Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2008, **18**, 244–245
Mendeleev Communications

Electrochemical equilibria in copper/cryolite-alumina melt systems

Alexander Yu. Filatov,* Marina I. Borzenko, Zoya V. Kuzminova, Sergey Yu. Vassiliev, Sergey M. Kazakov, Evgeny V. Antipov and Valerii V. Lunin

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 4788; e-mail: filatov@icr.chem.msu.ru

DOI: 10.1016/j.mencom.2008.09.04

Temperature and cryolite ratio effects on copper redox potentials in alumina-cryolite melts are reported in relation to the prospects of metal-containing anodes for aluminum electrolysis.

Recently,[1,2] we reported the redox potentials for metals recognized as the prospective components of inert anodes for cryolite-alumina melt electrolysis. These data are also important for melt thermodynamics, especially, if available for a wide range of NaF/AlF_3 ratios (so-called cryolite ratio, CR). In this communication we address copper† behaviour in the cryolite-alumina melt‡ within the range of CR 1.3–3.0 by means of cyclic voltammetry.§ To separate the dependence of copper potentials on the temperature and CR, for each CR the voltammetry was performed at two temperatures: any time we started with 30 K above the liquidus,[3] and later increased the working temperature up to the value of 30 K above the liquidus for higher CR (Table 1).

Voltammograms (Figure 1) demonstrate the existence of at least two well-separated redox couples I and II (in potential regions much lower than 2 V and close to 2 V, respectively). A number of overlapping features (peaks and waves) can be found in both regions, and data treatment appears to be complicated by the overlap of several electrode processes (sometimes including oxygen evolution), as well as by pronounced Ohmic drop. This is why to estimate formal potentials, we extrapolated the regions of cathodic and anodic current growth to zero current and averaged thus obtained values [Figure 1(*a*)].

In the absence of any complications, this procedure gives the same result as the averaging of peak potentials. Thus obtained dependences of formal potentials on CR were compared to calculated results. Various possible scenaria of copper oxidation in cryolyte-alumina melts can be presented by the following equations:

$$4Cu_{(met)} + O_{2(g)} = 2Cu_2O_{(s)}$$
$$2Cu_{(met)} + O_{2(g)} = 2CuO_{(s)}$$
$$2Cu_2O_{(s)} + O_{2(g)} = 4CuO_{(s)}$$
$$2Cu_{(met)} + 2Al_2O_{3(solv)} + O_{2(g)} = 2CuAl_2O_{4(s)}$$
$$3Cu_{(met)} + 2AlF_{3(solv)} + 1.5O_{2(g)} = 3CuF_{2(s/liq)} + Al_2O_{3(solv)}$$

Standard Gibbs energies and half reaction standard potentials E_T for all reactions were calculated using standard thermodynamic data[5] and assuming that all copper compounds are solid and therefore their activities are equal to unity. Note that our calculation ignores any contribution of copper compounds solvation by the melt. This means that the experimental values may be lower but never higher than calculated values. The difference of computed and experimental potentials is expected for equilibria with soluble species, in particular fluoride complexes (formally presented by solid or liquid CuF_2). However, the difference of 0.4 V is surely higher than the solvation energy. We escaped to consider CuF formation because its existence is doubtful. As for CuF_2 (undergoing melting at 770 °C[4]), we used formally the values of formation free energy[5] and obtained a bending of computed curve at the melting point.

For the processes involving aluminum oxide and fluoride, the activities[3] $a_{Al_2O_3}$ and/or a_{AlF_3} were substituted into the Nernst equation:

$$E = E_T + \frac{RT}{nF}\ln(a^A_{Al_2O_3}a^B_{AlF_3}),$$

where R is the gas constant; T is the temperature; n corresponds to the number of electrons involved in the reaction; F is the Faraday constant; A and B are corresponding stoichiometric coefficients.

The most natural hypothesis is to attribute the observed potentials to Cu/Cu_2O and Cu_2O/CuO redox couples because of evidently close computed values. XRD¶ analysis of copper samples after galvanostatic†† electrolysis indicated the formation of Cu_2O exclusively. One can assume that Cu^{II} forms more soluble compounds as compared to Cu^{I}. No copper fluoride was found, as well as copper aluminate (its formation can be surely

Table 1 Melting and working temperatures for melts under study.

