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*Mendeleev Commun.*, 2014, **24**, 12–14

Mendeleev Communications

# Wetting and spreading of molten NaCl and $CaCl_2$ over polycrystalline hydroxyapatite

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DOI: 10.1016/j.mencom.2013.12.003

**The contact angles of molten NaCl and $CaCl_2$ on hydroxyapatite (HAp) in air at 866 and 880 °C are close to zero. Wettability and the kinetics of spreading in the NaCl/HAp system were not affected by the reaction product presaturation of a melt or by substrate density and roughness; the rate of spreading for NaCl/HAp was described by the De Genes model of viscous dissipation, while it slowed down significantly in case of $CaCl_2$/HAp due to the interfacial reaction resulting in a surface tension gradient.**

Wettability by molten salts and interfacial reactions are the important factors of ceramics production processes. About 95% of ceramics is manufactured by liquid phase sintering[1] with different salts (often alkali or alkali-earth halides) used as low-temperature sintering additives. For example, we can consider the fabrication of artificial ceramic implants based on hydroxyapatite (HAp). The rate of liquid phase sintering depends on the efficiency of melt infiltration through the pores of a preform, processes of surface and grain boundary wetting, interfacial energy and solubility of ceramic material.

Wettability of ceramic materials by molten salts has not been studied systematically: a few publications were devoted to the wetting of solids by molten salts[2,3] and the main conclusion is that the spreading process could not be modeled adequately and the equilibrium contact angle could not be predicted (even semi-quantitatively).

The aim of this work was to study wetting in the molten NaCl/HAp and molten $CaCl_2$/HAp systems and to analyze the process of melt spreading.

HAp powders were prepared by a conventional wet precipitation technique:[4,†]

$$10\,Ca(NO_3)_2 + 6\,(NH_4)_2HPO_4 + 8\,NH_4OH = \\ = Ca_{10}(PO_4)_6(OH)_2 + 20\,NH_4NO_3 + 6\,H_2O. \qquad (1)$$

The surface tension of pure liquid NaCl and NaCl held in contact with HAp powder in the dispenser before drop formation at 866 °C was determined from the hanging drop profile. The density of liquid NaCl[5] (Table 1) was assumed to remain unchanged after the interaction with HAp. The experimental surface tension of 109±2 mJ $m^{-2}$ for pure NaCl is consistent with published data.[6] The surface tension of a liquid NaCl–HAp mixture of 112±2 mJ $m^{-2}$ is close to that of pure NaCl within the limits of experimental error. This result is consistent with data on the dissolution of HAp in molten NaCl: NaCl held in contact with HAp dissolves less than 0.01 mol of CaO per mole of sodium chloride at 866 °C. Since the surface tension of CaO is much higher than that of NaCl (670 mJ $m^{-2}$ at a CaO fusion temperature[7]), the dissolution of a small amount of CaO in NaCl should not affect the melt surface tension.

It takes a drop about 200 ms to spread completely over the sample surface; in a few tens of milliseconds, the dihedral angle $\theta$ decreases to ~5° and continues to tend to zero. The determination of drop parameters from a side view becomes difficult in this case. The rate of spreading decreases drastically with time.

In order to reveal the effect of the preliminary equilibration of NaCl melt with solid HAp on spreading, sodium chloride was mixed with HAp powder (10 wt%) before placing into a dispenser and kept for 15 min at 866 °C before drop formation. Similarly to pure NaCl, the equilibrated melt perfectly wets HAp substrate and spreads to $\theta < 5°$ within several tens of milliseconds (Figure 1). Difference in spreading behaviors is within a reproducibility range. Slight dissolution of HAp (as CaO) did not influence the melt surface tension and viscosity. The dissolution cannot change significantly the shape of a solid liquid interface, which is reasonable taking into account the short time needed for complete spreading.

**Table 1** Physicochemical parameters of molten NaCl and $CaCl_2$.

| Salt | $T_f$/°C | $T_{exp}$/°C | $\sigma_{LG}$/mJ $m^{-2}$ | $\rho$/g $cm^{-3}$ | $\eta/10^{-3}$ Pa s |
|---|---|---|---|---|---|
| NaCl | 801[11] | 866 | 109.49±0.07[6] | 1.52±0.02[5] | 0.930[14] |
| $CaCl_2$ | 775[11] | 880 | 143.31±0.03[12] | 2.041[13] | 2.60±0.03[12] |

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[†] As-sintered ceramic samples (dense and porous; 95 and 80% of theoretical density, respectively) were ground and polished down to 9 μm with a series of diamond pastes. Sodium chloride monocrystals (chemically pure, PLC LOMO) and anhydrous calcium chloride powder (Reag. Ph Eur, Merck) were used. The experimental setup for studying wetting in air consisted of a tube furnace, a melt deposition system, a high-speed video camera (FastVideo-400, max. resolution of 640×480, 400–18000 frames $s^{-1}$) and a backlight. The melt dispenser consisted of an alumina crucible with an alumina plunger and a thin capillary of hexagonal boron nitride. A melt drop can be extruded by moving the plunger inside the crucible.

