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SURFACE TENSIONS AND DENSITIES OF MOLTEN Al_2O_3 AND Ti_2O_3

Norihito Ikemiya*, Shigeta Hara* and Kazumi Ogino**

*Department of Materials Science & Processing, Faculty of Engineering; Osaka University, Yamadaoka 2-1, Suita, Osaka, 565, Japan
**Department of Materials Science & Processing, Faculty of Engineering; Osaka University, Now, Kagawa Polytechnic College, 3202 Gunkecho Marugame Kagawa, 763, Japan

Synopsis: Surface tensions and densities of molten Al_2O_3 and Ti_2O_3 were determined under Ar+10%H_2 gas by using the maximum bubble pressure method. Surface tension and density of molten Al_2O_3 near the melting point are $606 \pm 6 mNm^{-1}$ and $3.06 \pm 0.03 \times 10^3 kgm^{-3}$, and those of molten Ti_2O_3 are $584 \pm 5 mNm^{-1}$ and $3.91 \pm 0.03 \times 10^3 kgm^{-3}$, respectively. The results are compared with those of other molten pure oxides and fluorides having high melting points and discussed.

Key words: Surface tension, Density, Melt, Maximum bubble pressure method, Al_2O_3, Ti_2O_3.

1. Introduction

Al_2O_3 and Ti_2O_3 have been used as main components of fluxes for pyrometallurgical processes. Although, there are many works on the physico-chemical properties of molten multi-component slags and fluxes, we have limit information on the properties of the pure component oxides at the molten state. If we have them, the accuracies of the determinations are sometimes very poor. It is a typical example that with respect to surface tension and density of molten Al_2O_3, which have been measured by many workers[1-15], discrepancy among the results amounts up to as much as 20%. This arises from the complexity of experimental procedures at high temperature, difficulties encountered in the choice of container materials and so on.

The purpose in the present work is the accurate determinations of surface tensions and densities of molten Al_2O_3 and Ti_2O_3 ; moreover we establish the experimental procedure for the measurements of these properties at high temperature. The results are compared with those of other molten pure oxides and fluorides having high melting points and discussed.

2. Experimental

2.1 Experimental apparatus and method

The maximum bubble pressure method was applied. The sample was heated by the induction heating furnace. Molybdenum crucible having 30mm diameter and 50mm height was used as a a container of melts. Ar+10% H_2 gas is blown in melt through a molybdenum capillary tube having about 2.00mm in the inner diameter. Usually, a bubble was created at each 30 s. The bubble pressure was measured by a pressure transducer calibrated by a deionized water filled manometer. The bubble pressure changes linearly with the immersion depth of the capillary tube in melts. Surface tensions were computed by the Schrödinger's equation[16],

$$\gamma = (r \cdot H \cdot g/2)[1-(2/3)(r \cdot \rho /H)-(1/6)(r \cdot \rho /H)^2] \quad \cdots\cdots(1)$$

where, H: the maximum bubble pressure at surface of melt, r: the inner radius of the, ρ : the density of melt, g: the acceleration of gravity.

The inner radius of the capillary tube at the experimental temperature is calibrated by the value at room temperature and the thermal expansivity of molybdenum[17].

Densities of melts are also calculated from the differences of maximum pressure P at two positions separated vertically in melts by h.

$\rho = \Delta P / \Delta h \cdots\cdots (2)$

Temperature was measured by W-5mass%Re/W-26mass%Re thermocouple with molybdenum pipe set in melts below 2200K. Above 2200K, radiation pyrometer calibrated by the W-5mass%Re/W-26mass%Re thermocouple was used. Its relative error in the temperature range of 2200-2450K was within ± 0.5%.

2.2 Materials

Al_2O_3 (>99.9%) used in the present work was supplied from Wako Chemical Co. and Ti_2O_3 and TiO_2 (>99.9%) were supplied from Rare Metallic Co.. All of the samples were heated up to 453K under reduced pressure for dehydration before use.

2.3 The source of experimental error

The contribution of experimental errors on the determination of surface tensions and densities are listed below,

Factors	Error in determination	Error in surface tension	Error in density
1. Capillary radius	<± 0.01mm	<± 1.0%	-
2. Pressure measurement	<± 0.12mmAq.	<± 0.1%	<± 1.0%
3. Determination of surface	<± 0.2mm	<± 0.2%	-
4. Temperature	<± 12K	<± 0.2%	<± 0.4%
5. Density	<± 0.05g/cm3	<± 0.04%	
6. Immersion of capillary	<± 0.01mm	-	<± 0.3%
Total		<± 1.54%	<± 1.7%

3. Results and discussion

3.1 Surface tension and density of molten Al_2O_3

As details are shown in below, although molybdenum oxides lower surface tension, in our experimental condition molybdenum was not detected in the sample after melting. Fig.1 shows the results of present work compared with available data[1-11].

