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Viscosity and Dissociation Mechanism of a Cryolite Flux, Na_3AlF_6, during the Growth of Corundum Single Crystals

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The viscosities of the Na_3AlF_6–Al_2O_3 system, including Al_2O_3 of 0, 5, 10, and 15 wt%, during the growth of corundum single crystals at 1050°C were measured by the oscillating disk method, and used with Hallett's equation. Although the viscosity in such a system progressively increased with an increase in the Al_2O_3 concentration, from 1.57 cP (0 wt%) to 1.68 cP (10 wt%) at 1050°C, at 15 wt% it steeply increased to 2.40 cP. A plot of the logarithmic viscosity vs. the reciprocal absolute temperature gave a linear relation in the respective systems. The values of the mean molar volume and the activation free energy (ΔG^*) of the flow unit in a system including 15 wt% Al_2O_3 were calculated to be approximately 22.4 ml mol^{-1} at 1050°C and 12.74 kcal mol^{-1}, respectively. The dissociated ionic species and its mechanism in the molten state of such a system are discussed in terms of the free-energy-limited theory deduced from the reaction rate theory; the steep increment of the viscosity in a system containing Al_2O_3 of more than 10 wt% is conjectured to be caused by a clustering state of dissociated Al_2O_3.

In high-temperature solution growth a mass-transfer phenomenon in which the growth units are moved from the liquid phase to the crystal surface, the growth mechanism,[1] the change of habit, and the growth pattern are noticeably influenced by such factors as the viscosity of the solvent, diffusion of solute particles and thermal diffusion. The viscosities of typical solvents in solution growth have been measured by Oliver,[2] Bruton and White,[3] Elwell et al.,[4] as well as Elwell and Scheel.[5] Recently, the viscosities of phosphate solutions used for growing KTP crystals were measured by Bordui and Jacco,[6] as well as Iliev et al.[7]

In order to obtain information concerning the structural details of ion pairing and complexing as well as on association and dissociation in molten salts comprising a relatively simple component and low melting point, various static experimental techniques, such as ultraviolet and visible electronic spectroscopy, infrared and Raman spectroscopy, nuclear magnetic resonance, as well as X-ray and neutron diffraction techniques have now become applied widely. However, it is not easy to use these techniques for reactive compounds with a container, complex multi-component systems, highly concentrated solutions, high volatility, at higher temperatures than 1000°C. Above a temperature of 1000°C, such dynamical physico-chemical methods as electrical conductivity, viscosity, density, and cryoscopy have been employed more often than these techniques. Generally, dissociated ionic species in a molten salt that are determinable through measurement of the electrical conductivity are small cations possessing positive charges, which have a major effect on the conductivity. On the other hand, the species which have a major effect on the viscosity are large anions with negative charges.

The physical and chemical properties as well as dissociation mechanisms of the Na_3AlF_6–Al_2O_3 system have been extensively studied by numerous investigators, due to its importance to the aluminum industry. Førland and Patkje[8] discussed the dissociation mechanism of such a system based on cryoscopic measurements; Gilbert et al.[9] also discussed the dissociated ionic species in terms of the Raman spectra. The vapor pressure was measured by Kvande,[10] and the viscosity was measured by Tørklep and Øye[11] using the oscillating cylinder method. However, almost all of these studies were only for systems containing less than 10 wt% Al_2O_3. Moreover, there have been no papers concerning the dissociation mechanism of a system containing more than 10 wt% Al_2O_3. A high-temperature solution of the Na_3AlF_6–Al_2O_3 system has been available for many years for the growth of corundum single crystals with a seeded flux growth technique.[12—14]

The aim of the present study, based on the viscosity data of the Na_3AlF_6–Al_2O_3 system obtained by using the oscillating disk method, was to understand the dissociated ionic species and the mean molar volume of the flow unit in the molten salt, as well as the growth units of corundum crystals growing in a molten Na_3AlF_6 flux.