Solid salts were placed inside the crucible (without additives or with the addition of 10 wt% HAp powder); then, the crucible was mounted to the dispenser and placed inside the furnace above the HAp substrate. The furnace was heated to 866 °C for NaCl or to 880 °C for $CaCl_2$, and the temperature was stabilized for 15 min. Halide melt was gradually extruded through the capillary to form a drop and deposited on the HAp substrate. The process was recorded with a high-speed video camera. After the experiment, the sequence of separate drop images was extracted and geometrical drop parameters (contact angle $\theta$ and drop base diameter $D$) were measured.

The hanging drop profile before deposition on the substrate was used to define the melt surface tension $\sigma_{LG}$. The drop profile was fitted with the Laplace equation using the DropShape software (NPK Open Science).

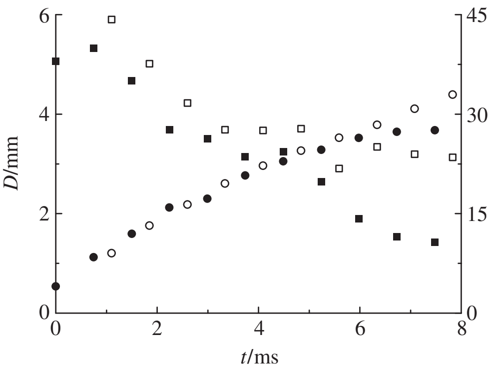

**Figure 1** (○), (●) Drop base diameter $D$ and (□), (■) contact angle $\theta$ *vs.* time for spreading of (○), (□) pure NaCl and (●), (■) NaCl equilibrated with HAp powder over dense HAp samples at 866 °C.

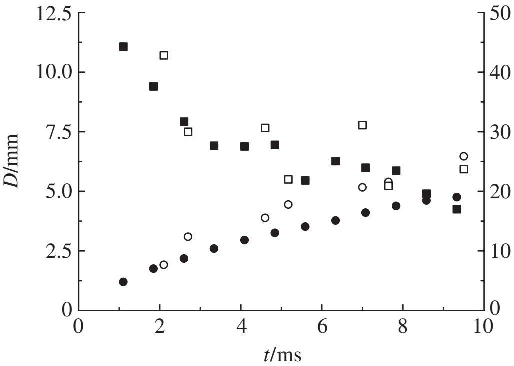

**Figure 2** (○), (●) Drop base diameter $D$ and (□), (■) contact angle $\theta$ *vs.* time for spreading of NaCl melt over (○), (□) rough and (●), (■) dense HAp samples at 866 °C.

The effect of surface structure (roughness and density) on the kinetics of spreading was studied by a comparison of the spreading behaviors of NaCl over dense and rough HAp samples (Figure 2). Spreading over low density HAp was similar (within data scattering) to that observed on a high density substrate.

The above experiments did not reveal any influence of dissolution on a solid / liquid interface or a surface relief on the spreading process for molten NaCl / HAp. Thus, the rate of spreading is controlled by viscous dissipation inside the drop, and it was compared with that predicted by the De Gennes model.[7] In terms of this model, the driving force of wetting is determined by a deviation of the instant contact angle from an equilibrium value, and viscous dissipation occurs inside the liquid volume in the triple line region

$$\frac{3\eta K_1}{\tan\theta}U = \sigma_{\mathrm{LG}}(\cos\theta_{\mathrm{F}} - \cos\theta), \tag{2}$$

where $\theta$ is the current contact angle, $\theta_{\mathrm{F}}$ is the equilibrium contact angle (assumed to be zero in our case as uncertainty in $\cos\theta_{\mathrm{F}}$ is less than 1% for $5 > \theta_{\mathrm{F}} > 0$), $U$ is the triple line velocity, $\eta$ is the liquid viscosity, and $\sigma_{\mathrm{LG}}$ is the surface tension of the melt, $K_1$ is a model parameter assumed to be 10.[7]

Thus, the final equation used to calculate the rate of spreading is

$$U = \frac{\sigma_{\mathrm{LG}}}{3\eta K_1}\tan\theta(t)[1 - \cos\theta(t)]. \tag{3}$$

Table 1 summarizes the physico-chemical parameters of NaCl and $CaCl_2$ melts used to calculate the rate of spreading. Experimental contact angles were inserted into equation (3) to calculate $U$ as a function of time. Figure 3 compares the calculated and experimental rates of spreading.

