Formation of metal fog during molten salt electrolysis observed in a see-through cell

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Visual observations of several molten salt electrolysis processes were made in a two-compartment, see-through quartz cell. The electrolyses of aluminium, magnesium, lead, zinc, sodium and potassium were studied. The colour of the melt in the anode compartment was pale yellow for fluoride–chloride melts and red for chloride melts, caused by the presence of dispersed anode gases during electrolysis. In the cathode compartment, streamers of metal fog were formed. The colours of the metal fog were purple for aluminium, grey for magnesium, lead and zinc, blue for sodium and green for potassium.

The metal fog tended to sink to the bottom of the cell, which indicated that it had a higher density than that of the melt. The metal fog also penetrated into the anode compartment, probable due to convection and diffusion in the melt. The most probable explanation of the nature of the metal fog is that it consisted of *dispersed* metal particles. This chemically unstable phase dissolved easily in the melt and was oxidized quickly by the anode gases.

1. Introduction

Most metals are somewhat soluble in their molten halide salts. This metal solubility is a decisive factor for the current efficiency and energy consumption obtainable in molten salt electrolysis processes. The range of metal solubilities in molten salts varies considerably, depending on the type of chemical reactions occurring between the metal and the molten salt. In most systems the nature of the dissolved metal is not very well known. However, it seems to be generally accepted that the metal–halide salt systems form true chemical solutions, although metal dispersions can be formed in several systems [1].

Visual observations have been highly informative in this respect, even though the previous observations were made by looking down into the melt. An important breakthrough came about 12 years ago when Haupin and McGrew [2] employed a see-through, bench-scale Hall–Héroult cell equipped with quartz walls to observe the dissolution of aluminium in cryolite melts. The present authors [3, 4] have recently reported similar studies in small, see-through Hall–Héroult cells.

The purpose of the present paper is to report the visual observations of several molten salt electrolysis processes in a see-through cell. In addition to aluminium electrolysis, the molten salt electrolyses of magnesium, lead, zinc, sodium and potassium were also studied. Observations concerning their anode and cathode reactions are described in detail.

2. Experimental details
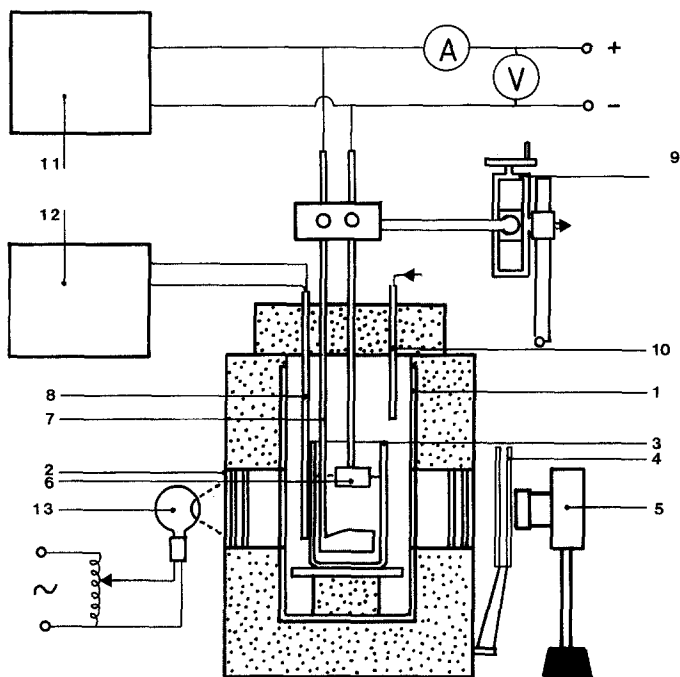
The experimental arrangement is shown in

Fig. 1. The experimental arrangement used in the electrolysis experiments with a see-through cell. 1, Heating element; 2, quartz window; 3, quartz crucible; 4, glass; 5, camera; 6, 7, electrodes made of high-purity graphite; 8, Pt/Pt 10% Rh thermocouple; 9, electrode elevating mechanism; 10, argon gas inlet; 11, x–y recorder for current and voltage measurements; 12, temperature controller; 13, tungsten lamp, with adjustable voltage from 0 to 30 V.

