporation. The mean surface tensions that they obtained from three sets of measurements made on three separate days are 1435 $\pm$ 25, 1445 $\pm$ 14, and 1346 $\pm$ 18 $mN \cdot m^{-1}$. The first two values were obtained on samples that were thoroughly outgassed until the pressure was in the low 10^{-7} Torr range. The last value was obtained on a sample kept at room atmosphere for more than 1.5 hr followed by image capture at 2 x 10^{-6} Torr. These results indicate the sensitivity of the surface tension measurements to sample preparation and vacuum conditions. The surface tension values obtained by Thiessen and Man are lower than the highest value obtained by Allen [1] using a drop-weight method. However, the best value reported by Thiessen and Man, 1463 $\pm$ 12 $mN \cdot m^{-1}$, agrees well with the value, 1469 $\pm$ 4 $mN \cdot m^{-1}$, obtained by Allen using a similar pendent-drop method.

Send comments to
jkfink@anl.gov

The recommended value for the surface tension of liquid zirconium is 1455 $\pm$ 50 mN· m^{-1}. This value is the mean of the last five values given in Table 1, which are the values from the measurements by Allen, Arkhipkin et al., Vinet et al., and Thiessen and Man. The values given in Table 1 are considered to be the best values obtained by each experimental group using each measurement method. Two values reported by Allen have been included in the determination of this recommendation because they are the best values obtained by two different experimental techniques. The values reported by Peterson et al. and by Shunk and Burr have not been included in the average because they are significantly lower than the more recent measurements under high vacuum. The 4% uncertainty in the recommendation is has been chosen to include not only the statistical variation in reported values but also the uncertainty in the liquid density. Measurements are needed to determine the density of liquid zirconium at the melting point and its variation with temperature. Surface tension measurements are needed to determine the temperature dependence.

References

1. B. C. Allen, "The Surface Tension of Liquid Transition Metals at Their Melting Points," Trans of Met. Soc. Of AIME 227, 1175 (1963).
2. V. I. Arkhipkin, A. D. Agaev, G. A. Girgor'ev, and V. I. Kotkikov, Ind. Lab (USSR) 39 (8), 1340, (1973), as referenced by Keene.
3. B. Vinet, J. P. Garandet, and L. Cortella, J. Appli. Phys. 73, 3830 (1993).
4. D. B. Thiessen and K. F. Man, "A Quasi-Containerless Pendant Drop Method for Surface Tension Measurements on Molten Metals and Alloys, Int'l J. of Thermophysics 16, 245-255 (1995).
5. B. J. Keene, "Review of Data for the Surface Tension of Pure Metals," International Materials Reviews 38, 157-192 (1993).
6. A. W. Peterson, H. Kedesdy, PH. Keck, and E. Schwartz, J. Appl. Phys. 29, (2) 213 (1958).
7. F. Shunk and A. A. Burr, Trans. ASM. 55, 786 (1962).