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On the Electrodeposition of Coherent Gadolinium Dendrites from Molten Fluoride Electrolytes

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The morphology of gadolinium dendrites deposited in molten fluorides may be linked with the stability of electroactive associates.

Quantum chemical calculations of moieties, based on the solid state structure of GdF_3, reveal an increased overall stabilizing attraction in the following order:

$$Gd_{1-x}Ba_xF_{3-x} < GdF_3 < Gd_{1-x}F_{3-2x}O_x < Gd_{1-x}Ca_xF_{3-x}$$

The stabilization of the 75 LiF-25 mol% GdF_3 electrolyte by oxyfluorocomplexes led to the deposition of essentially pure gadolinium dendrites. The fluorine contamination caused by salt inclusions was consequently reduced from the 1,500-2,000 ppm, as obtained in the pure LiF—GdF_3 electrolyte, to less than 3 ppm.

(Keywords: CNDO-Method; Electrode kinetics; Morphology of electrodeposits)

Zur elektrochemischen Abscheidung kohärenter Gadoliniumdendriten aus geschmolzenen Fluoridelektrolyten

Die Morphologie aus Fluoridschmelzen abgeschiedener Gadoliniumdendriten läßt sich mit der Stabilität elektroaktiver Assoziate korrelieren.

Quantenchemische Berechnungen von Assoziaten, deren Struktur auf jener des kristallisierten GdF_3 aufbauen, ergeben eine zunehmende Stabilisierung in der Folge

$$Gd_{1-x}Ba_xF_{3-x} < GdF_3 < GdF_{3-2x}O_x < Gd_{1-x}Ca_xF_{3-x}$$

Durch die Stabilisierung des 75 LiF—25 mol% GdF_3-Elektrolyten mittels Oxyfluorokomplexen konnte eine nahezu vollständige Kohärenz der abgeschiedenen Gadoliniumdendriten erreicht werden. Die durch Salzeinschlüsse bedingte Fluorkonzentration im gewonnenen Gadoliniummetall nahm dementsprechend von 1 500—2 000 ppm (LiF—GdF_3-Elektrolyt ohne Zusätze) auf < 3 ppm ab.

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Introduction

The electrodeposition of actinides in molten salts presents a challenge to electrochemists, because the method has a high potential for the reprocessing of nuclear fuel. In particular, high purity gadolinium has turned out to be an advantageous alloying agent for thermoelectric devices and these will likely replace the currently used solar cells in space vehicles.

The electrodeposition of low melting rare earths, e.g. cerium, is already commercially viable, but attempts to obtain the high-melting rare earths, e.g. yttrium, have been less successful, since the cathode product of these metals consists mainly of an impure mixture of salt and metal powder. Recent investigations[1, 2] have shown that gadolinium (mp. 1,312 °C) can be deposited in the form of well-developed dendrites, which can be further processed to yield essentially pure metal.

The small cathodic polarization of the electrodeposition process in the used molten salts leads to high values of the energy efficiency, but also to dendritic deposits which occlude solidified fluoride electrolyte (Fig. 1). Correspondingly, fluorine contamination of the gadolinium metal (1,500-2,000 ppm) was reduced to less than 10 ppm by an additional electron-beam melting step[2]. It is thus of interest to investigate electrolyte characteristics which lead to the elimination of these salt inclusions by the coherent growth of the dendrites (Fig. 2).

Cathode Process

The difference in the deposition morphology obtained by the experiments with $LiF—GdF_3$[1] and $BaF_2—LiF—GdF_3$ electrolytes[3] may be explained by the assumption that the deposition process is controlled by a rearrangement of ion complexes. This appears similar to a chemical reaction analogous to the reduction of a complexed high-oxidation-state metal ion which involves a shedding of the anionic constituents during the passage to the growing metal lattice. Furthermore this assumption of intermediates is supported by the reduction of tantalum and niobium fluorides; these are reported to have produced species which were reduced subsequently in a rate-controlling step[4]. Indirect evidence is adduced in that reduction of zirconium was only possible in baths containing K^+ ions. It is known that ZrF_6^{2-} exists in a polymeric eight-coordinated state in K_2ZrF_6[5]. In this context it may be mentioned that ion association can cause a coupling of different species at the phase boundaries. Corresponding coupled adsorption reactions have frequently been investigated[6–8].

