

Influence of oxide dopants on the wetting of doped graphite by cryolite/alumina melts

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Abstract

In the aluminium smelting industry, the wetting of the electrolyte on the carbon anode is an important property associated with the onset of the anode effect. The effect of dopants on the wettability of the anode was investigated in this study. The carbon material selected was graphite. The composition of the cryolite/alumina melts varied between a very low alumina content and 6 wt.% alumina. The sessile drop approach was adopted to measure the contact angle between the melt and the graphite at 1030 °C. The influence of oxide dopants, chromium III oxide and alumina, in the graphite on the wettability was studied. The wettability on a pure graphite surface depends to a small extent on the liquid surface tension but mostly on the liquid–solid interfacial tension that varies with the concentration of alumina in the liquid. The wettability on an oxide doped graphite surface depends on the dissolution of the oxide in the melt that changes the liquid–solid interfacial tension. The alumina dissolution has a double effect on the liquid–solid interfacial tension: the chemical reaction as well as the change in the oxy-anions concentration at the interface decrease the interfacial tension.

Introduction

In industrial alumina reduction cells, the anode effect is known to be due to the depletion of the alumina in the vicinity of the anode [1]. However, the reason for its onset is still under debate. Researchers have suggested that the deterioration of the wetting properties of the anode could accelerate the onset of the anode effect [2, 3].

One field of research is the use of dopants in the anodes to inhibit the anode effect [4]. Some studies have suggested that the inhibition of the anode effect on the doped anodes could be due to an improvement of the wettability of the electrolyte on the anode [2, 5]. However this was not verified experimentally in most cases.

Several parameters influence the wettability of electrolytes on carbon substrates. It is strongly dependent on the composition of the melt, the physical properties (mainly the structure) of the carbon material, the temperature and the composition of the gas phase [1]. The polarization of the carbon material, the potential imposed and the current density also influence the wettability [6]. Finally, the contact angles also vary with exposure time [2]. Consequently, the different experimental conditions used, explain the discrep-

ancies in the contact angle values found in the literature.

The angle of wetting of carbon substrates by cryolite/alumina melts with increasing concentration of alumina was studied by several researchers. Matiasovsky et al. [7] worked under an argon atmosphere and measured the contact angles at the time of melting on a graphite substrate. Belyaev et al. [8] measured the contact angles of cryolite/alumina melts on carbon plates under different atmospheres, argon, nitrogen, carbon monoxide and oxygen, 480 or 600 s after melting, at 1000 °C. No details are given regarding the nature of the carbon. Metson et al. [2] used pressed pellets on highly graphitised electrode materials and their measurements were done at the melting temperature of the specimen right after melting. The general trend of these results is that the contact angles decrease when the alumina concentration increases. These are summarized in Figure 1. It shows that significantly different values of contact angle were reported in the literature, this wide range of value (75–140°) is explained by the different experimental conditions used by the different authors. Antipin et al. [9] found an entirely different character of the dependence of the contact angle with alumina concentration, their curve passing through a series of minima and maxima, which become more pronounced with

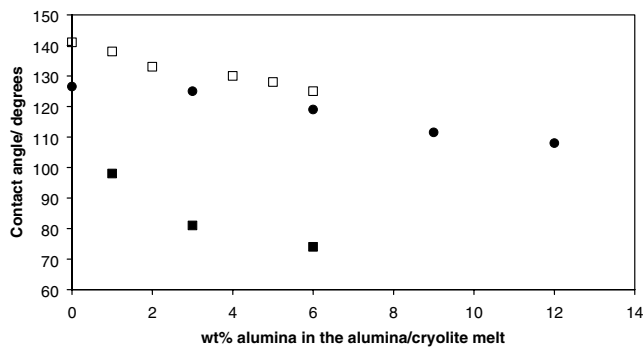


Fig. 1. Contact angle against alumina concentration in the system cryolite–alumina/carbon. Key: (□) Metson et al. [2], (■) Belyaev et al. [8], (●) Matiasovski et al. [7].

prolonged contact time between the melt and the graphite support. Other wettability measurements were done under polarization of the graphite material and show a larger decrease in contact angle with the increase in alumina concentration [10, 11].

The influence of several additives in the carbon on the wetting angle of cryolite–alumina melts has been studied. Yao et al. [12] studied the wettability of cryolite/5 wt.% alumina melts on carbon anodes doped with Li_2CO_3 . They showed that the wettability improved on the doped anode whether it is anodically polarized (decrease of contact angle by 46° to 80°) or not (decrease of contact angle by 50° to 60°). Yang et al. [13] prepared carbon anodes doped with different composite oxide powders by mechanical mixing. They found that melts of cryolite/5 wt.% alumina have good wettability on carbon anodes doped with LiAlO_2 and CaAl_2O_4 . No explanation for the improvement in wettability was given.

