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High Purity Gadolinium by the Electrolysis of GdF_3

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The anodic overvoltage on carbon and platinum electrodes in the electrochemical production of high purity gadolinium from molten 75 LiF-25 mol% GdF_3 solutions is discussed. At the cell temperature of 840 °C calciumimpregnated anodes led to the reduction of inert electrode films and to a current yield of nearly 100%.

The deposited gadolinium contained 75, 22, 54 and less than 100 ppm of the interstitial elements H, N, O and C respectively; the concentrations of the highest other analysed impurities were: Si (89), Fe (15), Y (5), Zr (3), Nd (3), Tb (71), Ta (49), W (23) and Re (< 3 ppm).

(Keywords: Electrolysis of gadolinium fluoride; Fluorine overpotentials; Gadolinium, high purity)

Hochreines Gadolinium durch die Elektrolyse von GdF_3

Es werden die anodische Überspannung an Graphit- und Platinelektroden bei der Herstellung von hochreinem Gadolinium durch die Elektrolyse von 75 LiF—25 mol% GdF_3 Schmelzen diskutiert. Bei der Zelltemperatur von 840 °C führten Calcium-imprägnierte Anoden zum Abbau polarisierender Elektrodenfilme und zu einer Stromausbeute von nahezu 100%.

Das abgeschiedene Gadolinium enthielt 75, 22, 54 und weniger als 100 ppm von den interstitiellen Elementen H, N, O und C; die Konzentrationen der höchsten anderen analysierten Verunreinigungen waren: Si (89), Fe (15), Y (5), Zr (3), Nd (3), Tb (71), Ta (49), W (23) und Re (< 3 ppm).

Introduction

High purity gadolinium (99.95%) is used for thermoelectric devices (prepared at the Ames Laboratory by metallothermic reduction[1]). The method involves a series of production steps which cause serious container problems, since gadolinium reacts with or dissolves most materials. Tungsten proved to be the best crucible material as far as

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* Partly performed at the Ames Laboratory—U.S. Department of Energy.

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metallic impurities are concerned (0.003% W in the final Gd). Unfortunately it suffers from the disadvantage, that the material is expensive, hard to fabricate and the crucible can frequently be used just once, since tungsten tends to crack when gadolinium solidifies. If tantalum is employed, vacuum melting at 1,800 °C, which is necessary to perform in any case, requires a subsequent distillation to reduce the tantalum concentration in gadolinium to less than 10 ppm. The distillation runs at a rate of 1 g/h in a vacuum of 10^{-9} Torr to protect the metal from impurities. However, it is not possible to reduce the oxygen contamination, since the vapor pressure of gadolinium oxides is high enough to distill along with the metal. The gaseous impurities (H, N, O), once present in any form in the reacting system, end up almost invariably in the gadolinium metal. This means that the process has to be started with extremely pure raw materials and all operations have to be carried out in a highly purified, inert atmosphere.

Recently, electrorefining methods proved to solve this expensive, time-consuming container and handling problem for the preparation of high purity gadolinium[2]. The employed molten fluoride electrolytes revealed a particular purification effect with respect to oxygen and tantalum. It is the objective of the present study to investigate the purity of electrocrystallized gadolinium using GdF_3 as the starting material.

Experimental

The electrolysis of gadolinium fluoride was started with a 75 LiF-25 mol% GdF_3 solution analogous to the liberation of alkali metal and halogen from the fused alkali halide. Fluorine atoms, liberated by the electrolysis, are capable of entering between the layers of the carbon anode. A pseudo polymer of carbon-fluoride is supposed to be formed, which will decompose into fluorcarbons of low molecular weight. One might expect that these fluoro-carbons would evolve from the anode and generate a renewed surface in contact with the melt[3]. However, the electrolysis could not be performed, since the graphite anode showed inert character (Fig. 1). Thus a cell current of 0.5 A was maintained at the cell voltage of 8 V; a value much higher than the theoretical decomposition voltage of pure GdF_3 (4.8 V).