Fig. 1. The electrolysis cell was positioned inside the heating furnace, which was equipped with quartz windows for visual observation and photographing. Rear illumination was provided by a tungsten lamp. The electrolysis was performed in a quartz crucible of square shape, with dimensions $40 \times 40 \times 80$ mm and a wall thickness of 3 mm. A smaller, square-shaped quartz tube ($20 \times 20 \times 80$ mm) was positioned inside the crucible. Then a high-purity graphite rod of diameter 6 mm was inserted into the small quartz tube to serve as the cathode. The small quartz tube thus formed the cathode compartment of the electrolysis cell. A similar graphite rod of 6 mm diameter served as the anode and was inserted into the large crucible, but outside the cathode compartment. Thus, the rest of the quartz crucible formed the anode compartment. The two compartments were then connected at the bottom of the small quartz tube. This arrangement is illustrated in Fig. 2, which shows the electrolysis cell seen from above. The camera was placed in front of the cell, so that both electrodes could be photographed without overlapping.

During the experiments the electrolysis temperature was kept at 800 or 900° C, depending on the melting point of the salt mixtures. The temperature was measured by a Pt/Pt 10% Rh thermocouple and kept constant by a temperature controller. At these temperatures the service lives of the quartz tube and crucible were as long as 3–4 h in fluoride melts, without being heavily attacked. In chloride melts the service lives were considerably longer, and slight attacks were observed after 12–14 h. Moreover, as stated by Haupin and McGrew [2], the etching of the quartz which occurred did not affect the visibility into the cell. This apparently happened
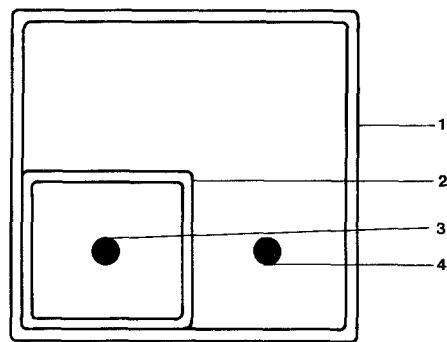

Fig. 2. Horizontal plane through the electrolysis cell (as seen from above). 1, Quartz crucible; 2, quartz tube; 3, carbon cathode; 4, carbon anode.
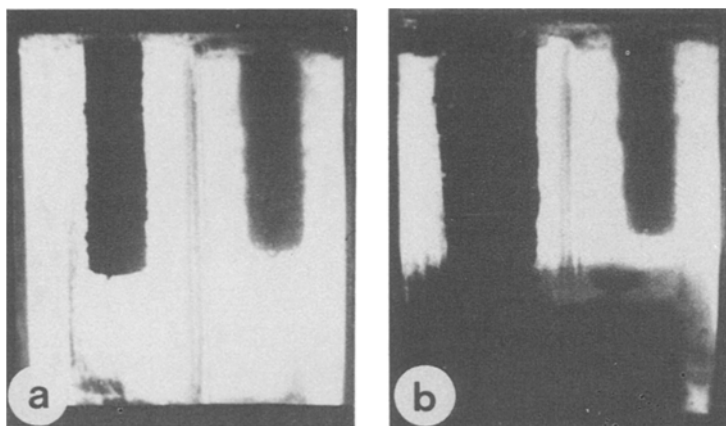
Fig. 3. Aluminium electrolysis in a two-compartment, see-through cell. Left, cathode; right, anode. (a) At the beginning of the electrolysis (4.0 A). (b) Metal fog has reached into the anode compartment. The upper surface of the metal fog was located about 5 mm below the bottom surface of the anode.

because the index of refraction of the quartz and the melt were similar.