In the present study, the dynamic wetting of cryolite/alumina melts on graphite substrates and on doped graphite substrates, was studied using the sessile drop approach. The first dopant studied was a chromium dopant as this has been shown to inhibit the anode effect in melts of pure cryolite and to multiply the critical current density by a factor of three in melts of cryolite/alumina [14]. The second dopant selected was alumina as it is more environmentally friendly and is more compatible with the industrial application. The doping procedures used were impregnation or mixing. Scanning electron microscopy observations and X-ray energy dispersive spectrometry were conducted to test the efficiency of the doping procedures. X-ray diffraction analyses were performed to identify the doping phase.

The objective of the investigation is to establish the influence of the dopants on the dynamic wetting

occurring at the solid/melt interface and to develop a fundamental understanding regarding the wettability. Furthermore, careful high temperature experiments were necessary to establish accurate contact angle values for these systems since there seems to be discrepancies in the values reported in the literature.

2. Experimental details

2.1. Preparation of substrates

The graphite substrates were polished with a 600-grit emery paper. They were then doped by a solution of $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ by impregnation as described in [14].

The alumina doped substrates were prepared by mixing of a graphite powder and an alumina powder. The two powders were mixed and crushed by wetmilling for 12 h in a solution of isopropanol, the grinding media being four alumina balls. The mixture was then dried at 110°C overnight to evaporate any alcohol residue followed by further drying at 400°C for 12 h to remove the moisture. The mixture was then pressed in a vertical press in a 20 mm diameter die at a pressure of 100 kg/cm^2 . To investigate the impact of the alumina content on the wettability, the alumina content was varied between 0 and 10 wt.%.

2.2. Preparation of the specimens

Cryolite/alumina batches were prepared, the composition of alumina varying from a very low content to 6 wt.%. The cryolite was purified by electrolysis in a laboratory cell described elsewhere [14]. Some alumina was added to the melt and sufficient time was left for dissolution and homogenization of the melt. Samples of 0.1 g were taken from each melt for the wettability measurements. This weight was low enough to overcome the influence of gravity on the drop formation. A sample of each melt was analyzed by an O-LECO analyzer to determine the alumina content accurately and the results are reported in Table 1. The difference between the theoretical value and the actual value is due to the quality of the pre-electrolysis. The theoretical alumina concentrations will be used to name the specimens in the present paper.

2.3. Experimental setup

The wetting experiments were conducted in the horizontal tube furnace shown in Figure 2. The temperature was set at 1030°C and the furnace was flushed with dry,

Table 1. Comparison of the theoretical alumina content of the cryolite/alumina batches and the results of the LECO analysis

| Theoretical alumina content/wt.% | Very low | 1 | 2 | 3 | 6 |
|----------------------------------|----------|------|------|------|------|
| Measured alumina/wt.% | 0.26 | 1.49 | 2.85 | 3.27 | 5.95 |

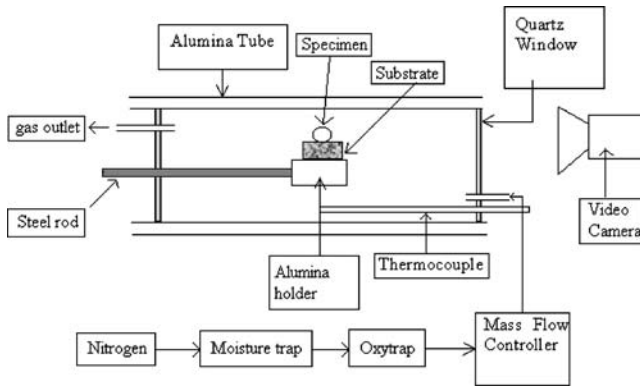


Fig. 2. Schematic diagram of the experimental setup for measuring the contact angle using the sessile drop approach.

oxygen-free nitrogen at a flow rate of 1 l/min. The experimental procedure was described by Wu and Sahajwalla [15]. The assembly of substrate and bath were introduced into the furnace hot zone. The melting of the sample on the substrate and then the reaction of the molten sample on the substrate was recorded by a high resolution video camera. The recorded film was then used to measure the contact angles. Digital images were captured from the film and special software was used to measure the contact angles with an accuracy of $\pm 5^\circ$.

3. Results and discussion

3.1. Wettability on pure graphite substrate

The evolution of the contact angle of a droplet of cryolite/alumina reacting on a pure graphite substrate was studied as a function of alumina concentration and the results are shown in Figure 3. The reported values are the values measured 10 min after the melting of the droplet. No significant evolution of the contact angles was observed in these experiments.