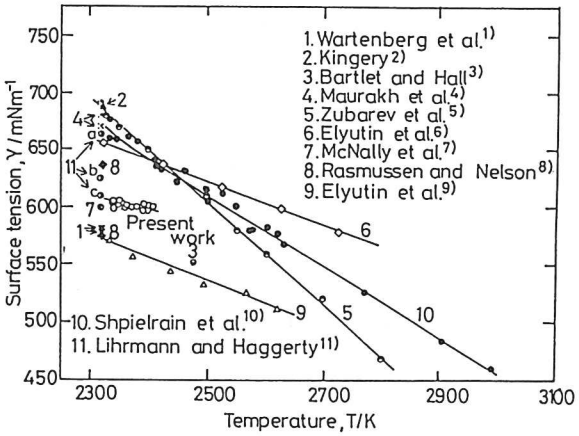

Fig.1 Surface tension of molten Al_2O_3.

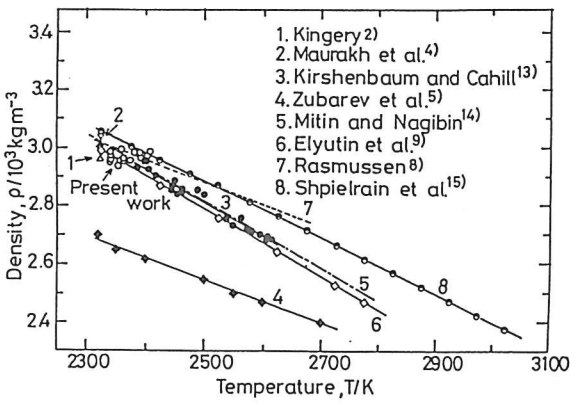

Fig.2 Density of molten Al_2O_3.

We suppose that the results of Wartenberg et al.[1] using the drop weight method contain systematic errors because the density obtained simultaneously is lower than those reported by other workers. The results of Zubarev et al.[5] using the sessile drop method cover wide temperature range from the melting point up to 2973K. According to the results, the

temperature coefficient of surface tension was abnormally large value of 0.46mNm^{-1}K^{-1} and densities obtained simultaneously were slightly lower than those reported by other workers.However ,we consider that the results are suspect because interaction between a drop and a graphite substrate was guessed. Elyutin et al.[6] measured surface tension by using the dipping cylinder method. The cylinder detached the melts was made of molybdenum and tungsten.Rasmussen et al.[8] have developed an X-radiographic technique to obtain profiles of molten Al_2O_3 pendant drops sealed in molybdenum or tungsten capsules under reduced pressure. In their work,Mo capsules lowered surface tension values. In the case of using the Mo capsules the results obtained by the pendant drop method were higher than those obtained by the contact angle method since the melt contacts the Mo container with small area. This suggests that measured value of surface tension is affected by atmospheric gas. The similar situation was also observed on the measurement for molten CaO-Al_2O_3 system[12]. The results obtained under Ar gas were lower than those obtained under Ar+10%H_2 gas and molybdenum was detected in the sample after melting. Therefore,we consider that the measured values lower due to the contamination of molybdenum oxide with much low surface tension[4]. The results of Shpilrain et al.[10] using the maximum bubble pressure method were different from those of Elyutin et al.[9] using the same method. The surface tension at the melting point and temperature coefficient reported by the former were 670mNm^{-1} and 0.30 mNm^{-1}K^{-1} respectively,but those reported by the latter were 570mNm^{-1} and 0.187mNm^{-1}K^{-1} respectively.The results of Lihrmann et al.[11] using the pendant drop method change slightly with vapour phase such as He gas, He+10%H_2 gas or air. The result in the present work is 606± 6mNm^{-1} and this value is close to the result of Lihrmann et al.[11] under He+10%H_2 gas. The temperature coefficient obtained in present work is lower than those of Zubarev et al.[5] and Shpilrain et al.[10] but it is close to that of Elyutin et al.[6,9].The considerable differences among their measurements for surface tension arise from not the experimental procedure applied but unexpected error factors due to the measurements at high temperature.

Fig.2 shows the density of molten Al_2O_3 compared with the available data. The scattering among their measurements was smaller than that of the results for surface tensions.

The result of 2.97± 0.03x10^{3}kgm^{-3}(from 2360K to 2407K) in present work is in good agreement with the results of Mitin et al.[14] and Kirshenbaum et al.[13] using the Archimedean method and Shpilrain et al.[15] using the maximum bubble pressure method. As mentioned above,the results of Zubarev et al.[5] were much lower than those of other many workers because they used the graphite as the substrate.