Each of the graphite, platinum and calcium-impregnated anodes was designed with a geometrical surface area of 10 cm^2. The corresponding current-voltage relations are given in Fig. 1. It is noted that the deposition of gadolinium does not cause a significant cathodic overvoltage[4]. Fig. 2 shows the shape of the grown [001] crystals using a calcium-impregnated anode. The cell voltage in the electrolyte was equal to 0.7 V. The chemical analysis of the deposited gadolinium is presented in Table 1, the deposition rate and current efficiency in Fig. 3.

Since commercially distilled calcium is likely to contain considerable quantities of hydrogen, carbon, oxygen and nitrogen, calcium was distilled at 825 °C under a helium pressure of about 6 Torr[5]. It was not necessary to purify the helium, because gaseous impurities react with hot calcium and remain at

Table 1. *Analysis of the electrolyte solution and electrolytically produced gadolinium (ppm)*

	LiF—GdF$_3$ solution	Gadolinium metal		LiF—GdF$_3$ solution	Gadolinium metal
a) Vacuum fusion					
H		75			
N		22			
O		54			
b) Wet chemistry					
C		< 100			
c) Standarized spark scourse mass spectrometric analysis					
Li		< 0.04	Ru	< 0.2	< 0.1
B		0.02	Rh	< 0.05	< 0.04
Na	< 0.06	0.4	Pd	< 0.1	< 0.7
Mg		0.15	Ag	< 0.3	< 0.04
Al	< 0.07	0.7	Cd	< 0.04	< 0.03
Si	< 0.4	89	In	< 0.02	< 0.02
P		0.08	Sn	< 0.09	< 0.05
S	< 0.04	< 0.2	Sb	< 0.04	< 0.02
K	0.2	< 0.25	Te	< 0.05	< 0.03
Ca		< 0.7	Cs	< 0.003	< 0.003
Ti	< 0.3	0.4	Ba	< 0.07	< 0.07
V	< 0.1	0.03	Hf	< 0.1	< 0.9
Cr	< 0.3	0.7 (700*)	Ta	< 0.3	49
Mn	< 0.03	0.07 (30*)	W	< 1	23
Fe	3	15 (10,300*)	Re	< 0.5	< 3
Co	< 0.2	< 0.01 (35*)	Os	< 0.8	< 2
Ni	0.6	0.07 (3,100*)	Ir	< 0.4	< 0.2
Zn	< 0.002	0.1	Pt	< 0.6	< 0.4
Ga	< 0.04	0.02	Au	< 0.09	< 0.08
Ge	< 0.2	< 0.1	Hg	< 0.09	< 0.06
As	< 0.03	0.02	Tl	< 0.06	< 0.04
Se	< 0.1	0.35	Pb	< 0.03	< 0.1
Rb	< 0.1	0.01	Bi	< 0.05	< 0.4
Sr	< 0.6	0.06	Ra	< 0.3	< 0.3
Zr	< 0.1	3	Th	< 0.6	0.7
Nb	< 0.5	0.2	U	< 0.3	0.3
Mo	< 0.4	1			
Rare earth impurities					
Sc	< 0.06	< 0.6	Tb	1	71
Y	1	5	Dy	0.6	2
La	2	2	Ho	0.3	0.7
Ce	5	5	Er	< 1	< 0.6
Pr	2	2	Tm	< 0.4	< 0.2
Nd	2	3	Yb	< 2	< 2
Sm	4	0.7	Lu	< 2	< 0.9
Eu	48	< 1			

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* Contamination obtained in stainless steel cells.

the bottom of the still. The obtained calcium showed almost no contamination from the stainless steel condensor; less than 1 ppm Fe, Co, Ni and Ti. The oxygen analysis averaged at about 30 ppm, nitrogen below 10 ppm, but hydrogen varied between 50-200 ppm.

The individual rare earths are separated from gadolinium by getting the Gd_2O_3 necessary for the preparation of GdF_3 free from the contamination of the other rare earths. This was indicated, because the individual standard electrode potentials of the rare earths differ not substantially. The total contamination of the used Gd_2O_3 by the other rare earths was less than 25 ppm. It was prepared at the Ames Laboratory US-DOE by the ion exchange method[5].