Experimental

Synthetic Na_3AlF_6 of high purity was employed as a solvent, and Al_2O_3 powder of pre-fused product as a solute. A chemical analysis of the source materials is given in Table 1. Various compositions of molten salt were prepared by accurately weighing appropriate quantities of the source materials, and then thoroughly mixing them in an agate mortar. The quantities of Al_2O_3 contained in the molten salt were 0, 5, 10, and 15 percent by weight.

The apparatus is shown schematically in Fig. 1. The

Table 1. Chemical Analysis of Source Materials

	Al_2O_3	Na	Al	F	SiO_2	Fe_2O_3	TiO_2	CaF_2	H_2O
Al_2O_3	99.85	—	—	—	0.01	0.01	Tr	—	—
Na_3AlF_6	—	32.4	12.8	53.7	0.07	0.005	—	0.02	0.0

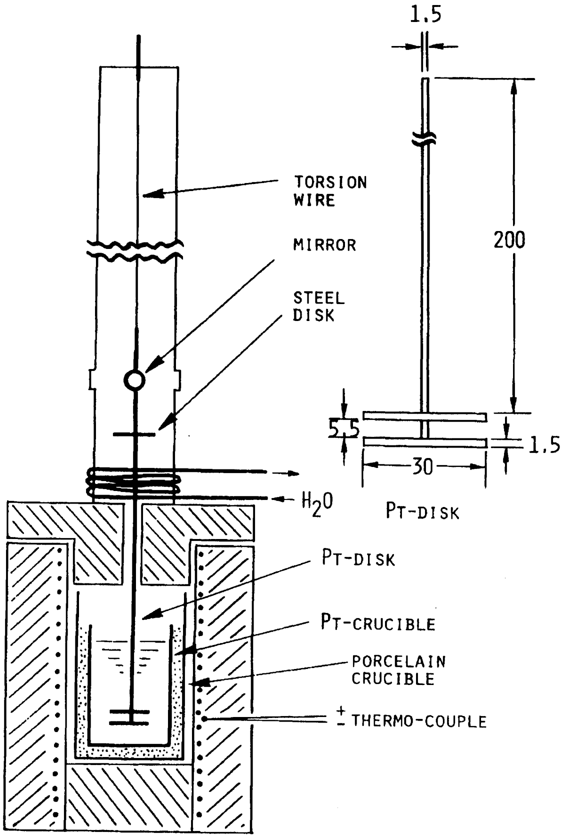

Fig. 1. Experimental apparatus and Pt-disk.

adopted oscillating system comprised two platinum disks (diameter is 30 mm, thickness of 1.5 mm, with a 5.5 mm space between the two, connected by a platinum stem of diameter 1.5 mm and a length of 200 mm). A steel disk (2 mm thick and 30 mm in diameter) which acts as a mass with a suitable moment of inertia, tightly grips the platinum stem. The top of the stem is fixed onto the lower end of the manganin (Cu–Mn alloy) torsion wire (0.125 mm in diameter and 600 mm in length). The head of the oscillating system is tightly grasped by a steel rod which is clamped outside through a teflon cap. In order to prevent any additional swing caused by dry air from the furnace, the upper part of the oscillating system outside the furnace is covered with a quartz glass tube, and cooled with water through a wound copper pipe. The oscillating motion of the system is initiatd by carefully turning a small magnetized steel pin fixed on the torsion wire with a permanent magnet; this is followed by observing a beam of light reflected from a mirror cemented on the platinum stem. The reflected beams are focused onto a one-meter straight scale placed two meters apart from the mirror by a lens system with a window. A Pt–Pt·13 % Rh thermocouple for the cotroller is inserted into the side of the furnace, constructed of upper and lower winding segments, through a suitable hole. The temperatures at different parts of the inside of the furnace are controlled to within ±2°C throughout the experiments, and the vertical temperature gradient in the crucible is less than $\pm 0.05^\circ\mathrm{C\,cm^{-1}}$. Before the oscillating system is suspended into the molten salt, the temperature of the latter is measured by inserting a Pt-sheathed Pt–Pt·13 % Rh thermocouple into the platinum crucible (40 mm in diameter and 70 mm in length) using a very sensitive (0.0001 mV) potentiometer, in combination with a chart recorder which includes an amplifier. Temperature control of the furnace is performed by means of a PID with stabilized power supply within an error of 0.1 %. Source materials of about 130 g are put into the crucible; when it is melted, the depth of the molten salt is approximately 5 cm above the bottom of the crucible. The decay of torsional oscillations is measured with the disk immersed in the molten salt at 2 cm distance above the bottom of the crucible, and is located along the center axis of the crucible.