The following metal–molten salt systems were studied:

(i) aluminium–cryolite + alumina + sodium chloride

(ii) magnesium–sodium chloride + potassium chloride + magnesium chloride

(iii) lead–sodium chloride + potassium chloride + lead chloride

(iv) zinc–sodium chloride + potassium chloride + zinc chloride

(v) sodium–sodium chloride

(vi) potassium–potassium chloride.

All these salts were chemically pure reagents and were dried at $400°$ C for 2 h before use. A stream of dry argon was passed into the cell to protect the molten salts from air oxidation. After the melting of the salt mixture both electrodes were immersed into the melt to a depth of about 30 mm.

In some experiments the location of the electrodes were purposely changed by inserting the anode in the quartz tube and the cathode in the quartz crucible. This was carried out in order to avoid the effect of overlapping of the colour in the molten salts in the quartz tube.

3. Results

3.1. *Aluminium electrolysis*

The main component of the molten salt mixture in these experiments was a sodium fluoride–aluminium fluoride melt with a cryolite ratio of 1.2, which corresponds to 37 wt% aluminium fluoride in excess of the cryolite composition. Furthermore, 5 wt% alumina and 10 wt% sodium chloride were added. This is a low-melting electrolyte which allowed the electrolysis to be carried out at $800°$ C. After melting, the electrolyte was white and transparent.

The electrolysis was started at the low current of 0.1 A, corresponding to a current density of only $0.018\,A\,cm^{-2}$. Small gas bubbles were formed at the anode and the melt in the vicinity of the anode immediately began to turn yellowish in colour. At this low current there were no streamers of metal fog evolved from the cathode. The situation is shown in Fig. 3a. The current was then increased gradually to 4.0 A. This gave a current density of $0.72\,A\,cm^{-2}$, which is typical for the values commonly used in large industrial cells. Many more small gas bubbles were formed at the anode, and the upper part of the anode compartment became yellowish in colour. At the same time, streamers of purple metal fog were liberated from the graphite cathode. These streamers apparently had a higher density than the melt, and they settled down at the bottom of the cathode compartment.

As electrolysis continued, the colour of the metal fog turned dense purple. Then parts of the metal fog escaped from the cathode compartment through fissures at the bottom of the quartz tube. The fog rose progressively in the anode compartment, but when the upper surface level of the metal fog was about 5 mm from the bottom surface of the anode it started to fluctuate vigorously, because the fog came in
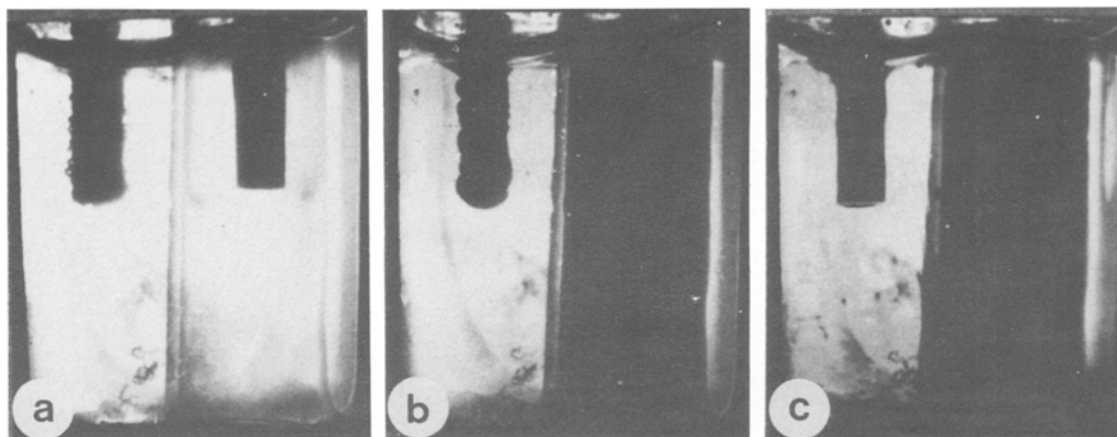
Fig. 4. Magnesium electrolysis in a two-compartment, see-through cell. Left, anode; right, cathode. (a) At the beginning of the electrolysis (1.0 A). (b) After 10 min of electrolysis at 2.0 A. (c) During an anode effect at 10 A and 50 V.

contact with the anode gas dispersed in the electrolyte. Then the colour of the melt between the carbon anode and the upper surface of the metal fog became white and transparent. This is shown in Fig. 3b.