CR	Melting temperature/°C	Working temperatures/°C
1.3	717	750, 840
1.5	811	840, 935
1.8	906	935, 960
2.0	942	960, 1010
2.3	979	1010, 1030
2.7	996	1030
3.0	997	1030

† Technical copper wires 2.8 mm in diameter were used as working electrodes.

‡ Melts were prepared by mixing cryolite (Na_3AlF_6) with aluminium fluoride (AlF_3) (the ratio corresponded to certain CR) and with 2 wt% of alumina (Al_2O_3).

§ Cyclic voltammetry and chronopotentiometry were performed in a three-electrode cell, with Pt wire as a reference electrode, and graphite rod as a counter electrode. For voltammetry, scan rate was 10 mV s^{-1}. All potentials E are reported in Al electrode scale. Current densities are normalized to geometric surface area; the latter was determined within the accuracy of factor 2 because of comparable areas in the melt and in meniscus. The current densities are not involved into any quantitative considerations presented below.

¶ XRD patterns were recorded at room temperature with a Huber IMAGE FOIL Guinier Camera 670 [$\lambda(CuK\alpha_1)$ = 1.5406 Å].

†† Current density 0.3–0.9 A cm^{-2}, polarization time 20 min, potentials changes 2.3–2.7 V.

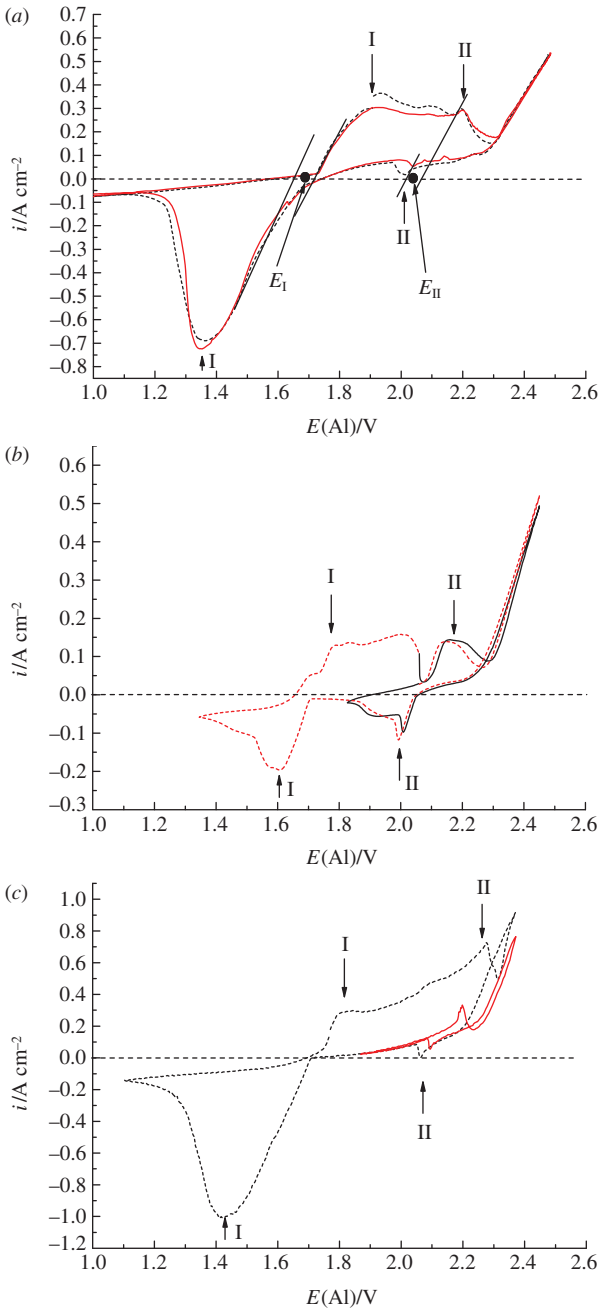

Figure 1 Copper cyclic voltammograms (10 mV s^{-1}) in the melts of various CR: (*a*) 1.3; (*b*) 1.8; (*c*) 3.0.

excluded in frames of a comparison shown in Figure 2). To summarize, we observed a two-step process of subsequent copper oxidation, Cu to Cu^{I} and then to Cu^{II}, but not parallel oxidation processes with the formation of oxide and fluoride.

