

Electrorefining and Electrowinning of Gadolinium in a Molten Fluoride Electrolyte Purified by Pre-electrolysis

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Commercial gadolinium was electrorefined in an $\text{LiF}-\text{GdF}_3$ melt that had been pre-electrolyzed in an anodic graphite cell to remove dissolved oxide and hydroxide. When the metal was *electrorefined* with a stationary cathode, the impurities of oxygen, hydrogen and nitrogen were higher than when the cathode was gradually pulled out of the electrolyte. The effect is particularly pronounced for nitrogen.

The metal *electrowon* from a purified electrolyte contained about the same amount of oxygen and hydrogen impurities, but only about one tenth as much nitrogen as the electrorefined metal.

The purification with respect to oxygen, hydrogen and nitrogen was comparable or better than results obtained in an electrolyte where the constituents, LiF and GdF_3 , were ultrapure.

Previous work on electrowinning of gadolinium dendrites by direct electrolysis of gadolinium oxide dissolved in a molten $\text{LiF}-\text{GdF}_3$ electrolyte revealed that the oxygen contamination of the metal decreased with decreasing oxide concentration in the bath.¹ A minimum contamination of about 80 p.p.m.w. of oxygen was obtained when an oxide deficient melt was electrolyzed, although even this melt probably contained some oxide. Zwilling and Gschneidner,² using purified lithium fluoride, and gadolinium fluoride, containing less than 20 p.p.m.w. oxygen, and adding no oxide, found in their *electrorefined* gadolinium dendrites a minimum of 40 p.p.m.w. oxygen. Since the difference in contamination level was not larger, it was assumed

that a purer metal might be obtained by electrorefining in an electrolyte purified by pre-electrolysis.

EXPERIMENTAL

The apparatus was described previously.¹

The lithium fluoride was purchased from Fisher Scientific Co. (catalog No. L-124) and the gadolinium fluoride was prepared at Ames Laboratory-DOE by passing a mixture of anhydrous HF and 60% Ar over gadolinium oxide at 700 °C for 16 h.³ Neither fluoride was purified before mixing to make the 35 mol % gadolinium fluoride electrolyte. The gadolinium metal which was to be electrorefined was purchased from Research Chemicals. The nonmetallic impurity concentrations are given in Table 1. A graphite crucible, which was made from Union Carbide grade ECV, was machined to a 90 mm inside diameter and a 100 mm depth, and contained 1.6 kg of the electrolyte.

The fluoride mixture was purified by pre-electrolysis. Both in the pre-electrolysis and in the electrowinning experiments the graphite crucible was used as the anode, and a 6 mm diameter tantalum rod was the cathode. The electrorefining was done in the same crucible but a gadolinium rod served as the anode. The temperature was 900 ± 10 °C in all cases.

The electrorefined gadolinium was consolidated by arc-melting as in previous work.^{1,2}

RESULTS AND DISCUSSION

Pre-electrolysis. Before the pre-electrolysis, it was found that the anodic current density (acd) was a maximum (8 mA cm⁻²) at about 2.8 V, and thus the

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Table 1. Analysis of impure and electrorefined gadolinium metal, p.p.m.w.

Expt. No.	O	H	N	C	Remarks
1	50	50	140	n.d. ^a	Stationary cathode
2	34	21	43	253	Cathode gradually withdrawn
Impure anode	1100	88	400	209	

^a n.d.: Not determined.

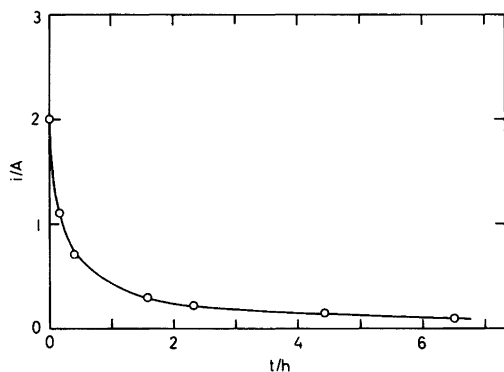


Fig. 1. Pre-electrolysis of a 35 mol.% GdF_3 -65 mol.% LiF electrolyte at a constant voltage of 2.7 V and a temperature of 900 °C. Anode area 260 cm^2 .