After 30 min of electrolysis the upper surface of the metal fog still extended only about 5 mm below the bottom of the anode. Apparently, an equilibrium condition had been reached, in which the rate of metal fog entering the anode compartment was equal to the rate of its oxidation by the dispersed anode gases in the melt. To investigate this further, the anode was *raised* by 15 mm. The metal fog in the anode compartment also rose, but after 2 min it again appeared to reach an equilibrium condition at a distance of about 5 mm below the bottom surface of the anode. The anode was then *lowered* by 15 mm, and reached down into the metal fog. The purple metal fog rapidly reacted with the anode gases, and finally the melt below the anode became white and transparent over a downward distance of about 5 mm. A new equilibrium condition was established. From these observations it is clear that the oxidation of the metal fog by the dispersed anode gases occurred rapidly once the two reactants came in contact with each other.

Finally, some observations during the anode effect may be mentioned. When the voltage and current of the cell were increased further, an anode effect occurred at 50 V and 10 A (or 1.8 A cm^{-2}). Within 2 min the melt in the anode

compartment became white and transparent, and all the metal fog entering that area quickly reacted with the anode gases. During an anode effect the dominating anode gas is carbon monoxide [1], and this gas obviously oxidized the metal fog just as well as carbon dioxide had done during the normal electrolysis experiments.

3.2. *Magnesium electrolysis*

The melt composition used in the magnesium electrolysis experiments consisted of sodium chloride and potassium chloride in equimolar amounts, plus 5 wt % magnesium chloride. The temperature was kept at 800° C, and at the beginning of the electrolysis the melt was colourless and transparent.

The electrolysis was started at a current of 1.0 A, which corresponded to a current density of 0.18 A cm^{-2}. After about 3 min the electrolyte in the anode compartment began to turn yellow and tiny streamers of grey metal fog developed from the cathode (Fig. 4a). After 5 min of electrolysis the colour of the metal fog had turned black. It should be noted that the density of magnesium is lower than the melt, which is opposite to the situation in aluminium electrolysis. The current was then increased to 2.0 A (0.36 A cm^{-2}), and the electrolyte in the anode compartment became red. After about 10 min of electrolysis some metal fog escaped into the anode compartment, as shown in Fig. 4b. The
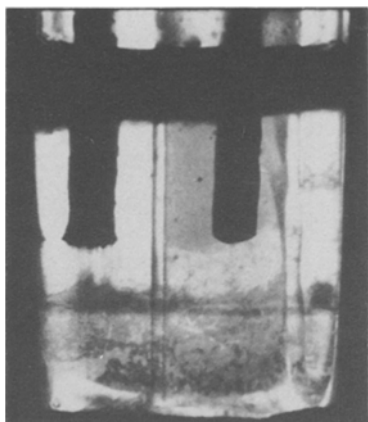
Fig. 5. Lead electrolysis in a two-compartment, see-through cell. Left, cathode; right, anode.

metal fog could be observed at the bottom of the anode compartment but it did not rise very high in the electrolyte. Obviously, it reacted easily with dispersed anode gas (chlorine) closer to the anode.

Also in this case an anode effect was initiated at 50 V and 10 A (Fig. 4c). The electrolyte in the anode compartment then became white and transparent again.

3.3. Lead electrolysis

The composition of the melt used in the lead electrolysis experiments was an equimolar mixture of sodium chloride and potassium chloride, containing 5 wt % lead chloride. The temperature was kept at 800° C, and the melt was colourless and transparent. Fig. 5 shows a photograph of the cell and the electrodes used.