Results

Determination of the Decrement. The amplitudes of swing ϕ on each side of the rest position of the reflected light from the mirror were observed and recorded for as large a number of oscillations as possible. When the disk oscillated with a period of about 18.7 seconds in the molten salts at a given temperature, good linear lines were obtained on the plots of log ϕ_n versus n, the serial number of a swing of amplitudes ϕ_n. Usually, five runs were carried out at each temperature. Plots of log ϕ_n vs. n were obtained by a least-squares method, and the average value of the slopes of the lines was evaluated. The decrement (Δ), defined by Eq. 1, was deduced from the slope of the lines, dln $\phi_n/\mathrm{d}n$,

$$\Delta = -\frac{1}{2\pi}\cdot \mathrm{dln}\,\phi_n/\mathrm{d}n. \tag{1}$$

The accuracy in the determination of the decrement is of the order of 3%. The period of oscillation in molten salt (T) and in air (t), which were determined from the total time of a large number of swings (ca. 30), were measured with an accuracy of 1/100 second. A through the experimental accuracy was calibrated with standard viscous oils at room temperature, it was not made at high temperatures. Therefore, the final values of the viscosity in the present study may contain an error of about 10%, considering the expansion of the disk upon heating at high temperatures as well as the inaccuracy in measuring the reflected light.

Calculation of the Viscosity Using Hollis–Hallett's Equation.[15] A calculation of the viscosity (η) was made using Hallett's equation,

$$(\eta\rho)=\frac{4I^2}{\pi R^8}\cdot\frac{\left\{\Delta\left(\tau^2+1\right)-2\tau\delta\right\}^2}{T(1-\Delta)}\cdot\left[1+\frac{2d}{R}+\frac{2}{R\Lambda}\right]^{-2}, \tag{2}$$

where ρ is the density of the molten salt at measured temperature, Δ the decrement of oscillation in a molten salt, T the period of oscillation in the molten salt at the measured temperature, and δ the decrement of oscillation in air at room temperature; $\tau = T/t$ with t the period of oscillation in air at room temperature; $4I^2/\pi R^8$ is a constant value for the oscillating system with I being the moment of inertia, R the radius of the disk, d the thickness of the disk, $\Lambda=\sqrt{\omega\rho/2\eta'}$ and $\omega = 2\pi/\mathrm{T}$. The constant value of $4I^2/\pi R^8$, which is required in the calculation, was determined from the decrements and the periods of oscillation in the two molten salts, KNO_3 and KCI,[16] whose the values of viscosity and density were already known at various temperatures. The arithmetical mean value of $4I^2/\pi R^8$ obtained from the model systems at various temperatures is 9.8×10^2 g^2 cm^{-4}. The decrement (δ) and period (t) of oscillation in air were measured to be 18.05 seconds and 4.5×10^{-4} at 28.5°C, respectively. The values of η' were calculated by the method of successive approximation, the first approximation being

$$(\eta'\rho) = \frac{4I^2}{\pi R^8}\cdot\frac{\left\{\Delta\left(\tau^2+1\right)-2\tau\delta\right\}^2}{T(1-\Delta)}, \qquad (3)$$