As seen in Figure 3, the contact angle of a droplet of cryolite/alumina on the graphite substrate shows a step at around 3 wt.% alumina. If the specimen contains less than 3 wt.% alumina, the contact angle value is 105°

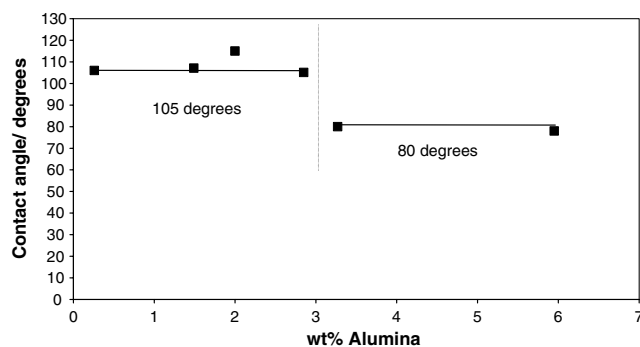


Fig. 3. Contact angle of a droplet of cryolite/alumina on a graphite substrate.

whereas if the specimen contains greater than 3 wt.% alumina, the contact angle value is 80° .

The degree of wetting of the graphite by the melt is affected by the values of the three interfacial tensions [1]: the interfacial tension of the electrolyte(E)/gas(G) interface (surface tension of the liquid), $\gamma_{G/E}$, the interfacial tension of the solid(C)/gas(G) interface (surface tension of the solid), $\gamma_{G/C}$ and the interfacial tension at the boundary liquid(E)/solid(C), $\gamma_{E/C}$, the dependence being given by Young's equation:

$$\cos \Theta = \frac{\gamma_{G/C} - \gamma_{E/C}}{\gamma_{G/E}} \quad (1)$$

where Θ is the contact angle. The conversion from wetting to non-wetting takes place when the contact angle becomes larger than 90° .

The presence of alumina in the cryolite/alumina melt modifies two of the above interfacial tensions: the liquid surface tension and the liquid/solid interfacial tension.

Alumina has been previously reported to act as a surface active compound in the cryolite/alumina melt. Measurements of the liquid surface tension of cryolite/alumina melts found in the literature [16, 17] show that the liquid surface tension decreases when the alumina content increases. For an alumina concentration in the 0.4–12 wt.% range and for temperatures between 1000 and 1100 $^\circ\text{C}$, the liquid surface tension γ can be expressed, in mN m^{-1} , as [17]:

$$\gamma = 264.3 - 0.1318t - 4.6 \log(C_{\text{Al}_2\text{O}_3}) - (3.29 - 0.00329t)C_{\text{Al}_2\text{O}_3} \quad (2)$$

where t is the temperature in Celsius and $C_{\text{Al}_2\text{O}_3}$ is the alumina concentration in wt.%.

At 1030 $^\circ\text{C}$, the surface tension decreases from 130 mN m^{-1} at low alumina content to 125 mN m^{-1} at 6 wt.% alumina. If we assume that the interfacial tension liquid–solid does not change with the alumina concentration, when the alumina concentration varies from 0.4 to 6 wt.%, the contact angle decrease is 0.4° . The contribution of the liquid surface tension alone cannot explain the decrease in contact angle observed in this work.

According to Metson et al. [2], the wettability of the melt on the carbon anode is determined by the interfacial tension at the anode/electrolyte interface. The role of the alumina is to provide the surfactant species which control the interfacial tension, the surfactants being the oxy-anionic species.

When alumina dissolves in the cryolite, oxygen-containing species are formed. Kvande [18] calculated the anionic molar fraction of the different Al–O–F species. It is interesting to note the shift from $\text{Al}_2\text{OF}_8^{4-}$ and $\text{Al}_2\text{OF}_6^{2-}$ as dominating at low alumina contents to the dominance of $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ for higher alumina contents, the transition occurring around 3 wt.% alumina in the melt. These complexes are

covalent in nature relative to the cryolite melt and will concentrate on the surface of the droplet to minimize the free energy of the system.

The decrease in contact angle observed in this work (105° – 80°) might then be due to a change in the dominant ionic species in the melt that occurs at approximately the same concentration. Indeed, the ions present at the interface melt/graphite are changing as the alumina concentration changes. A change in the interfacial tension might result from these changes.

The values of the contact angle found in this study are within the range of the contact angle found in the literature, but are closer to the values found by Belyaev et al. [8] who performed the measurements 10 min after the specimen melting, under a nitrogen atmosphere, as in the present study. However, it has been reported that the contact angle value decreases steadily when the alumina concentration increases in the cryolite/alumina melt [3] and this was not observed in this study. This statement applies fully to the contact angle measurements that were done under anodic polarization of the carbon substrate [10, 11] which is not the case of the present work. As shown in Figure 1, Matiasovsky et al. [7] did not report a decrease of contact angle value between 0 and 3 wt.% alumina, a lower contact angle value is only reported at 6 wt.% alumina. Metson et al. [2] reported a linear decrease of the contact angle value; when the alumina concentration increases by 1 wt.%, the contact angle decreases by 3 – 5° , these values being within the range of the usual experimental error. For experiments done without polarization of the substrate, a steady decrease in contact angle with an increase in alumina concentration may be questionable.

