RI 7710

BuMines RI 7710

Bureau of Mines Report of Investigations/1973

PB 214 763

Purification of Yttrium by Electrorefining

UNITED STATES DEPARTMENT OF THE INTERIOR

BIBLIOGRAPHIC DATA SHEET	1. Report No. BuMines RI 7710	2.	3. Recipient's Accession No. PB-214 763
4. Title and Subtitle Purification of Yttrium by Electrorefining			5. Report Date January 1973 6. Performing Organization Code
7. Author(s) D. C. Fleck, E. K. Kleespies, and D. G. Kesterke			8. Performing Organization Rept. No. BuMines RI
9. Performing Organization Name and Address Reno Metallurgy Research Center Bureau of Mines, USDI 1605 Evans Avenue Reno, NV 89505			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Agency Name and Address Division of Metallurgy Bureau of Mines U.S. Department of the Interior Washington, DC 20240			13. Type of Report & Period Covered Research, 1971-72 14. Sponsoring Agency Code
15. Supplementary Notes			

16. Abstracts Electrorefining yttrium from selected low-melting yttrium-base alloys was investigated, and various halide systems were studied as potential electrolytes for use in preparing low-oxygen yttrium by electrorefining unalloyed yttrium.

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17. Key Words and Document Analysis. 17a. Descriptors

Metallurgy
Electrorefining
Yttrium
Halide systems

17b. Identifiers/Open-Ended Terms

Impurity transfer
Molten-halide electrolytes

17c. COSATI Field/Group 11F

18. Distribution Statement	19. Security Class (This Report)	21. No. of Pages
Release unlimited by NTIS.	UNCLASSIFIED	17
	20. Security Class (This Page) UNCLASSIFIED	22. Price $3.00/$0.95

Report of Investigations 7710

Purification of Yttrium by Electrorefining

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UNITED STATES DEPARTMENT OF THE INTERIOR
Rogers C. B. Morton, Secretary

BUREAU OF MINES
Elburt F. Osborn, Director

This publication has been cataloged as follows:

Fleck, Delbert C

Purification of yttrium by electrorefining, by D. C. Fleck, E. K. Kleespies, and D. G. Kesterke. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1973]

12 p. illus., tables. (U.S. Bureau of Mines. Report of investigations 7710)

Includes bibliography.

1. Yttrium—Electrometallurgy. I. Kleespies, Ernst K., jt. auth. II. Kesterke, Donald G., jt. auth. III. Title. (Series)

TN23.U7 no. 7710 622.06173

U.S. Dept. of the Int. Library

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PURIFICATION OF YTTRIUM BY ELECTROREFINING

by

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ABSTRACT

Electrorefining yttrium from selected low-melting yttrium-base alloys is investigated, and various halide systems are studied as potential electrolytes for use in preparing low-oxygen yttrium by electrorefining unalloyed yttrium.

Yttrium cathode products having significantly less metallic impurities than the anode materials were prepared from alloys containing nickel, iron, and manganese by electrorefining in LiCl-YCl_3 electrolytes at 900° to 1,000° C. Yttrium-copper and yttrium-magnesium alloys are not suitable as anode feed materials.

An evaluation of chloride, fluoride, bromide, and mixed chloride-fluoride electrolytes showed that cathode products containing much less oxygen than the anode material can be obtained in the fluoride and mixed chloride-fluoride systems. Initial cathode current density has no apparent effect on the purity of the products obtained in both phases of the investigation.

INTRODUCTION

The electrorefining of yttrium and rare-earth metals is a part of a Bureau of Mines research program to study the preparation of high-purity reactive metals by electrochemical methods.

Consideration of yttrium metal in nuclear applications, and as an alloying agent has stimulated interest in the preparation of high-purity metal. Further research of its properties is a requisite to evaluating potential uses.

In current practice, yttrium metal is prepared by thermochemical reduction of an yttrium halide (2-3).[4] The resulting sponge, however, requires several processing steps to obtain massive yttrium, and the final product

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[2] Metallurgist (now with the Metalrex Co., Reno, Nev.).

[3] Supervisory metallurgist.

[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

contains appreciable amounts of oxygen and metallic contaminants originating in the reaction chamber. Further purification of the metal has been studied by several methods. Anable and Beall (1) attempted to achieve purification by electron-beam melting. This method resulted in a significant lowering of most metallic impurities but was unsuccessful with respect to oxygen and nitrogen. Habermann and Daane (4) obtained a product containing less than 150 ppm oxygen by a distillation technique. Merrill and Wong (5) electrorefined solid yttrium in a chloride bath, which resulted in a marked reduction in metallic contamination, although there was little decrease in the oxygen content. In a recent study, Morrice, Shedd, and Henrie (6) demonstrated the preparation of yttrium-nickel and yttrium-iron alloys in fluoride melts by electrodeposition of yttrium on a consumable cathode.

