

Wettability of carbon surfaces by pure molten alkali chlorides and their penetration into a porous graphite substrate

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Abstract

The wettability of graphite and glassy carbon surfaces by pure molten alkali chlorides (NaCl, KCl, RbCl, CsCl) was measured by the sessile drop method. The contact angle was found to decrease with increase of the cation radius of the chloride. Using our measured and available literature data, a new, semi-empirical model is established to estimate the adhesion energy between the 20 alkali halide molten salts and graphite (or glassy carbon). The adhesion energy is found to increase with square of the radius of the cation, and the inverse of the radius of the anion of the salt. The minimum possible value for the surface energy of graphite (and glassy carbon) was found as $150 \pm 30 \text{ mJ/m}^2$. The critical contact angle of spontaneous penetration (infiltration) of the molten chlorides into a porous graphite substrate was found experimentally below 90° , in the interval between 31° and 58° . This is explained by the inner structure of the porous graphite.

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1. Introduction

The wettability of solid surfaces by molten salts is an important part of high temperature capillarity. However, the number of papers published on wetting by molten salts is by at least one order of magnitude less compared to the number of papers published on wetting by liquid metals. The reason for that is practical: while liquid metals are phases of primary importance for different technologies, molten salts usually play only a secondary role. Nevertheless, the meaningful control and design of different high-temperature technologies is not possible without the detailed knowledge on the wettability of different solid surfaces by molten salts. Examples when solid surfaces and molten salts appear to be in contact are numerous: electrolysis of metals from molten salts [1,2], production of carbon nanotubes from molten salts [3–5], energy storage, fuel cells [6–8], production of composite materials [9–12], fluxes in liquid metal purification [13,14], etc.

This paper is devoted to the exploratory results on the wettability of carbon (graphite and glassy carbon) surfaces by molten chlorides. The existing literature of this question is scarce and thus can be briefly reviewed.

Grjotheim et al. [1] (pp. 146–152) reviews literature for wettability of graphite by fluoride-based melts, being essential for Al electrolysis. Eustathopoulos et al. [15] (p. 346) refers to a report of Morel [16]. This report shows that graphite in dry inert gas at 1000°C is not wetted by the bromides, chlorides and fluorides of Na and Li (the contact angle of LiCl and NaCl is 136° and 128° , respectively). However, the wettability improves for KBr, KCl and KF (the contact angle for KCl is 73°). The wettability is further improved for RbCl ($\theta = 47^\circ$).

The wettability of graphite by molten NaCl–KCl melts at $820\text{--}850^\circ\text{C}$ was measured by Borisoglebskii et al. [17]. The contact angle of pure NaCl melt was found in the range of $110\text{--}120^\circ$ being somewhat below the results of [16]. However, the contact angle of pure KCl was found in the range $20\text{--}30^\circ$, being in significant contradiction with data of [16]. The concentration dependence of contact angle in the NaCl–KCl system showed some positive deviations from additivity [17]. When AlCl_3 was added to NaCl–KCl eutectic, some small decrease of the contact angle was observed [17].

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The NaCl–KCl–KF melt was reported to spontaneously infiltrate into the wall of a graphite crucible [13]. Thus, the contact angle must have been below 90°.

2. Experimental conditions

Pure NaCl, KCl, RbCl and CsCl salts of analytical purity (at least 99.9%) were used for the experiments. The salts were pre-melted above their melting points under low-pressure argon and held for 30 min. Then the furnace was switched off and the salt was left to cool spontaneously under argon atmosphere. Small pieces (of about 0.02 g) were broken from the middle parts of the prepared salts for the wettability tests.

Graphite and glassy carbon plates of chemical purity (>99.99%) were used as substrates for the sessile drop experiments. The substrates were produced by Carbone Lorraine Composants, France. The polycrystalline graphite plates (grade 1940 PT) have bulk density of 1.76 g/cm³, open porosity of 16% and average grain size of 12 μm. The bulk density of glassy carbon plates is 1.51 g/cm³, with no measurable open porosity. The size of the plates were 13 mm × 10 mm × 3 mm. The roughness was measured by atomic-force microscopy (AFM) using a NTEGRA PRIMA instrument. The initial graphite surface had a roughness of about 1 μm, which was decreased to about 250 nm by polishing. The as-received glassy carbon substrate had an average roughness of 5 nm. These observations on the achievable roughness of different carbon materials are in accordance with [18].