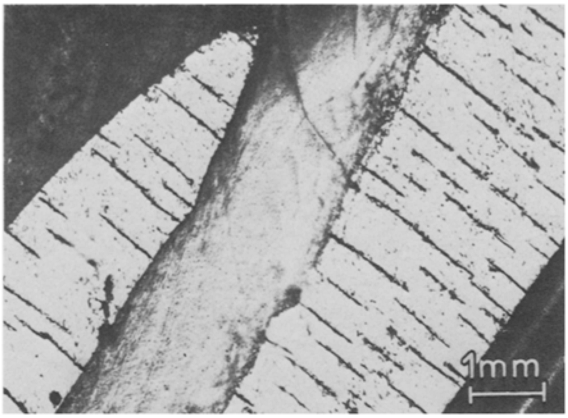

Fig. 1. Salt inclusions of gadolinium dendrites deposited in the 75 LiF-25 mol% GdF_3 electrolyte at 870 °C

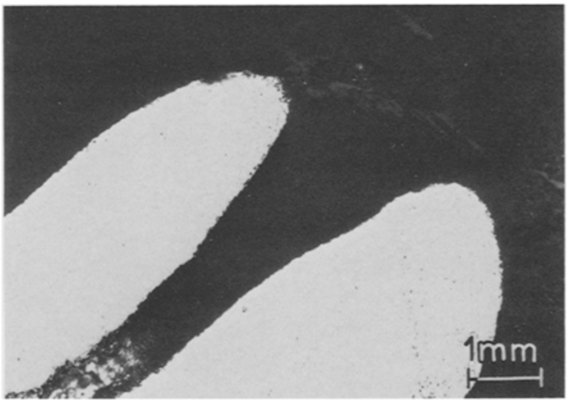

Fig. 2. Coherent gadolinium dendrites deposited at 870 °C after stabilization of the 75 LiF-25 mol% GdF_3 electrolyte by oxyfluorocomplexes

Now, the addition of BaF_2 to the LiF—GdF_3 electrolyte is supposed to exert a destabilization effect because of the relative size of the barium ion. Thus, due to the changed shape of the gadolinium crystals by additives, it may be expected that the stability of electroactive complexes in the electrolyte influences significantly the deposition morphology of the dendrites. In order to prove the effect of various additives experiments are carried out on the basis of quantum chemical calculations of model-complexes.

Quantum Chemical Aspects

In molten salts, solute and solvent share the same nature and all ions react qualitatively in the same way towards internal and external electric fields. Therefore, the rearrangement properties of fluoride intermediates are characterized to a high degree by the structure, and hence, the transport properties of the electrolyte. Although the history of such measurements dates back to conductivity measurements in 1809[9], the present knowledge with respect to the fluorides is very sparse. The collected data on diffusion coefficients and mobilities of ions can not be explained by a single model. The proposed theories seem to be too limited for quantitative correlations[10]. Nevertheless, an approximation of the molten salt structure may be reasonably assumed by the analogy with the corresponding solid-state structures. The basis of this conclusion is provided by the fact that the heat of fusion, which is necessary for the change from the solid to the liquid state, amounts only to 3-5% of the lattice energy. Since the entropy of fusion is also low the melts contain units of which the geometrical structure must be somewhat similar to that of the crystallized electrolyte. Thus the characteristics of molten gadolinium fluoride and its "complexes" may be elicited through the medium of quantum chemical calculations.

As quantum chemical method a modified CNDO approach is chosen[11]. This approach is based on the work of *Pople*, *Santry*, and *Segal*[12] in which one sets up a *Fock* matrix and performs the calculation iteratively to self-consistency. The density matrix is used to allow redefinition of the new *Fock* elements.

