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Abstract

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SURFACE PROPERTIES OF MELTS BASED ON CaF_2

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The study of the surface properties of oxide melts makes it possible to establish a connection between them and the nature of the cations of the melt. The introduction of CaF_2 into the latter leads to systems in which it is possible to vary the relative amounts not only of different cations, but also of anions.

Investigation of the dependence of the surface tension (σ), measured by the sessile-drop method ([1,2]), on the composition of the melt at 1470–1550° C showed that, to a first approximation, there is a definite parallelism between σ and the ionic fraction of oxygen ($N_{O^{2-}}$) in the melt ([3]) (see Table 1). Indeed—

Table 1

Surface tension of oxide-fluoride melts at 1470-1550°

No.	CaF_2	CaO	Al_2O_3	SiO_2	MgO	Ionic fraction of oxygen $N_{O^{2-}}$	σ, erg/cm^2
1	100	–	–	–	–	0	280
2	95	5	–	–	–	0.036	290
3	85	15	–	–	–	0.110	300
4	74	26	–	–	–	0.200	315
5	86	–	–	14	–	0.180	285
6	80	–	20	–	–	0.225	295
7	71	–	26	–	–	0.325	330
8	65	7	10	12	6	0.380	340
9	52	21	27	–	–	0.440	375

the addition of calcium oxide to CaF_2 up to 26 wt.% raises σ from 280 to 315 erg/cm^2. This increase in σ may be associated with the appearance in the surface layer of the melt of oxide anions with a charge twice as large as that of the fluoride anion. Evidence in favor of this assumption is provided by the results of a comparison, by the method (4), of the surface potentials of liquid CaF_2 and of a melt with 26 wt.% CaO. Their difference ($\Delta\varepsilon_\omega$) was determined from the relation

$$\Delta\varepsilon_\omega = \Delta\varepsilon'' - \Delta\varepsilon' - \Delta\varepsilon_x. \tag{a}$$

To determine $\Delta\varepsilon_x$, a galvanic cell was assembled in corundum crucibles:

$$\mathrm{Pt\,(I)} \mid \underset{\text{(traces of CaO)}}{\mathrm{CaF_2}} \mid \mathrm{CaF_2 - CaO} \mid \mathrm{Pt\,(II)},$$

for which

$$\Delta\varepsilon_x = \varepsilon_{\mathrm{II}} - \varepsilon_{\mathrm{I}} = 32\ \mathrm{mV}. \tag{b}$$

The values of $\Delta\varepsilon''$ and $\Delta\varepsilon'$ were determined as the difference in potentials, respectively, between electrodes I or II and platinum electrode III, located above the surface of the melts under study, i.e.,

$$\Delta\varepsilon'' = \varepsilon_{\mathrm{III}} - \varepsilon_{\mathrm{I}} = 150\ \mathrm{mV}, \tag{c}$$

and

$$\Delta\varepsilon' = \varepsilon_{\mathrm{III}} - \varepsilon_{\mathrm{II}} = 90\ \mathrm{mV}. \tag{d}$$

All electrodes were in a stream of unpurified nitrogen (2-4% O_2). As a result of the measurements it was found that the surface potential of the melt with 26% CaO is 28 mV more negative than that for CaF_2.* The introduction of aluminum oxide into CaF_2 up to 15 wt.% reduced $\Delta\varepsilon_\omega$ almost to zero. Apparently, in the $CaF_2 - Al_2O_3$ system the surface layer also contains an appreciable amount of oxygen anions, which increases σ of the melt when Al_2O_3 is introduced into it. The addition of SiO_2 to CaF_2 has almost no effect on σ, which is promoted by the form in which SiO_2 exists in the melt (5). The simultaneous introduction of various oxides into CaF_2 appreciably increases σ.

By an approximate estimate, based on the shape of solidified drops (6), of the interfacial tension (σ_m) of certain metallic alloys based on nickel and iron, a parallelism was found between σ_m, σ, and $N_{O^{2-}}$ in the melt (see Table 2). From the electrocapillary motion (7) of metallic drops in the bulk of oxide-fluoride melts (8) toward the anode, it was established that the surface of the metal at the interphase boundary with the melt has a negative electric charge.

Table 2

Interfacial tension of metallic alloys at the boundary with an oxide-fluoride melt

Composition of melt	$N_{O^{2-}}$	20% Cr, 77% Ni, 2% Ti, 1% Al	20% Cr, 79.5% Ni, 0.5% (Ti+Al)	75% Fe, 15% Cr, 9% Ni, 1% Al	73.5% Fe, 18% Cr, 8.8% Ni, 0.5% Ti
100% CaF_2	0.000	1230	1300	1315	1150
74% CaF_2, 26% CaO	0.200	1250	1300	1350	1200
71% CaF_2, 29% Al_2O_3	0.325	1300	1370	1520	1300
65% CaF_2, 12% SiO_2, 6% MgO, 10% Al_2O_3, 7% CaO	0.380	1350	1430	1500	1380
52% CaF_2, 21% CaO, 27% Al_2O_3	0.440	1300	1380	1530	1310

Apparently, replacement in the melt of F^- ions by O^{2-} decreases the negative charge of the metal surface (^{9}) and thereby increases σ_m (^{10}).

The parallelism between σ_m and σ indicates, in particular, the constancy of the work of adhesion of metals to oxide-fluoride melts

$$W = \sigma + \sigma' - \sigma_m,$$

where σ' is the surface tension of the metal at the boundary with the gas. Indeed, a simultaneous increase in σ and σ_m does not change W.

Wetting of these same solid metals by oxide-fluoride melts in a furnace atmosphere with a carbon heater was very good ($\theta = 3 \div 5^{\circ}$), which can be explained by some oxidation of the metal. This is confirmed under the same conditions by the direction of the electrocapillary motion of metal drops over the surface of the melt toward the cathode.

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* In determining $\Delta\varepsilon_{\omega}$, the minimum value $\Delta\varepsilon''$ and the maximum values $\Delta\varepsilon'$ and $\Delta\varepsilon_x$ observed over the course of 10 min were used.

Note: Figure translations are in progress. See original paper for figures.

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