A sessile drop furnace with a high vacuum and pure argon system was used for the experiments. First, the substrate with a salt on its surface was placed into the furnace chamber. Then, high vacuum was created in the chamber, followed by filling it by pure (>99.999%) Ar gas till about 1 bar. This gas pressure was necessary to avoid strong evaporation of the salts. The samples were heated and melted at a rate of 10 K/min. Several photographs were taken in the temperature interval exceeding the liquidus temperature of the salt by 10–20 K. Then the system was switched off immediately and cooled spontaneously. Thus, temperature and time dependence of wettability was not studied to avoid severe evaporation of the samples. Rather, first contact angles were detected around the melting point of the salt. Due to the above experimental technique, the contact angle was an advancing angle and the weight loss during all experiments was below 0.5 wt.%. Only a few experiments were run to study the temperature dependence of wettability. In this case the sample was

heated with the same rate of 10 K/min till a higher temperature.

Photographs were taken with a digital camera, and were analyzed digitally using an image analysis software. The deviation between the contact angles on the two sides of the sessile drop was usually less than 5°. If the deviation was larger, the experiment was rejected, what usually happened to results on graphite substrate with a high roughness. The same reproducibility was ensured between the few photographs taken shortly after melting in a narrow temperature interval. The maximum deviation between parallel experiments never exceeded 10°.

3. Experimental results

The average measured contact angle data are presented in Table 1. The pre-last column shows the work of adhesion values, calculated by the Young-Dupré equation [15]:

$$W = \sigma_{l/v}(1 + \cos \Theta) \quad (1)$$

where $\sigma_{l/v}$ is the surface tension of molten salt (mJ/m²) and W is the adhesion energy between the carbon substrate and molten salt (mJ/m²).

As one can see from Table 1, contact angle values of CsCl, measured on the graphite and on the glassy carbon substrates are identical within the uncertainty of the measurements. Let us remind that contact angles were found proportional to the density of the carbon substrates (with zero open porosity) by Dezellus and Eustathopoulos [18]. In our case, the effective density of the graphite is close to the density of glassy carbon. Thus, our observed results (the approximated equality of contact angles on graphite and glassy carbon surfaces) are in accordance with the results of [18].

One can also see from Table 1 that by increasing the radius of the cation (R_M), the contact angle decreases (wettability improves) and the work of adhesion increases in the molten alkali chlorides/carbon systems. This observation is in accordance with literature data [15–17]. As one can see from Table 1, our contact angle value for NaCl (113°) is in good agreement with that of Ref. [17] (115°) and is somewhat lower than that of Ref. [16] (128°). On the other hand, our contact angle values for KCl and RbCl (78° and 58°, respectively) are in a relatively good agreement with that of Ref. [16] (73° and 48°, respectively), but are in a serious contradiction with that measured for KCl (25°) [17]. Although the value obtained for pure CsCl (31°) is new in the literature, it follows nicely the trend obtained by Morel [16], i.e., it decreases further along the row:

Table 1

Summary table of average contact angles of molten salts measured on graphite and glassy carbon plates immediately after melting (contact angle data with ±5°), and penetration ability of different molten salts into the porous graphite substrate

Salt	R_M (pm) [20]	T (°C)	Θ (°) on graphite	Θ (°) on glass-carbon	$\sigma_{l/v}$ (mJ/m ²) [19]	W (m ²) Eq. (1)	Penetration ^a
NaCl	98	810	113	–	114	69	No
KCl	133	780	78	–	99	120	No
RbCl	149	740	58	–	95	145	No
CsCl	165	645	31	30	92	171	Yes

^a Spontaneous penetration of the salt into the porous graphite was (yes) or was not (no) observed.

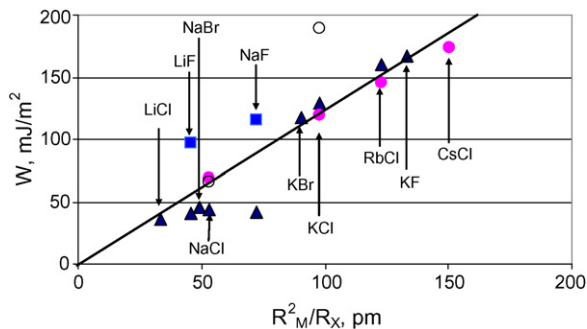


Fig. 1. Adhesion energies in molten alkali halide/graphite systems, checked against the semi-empirical Eq. (2). Triangles from [16]; squares, [1]; empty circles [17]; full circles, this paper (note: the full and empty circles for NaCl overlap).