The values of density (ρ) in the Na_3AlF_6–Al_2O_3 system were from the data of Edwards et al.[17] Using the values of η' derived from Eq. 3, after the values of Λ were calculated a calculation of Eq. 2 was carried out. As an example, the calculated values of the viscosity of a 90 wt% Na_3AlF_6–10 wt% Al_2O_3 melt at various temperatures are tabulated in Table 2 together with the first approximation η'. The viscosities of such a system gradually decrease upon raising the temperature. Figure 2 shows the viscosity change of molten Na_3AlF_6 with varying Al_2O_3 concentration at a temperature of 1050°C. The viscosity tends to gradually increase with increasing Al_2O_3 concentration, and then sharply above 10 wt%. According to the equilibrium phase diagram of the Na_3AlF_6–Al_2O_3 system,[18] the primary phase in such a system is Na_3AlF_6 up to 10 wt% of the Al_2O_3 concentration; above that it is Al_2O_3. It is therefore expected that a sharp change in the viscosity (Fig. 2) is due to a difference in the dissociation mechanism between the regions of lower and higher concentration of Al_2O_3 in molten salt.[19]

Discussion

With respect to the liquid viscosity, there are two major semiempirical theories based on free-energy limited[20,21] and free-volume limited models.[22—24] It is of interest that the fluid flow mechanism in the present system may be either free-energy limited or free-volume limited.

Table 2. Viscosities of the 90 wt% Na_3AlF_6–10 wt% Al_2O_3 System

Temp/°C	T/second	Δ	ρ/g cm^{-3} a)	η'/cP	η/cP
1061	18.7	0.0177	1.992	3.42	1.64
1051	18.7	0.0180	2.000	3.53	1.68
1037	18.7	0.0185	2.012	3.75	1.76
1024	18.8	0.0190	2.025	3.92	1.83
1011	18.8	0.0196	2.033	4.17	1.92
994	18.8	0.0204	2.047	4.50	2.04
981	18.8	0.0216	2.057	5.04	2.23
970	18.8	0.0231	2.067	5.76	2.47

a) The density was calculated from the data of Edwards et al.[17]

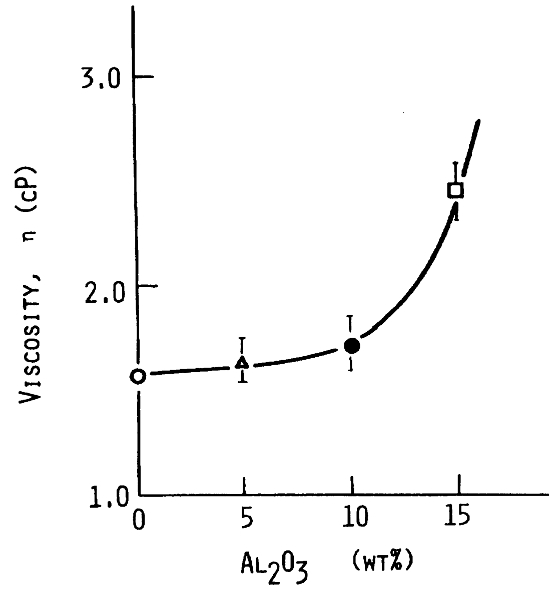

Fig. 2. Viscosity change depending on the Al_2O_3 concentration at 1050°C.

By combining two the theories,[25] the viscosity (η) of the liquid can be represented by

$$\eta = A\exp\left[\gamma v_0/v_f + \Delta G^*/RT\right], \qquad (4)$$

where the pre-exponential factor (A) varies with temperature, but is usually far less than the exponential term, and is roughly constant for a small temperature range; ΔG^* is the activation free energy per mole of liquid, R the gas constant (1.987 cal mol^{-1} degree^{-1}) and T the absolute temperature. v_0 is the close-packed molecular volume of liquid extrapolated to absolute zero without a change of phase, v_f is the free volume per molecular segment in the liquid at any temperature, related to the value of reciprocal density,[20] and γ is a numerical factor introduced in order to correct for any overlap of the free volume (lying between 0.5 and 1). Moreover, the free volume per molecule (v_f) is defined as