The diagonal elements of the *Fock* matrix are,

$$F_{\mu\mu} = H_{\mu\mu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[\langle \mu\mu | \lambda\sigma \rangle - \frac{1}{2} \langle \mu\lambda | \mu\sigma \rangle \right]$$

where $H_{\mu\mu}$ represents the energy of an electron in the atomic orbital μ and $P_{\lambda\sigma}$ is a density matrix element. The remaining quantities are exchange and *Coulomb* repulsion integrals.

Under zero differential overlap $F_{\mu\mu}$ becomes,

$$F_{\mu\mu} = H_{\mu\mu} + \sum_{\lambda} P_{\lambda\lambda} \langle \mu\mu | \lambda\lambda \rangle - \frac{1}{2} \mathrm{P}_{\mu\mu} \langle \mu\mu | \mu\mu \rangle$$

When the atoms are completely separated,

$$P_{\lambda\sigma} = 0, \; P_{\lambda\lambda} = P^{g}_{\lambda\lambda}$$

i.e. the occupancy of the orbital λ in the isolated atom; $F_{\mu\mu}$ is then the self-consistent energy of an electron in the orbital μ. Now for an atom of the configuration $n\mathrm{s}^{p}\, n\mathrm{p}^{q}\, n\mathrm{d}^{r}$, the following expression for the energy of an electron in any orbital λ holds,

$$E_\lambda = \frac{1}{2} P^g_{\lambda\lambda} (U^0_{\lambda\lambda}) + \left(1 - \frac{1}{2} P^g_{\lambda\lambda}\right) U^{-1}_{\lambda\lambda}$$

where $U^0_{\lambda\lambda}$ and $U^{-1}_{\lambda\lambda}$ are the valence-state ionisation potentials of the same orbital in the neutral atom and negative ion respectively. If one writes,

$$\gamma_{\lambda\lambda} = U^{-1}_{\lambda\lambda} - U^0_{\lambda\lambda}$$

where γ is a one-centre electron repulsion integral then,

$$E_\lambda = \frac{1}{2} P^g_{\lambda\lambda} U^0_{\lambda\lambda} + \left(1 - \frac{1}{2} P^g_{\lambda\lambda}\right) (U^0_{\lambda\lambda} + \gamma_{\lambda\lambda})$$

Thus,

$$\begin{aligned} F_{\mu\mu} &= U^0_{\mu\mu} + \gamma_{\mu\mu}\left(1 - \frac{1}{2} P^g_{\mu\mu}\right) \\ &= \mathbf{H}_{\mu\mu} + \sum_\lambda P^g_{\lambda\lambda} \gamma_{\lambda\mu} - \frac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} \end{aligned}$$

If the atoms are now considered to be at positions where there is significant interaction, then the orbital occupancy $P^g_{\lambda\lambda}$ will deviate from that of the free atom (i.e. an integral number). Thus we find,

$$F_{\mu\mu} = U^0_{\mu\mu} - \sum_\lambda P^g_{\mu\mu} \gamma_{\lambda\mu} + \gamma_{\mu\mu} + \sum_\lambda P_{\lambda\lambda} \gamma_{\lambda\mu} - \frac{1}{2} P_{\mu\mu} \gamma_{\mu\mu}$$

i.e.

$$F_{\mu\mu} = U^0_{\mu\mu} + \sum_\lambda (P_{\lambda\lambda} - P^g_{\lambda\lambda}) \gamma_{\lambda\mu} + \left(1 - \frac{1}{2} P_{\mu\mu}\right) \gamma_{\mu\mu}$$

This is the form of diagonal element employed in the present calculation. It reduces to the *Pople* et al. element when atomic repulsion rather than orbital repulsion integrals are employed.