Electrolysis was started at 3.0 A, which gave a current density of $0.54 \, A \, cm^{-2}$. The electrolyte in the anode compartment became red and a black metal fog appeared from the cathode. At first the metal fog floated in the upper part of the melt, but some small black particles sank to the bottom of the crucible. These particles were afterwards identified to be metallic lead by use of X-ray analysis. Later, the melt in the whole cathode compartment became opaque. Parts of the metal fog escaped into the anode compartment, where it quickly reacted with the anode gases dispersed in the red-coloured melt.

It was considered interesting to make a closer

comparison between the aluminium and the lead electrolyses. Thus, a lead electrolysis experiment was performed in a single quartz cell with no separation between anode and cathode, and with the electrodes positioned horizontally, as in experiments reported previously with aluminium [3, 4]. Electrolysis was then started at 4.0 A, or $0.72 \, A \, cm^{-2}$. First the colour of the melt close to the anode turned reddish and then the whole volume of the melt became red. Gas bubbles of chlorine evolved from the anode, while very little fog developed from the pool of molten lead, as with the aluminium electrolysis [4]. The main difference was the colour of the melt in the anode compartment, which was red in the lead electrolysis and yellowish in the aluminium electrolysis. This difference is probably caused by the presence of different types of anode gases in the melts. Furthermore, there seemed to be less fog evolved in the lead electrolysis experiments after the current was cut off. Fig. 6(a–d) shows a comparison of the lead and aluminium electrolysis observations.

Apparently, a passivation of the anode occurred during the lead electrolysis in the two-compartment cell. The current suddenly dropped to 0.5 A, while the cell voltage reached 10 to 15 V. At this time the voltage was increased to 50 V, and an anode effect occurred (at 10–15 A). Tiny gas bubbles were then injected from the anode into the melt and caused a violent stirring of the surface of the molten lead, which in turn lead to the formation of metal fog. This metal fog reacted quickly with the anode gases and the colour of the melt turned from red to white.

After the anode effect had been quenched and normal electrolysis resumed, the melt in the anode compartment became red again. At the same time the grey metal fog ceased to evolve from the cathode.

3.4. Zinc electrolysis

The melt composition used in the zinc electrolysis experiments was identical to that of the lead electrolysis, but contained 5 wt % zinc chloride instead of lead chloride. The temperature and the colour of the melt were the same as in the previous lead electrolysis experiments.

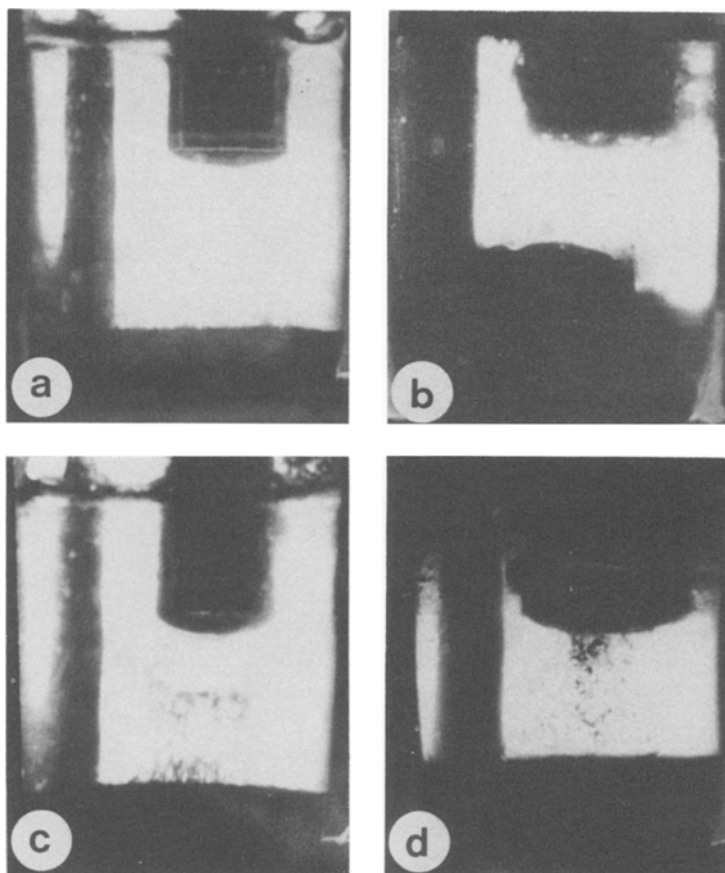At a current of 3.0 A the colour of the melt