LiCl (136°)–NaCl (128°)–KCl (73°)–RbCl (47°)–CsCl (31° , our new data), and also the trend, measured in this paper NaCl (113°)–KCl (78°)–RbCl (58°)–CsCl (31°).

The temperature dependence of the contact angle was studied for the KCl samples from its melting point till 860°C . During the experiment the geometry of the drop (diameter and height) and the contact angle were observed as function of time and temperature. It was found that during 6 min, i.e. in the T -range of 780 – 840°C the visible volume of the drop was unchanged, i.e. nor penetration, neither evaporation of the drop was taking place. In this T -interval the measured contact angle changed from 78° to 75° . According to Eq. (1), the adhesion energy due to the $(1 + \cos \Theta)$ term increases by about 4% if the contact angle decreases from 78° to 75° . On the other hand, the surface tension of KCl decreases in the same T -interval by about 5% [19]. Thus, the two effects (both contact angle and surface tension decrease with T) almost perfectly compensate each other in Eq. (1). As a consequence, we can state within the accuracy of the experiments that the adhesion energy in the non-reactive MX/C systems is independent of T . Thus, the adhesion energy values of Table 1 can be treated as T -independent values.

4. A semi-empirical model for the adhesion energy between pure alkali halides and carbon

Let us model the adhesion energy between alkali halide (MX) salts on graphite (C) in order to put our experimental data into a wider perspective. Using only the Goldschmidt ionic radii (R_M and R_X for the cation and the anion) as fitting parameters, the following semi-empirical equation was found to reproduce in the best way all available experimental data:

$$W \cong k \frac{R_M^2}{R_X} \quad (2)$$

Calculated adhesion energy values are checked against Eq. (2) in Fig. 1. One can see a good correlation with the semi-empirical coefficient of Eq. (2): $k \approx 1.25 \pm 0.20 \text{ mJ/m}^2 \text{ pm}$.

Eq. (2) can be rationalized as follows. The adhesion energy in the alkali halide/carbon systems (MX/C) is expected to be proportional to the polarizability of the cation of the salt. Polar-

izabilities of ionic ceramics are known to be proportional to their molar volumes [21]. That is why the polarizability of a cation in a molten salt can be taken in first approximation to be proportional to the cube of the ionic radius of the cation (R_M^3). On the other hand, the adhesion energy is expected to be inversely proportional to the molar surface area of the salt, what is proportional to the $2/3$ power of molar volume [22], and thus in the first approximation to the product of the radii of the cation and anion of the salt ($R_M R_X$). Dividing (R_M^3) by ($R_M R_X$), Eq. (2) follows. Calculated by Eqs. (1) and (2) values are given in Table 2. One can see that our measured contact angle values appear to be within the interval of calculated values.

5. Estimation of the surface energy of graphite and glassy carbon

Coupling Eq. (1) with the Young equation ($\sigma_{l/v} \cos \Theta = \sigma_{C/g} - \sigma_{C/l}$, where $\sigma_{C/g}$ and $\sigma_{C/l}$ are the carbon/gas and carbon/liquid interfacial energies, respectively), and using the obvious boundary condition $\sigma_{C/l} \geq 0$, the minimum value of the carbon/gas interfacial energy can be obtained as:

$$\sigma_{C/g} \geq W - \sigma_{l/v} \quad (3)$$

The maximum value found in the last column of Table 2 is: $\sigma_{C/g} \geq 150 \pm 30 \text{ mJ/m}^2$. Although this possible minimum value follows from our approximated model of Eq. (2), it is in perfect agreement with the value of the dispersion component of the surface energy of the basal plane of graphite, measured by Donnet et al. [23] and accepted as the full surface energy of the basal plane of graphite by Eustathopoulos et al. (see Ref. [15], p. 170). It should be mentioned that this minimum value is much lower compared to those, obtained and referred to by Rhee [24]. In this paper this minimum value is extrapolated also to glassy carbon, what is about five times higher than the dispersive term (see Ref. [15], p. 170).

6. Spontaneous penetration of molten salts into the porous graphite substrate

In the last column of Table 1 the results of spontaneous penetration observations are recorded. As the visible volume of the drop was observed and calculated during the experiment and the weight was measured before and after the experiment, the volume changes due to evaporation and penetration could be separated.