Calculations

For calculational purposes a basic model, in which the Gd-atom occupies the centre of a regular octahedron, was first assumed. The Gd—F bond length was 2.42 Å as in LaF_3[13]. This unit was then modified to represent other structural units in the "mixed complexes" (Fig. 3). The position of oxygen in the model was chosen by a structural analogy, since it is not possible to quench $GdF_{3-2x}O_x$ phases and to determine the mechanism of the heterovalent substitution of fluorine by oxygen through density measurements[14]. The corresponding measurements on the density of $BiF_{3-2x}O_x$ phases (with the tysonite structure of $GdF_{3-2x}O_x$) formed during the pyrohydrolysis of BiF_3 elicit indirect evidence for a vacancy mechanism[15]. This is further confirmed by the low energy of activation of the vacancies in LaF_3 at high temperatures, since near the melting point GdF_3 may be characterized as a high temperature modification of LaF_3[16]. Thus to characterize $GdF_{3-2x}O_x$ solutions two fluorine atoms were replaced in the model by oxygen, whilst for solutions of the type $Gd_{1-x}Ba_xF_{3-x}$ and $Gd_{1-x}Ca_xF_{3-x}$ the alkaline earth metals were positioned in the centre of one trigonal face of the GdF_6 octahedron. The M—F distances were assumed to be as those in the known binary calcium and barium difluorides. The electronic structure and charge distribution in these basically octahedral structures was calculated by means of a variant of the CNDO method[11]. The input data for fluorine, oxygen, barium and calcium with respect to the electronic configurations were abstracted from the literature. The f-electrons of gadolinium were treated as d-electrons for calculational purposes and the valence-state ionisation potentials were Gd 6s, Gd 4f, 6.2 eV and 12.0 eV respectively. The repulsion integral for gadolinium was 5.0 eV. The whole calculation was finally cycled to self consistency in each case.

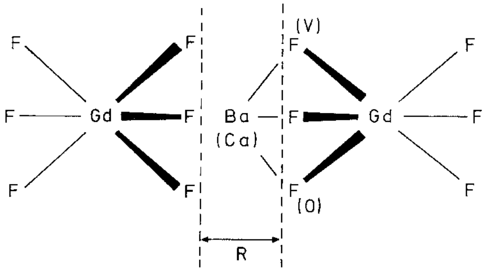

Fig. 3. Geometries of interacting moieties in the electrolyte, V vacancy, O oxygen, $R = 2.72$ Å when no Ba or Ca are present, $R = 2.35$ Å for the Ca derivative, $R = 4.08$ Å for the Ba derivative

From the calculated electronic charge distribution, Table 1, a *Coulombic* interaction energy between the unit under examination and a second GdF_3 moiety was computed by pairwise summation. Both attractive and repulsive interactions are found. From this exercise resulted an increasing stabilizing effect between the two units in the following order

$$GdF_6Ba < GdF_6 < GdF_4O < GdF_6Ca$$

i.e. in mixed structures which contain barium ions the attraction between the melt units is expected to be less than that of the pure fluoride, while the addition of calcium-ions leads to an increasing stability of the melt.

Table 1 a. *Relative atomic charge distributions computed by the CNDO-method for the models of interacting gadolinium moieties (Fig. 3)*

Moiety	Relative Atomic Charge Distribution					
	Gd	F		O	Ca	Ba
GdF_6	+ 3.55	—0.59		—	—	—
GdF_4O	+ 3.07	—0.29		—1.89	—	—
GdF_6Ca	+ 2.90	—0.49,	—0.51	—	+ 0.10	—
GdF_6Ba	+ 2.78	—0.38,	—0.56	—	—	+ 0.05

Table 1 b. *Relative interaction energies referred to* GdF_6 *in arbitrary units (only the ordering of the quantities is significant, not the absolute values)*