The pure Gd_2O_3 was then converted to anhydrous fluoride in a platinum lined inconel furnace. A gas stream of 60% argon and 40% HF was turned on and the temperature slowly, over a period of hours, increased to 850 °C. Thus a low water vapor concentration was maintained in the furnace. Otherwise considerable amounts of oxyfluorides were formed, which can not be reconverted. The resultant GdF_3 sponge contained about 100 ppm oxygen. Additional melting of the sponge in a stream of argon and HF completed the conversion and solid GdF_3 with about 20 ppm oxygen was obtained[5]. A similar process was applied for the fluorination of LiF. The chemical analysis of the electrolyte is given in Table 1.

Electrodics

Besides the many difficulties inherent in the preparation of fluorine electrodes and reference electrodes, the reason for the paucity of reports on electrode kinetics of fluorine evolution stems from problems with the container durability and the purity of the electric bath. A review of papers on chlorine overpotentials[6], on the resistance overpotential by discharge of the chloride ion[7], on the hydrogen overpotential in fused $KHSO_4$[8] and a study on the mechanism of the anodic discharge in cryolite-alumina[9], has led to the assumption that the cell current is determined by reactions in connection with fluorine evolution rather, than by the wettability of the anode by the electrode.

As is known from gadolinium refining experiments[4], the deposition overpotential of gadolinium is extremely low. Consequently, the observed cell voltage is determined by the anodic overvoltage, which is subdivided into three reaction steps,

I. Discharge of fluorine ions

a) $GdF_4^- \rightleftarrows C \ldots . F + GdF_3 + e^-$
$GdF_4^- \rightleftarrows Pt \ldots F + GdF_3 + e^-$

b) $C \ldots . F + GdF_4^- \rightleftarrows F_2 + GdF_3 + e^-$
$Pt \ldots F + GdF_4^- \rightleftarrows F_2 + GdF_3 + e^-$

II. Atomic recombinations

$$C \ldots . F + C \ldots . F \rightleftarrows F_2$$
$$Pt \ldots F + Pt \ldots F \rightleftarrows F_2$$

C....F, Pt...F represent atomic fluorine adsorbed on graphite and platinum electrodes respectively. Although it was not possible to obtain experimental values of the *Tafel* equation, the fact that fluorine was not directly observed as fluorine gas, and because of the high atomic resistance of the current-voltage curves (Fig. 1), it may be assumed that fluorine desorption controls the rate of the anode reaction. This is reasonable since in the first place fluorine is a highly oxidizing element with a low solubility in the electrolyte. Secondly, studies of chlorine evolution on different types of graphite materials in a NaCl—AgCl melt at 750 °C by the double pulse method[10] reveal that charge transfer is a fast reaction. Furthermore *Hoff*[11] found considerable retardation of the chlorine evolution in various melts. In correspondence with the slow recombination reaction $\mathrm{Cl_{ad}} + \mathrm{Cl_{ad}} \rightleftarrows \mathrm{Cl_{2(g)}}$ the *Tafel* slopes were consistent with the theoretical slope $RT/2F$ (Lit.[12,13]).

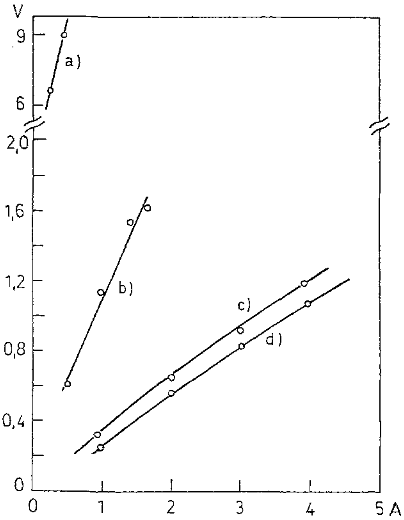

Fig. 1. Voltage—current diagram for the deposition of gadolinium in the 75 LiF-25 mol% $\mathrm{GdF_3}$ electrolyte. *a* Graphite anode (1,050 °C), *b* Platinum anode (1,050 °C), *c* Calcium-impregnated anode (840 °C), *d* Gadolinium anode (870 °C)