3.2 Surface tension and density of molten TiO_2 and Ti_2O_3

Although we have measured surface tensions and densities of molten TiO_2 and Ti_2O_3, it was difficult to obtain a stable bubble pressure for the molten TiO_2. We examined the chemical state of TiO_2 and Ti_2O_3 before and after melting in molybdenum crucible under the Ar+10%H_2 atmosphere by the X-ray powder diffraction method(using CuKα line). According to the results, TiO_2 was rutile containing a small amount of the anatase before melting. However the chemical state changed toward the compound Ti_2O_3 after melting. For Ti_2O_3 ,little change was observed in the diffraction pattern before and after melting.Surface tension and density of molten Ti_2O_3 are as follows,

$$\gamma\ /\mathrm{mNm^{-1}} = 742.5 - 0.0744T \cdots\cdots\cdots (3)$$

$$\rho\ /10^3\mathrm{kgm^{-3}} = 4.59 - 0.328\times10^{-3}T \cdots\cdots (4) \quad (2158<T/K<2289)$$

We consider that the surface tension and the density of molten Ti_2O_3 near the melting point are 587mNm^{-1} and 3.90 x10^{3}kgm^{-3} respectively by extrapolating our experimental data. Surface tension of molten Ti_2O_3 is about two times higher than that of molten TiO_2 near the melting point reported by Elyutin et al.[18] by using the dipping cylinder method. In the case of the starting material was TiO_2, the maximum bubble pressure increased with time at a constant immersion depth of the capillary in the melt. This phenomenon is interpreted as follows; under our experimental condition, it is considered that oxygen in molten TiO_2 is lacking with time and hence the chemical composition is shifted toward Ti_2O_3. Consequently the surface tension of melt increase. The densities of molten TiO_2 reported by Maurakh et al.[4,19] using two methods are 4.0x10^{3}kgm^{-3} and 3.65x10^{3}kgm^{-3} ,respectively. These are remarkably different from each other. We suppose the results of Maurakh et al.[19]using the maximum bubble pressure method should be acceptable because an increase of an atomic ratio of Ti/O results in an increase of the density.

3.4 The surface tensions of molten pure oxides near the melting points

An electrostatic force acting between a cation and an anion is defined as follows,

$$F=e^2Z_aZ_c/(r_a+r_c)^2 \cdots\cdots\cdots (5)$$

where, r_a & r_c ,Z_a & Z_c:ionic radii and valencies for anion and cation respectively.

Previous reports[20,21] showed that surface tensions of molten fluorides near the melting points represent as a function of the F value. Fig.3 shows relationship between surface tensions near the melting points and the F value for molten oxides[22-39].

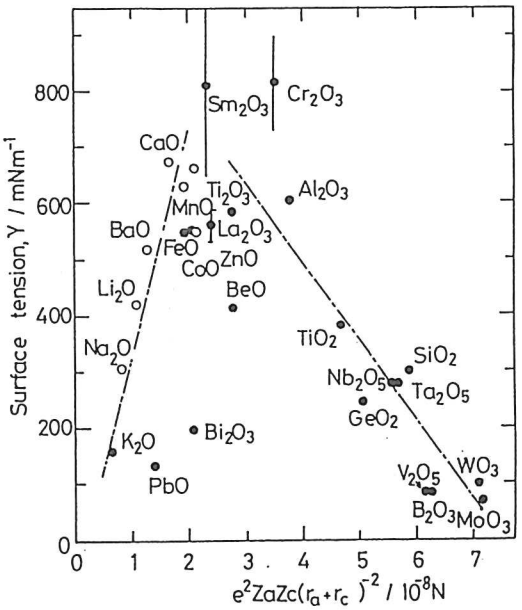

Fig.3 Surface tensions of molten pure oxides at the melting points as a function of attractive force between cation and oxygen.

In this figure closed circles represent the measured value and the open circles represent the estimated value from the measured value of molten binary systems. As the F value increase, surface tensions of molten oxides increase in proportion to the F value at first,then decrease after reaching a certain maximum surface tension value. For molten oxides such as SiO_2,B_2O_3 and V_2O_5 , surface tensions decrease as the F value increase. They are known to be network formers due to their strong cation-anion attractions, in other words,a covalent character rather than an ionic character appear strongly in them. Consequently, effective electrostatic forces between the cation and the anion decrease.

Surface tension of molten TiO_2 is lower than that of molten Ti_2O_3. This suggests that a tendency of network forming of the molten TiO_2 should be stronger than that of the molten Ti_2O_3.