When a droplet gradually ‘disappeared’ from the surface of the substrate without any notable change in the total weight of the system in the course of the experiment, spontaneous penetration of the molten droplet into the porous graphite substrate is detected. It was confirmed only for the CsCl sample, which fully ‘disappeared’ into the porous graphite sample within 4 min after its melting started. It should be noted that the total volume of the pores within the graphite sample was by about five times larger than the total volume of the molten salt sample.

Table 2

Adhesion energy predicted by Eq. (2) ($k \approx 1.25 \pm 0.20$) and contact angle in MX/C systems at the melting point of the salt calculated from Eq. (1)

MX	R_M (pm) [20]	R_X (pm) [20]	σ_{lv} (mJ/m ²) [19] $\pm 3\%$	W (mJ/m ²) Eq. (2) $\pm 16\%$	Θ (°) Eq. (1) interval	$\sigma_{C/g}^{\min}$ (mJ/m ²) Eq. (3) ^a $\pm 19\%$
LiF	78	133	236	57	135–143	0
NaF	98	133	186	90	115–127	0
KF	133	133	144	166	68–93	22
RbF	149	133	126	209	9–69	83
CsF	165	133	106	256	0–14	150
LiCl	78	181	128	42	127–137	0
NaCl	98	181	114	66	108–122	0
KCl	133	181	99	122	62–90	23
RbCl	149	181	95	153	20–71	59
CsCl	165	181	92	188	0–48	96
LiBr	78	196	110	39	125–135	0
NaBr	98	196	95	61	103–118	0
KBr	133	196	90	113	60–89	23
RbBr	149	196	87	142	17–71	55
CsBr	165	196	83	174	0–44	91
LiI	78	220	94	35	124–134	0
NaI	98	220	82	55	102–117	0
KI	133	220	79	101	58–88	22
RbI	149	220	76	126	9–69	50
CsI	165	220	72	155	0–41	83

^a When a negative value follows from Eq. (3) for non-wetting systems, zero is shown in the Table, as negative surface energies have no physical sense.

When the visible volume of the droplet did not change, or its decrease was quantitatively explainable with the decrease of the total weight of the system during the course of the experiment, only some evaporation of the droplet was taking place, without any penetration. This was observed for RbCl, KCl and NaCl samples.

As a summary to the above, the CsCl droplet with contact angle of 31° was able to spontaneously penetrate, while the RbCl, KCl and NaCl droplets with contact angles of 58° , 78° and 113° , respectively, were not able to penetrate spontaneously into the porous graphite substrate. Thus, the critical contact angle of spontaneous penetration (Θ_{cr}) is measured in this work to be between 31° and 58° ($45 \pm 14^\circ$).

This result seems to be in contradiction with a common believe that liquids spontaneously penetrate into porous solids at $\Theta_{cr} = 90^\circ$. Let us remind that this critical value is valid only, if the pores in the solid body are cylindrical [25]. However, it is obviously not the case for the graphite samples used in this work. Our graphite samples are composed of rounded graphite grains of $12 \mu\text{m}$ in size. These grains provide a difficult 3D structure of the pores. Our experimental data ($31^\circ < \Theta_{cr} < 58^\circ$) are in good accordance with some previous experimental [26–30] and theoretical [25,31–34] results.

7. Conclusions

- (i) The wettability of graphite and glassy carbon surfaces by pure NaCl, KCl, RbCl and CsCl molten alkali chlorides was measured by the sessile drop method.
- (ii) A new, semi-empirical model (Eq. (2)) is proposed to estimate the adhesion energy between the 20 alkali halide molten salts and graphite (or glassy carbon) using our measured and available literature data. The adhesion energy is

found to increase with square of the radius of the cation, and the inverse of the radius of the anion of the salt.

- (iii) The minimum possible value for the surface energy of graphite (and glassy carbon) was found to equal $150 \pm 30 \text{ mJ/m}^2$.
- (iv) The critical contact angle of spontaneous penetration of pure molten salts into porous graphite was experimentally found between 31° and 58° , i.e. definitely below the commonly accepted 90° value. This is explained by the structure of the pores in graphite. The pores are formed between small graphite grains, instead of being cylindrical.