3.2. Influence of chromium doping on wettability

The wettability of cryolite/alumina melts was studied on chromium doped graphite substrates and the results are presented in Figure 4. The contact angle values presented were measured 10 min after melting for the same reason as for the graphite substrate. Two main features appear: if there is alumina in the specimen, the wettability is the same on the doped substrate as on a pure graphite substrate. If the alumina content in the

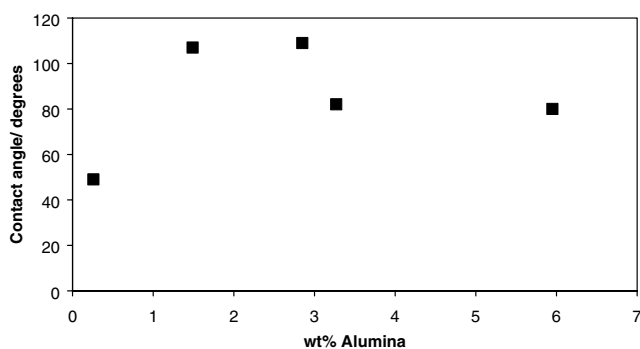


Fig. 4. Contact angle of a droplet of cryolite/alumina on a chromium doped graphite substrate.

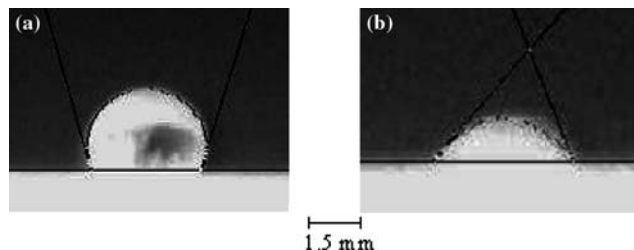


Fig. 5. Contact angle measurements, (b) a droplet of purified cryolite wets the chromium doped graphite substrate ($\theta = 49^{\circ}$), (a) but does not wet the graphite substrate ($\theta = 106^{\circ}$).

specimen is very low (0.26 wt.%), the specimen wets the chromium doped substrate (49°) as shown in Figure 5b but does not wet the graphite substrate (106°) as shown in Figure 5a.

SEM observations and EDX analysis evidenced the efficiency of the doping procedure and showed the distribution of chromium on the surface of the substrate and in the cross section. As shown in Figure 6, chromium appears to be distributed on the surface with a higher concentration in the pores of the graphite. The maximum depth of penetration of the dopant was seen to be around 100 microns.

XRD analysis was used to identify the chromium compound present at the surface of the substrate. Two samples were prepared: sample 1 was pure graphite, used as a blank, while sample 2 was a chromium doped graphite sample. The samples were ground to produce powders that were analysed by XRD. For each of the two samples, the XRD spectra were obtained over the range 10 – 90° . A slow scan rate, 0.5 degree min^{-1} , was used with sample 2 to allow better detection of the low chromium level, while a scan rate of 1 degree min^{-1} was used with sample 1. XRD analysis proves that a new crystalline compound, identified as Cr_2O_3 , is present on the doped sample as shown in Figure 7. This compound formed at the heat treatment of 400°C , which is a step of the doping procedure.

The solubility of Cr_2O_3 in the cryolite or cryolite/alumina melts has been studied and is reported in the literature. Rolin and Bernard [19] used a visual method and found a solubility of 0.12 wt.% for Cr_2O_3 in pure cryolite at 1030°C with an error of 4%. Rolin and Gallay [20] reported a value of 0.13 wt.% for the solubility in pure cryolite and 0.05 wt.% for the solubility in cryolite + 5 wt.% alumina. Sterten and Skar [21] used a thermal method to measure the solubility of Cr_2O_3 in pure cryolite and found a larger value of 1.03 wt.%. Like other oxides, because of the common oxide anion formed on dissolving, the solubility of Cr_2O_3 in liquid mixtures of cryolite–alumina is strongly dependent on the alumina concentration. Consistent with this, Sterten and Skar [21] attribute the discrepancy between their value and the values found previously, to the presence of oxide impurities in the cryolite. Consequently, a certain amount of alumina in the cryolite implies a decrease in solubility of the Cr_2O_3