Fig. 6. Comparison of lead electrolysis and aluminium electrolysis with horizontal electrodes. (a) Lead electrolysis at 4.0 A. (b) Aluminium electrolysis at 4.0 A. (c) Anode effect in lead electrolysis. (d) Anode effect in aluminium electrolysis.

turned red in the anode compartment. Some pale grey streamers of metal fog evolved from the molten zinc, but less than for the aluminium and magnesium electrolyses. Some particles of metallic zinc sank to the bottom of the crucible, as identified later by chemical analysis. Parts of the metal fog entered into the anode department. The surface of the melt in the cathode compartment was concave downwards and about 5 mm lower than in the anode compartment, where the surface was concave upwards. When the current was cut off, the heights of the surfaces became equal, and when electrolysis was resumed, the difference in surface levels reappeared again. The reason for this difference in melt level may simply be different wettabilities of the two electrodes by the molten salts. The zinc electrolysis cell is shown in Fig. 7.

Also for zinc electrolysis, a passivation of the anode appeared after 10–15 min of electrolysis.

The current dropped suddenly to 0.5 A and the cell voltage increased to 8–10 V. An anode effect occurred after the voltage was raised to 40–50 V, and the current then was 10–12 A.
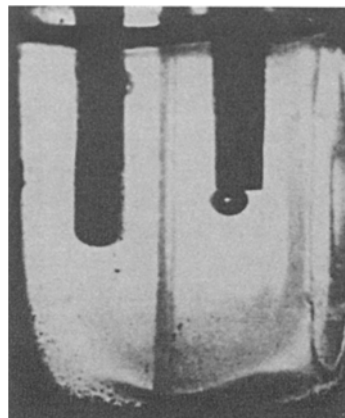

Fig. 7. Zinc electrolysis in a two-compartment, see-through cell. Left, cathode; right, anode.
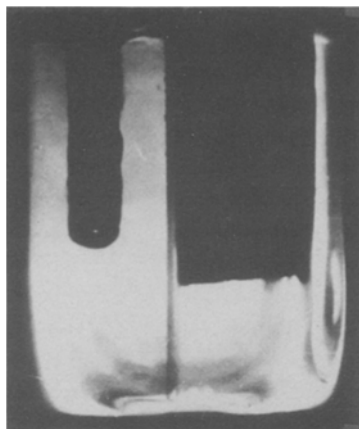
Fig. 8. Sodium electrolysis in a two-compartment, see-through cell. Left, anode; right, cathode.

3.5. *Sodium electrolysis*

The sodium electrolysis was performed in pure molten sodium chloride at 900° C. The molten electrolyte was white and transparent. Electrolysis was carried out at 3.0 A. In the anode compartment the colour of the melt then changed from white, via pale yellow and dense yellow, to red. Blue metal fog developed in the cathode compartment, which turned to dense blue and then black. Parts of the metal fog entered the anode compartment, as seen from Fig. 8.

The current was then interrupted for 5 min. The red fog in the anode compartment disappeared, while the metal fog in the cathode compartment disappeared only partly. This was
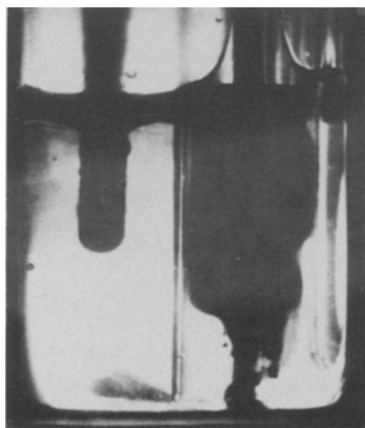

Fig. 9. Potassium electrolysis in a two-compartment, see-through cell. Left, anode; right, cathode.

caused by a chemical reaction occurring, and it may be inferred from this that the available amount of dispersed chlorine gas was considerably less than the amount of metal fog in the melt.