$$v_f = v - v_0, \qquad (5)$$

where v is the volume per molecule in the liquid at any temperature. The first term in brackets in Eq. 4, exp $(\gamma v_0/v_f)=P_V$, describes the contribution of the free volume to the viscosity of the liquid; the second term in the brackets, exp $(\Delta G^*/RT)=P_E$, describes that of the free energy. Liquids can be viewed as being either free-volume-limited or energy-limited in their transport processes, such as viscosity or diffusion. This depends upon whether P_E is greater or less than P_V. The ratio P_V/P_E can be written as exp $[\gamma v_0/v_f)-(\Delta G^*/RT)]$. If the value of P_V/P_E is less than unity, the liquids are defined as being free-volume-limited. On the other hand, if the value of P_V/P_E is greater than unity, the liquids are denoted as being energy-limited.

Taking logarithms, Eq. 4 becomes

$$\ln \eta = \Delta G^*/RT + (\ln A + \gamma v_0/v_f)\,, \tag{6}$$

From the slope of the straight line obtained by plotting the viscosity vs the reciprocal of the absolute temperature, according to Eq. 6, the activation free energy (ΔG^*) is determined. In addition, from the intercept the value of ($\ln A+\gamma v_0/v_f$) is determined. Figure 3 shows Arrhenius-type plots of $\ln \eta$–$1/T$ for the Na_3AlF_6–Al_2O_3 system. It can be seen that all of the data fit quite well the straight line, as can be predicted from Eq. 6. The activation free energy (ΔG^*) for fluid flow of the respective systems obtained from the straight lines, in Fig. 3 are 11.91 kal mol^{-1} in the 100 wt% Na_3AlF_6 system, 13.25 kcal mol^{-1} in the 95 wt% Na_3AlF_6–5 wt% Al_2O_3 system, 12.74 kcal mol^{-1} in the 85 wt% Na_3AlF_6–15 wt% Al_2O_3 system. In the case of the 90 wt% Na_3AlF_6–10 wt% Al_2O_3 system, however, the plot consists of two lines, gentle and steep, having respective activation free energies of 11.93 and 28.80 kcal mol^{-1}. The temperature of the intersection of the two lines (about 982°C) is found to be near to the solidus line of the primary phase (Na_3AlF_6) in such a system. Therefore, the higher one in two values of the activation free energy may be taken as cooresponding to that for fluid flow of a solution in which the precipitation of Na_3AlF_6 begins to occur partly. Calculated examples of the 100 wt% Na_3AlF_6 and the 85 wt% Na_3AlF_6–15wt% Al_2O_3 systems are shown in detail in Tables 3 and 4. The values of pre-expomemtial term A in the expression of ($\ln A+\gamma v_0/v_f$) were calculated by using the values from the intercept and of the reciprocal relative free-volume (v_0/v_f) and assuming that $\gamma=1$, where the values of v_0 and v_f were obtained by extrapolating the reciprocal of its density[17] (v) at various temperatures to absolute zero and substituting their values in Eq. 5 respectively. For the 100 wt% Na_3AlF_6 system the value of v_0 and an average of A were 0.306 and 0.00306, respectively. In the case of a 85 wt% Na_3AlF_6–15 wt% Al_2O_3 system they were 0.342 and 0.00223, respectively. Using the respective values given in Tables 3 and 4 the values of P_V/P_E for both systems of 100 wt% Na_3AlF_6 and 85 wt% Na_3AlF_6–15 wt% Al_2O_3 were calculated. The obtained values were 0.06 and 0.07 less than unity, respectively. Thus, as described above, for the fluid-flow mechanism in the present system applying the free-energy-limited theory is reasonable.