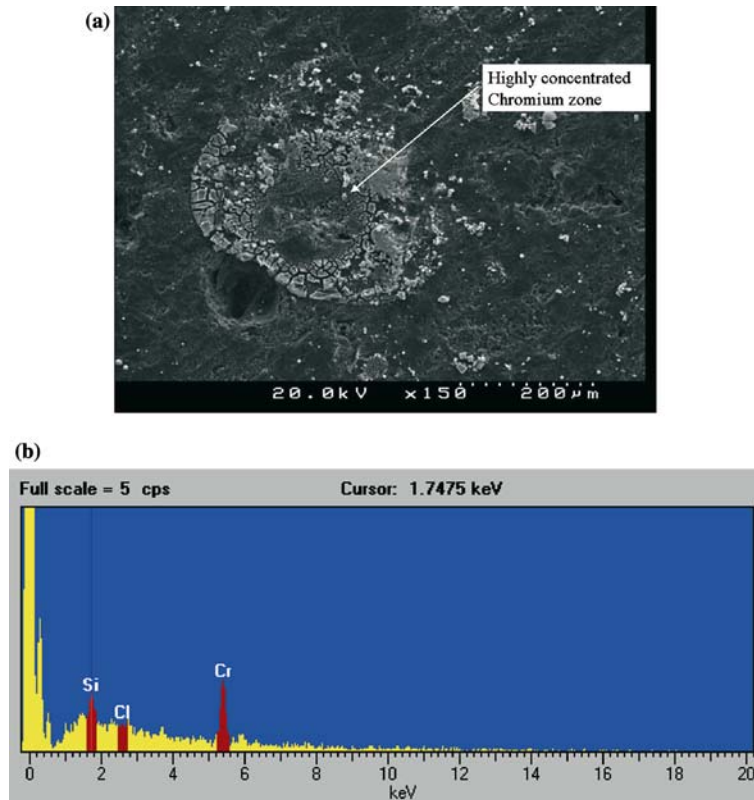


Fig. 6. SEM micrographics (a) and EDX analysis (b) evidencing a chromium compound at the surface of the chromium doped graphite substrate.

in the liquid cryolite/alumina melt. In the present work, the chromium oxide must be soluble in the very low alumina melt (0.26 wt.%) but the solubility must decrease for the other melts.

The wettability of the purified cryolite droplet on the chromium doped substrate can be explained by the dissolution of the chromium oxide in the cryolite. This wetting therefore occurs under chemical non-equilibrium conditions and would be significantly different from wetting under chemical equilibrium, where wettability is determined by molecular structural differences between the two contacting phases. Indeed, as the chromium oxide dissolves in the cryolite, a mass transfer from the substrate to the specimen occurs.

In a reactive wetting system, in light of thermodynamic considerations, it is agreed that the free energy

decrease which keeps the wetting line moving, results from the interfacial interaction ($\Delta\sigma_r$) and chemical reactions (ΔG_r). The term ΔG_r refers to the free energy decrease related to the mass transfer across the interface or formation of new substances at the interface. If mass transfer is the only reaction involved in the wetting process, the decrease in the system free energy will contribute to the interfacial region and result in a net decrease in interfacial tension. This will result in the spreading of the wetting line on the solid surface.

The dissolution of the chromium oxide in the cryolite therefore leads to a decrease in the solid/liquid interfacial tension and consequently to a wetting of the substrate by the specimen.

A higher concentration of alumina in the specimen minimizes the effect of the chromium doping on the wettability. Indeed, the mass transfer reaction is limited by the low solubility of the chromium oxide in the cryolite/alumina melt.

3.3. Influence of alumina doping on wettability

3.3.1. Influence of alumina in the substrate

The distribution of the alumina particles on the surface of the substrate was studied by SEM/EDX analysis. Figure 8 shows several alumina particles at the surface of the pressed substrate. From EDX analysis the aluminium mapping was seen to match with the oxygen mapping, allowing the light particles to be identified as alumina. As the size range of the alumina particles is

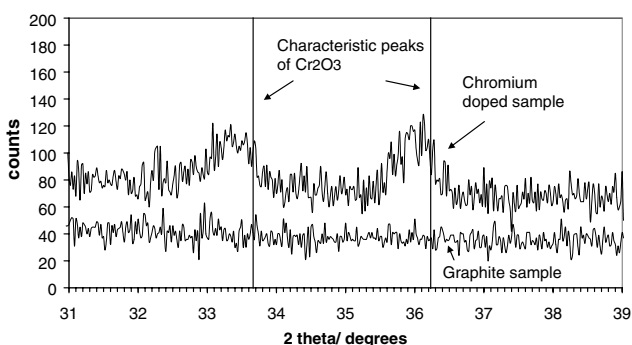


Fig. 7. XRD spectrum evidencing the presence of Cr_2O_3 on the doped graphite.