An oxygen packing density N_o of molten oxides near the melting points is given in Eq.(6). The N_o value also change with the F value.

$$N_o=\rho\, yN/W \cdots\cdots\cdots (6)$$

Where,N:Avogadoro's number,W:molecular weight,ρ :the density of the melt.

As previously reported[21],for alkaline metal , alkali-earth metal,rare-earth metal and a part of tetravalent metal molten fluorides(UF_4,ThF_4),a fluoride packing density in melts increase monotonously as the F value increase. However, as shown in Fig.4, for molten oxides the N_o increase in proportion to the F value at first and then decrease as the F value increase. The difference between fluorides and oxides should be explained as follows,in molten fluorides only monomer anions are stable,while in molten oxides such as SiO_2,B_2O_3,etc. polymerized complex anions have much vacancies in the structure. We suppose that this feature relates to decrease of oxygen packing densities with the F value. Mishin et al.[40] tried to classify some of surface tensions of molten oxides as a function of the melting points and the molar volume,but they do not always succeed. However as previously reported[20,21],if one chose the average atomic volume as V_{av} instead of the molar volume V_m,fairly good linear relationship between surface tensions of molten fluorides near the melting points and $RT_m(V_{av})^{-2/3}$ is obtained. Here T_m is a melting point and R is gas constant.V_m and V_{av} are defined as follows,

$$V_m=W/\rho \cdots\cdots\cdots (7)$$

$$V_{av}=W/((x+y)) \cdots\cdots\cdots (8)$$

For molten oxides and molten fluorides, Fig.5 shows relationship between surface tensions

and $RT_m(V_{av})^{-2/3}$. Here,open circles represent molten oxides and close circles represent molten fluorides. Except of several oxides,a fairly good relationship between surface tensions and $(V_{av})^{-2/3}$,which is a packing density at surfaces of melts was observed. However,as previously reported[20],surface structure of melts relates the crystal structures of solids. Hence,it will be required that the surface structure of melts is taken into the classification of surface tensions of molten pure oxides.

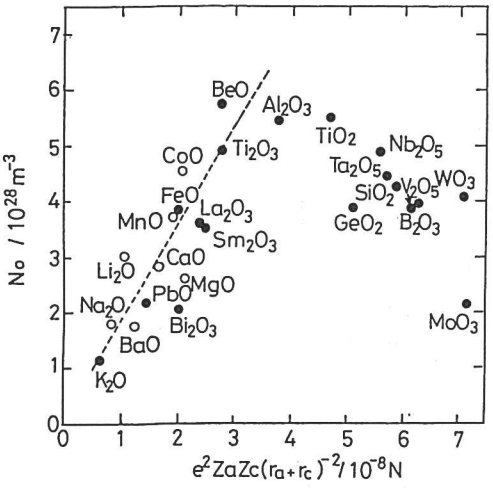

Fig.4 Oxygen density of molten pure oxides at the melting points as a function of attractive force between cation and oxygen.

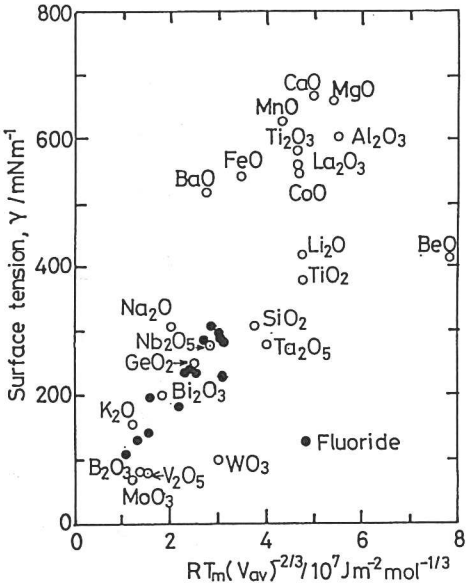

Fig.5 Surface tensions of molten pure oxides and fluorides at the melting points as a function of $RT_m(V_{av})^{-2/3}$.

4. Conclusions

Surface tension and density of molten Al_2O_3 and Ti_2O_3 were determined under Ar+10%H_2 gas by using the maximum bubble pressure method. Surface tension and density of molten Al_2O_3 near the melting point are $606\pm 6mNm^{-1}$ and $3.06\pm 0.03x10^3kgm^{-3}$, and those of molten Ti_2O_3 are $584\pm 5mNm^{-1}$ and $3.91\pm 0.03x10^3kgm^{-3}$,respectively.The results are compared with those of other molten pure oxides and fluorides having high melting points and discussed.

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