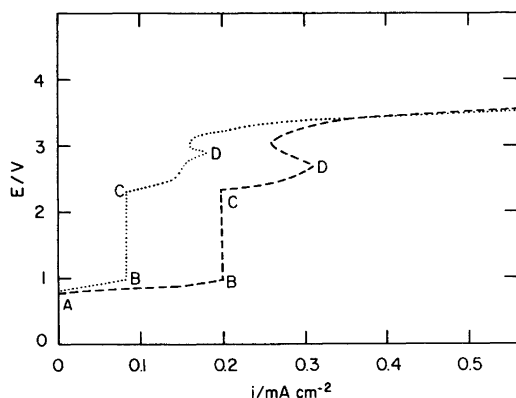


Fig. 2. Polarization curve at steady state in a 35 mol.% GdF_3 -65 mol.% LiF electrolyte. ----. After 8 h of pre-electrolysis at 2.7 V. After a total of 14 h of pre-electrolysis at 2.7 V. AB, probably discharge of OH^- ; CD, discharge of Gd_2O_3 (residual oxide in fluoride electrolyte).

pre-electrolysis was carried out at 2.7 V. After 8 h the acid had dropped to 0.4 mA cm^{-2} (see Fig. 1). A polarization curve, obtained by stepwise increasing voltage, showed that no appreciable current flowed at voltages below about 3.6 V (Fig. 2). From the curve it appears that an electrode reaction takes place at around 1.0 V (the wave AB). This is presumably discharge of hydroxyl ions. The reaction taking place at voltages above 2.0 V (wave CD) is certainly the decomposition of gadolinium oxide. The maximum acid is reduced to about 0.3 mA cm^{-2} , which is about 4% of the maximum acid before the electrolysis. This implies that somewhere near 96% of the original amount of oxide and hydroxide has been decomposed. From Fig. 1 it is seen that a 90% reduction of the oxide concentration was attained after 2 1/2 h. Continued electrolysis of the melt for 6 h reduced the terminal oxide concentration further (Fig. 1). A discussion of the current/voltage relationship in this melt will appear elsewhere.⁴

Electrorefining. At the stage of purification as described above, the electrolyte was considered ready for electrorefining of the gadolinium metal.

In the first experiment the cathode (tantalum rod) was inserted 6 mm into the electrolyte for the entire run. In the next experiment it barely touched the surface in the beginning of the experiment, and as metal formed on the cathode, it was gradually pulled upwards in increments of 5 mm for a total of 35 mm. This was an attempt to improve the salt drainage of the cathode deposit, which is a problem in all molten salt electrorefining where crystalline deposits are obtained.

The current was 4 A and the amount of current passed was 5 Ah in each case.

The current efficiency, based on the amount of metal recovered after arc-melting two times, was 69.2 and 84.0%, respectively. The difference is probably due to the fact that a larger amount of Ta cathode surface area was exposed to the bath in the

Table 2. Gadolinium metal electrowon from oxide-free electrolyte, p.p.m.w.

Expt. No.	Oxygen	Hydrogen	Nitrogen
1	55	49	5
2	55	31	6

former case. Removal of the gadolinium deposit was more efficient in the second experiment, where only the tip of the cathode (or metal) was exposed to the bath. Another reason may be that in the latter experiment the metal was exposed to the bath for a shorter time, thus minimizing any redissolution of the metal.

The salt to metal ratio in the deposit was in each case 2.3, which indicates that the salt drainage was not improved by pulling the cathode gradually out of the bath.

The oxygen, hydrogen, nitrogen and carbon contents in the electrorefined gadolinium are given in Table 1.