Graphite anodes tried for the electrolysis of $\mathrm{GdF_3}$ (Fig. 1) turned out to be highly polarized although the formation of fluorocarbons is proposed[14–16]. Their inertness may be rationalized by liberated fluorine atoms, which are adsorbed at the electrode. Such a film would prevent the wetting of the electrode by the bath. By the use of platinium electrodes the polarization decreased approximately by a factor of ten (Fig. 1). The lower polarization may be related to the chemical structure of the electrodes, since the π-electrons of the carbon atoms attract fluorine with the force of a covalent bond while the consumption of platinum metal may lead to the formation of the volatile hexafluoride and the more ionic tetrafluoride. In the absence of easily oxidized elements PtF_6 is very stable and shows a high oxidizing power. It may even remove an electron from the oxygen. Therefore, platinum hexafluoride is probably present in the electrolyte as an $O_2^+[PtF_6]^-$ type of complex.

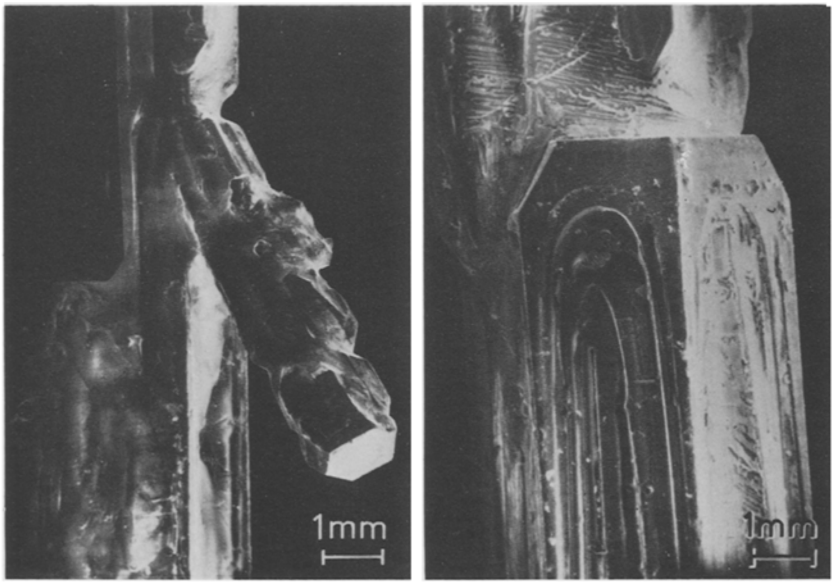

Fig. 2. High purity gadolinium dendrites grown from the 75 LiF-25 mol% GdF_3 solution at 840 °C. Growth direction perpendicular to the hexagonal basis plane of the gadolinium crystals, a/c ratio 0.629, cell voltage 0.7 V

In order to lower the anodic overpotential the

$$\mathrm{Pt},\ F_2 \mid \mathrm{LiF—GdF_3} \mid \mathrm{Gd}$$

cell was modified by the introduction of calcium impregnated anodes into a cell of the type

$$\mathrm{Ta} \mid \mathrm{Ca} \mid \mathrm{CaF_2—LiF—GdF_3} \mid \mathrm{Gd}$$

in which the following electrode reactions occur:

$$3\,Ca + 6\,F^- \rightarrow 3\,CaF_2 + 6\,e^-$$
$$2\,GdF_3 + 3\,e^- \rightarrow 2\,Gd + 6\,F^-$$

This technique led to an approximately *Faradayic* yield in the electrolysis (Fig. 3), and the initial cell voltage of 6-10 V experienced with graphite anodes was reduced to values (~ 0.7 V) comparable to those of electrorefining cells. The thermochemical dissolution of calcium in the salt was negligible, because of its low solubility in the electrolyte. CaF_2 integrates completely into the electrolyte; its thermodynamic stability prevents an undesired interference with the deposition of ultrapure gadolinium (0.7 ppm Ca).