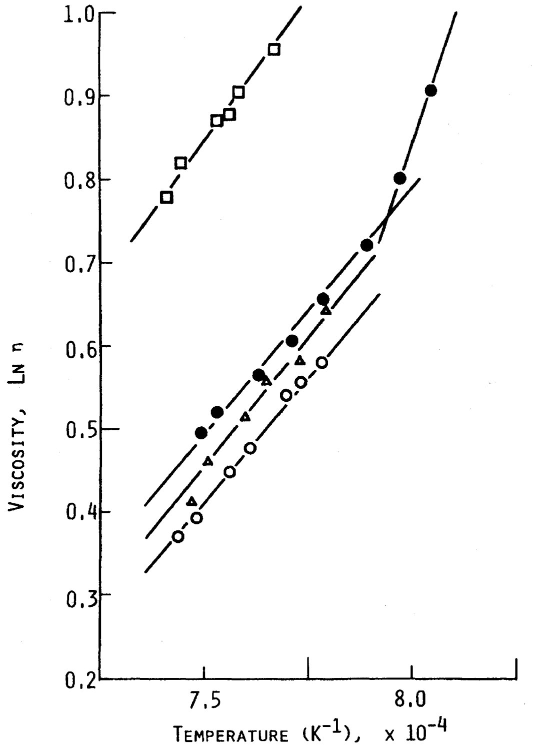

Fig. 3. Plots of logarithmic viscosity as a function of temperature ($1/T$). —○—: 100 wt% Na_3AlF_6, —△—: 95 wt% Na_3AlF_6–5 wt% Al_2O_3, —●—: 90 wt% Na_3AlF_6–10 wt% Al_2O_3, —□—: 85 wt% Na_3AlF_6–15 wt% Al_2O_3.

For the activation free energy ($\Delta G^*{}_M$) of the mixture, the following equation holds.[26]

$$\Delta G^*{}_M = X_1 \Delta G^*{}_1 + X_2 \Delta G^*{}_2 - \alpha \Delta G_E, \tag{7}$$

where X_1 and X_2 are the mole fractions, $\Delta G^*{}_1$ and $\Delta G^*{}_2$ are the activation free energies of two compounds (1 and 2) in a binary mixture, α is a constant of order unity, and ΔG_E is the excess free energy of mixing, which is given by

$$\Delta G_E = RT\,(X_1 \ln \gamma_1 + X_2 \ln \gamma_2)\,, \tag{8}$$

here, γ_1 and γ_2 are the respective activity coefficients of two compounds 1 and 2. Substituting the respective activity coefficients ($\ln \gamma_1=0.064$ and $\ln \gamma_2=0.483$[27]) and the mole fractions ($X_1=0.73$ and $X_2=0.27$) for Na_3AlF_6 and Al_2O_3 at a temperature of 1050°C into Eq. 8, the excess free energy of mixing (ΔG_E) was calculated as 460.8 cal mol^{-1}. As can be seen in Tables 3 and 4, the activation free energies ($\Delta G^*{}_1$ and $\Delta G^*{}_M$) for the systems of 100 wt% Na_3AlF_6 and of 85 wt% Na_3AlF_6–15 wt% Al_2O_3 were 12.74 and 11.91 kcal mol^{-1}, respectively. Upon substituting the respective values of $\Delta G^*{}_M$, $\Delta G^*{}_1$, ΔG_E, X_1, and X_2 into Eq. 7, the activation free energy corresponding to Al_2O_3 ($\Delta G^*{}_2$) in the system of 85 wt% Na_3AlF_6–15 wt% Al_2O_3 can be estimated to be 13.29 kcal mol^{-1}.