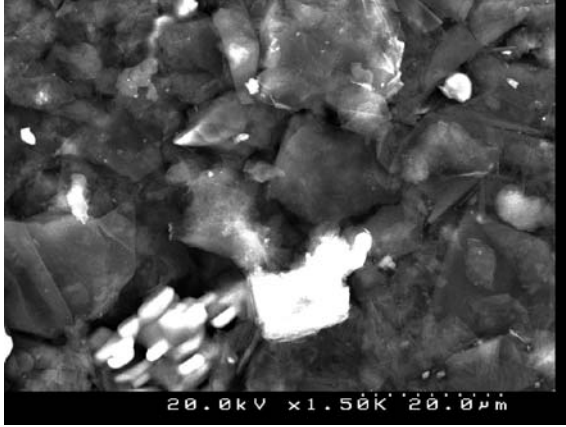


Fig. 8. SEM micrographics of the surface of a 10 wt.% alumina doped graphite substrate.

between 4 and 26 μm , it enables a distribution of the alumina on the surface of the substrate that is homogeneous enough for the wettability measurements.

The influence of the alumina content in the substrate on the wetting of a droplet of purified cryolite was studied. The droplet was allowed to react on the substrate for 1 hour, but only the interesting variations of the contact angles are reported here. The evolution of the contact angles for substrates with alumina content varying between 0 and 10 wt.% is presented on Figure 9 during the first 30 min of reaction.

On the substrate containing 10 wt.% alumina, the droplet of purified cryolite evolved from being nonwetting (105°) to wetting (79°) within 2 min, after which a steady state value for the contact angle is reached. This transition is illustrated in Figure 10. On the other substrates containing less than 5 wt.% alumina, no wetting of purified cryolite was observed, the contact angle staying between 100° and 110° . If we compare the contact angle of a melt of cryolite/alumina on a pure graphite substrate and the contact angle of a melt of purified cryolite on an alumina doped substrate, it can be noted that in both cases, when the droplet is wetting,

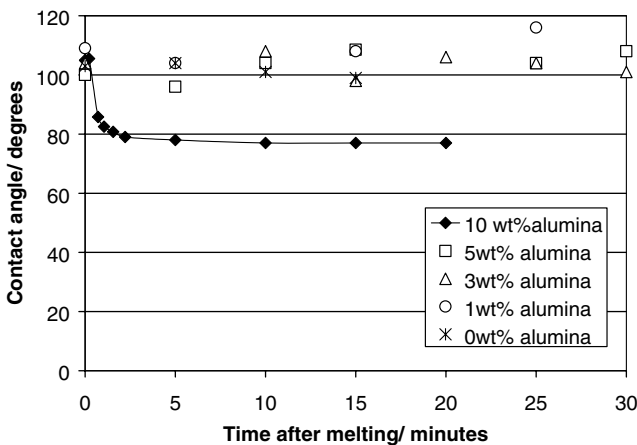


Fig. 9. Evolution of the contact angle of a droplet of purified cryolite on graphite substrates containing various percentages of alumina.

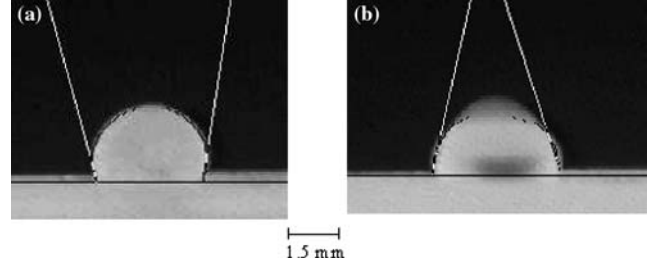


Fig. 10. Evolution of the contact angle of a droplet of pure cryolite on a 10 wt.% alumina/graphite substrate, at the time of melting, the droplet is non-wetting (a: $\theta = 105^\circ$) whereas 10 min later it is wetting (b: $\theta = 77^\circ$).

the contact angle value is around 80° and when it is non-wetting, the contact angle value is around 105° .

Thermodynamic considerations dictate that the movement of the wetting line in a wetting system is governed by the system's free energy decrease. Aksay et al. [22] related the system free energy change due to the change of surface area for a system in chemical equilibrium as given by:

$$\Delta G = \Delta \int_{sl} \gamma_{sl} dA_{sl} + \Delta \int_{sv} \gamma_{sv} dA_{sv} + \Delta \int_{lv} \gamma_{lv} dA_{lv} \quad (3)$$

Here ΔG is the interfacial free energy; γ_{sl} , γ_{sv} and γ_{lv} are the interfacial tensions at the solid/liquid, solid/vapor and liquid/vapor interfaces, respectively; dA_{sl} , dA_{sv} , dA_{lv} represent the surface area changes at the solid/liquid, solid/vapor, liquid/vapor interfaces caused by the movement of the wetting line. Wetting can proceed whenever ΔG is negative and the system will achieve its mechanical equilibrium when ΔG equals zero. Therefore, ΔG is the free energy available for wetting.