Rare data on the potentials for pure copper in the melt saturated with Al_2O_3 at 970 °C with CR ≈ 2.2 are available: potential corresponding to intersection of cathodic and anodic Tafel plots for Cu electrode is 1.68 V;[6] 2.16–2.20 V formal voltammetric potential was found for Cu_2O/CuO redox couple.[7] Both values (triangles in Figure 2) are in satisfactory agreement with our data.

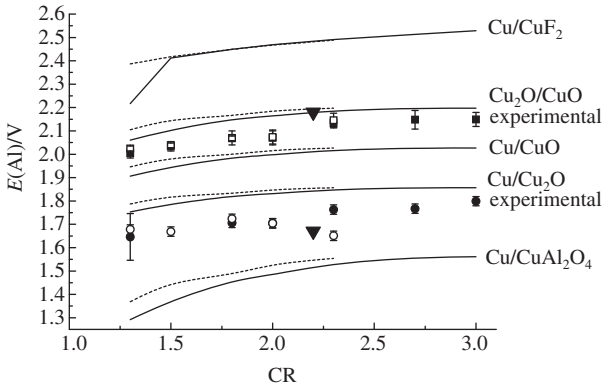

Figure 2 The dependences of experimental (points) and calculated (lines) potentials on CR. Bars demonstrate the scatter of potentials determination. Solid and dashed lines correspond to lower and higher temperature values (Table 1), the same is for solid and open symbols. Triangles correspond to the data of refs. 6, 7, CR 2.2, 970 °C.

Formation of fluorides presents the most important risk for any material applied as a component of low-consumable anode. Our findings demonstrate the prospects of using Cu as the main component of metallic or cermet anodes in a wide range of CR, in contrast to Fe and Ni easily forming fluorides at mid and low CR.[8] The slope of monotonous potential *vs.* CR dependeces is close to the slope thermodynamically predicted for both Cu/Cu_2O and Cu_2O/CuO redox pairs. For further optimization of melt electrolysis with Cu-containing anodes, CR effect on the solubility of Cu compounds is crucial, and the solubility data are currently available only for CR ≥ 3.[9] According to our preliminary results, solubility becomes lower with CR decrease, undergoing the most sharp decrease at CR of *ca*. 1.8–2.0.

We are grateful to Professor G. A. Tsirlina for useful discussions. This work was supported by Russian Engineering Company in frames of a joint RUSAL–MSU project.

References

1 E. V. Antipov, A. G. Borzenko, V. M. Denisov, A. Yu. Filatov, V. V. Ivanov, S. M. Kazakov, P. M. Mazin, V. M. Mazin, V. I. Shtanov, D. A. Simakov, G. A. Tsirlina, S. Yu. Vassiliev and Yu. A. Velicodny, in *Light Metals*, ed. T. J. Galloway, TMS, Warrendale, PA, 2006, p. 403.
2 D. A. Simakov, E. V. Antipov, M. I. Borzenko, S. Yu. Vassiliev, Yu. A. Velicodny, V. M. Denisov, V. V. Ivanov, S. M. Kazakov, Z. V. Kuzminova, A. Yu. Filatov, G. A. Tsirlina and V. I. Shtanov, in *Light Metals*, ed. M. Sorlie, TMS, Warrendale, PA, 2007, p. 489.
3 J. Thonstad, P. Fellner, G. M. Haarberg, H. Kvande and A. Sterten, *Aluminium Electrolysis. Fundamentals in the Hall-Heroult Process*, 3rd edn., Aluminium-Verlag, Dusseldorf, 2001.
4 H. M. Haendler, L. H. Towle, E. F. Bennett and W. L. Patterson, *J. Am. Chem. Soc*., 1954, **76**, 2178.
5 *HSC Chemistry 5.11 Database*. Outokumpu Research Oy, Pori, Finland.
6 P. G. Russell, *J. Appl. Electrochem*., 1986, **16**, 147.
7 C. F. Windisch, Jr. and S. C. Marschman, in *Light Metals*, ed. R. D. Zabreznik, TMS, Warrendale, PA, 1987, p. 351.
8 L. Cassayre, P. Chamelot, L. Arurault and P. Taxil, *J. Appl. Electrochem*., 2005, **35**, 999.
9 O. A. Lorentsen, T. E. Jentoftsen, E. W. Dewing and J. Thonstad, *Metall. Mater. Trans. B*, 2007, **38**, 833.

Received: 5th June 2008; Com. 08/3151