From reaction-rate theory,[26] the viscosity for a mixture of two compounds is generally expressible as

$$\eta = \frac{Nh}{V_{1,2}} \cdot \exp{(X_1 \Delta G^*{}_1 + X_2 \Delta G^*{}_2)/RT}, \tag{9}$$

where N is Avogadro's number (6.02×10^{23} mol^{-1}), h is Plank constant (6.62×10^{-27} erg·sec), $V_{1,2}$ is the mean molar volume of flow unit, X_1 and X_2 are the respective

Table 3. Calculation on the Free Volume and the Pre-Exponential Term 'A' in the 100 wt% Na_3AlF_6

Run No.	T/°K	$1/T$	η/cP	ln η	ρ/g cm^{-3}[a)]	$1/\rho$	A/cP
1	1344	7.441×10^{-4}	1.445	0.368	2.028	0.493	0.00323
2	1336	7.485×10^{-4}	1.481	0.393	2.036	0.491	0.00319
3	1322	7.564×10^{-4}	1.567	0.449	2.049	0.488	0.00313
4	1314	7.610×10^{-4}	1.61	0.476	2.057	0.486	0.00307
5	1299	7.698×10^{-4}	1.72	0.542	2.071	0.483	0.00302
6	1293	7.734×10^{-4}	1.74	0.554	2.077	0.481	0.00295
7	1284	7.788×10^{-4}	1.78	0.577	2.085	0.480	0.00287

a) Density was cited from Ref. 17.

Table 4. Calculated Result of the Pre-Exponential Term 'A' in the 85 wt% Na_3AlF_6–15 wt% Al_2O_3 System

Run No.	T/°K	$1/T$	η/cP	ln η	ρ/g cm^{-3}[a)]	$1/\rho$	A/cP
1	1351	7.402×10^{-4}	2.18	0.779	1.977	0.506	0.00235
2	1343	7.446×10^{-4}	2.27	0.820	1.983	0.504	0.00234
3	1328	7.530×10^{-4}	2.39	0.871	1.993	0.502	0.00225
4	1323	7.559×10^{-4}	2.40	0.875	1.997	0.501	0.00219
5	1218	7.587×10^{-4}	2.47	0.904	2.001	0.500	0.00218
6	1304	7.669×10^{-4}	2.59	0.952	2.011	0.497	0.00210

a) Density was cited from Ref. 17.

mole fraction (0.73 and 0.27) in the system, and $\Delta G^*{}_1$ and $\Delta G^*{}_2$ are the free energy of activation, per mole for each compound (1 erg=10^{-7} J). $\Delta G^*{}_1$ is the free energy of activation, 12.74 kcal mol^{-1}, for fluid flow of the molten Na_3AlF_6. $\Delta G^*{}_2$ is that of Al_2O_3, 13.29 kcal mol^{-1}. By substituting these values into Eq. 9, the value of $V_{1,2}$ is estimated to be about 22.4 ml mol^{-1}.

Regarding the dissociated ionic species of the Na_3AlF_6–Al_2O_3 system in molten salt, the following have been proposed by many invesigators.[8—10)]

I. Al_2O_3, simple solution without ionization,
II. $Al^{3+} + O^{2-}$,
III. AlO^-,
IV. $Al_2OF_X{}^{4-X}$ (X=6 or 8),
V. $Al_3O_2F_X{}^{5-X}$ (X=6 or 8),
VI. $Al_2O_2F_Y{}^{2-Y}$ (Y=2, 3, 4 or 5),
VII. $AlOF_Y{}^{1-Y}$ (Y=3, 4, 5 or 6).