When a liquid spreads over a solid, it occurs with an increase in energy at the liquid–vapor interface ($\Delta\gamma_{lv} dA_{lv}$) and solid–liquid interface ($\Delta\gamma_{sl} dA_{sl}$) but a decrease in energy at the solid–vapor interface ($\Delta\gamma_{sv} dA_{sv}$). The wetting line will move if $\Delta\gamma_{lv} dA_{lv} + \Delta\gamma_{sl} dA_{sl} + \Delta\gamma_{sv} dA_{sv}$ is negative. In a non-reactive wetting system, the interfacial energy change is brought about by the change of interfacial areas. This is the phenomenon observed when a droplet of cryolite/alumina wets a substrate of pure graphite.

However, in a reactive system, if a reaction occurs at an interface, the system free energy change will contribute to the change in interfacial tension. An interfacial energy change may not only result from a change in interfacial area, but a decrease of solid/liquid interfacial tension resulting from the reaction, could be another reason to move the wetting line, according to Defay et al. [23]:

$$\gamma_{\alpha\beta} = \Delta G_{\alpha\beta} - \sum_i \mu_i^{\alpha\beta} \Gamma_i \quad (4)$$

where $\gamma_{\alpha\beta}$ is the interfacial tension, $\Delta G_{\alpha\beta}$ is the specific interfacial free energy associated with the chemical

reaction, $\mu_i^{\alpha\beta}$ is the chemical potential difference resulting from component i and Γ_i is the surface excess of component i .

After completion of the reaction at the interface, the interfacial tension gradually increases towards its static value. When the reaction is between the solid and the liquid, this transient lowering of the interfacial tension can cause the liquid drop to spread on the solid substrate if the interfacial tension reduction is large enough. The larger the potential difference between the solid and liquid, the more the interfacial tension decreases.

If the dissolution reaction from the solid to the liquid involves surface active species, the interfacial tensions γ_{sl} and/or γ_{lv} are modified by the reaction occurring at the interface. Eustathopoulos et al. [24] discussed the validity of the Aksay model and emphasized that the spreading of the droplet on the substrate in such a reactive wetting system is also due to the complementary effect of decrease of the solid–liquid interfacial tension due to the mass transfer of surface active species. Indeed the increase in contact angle foreseen by the Aksay model is rarely observed experimentally.

When the droplet of purified cryolite melted on the alumina doped substrate, there was a chemical potential difference between the liquid and the substrate mostly due to the alumina concentration difference between the liquid and the substrate. The larger the concentration difference, the larger the energy released from the mass transfer and thus the larger the decrease in liquid–solid interfacial tension.

As the alumina dissolved from the solid to the liquid, the solid/liquid interfacial tension evolved due to the presence of the oxy-anions at the interface. The kinetics of the alumina dissolution in the melt influence this aspect of the interfacial tension reduction, and indeed, if the dissolution rate is very quick, the interfacial tension will decrease more quickly.

The phenomena in Figure 9 could be explained as follows. The difference in the alumina potential between the liquid phase and the solid phase is the highest when the substrate contains 10 wt.% alumina, so the decrease in interfacial tension due to the dissolution reaction is the highest in that case. Furthermore, the increase in alumina concentration in the liquid at the interface is the highest in this case, so that the threshold value of 3 wt.% alumina in the cryolite at the interface is reached with resultant decrease in interfacial tension. For these two reasons, the droplet spreads on the substrate and the static contact angle value corresponds to an alumina content in the liquid above 3 wt.% as shown by Figure 3.

When the substrate contains less than 5 wt.% alumina, the dissolution of the alumina also takes place but the decrease in interfacial tension is not high enough to create wetting. Furthermore, the amount of alumina dissolved is not high enough to increase the interfacial alumina concentration to 3 wt.% and to decrease the interfacial tension. The droplet remains nonwetting.

3.3.2. Influence of alumina in the melt

The influence of the alumina content in the droplet for a substrate containing a fixed amount of alumina, 5 and 3 wt.%, is represented in Figures 11 and 12, respectively. The two levels of 105° (non-wetting scenario) and 80° (wetting scenario) exist in those cases also. When wetting occurs, the droplet evolves from a non-wetting to a wetting case within 1 or 2 min after melting and then reaches an almost steady value.

The wetting and non-wetting cases can be explained using the same arguments as in the previous section 3.3.1. When the alumina concentration is increased in the droplet, the chemical potential difference of the alumina in the solid and the liquid which is the driving force for the dissolution reaction is decreased and consequently, the interfacial surface tension does not decrease as much when the mass transfer takes place. On the other hand, the bulk concentration of alumina in the droplet is higher, so a lesser alumina dissolution is needed to increase the concentration of oxy-anions at the interface and to reach the threshold value of 3 wt.% at the interface.