The spreading of NaCl is satisfactorily described by a viscous dissipation model, but the experimental rate of spreading for $CaCl_2$ is significantly lower than that calculated at $t < 10$ ms. An inverse behavior was frequently reported: the interfacial reaction promotes wetting and accelerates spreading. In the case of metallic systems, this is due to a specific role of reaction in removing wetting barriers (oxide films).[8] In the molten salt / HAp system, there is no evidence for the occurrence of such barriers. Calcium chloride melt reacts with HAp producing spodiosite $Ca_2PO_4Cl$ (confirmed by XRD analysis of an HAp–$CaCl_2$ mixture heated to 830 °C) and water. We suppose that water acts as a surfactant on the $CaCl_2$ melt/gas interface decreasing surface tension locally at the triple line region (where the diffusion path from interface is minimal). This leads to the initiation of Marangoni flow from the triple line toward a drop apex, which is inverse to viscous spreading flow and thus slows down spreading. A similar effect was observed when liquid copper spread over silicon: at $t < 10$ ms, the spreading of pure copper is slower than the spreading of copper presaturated with silicon[9] due to the dissolution of silicon (which is surface active in liquid copper) in the triple line region. The Marangoni effect can influence the rate of spreading, as shown experimentally for the mixtures of organic liquids on Pyrex.[10]

In conclusion, wettability of HAp surfaces by molten NaCl and $CaCl_2$ was systematically studied for the first time; the contact angle becomes smaller than 5° within ~100 ms. Neither the saturation of NaCl melt by reaction products with solid HAp nor the variation of substrate density and roughness affected the kinetics of spreading, which was successfully described in terms of viscous spreading. In the $CaCl_2$ / HAp system, the experimental rate of spreading is lower than that calculated for $t < 10$ ms. This effect could be attributed to the formation of a Marangoni flow provoked by the adsorption of a surface active reaction product (water) on the melt surface in the triple line region.

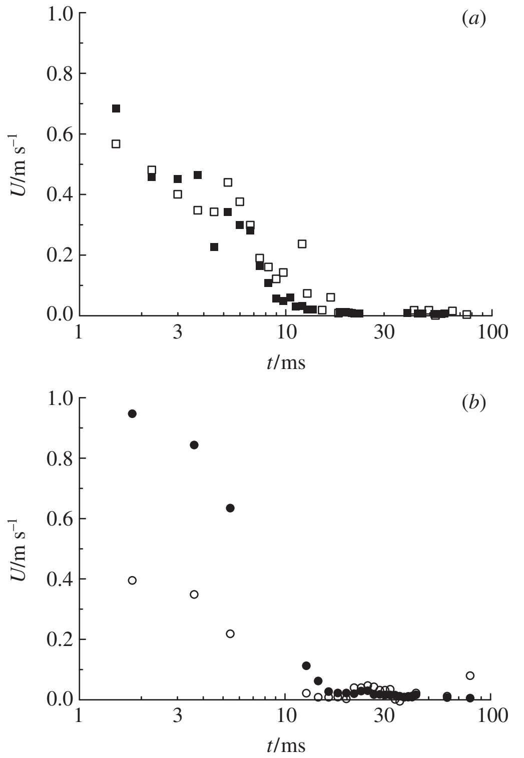

**Figure 3** (□), (○) Experimental and (■), (●) calculated spreading rates of (*a*) NaCl at 866 °C and (*b*) $CaCl_2$ at 880 °C over dense HAp samples.

This work was supported in part by the Federal Programmes 'R&D on High-Priority Directions of Science and Technology in Russia for 2007–2012' and 'Personnel' (state contract no. 14.740.11.0277), the Russian Foundation for Basic Research (grant nos. 11-08-01244, 12-03-01025, 12-08-00681, 12-08-33125, 13-08-12236 and 13-08-01056) and the M. V. Lomonosov Moscow State University Programme of Development.

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*Received: 16th July 2013; Com. 13/4168*