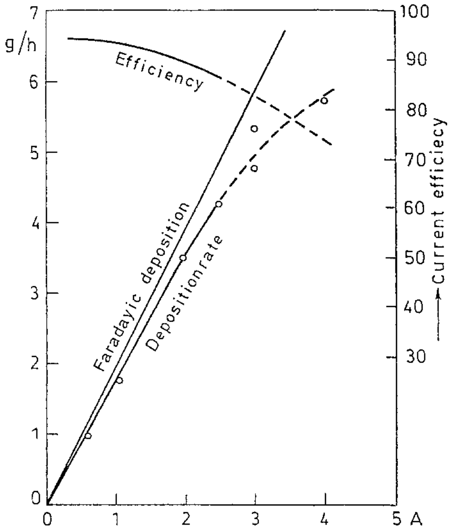

Fig. 3. Deposition rate and efficiency of the electrolysis of GdF_3; electrolyte: 75 LiF-25 mol% GdF_3; temperature: 840 °C

Furthermore, thermodynamic equilibria allow an approach to predict the reaction of container materials with the molten electrolyte. They may be expected to corrode until their potential is raised by oxidation to the redox-potential of the melt. The corresponding diagrams, constructed similarily to those suggested by *Edeleanu* et al.[17], revealed an activity for Fe^{2+}, Ni^{2+} and Cr^{2+} ions in the electrolyte of less than 10^{-5}. This low metal ion activities indicate stainless steel as a reasonable construction material. Even though, the gadolinium dendrites deposited in a stainless steel crucible contained 700 ppm Cr, 10,300 ppm Fe and 3,100 ppm Ni.

A thermodynamic evaluation of the compatibility of niobium, tantalum and molybdenum was not carried out, because the identity and stability of their lower fluorides in the molten salt are not known. However, it was found experimentally that the contamination of electrocrystallized gadolinium by a tantalum container is several magnitudes below that caused by the stainless steel cell. The analysis of Table 1 refers to gadolinium (49 ppm Ta) deposited in a tantalum cell.

Conclusions

Information available at present on kinetic parameters at solid electrodes in halogenide salt solvents is insufficient to allow any generalisation. In particular those concerned with the study of fluorides face serious problems in attributing certain phenomena to particular data.

The rate-determining fluorine dissolution linked with graphite and platinum anodes is avoided by using calcium-impregnated electrodes. By the discharge of electrode films at the anode, the deposition current increased from 0.3 to 5 A, and the cell voltage for the electrolysis of gadolinium fluoride was reduced to values comparable with those obtained in refining cells (0.7 V).

The chemical analysis of the electrochemically produced gadolinium metal resulted in 75, 22, 54 and 100 ppm for the interstitial elements H, N, O and C respectively. The highest concentrations of rare earth impurities were Y (5), Ce (5), Nd (3), and Tb (71 ppm). Tantalum crucibles provided a substantial improvement over the ceramic containers mostly used till now. Thus a principal problem of high-temperature molten salt chemistry is solved, and further experimental work on electrode kinetics may result in more reliable data.

A number of industrial firms state that their gadolinium is four or five 9's pure. Usually only certain impurities present are analysed and subtracted from 100% or alternatively, it is the purity with regard to other rare earths or to other metallic ions which is expressed.

With care it is not difficult to produce metal which is 99.9% pure in this respect, but the problem becomes complex if nonmetallic impurities are included, since the rare earths getter these elements at all stages of manufacturing and handling. The gadolinium (approximately 99.95% pure) prepared by the processes described in this series of papers is to be considered as ultrapure in comparison with the gadolinium of highest purity presently available, because the present specification represents a total chemical analysis.

Reduction of all the other rare earths to less than 100 parts per million impurity content was mainly achieved by the separation of the initial starting material of the experiments, Gd_2O_3, through ion exchange methods. In most cases emission spectroscopy failed to give accurate data in the concentration range of 10 parts per million, and it was necessary to use a specially calibrated mass spectrograph. These two methods, which have proved essential to the present studies, were originally developed by the metallurgical and analytical group of the Ames Laboratory—USDOE and the Iowa State University.

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