As shown in Figure 11, on a substrate containing 5 wt.% alumina, a droplet of cryolite/2 wt.% alumina

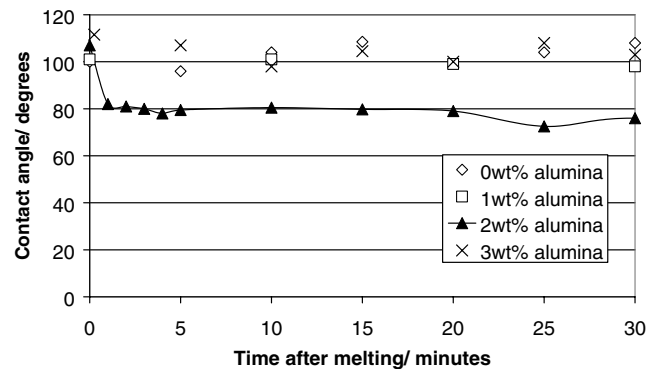


Fig. 11. Evolution of the contact angle of droplets containing various percentages of alumina on a 5 wt.% alumina/graphite substrate.

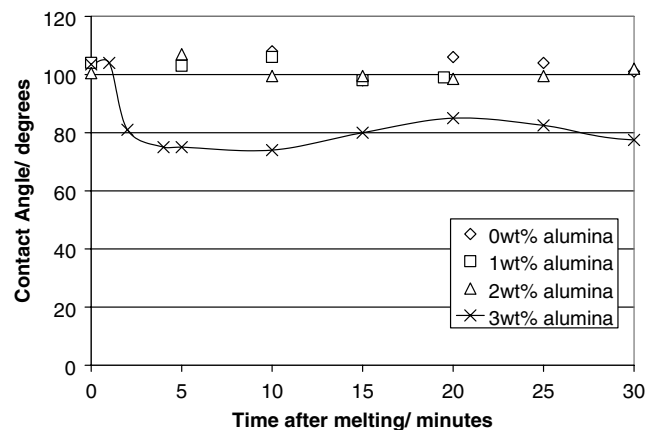


Fig. 12. Evolution of the contact angle of droplets containing various percentages of alumina on a 3 wt.% alumina/graphite substrate.

becomes wetting because the alumina dissolution first decreases the interfacial tension by its direct effect and by increasing the alumina concentration in the droplet at the interface. The droplet of cryolite/3 wt.% alumina shows an unusual behavior since it does not wet the substrate, this could be due to a local lower alumina concentration in the droplet.

As shown on Figure 12, in the cases of 3 wt.% alumina doped substrate, the alumina mass transfer for the droplets containing less than 3 wt.% alumina is not sufficient to decrease the interfacial tension, so the droplets remain non-wetting. The droplet containing 3 wt.% alumina is wetting because the alumina concentration was high enough to start with so the liquid–solid interfacial tension was already low enough to create a wetting.

It could be proposed that the wetting between an alumina doped substrate and a drop of cryolite/alumina depends on the chemical reaction that happens at the interface. The wetting is the net effect of two phenomena, the decrease in interfacial tension resulting from the chemical reaction and the decrease in interfacial tension resulting from the increase in the oxy-anions concentration in the liquid at the interface. The alumina dissolution only decreases the initial interfacial tension to create a wetting in a few cases.

4. Conclusions

The contact angle value of cryolite/alumina drops on graphite substrates was found to decrease from 105° to 80° for an alumina concentration in the liquid around 3 wt.%. This is mostly due to a decrease in liquid–solid interfacial tension when the alumina concentration increases.

The presence of Cr₂O₃ as a dopant in the graphite increases the wettability only at a very low alumina concentration. This could be due to the dissolution of the oxide in the cryolite that decreases the interfacial tension. The doping has no effect on contact angle for concentrations above 1.49 wt.% alumina in the liquid, this difference could be due to a drop in the oxide solubility in the liquid.

The presence of Al₂O₃ as a dopant in the graphite has an influence on the wettability depending on both the alumina content in the substrate and the specimen. Whether the droplet is wetting or non-wetting, the equilibrium contact angle value is one of the two values evidenced on a pure graphite substrate. The wetting depends on the chemical reaction that occurs at the interface. Indeed, the alumina dissolution has a double effect on the liquid–solid interfacial tension: the chemical reaction as well as the change in the oxy-anions concentration at the interface decrease the interfacial tension. The chemical potential difference between the solid and the liquid as well as the kinetics of the alumina dissolution determine whether the droplet will be wetting or not.

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