The contamination is significantly lower in the second experiment, where the metal is gradually withdrawn from the bath. This indicates that the contaminations originate from the bath and/or the anode metal and not from the furnace atmosphere.

The nitrogen contamination of the presently electrorefined gadolinium was much higher than that of metal electrowon in a similar graphite cell (9 ± 5 p.p.m.w.)¹ (also see Table 2). There are no data available on the mechanism of the nitrogen transport in these melts, but obviously nitrogen is very effectively transferred through the electrolyte from the anode to the cathode. Although hydrogen and oxygen also are transferred to the electrolyte by anodic dissolution, apparently the *a priori* concentration of these elements, as oxide and hydroxide impurities in the electrolyte, are determining factors for their contamination of the electrorefined metal.

The carbon contamination is higher than in the impure gadolinium (Table 1), but not much higher than in metal electrowon in a tantalum crucible with platinum anode (177 p.p.m.w.). (This work was reported elsewhere,¹ but the carbon analysis was not given.) This is surprising considering that the electrorefining took place in a graphite cell that had been used as anode in the pre-electrolysis of the electrolyte. Zwilling and Gschneidner found a lower contamination (60–100 p.p.m.w. C) when the

electrorefining was carried out in a tantalum crucible.² Their results may actually be interpreted as indicating that the lithium fluoride is the source of carbon contamination, but more work is clearly warranted to verify this. At any rate it is doubtful that the gadolinium anode is the principal source of carbon contamination.

The oxygen content of the metal electrorefined in the second experiment is lower than any previously electrorefined or electrowon gadolinium metal.^{1,2} This implies that pre-electrolysis of the electrolyte is at least as efficient as other methods of purification, including the treatment of the molten gadolinium fluoride under a dynamic HF:60% Ar atmosphere.³ Since it is performed *in situ*, pre-electrolysis is also a more convenient method.

However, the carbon contamination from the graphite cell is probably intolerable. A small, immersed graphite anode may reduce the contamination and eliminate the need for a graphite cell. This highly purified GdF₃ was used by Zwilling and Gschneidner in their work.² They also used commercial ultrapure LiF.

Polarization curves obtained after the electrorefining experiments indicated an increased concentration of both oxide ions and the supposed hydroxide ions, and also possibly the presence of other species introduced from the dissolved anode material.

The electrolyte was purified again by electrolyzing for 5 1/2 h during which time the acid dropped from 0.6 to 0.2 mA cm⁻² (see Fig. 2).

Polarization curves obtained with two different electrodes showed that the oxide concentration was significantly reduced, whereas the other major contaminant (probably hydroxide ions) still persisted.

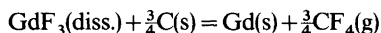
Electrowinning. During the determination of the last two polarization curves sufficient metal was electrowon to be consolidated by arc-melting. The samples were analyzed for gaseous impurities only (see Table 2).

The oxygen contamination is somewhat higher than in the electrorefined metal (Table 1), but lower than in the electrowon metal reported previously.¹

The hydrogen contamination is about the same, whereas the nitrogen content is significantly lower in the electrowon metal, and is in agreement with our previous findings for electrowon gadolinium.¹

As the polarization curves referred to were obtained over a large voltage range, (0–5 V) in a melt containing only a trace of oxide, these metal

samples clearly were electrowon by direct electrolysis of gadolinium fluoride dissolved in molten lithium fluoride. No attempt was made to identify the anode product, but the most likely cell reaction would be



CONCLUSION

A purified LiF–GdF₃ molten electrolyte has been found to be effective for electrorefining and for electrowinning of gadolinium. Pre-electrolysis is at least comparable to any other known purification method. But the last traces of hydroxide and oxide are virtually impossible to remove, as judged from polarization curves. The LiF–GdF₃ electrolyte apparently contains no nitride or nitrogen, since electrowon gadolinium is extremely low in this element, but carbon remains a problem.

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