It is now believed that Na_3AlF_6 in he molten state is dissociated into $AlF_6{}^{3-}$ and Na^+ ions, and that the $AlF_6{}^{3-}$ ions are partly separated into $AlF_4{}^-$ and F^- ions to the extent of ca. 25%[9)] By a reaction between ions which are produced by the dissolution of Al_2O_3 and aluminium fluoride or fluoride ions produced by the decomposition of Na_3AlF_6, it is conjectured that complex ions of aluminium fluoride oxide, as described above (IV—VII), are formed. The electrical conductivity of the molten Na_3AlF_6–Al_2O_3 system depends mainly on the transportable quantity of free Na^+ ions, and decreases with increasing Al_2O_3. It is therefore considered that the complete ionic dissociation of Al_2O_3 into Al^{3+} and O^{2-} ions (II) does not occur in this system; if it does occur, the increment of the electrical conductivity due to free Al^{3+} ions should necessarily be measured in the associated system. From the results of Raman spectroscopy Gilbert et al.[9)] confirmed the absence of $AlOF_Y{}^{1-Y}$(VII) and AlO^-(III) ionic species consisting of a bridging of Al–O bonds. Kvande,[10)] who measured the vapour pressure of such a system, reported that both ionic species of $Al_3O_2F_X{}^{5-X}$(V) and $Al_2O_2F_Y{}^{2-Y}$(VI) and a simple solution of Al_2O_3(I) showed a large negative deviation from Raoult's law. He also claimed that only ionic species of $Al_2OF_8{}^{4-}$ follow Raoult's law to an extent of 7.5 wt% in Al_2O_3 content. Foster and Frank,[28)] who employed the integrated cryoscopic equation by Temkin's formulation, suggested the possibility that, at higher Al_2O_3 content than 5 wt%, the molten state of the Na_3AlF_6–Al_2O_3 system gives rise to partial dimerization due to an interaction between $AlO_2{}^-$ ions. Rolin and Bernard[29)] also described from the cryoscopic result that the dissociation mechanism of Al_2O_3 in the molten state of the Na_3AlF_6–Al_2O_3 system containing Al_2O_3 more than 10 wt% gradually approached to the dissociated equation of $Al_2O_3 = AlO^+ + AlO_2{}^-$ with an increment of Al_2O_3 concentration, associating the phenomenon of clustering in the respective dissociated ionic species. It is very difficult to exactly determine the dissociated ionic species in the molten state of the present system. However, judging from the value of 22.4 ml mol^{-1} obtained from its viscosity as s mean molar volume of flow unit, the minimum step height, 26 Å (measured from the growth step pattern observable on (0001) face of Al_2O_3 single crystals grown at higher temperatures than 1000°C in the present system by using a very sensitive phase contrast microscope with a multiple interferometry,[1] which is now considered to be approximately equal to the minimum size of solute particle or growth unit existing in the solvent); the steep increment of viscosity in the molten salt containing Al_2O_3 more than 10 w%, there is expected to be a high probability that in molten Na_3AlF_6–Al_2O_3 containing Al_2O_3 concentration more than 10 wt%, the dissociated ionic species of Al_2O_3 exist as the clustering state or polymerizing state of AlO^+ or AlO_2^- rather than as aluminium fluoride oxide ions. We consequently speculate that these aluminium oxide ions existing in the clustering state are transferred by thermal convection and diffusion to the surface of a growing corundum crystal and are incorporated into the crystal as a growth unit.

Summary

The viscosity in the molten state of Na_3AlF_6–Al_2O_3 was measured by the oscillating disk method. The viscosity in such a system progressively increases with an increase in the Al_2O_3 concentration at 1050°C, from 1.57 cP (0 wt%) to 1.68 cP (10 wt%), and at 15 wt% it steeply increased to 2.40 cP (1 cP = mPa s). The temperature dependence of the viscosity exhibited an Arrhenius behavior, and it was found that the free-energy-limited theory for such a system is applicable, rather than free-volume-limited theory. The mean molar volume and activation free energy of the flow unit in a system containing 15 wt% Al_2O_3 were calculated to be 22.4 ml mol^{-1} and 12.74 kcal mol^{-1} at 1050°C, respectively. We believe that the dissociated ionic species of Al_2O_3 in the molten salt of the Na_3AlF_6–Al_2O_3 system containing Al_2O_3 of 15 wt% exist at a clustering state of AlO^+ or AlO_2^-, although the existence of aluminium fluoride oxide ions cannot be eliminated; these ions at the clustering state are incorporated into the crystal as a growth unit.

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