GdF_6Ba	GdF_6	GdF_4O	GdF_6Ca
—0.3	0.0	+ 0.4	+ 2.0

Experimental

An inert atmosphere was maintained within the electrochemical cell by helium gas[1]. The operating temperature of 870 °C was brought about by an external resistance furnace and controlled by a chromel-alumel thermocouple. The composition of the solvent may be varied widely without any impact on the salt inclusions in the matrix of the grown crystals. The eutectic composition (75 LiF-25 mol% GdF_3) was chosen for the experiments involving reduction of the melting point of the electrolyte. Lower concentrations of GdF_3 decreased the limiting current, whilst higher concentrations would have raised considerably the operating temperature. Fig. 1 shows the salt inclusions in the matrix of a gadolinium dendrite (1,500-2,000 ppm F) deposited in the 75 LiF-25 mol% GdF_3 electrolyte. Fig. 2 illustrates the micrograph of a dendrite grown after the increase of the rearrangement potential of the electroactive associates through oxyfluorocomplexes. The salt inclusions are seen to have disappeared and this corresponds to less than 3 ppm fluorine contamination of the gadolinium metal.

Discussion

In aqueous solutions the dipoles of neutral water molecules interact with the potential gradients surrounding dissolved ions. Thus the dissolved ions can respond to extremely weak electric fields. This allows the distinction between solute and solvent to be drawn; this is very important when the mobility of ions has to be defined. In molten salts these two entities possess the same nature and properties. The ions differ only in size, polarizibility, and their electric charge, but they react qualitatively in the same way towards electric fields and form associates. Characteristics, of the melt, are determined by the structure of these complex ions. The melts contain units of which the geometrical structure must be somewhat similar to that of the corresponding crystals, since the heat of fusion and entropy are low. Thus, although the detailed nature of the complex ions in the molten electrolyte is not known *a priori*, nevertheless plausible models can be constructed. They are used as qualitative approach to describe changes of the interaction between Gd-containing species in GdF_3 solutions. Therewith the relative stabilizing effect calculated by the models is associated with a stabilization of the solutions in the following order,

$$Gd_{1-x}Ba_xF_{3-x} < GdF_3 < Gd_{1-x}F_{3-2x}O_x < Gd_{1-x}Ca_xF_{3-x}$$

It indicates that in salts which contain barium ions the overall attraction between the melt units is less than in that with unchanged gadolinium trifluoride, while the stabilizing effect of oxygen might be replaced by calcium. Accordingly the melting point of mixtures containing oxygen or calcium should increase, which is in qualitative agreement with the experimental literature[17].

The approach does not include surface properties like the attachment of inhibitors and their potential dependence on metal surfaces. It outlines—corresponding to solution catalysis in the chemical sense of the term—an interaction of ions in the molten salt. In this context it is interesting to note that the stabilization of the electroactive gadolinium species through oxyfluoro-complexes goes along with a reduction of the fluorine contamination in the deposited gadolinium metal from 1,500–2,000 ppm (Fig. 1) to 3 ppm (Fig. 2). A further investigation of surface tension phenomena and the kinetics of adsorption processes during the deposition is considered to be a necessary supplement for the description of a detailed electrogrowth mechanism. One could investigate how far the implied increase of the surface tension of the electrolyte or the change in the kinetic of the electrocrystallization mechanisms itself contributes to the observed change in the deposition morphology. It should be pointed out that the change from the gadolinium crystallization with salt inclusions in the LiF—GdF_3 electrolyte to a cathode process which favors a theoretical bulk growth density is also linked with specific structural features. Solid solutions of $GdF_{3-2x}O_x$ are formed on the basis of a high temperature modification of the LaF_3 structure and a universal effect of oxygen, in raising the fusion temperature may be expected. The interaction of oxygen with the trifluorides of Tb and Ho, for example, leads also to solid solutions of $Ln\,F_{3-2x}O_x$. In the latter systems, however, the presence of small proportions of oxygen makes virtually no difference to the fusion temperature, since these materials are topologically different from the $GdF_{3-2x}O_x$ structure. They are separated by two-phase areas from the pure trifluorides and form eutecties with nearly unchanged melting temperatures.

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