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References

- [1] K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky, J. Thonstad, Aluminium Electrolysis, 2nd ed., Aluminium-Verlag, Düsseldorf, 1982.
- [2] D.A. Weirauch, Curr. Opin. Solid State Mater. Sci. 9 (2005) 230–240.
- [3] W.K. Hsu, M. Terrones, J.P. Hare, H. Terrones, H.W. Kroto, D.R.M. Walton, Chem. Phys. Lett. 262 (1996) 161–166.
- [4] A.T. Dimitrov, G.Z. Chen, I.A. Kinloch, D.J. Fray, Electrochim. Acta 48 (2002) 91–102.
- [5] J. Miklósi, P. Póczik, I. Sytchev, K. Papp, G. Kaptay, P. Nagy, E. Kálmán, Appl. Phys. A72 (2001) S189–S192.
- [6] L. Suski, A. Godula-Jopek, J. Oblakowski, J. Electrochem. Soc. 146 (1999) 4048–4054.
- [7] A. Godula-Jopek, L. Suski, J. Electrochem. Soc. 147 (2000) 910–915.
- [8] M. Kawase, Y. Mugikura, R.T. Watanabe, J. Electrochem. Soc. 147 (2000) 854–860.
- [9] T. Choh, R. Kammel, T. Oki, Z. Metallkd. 78 (1987) 286–290.
- [10] J.P. Rocher, J.M. Quenisset, R. Naslan, J. Mater. Sci. 24 (1989) 2697–2703.

- [11] A.R. Kennedy, A.E. Karantzalis, *Mater. Sci. Eng. A* 264 (1999) 122–129.
- [12] Y. Birol, *J. Alloys Comp.* 420 (2006) 71–76.
- [13] B. Masson, M.M. Taghei, *Mater. Trans. JIM* 30 (1989) 411–422.
- [14] R.R. Roy, Y. Sahai, *Mater. Trans. JIM* 38 (1997) 995–1003.
- [15] N. Eustathopoulos, M.G. Nicholas, B. Drevet, *Wettability at High Temperatures*, Pergamon, 1999.
- [16] C.F. Morel, EUR 4482 e, Commission of the European Communities—Euratom, Joint Nuclear Research Centre, Petten Establishment, Netherlands, 1970.
- [17] Y.V. Borisoglebskii, M.M. Vetukov, M.I. Karimov, G.L. Zhunkovskii, *Cvetniie Metalli* 11 (1989) 57–58.
- [18] O. Dezellus, N. Eustathopoulos, *Scripta Mater.* 40 (1999) 1283–1288.
- [19] G.J. Janz, *Molten Salts Handbook*, Academic Press, NY, 1967.
- [20] J. Emsley, *The Elements*, Clarendon Press, Oxford, 1989.
- [21] P.W. Atkins, *Physical Chemistry*, 4th ed., University Press, Oxford, 1990.
- [22] G. Kaptay, *Mater. Sci. Forum.* 473/474 (2005) 1–10.
- [23] J.B. Donnet, J. Schultz, M.E.R. Shanahan, *Proc. Intern. Symp. On Carbon: New Processing and New Applications*, Toyohashi, Japan, 1982, pp. 57–62.
- [24] S.K. Rhee, *J. Am. Ceram. Soc.* 55 (1972) 300–302.
- [25] G. Kaptay, T. Bérczy, *J. Mater. Sci.* 40 (2005) 2531–2535.
- [26] Y.W. Yang, G. Zografi, *J. Colloid Interface Sci.* 122 (1988) 24–34.
- [27] Y.W. Yang, G. Zografi, E.E. Miller, *J. Colloid Interface Sci.* 122 (1988) 35–46.
- [28] E.J. Gonzalez, K.P. Trumble, *J. Am. Ceram. Soc.* 79 (1996) 114–120.
- [29] E. Candan, H.V. Atkinson, H. Jones, *Scripta Mater.* 38 (1998) 999–1002.
- [30] W. Shi, M. Kobashi, T. Choh, *Z. Metallkd.* 90 (1999) 294–298.
- [31] G. Kaptay, D.M. Stefanescu, *AFS Trans.* 100 (1992) 707–712.
- [32] X.F. Yang, X.M. Xi, *J. Mater. Sci.* 30 (1995) 5099–5102.
- [33] K.P. Trumble, *Acta Mater.* 46 (1998) 2363–2367.
- [34] G. Kaptay, *Mater. Sci. Forum* 414–415 (2003) 419–424.