When the cell voltage was increased to 50 V, the current became very high (30 A). With this anode effect, long electric sparks passed through the quartz boundary between the two compartments and an explosion-like sound could be heard. After the experiment was finished it was found that the carbon cathode became swollen and was split due to penetration and intercalation of sodium.

3.6. *Potassium electrolysis*

The potassium electrolysis was carried out in pure molten potassium chloride at 900° C, which then was white and transparent. Electrolysis was performed at 0.5 A, or 0.09 A cm^{-2}. The melt in the anode compartment became red, while green metal fog appeared in the cathodic region (Fig. 9). After 10 min the melt in the whole cathode compartment became dark green and opaque. Parts of the metal fog then entered the anode compartment.

When the current was cut off, the colours of the melts in both compartments disappeared within 2 min. It was observed that the carbon cathode swelled, cracked and broke into small pieces, caused by intercalation of potassium into the carbon lattice.

4. Discussion

The observations of the colours of the melts in the anode and cathode compartments before and after the electrolysis experiments are summarized in Table 1. During electrolysis the following melt colours were observed.

(i) In the anode compartment the colour was pale yellow for the fluoride–chloride melt and red for the chloride melts.

(ii) In the cathode compartment the colours of the metal fog were purple for aluminium, grey for magnesium, lead and zinc, blue for sodium and green for potassium.

The colours of the molten salts in the anode compartment were probably due to the presence

Table 1. Colours of molten salts before and after electrolysis in a two-compartment, see-through cell

Metal	Molten salt composition[a]	Bath temperature (°C)	Colours		
			Before electrolysis — both compartments	After electrolysis	
				Anode compartment	Cathode compartment
Al	$NaF-AlF_3-Al_2O_3-NaCl$	800	White transparent	Pale yellow	Purple
Mg	$NaCl-KCl-MgCl_2$	800	White transparent	Red	Grey
Pb	$NaCl-KCl-PbCl_2$	800	White transparent	Red	Grey
Zn	$NaCl-KCl-ZnCl_2$	800	White transparent	Red	Grey
Na	NaCl	900	White transparent	Red	Blue
K	KCl	900	White transparent	Red	Green

[a] See text for exact melt compositions.

of the anode gases, as mentioned previously. Literature data [5] show that the solubility of chlorine in molten alkali chlorides is of the order of 10^{-6} to $10^{-7}\,mol\,cm^{-3}$. The solubility increases with increasing temperature and size of the alkali metal ion.

The colours of the melts in the cathode compartment were obviously caused by the presence of the metal fog. As seen from Table 1 the colours showed large variations, depending on the type of metal formed at the cathode.

What is then the *nature* of the metal fog? There seem to be two possibilities:

(i) metal fog may be *dispersed* metal in the process of being dissolved or oxidized in the melt;

(ii) metal fog may be dissolved monovalent or low-valent *ions*, which are chemically stable in the melt.

The colours observed seem to contradict the second explanation. Monovalent or low-valent ions certainly exist in these melts, but they would not in general be expected to have a typical colour which is different from the colour of the melt containing the more common ions. However, it has been suggested [2] that the colour of the fog may be due to 'solvated' electrons (F-centres), so the second explanation cannot be completely ruled out.

The possibility that the metal fog is dispersed metal in the melt, and that it is therefore not chemically stable in the melt, is more appealing. During the lead and zinc electrolyses some large particles settled at the bottom of the cell and these were identified later as metal particles. The

tendency for the metal fog to sink indicates that it has a density which is higher than the melt. The transport of the metal fog up into the melt in the anode compartment may be due to convection and diffusion. The rate with which the metal fogs were oxidized by the anode gases also points to the fog containing the metal in its reduced form, since these metals are easily oxidized in general.

Acknowledgements

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