As an extension of the electrowinning efforts, the objectives of this research were (1) to obtain impurity transfer data useful for evaluating a metallurgical processing sequence involving the electrorefining of yttrium from low-melting alloy intermediates and (2) to investigate the effect of electrolyte composition on oxygen transfer from unalloyed yttrium anodes.

Because of the reactive nature of yttrium at elevated temperatures, special precautions were taken to conduct the refining in an inert atmosphere and to minimize air and moisture contamination in the subsequent handling of the products.

Investigations of the electrotransport of metallic contaminants were made on binary yttrium-base alloys containing iron, nickel, copper, and magnesium, as well as on the ternary yttrium-manganese-iron alloy. These systems were selected because their relatively low melting points of 850° to 1,000° C make them potentially amenable to preparation by molten salt electrolysis. The electrolyte used in this phase of the research was confined to the $LiCl-YCl_3$ system. Other alkali-metal chlorides were not suitable as bath constituents because they would react with yttrium to form YCl_3.

In the investigations of oxygen transfer from solid anodes, selected iodide, bromide, fluoride, and chloride-fluoride systems were evaluated in addition to the chloride electrolyte to determine whether a significant reduction in oxygen transfer from the anode material to the cathode product could be achieved.

APPARATUS AND MATERIALS

Yttrium metal and molten halides react with air and moisture at elevated temperatures, thus all experiments were conducted in a helium atmosphere. In addition, yttrium metal readily reacts with most metals and metal oxides commonly used as materials of construction. However, yttrium does not alloy with tungsten at the temperatures used in this investigation, and a tungsten crucible, 3 inches in diameter by 6 inches in length, was used to contain the anode material and the electrolyte. The metal was deposited on 1/4-inch-diameter tungsten cathodes.

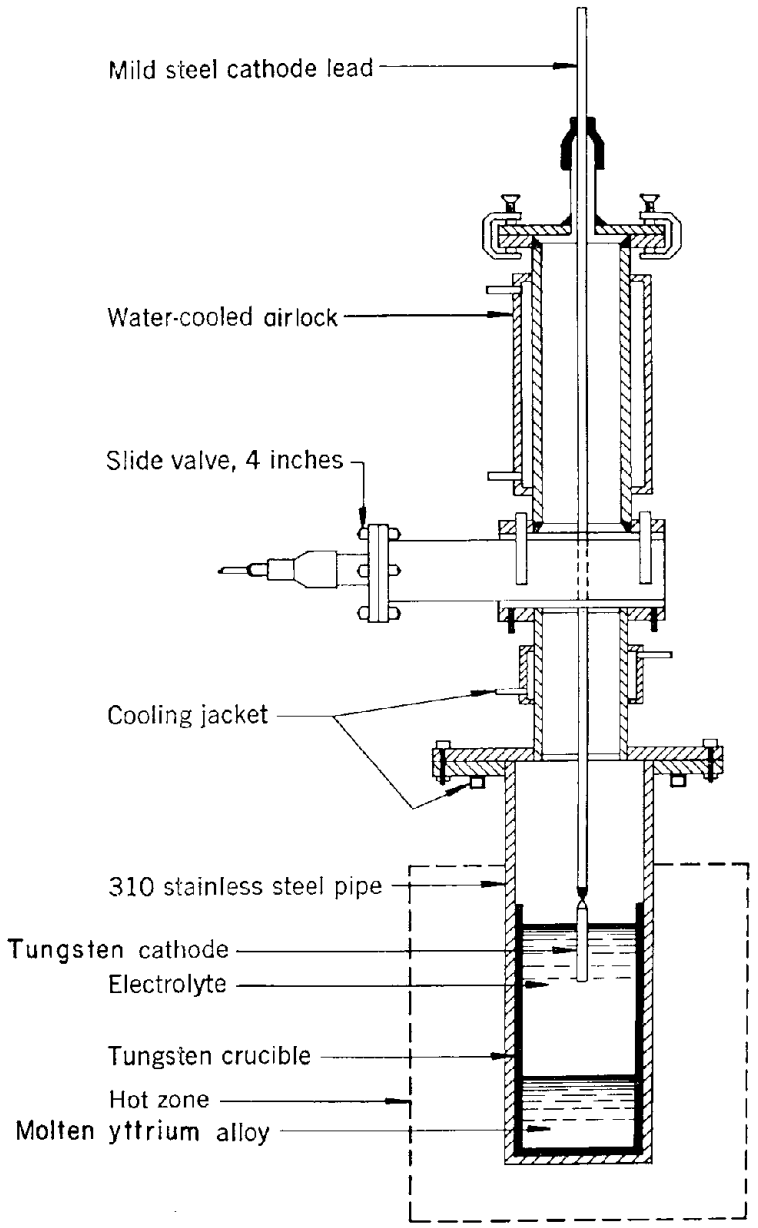

FIGURE 1. - Electrorefining Apparatus.

Figure 1 shows the electrorefining apparatus. The cell enclosure was constructed from type 310 stainless steel. It incorporated a water-cooled jacket near the top flange, and was connected to an aluminum air lock assembly by a 4-inch slide valve. The slide valve housing was constructed of aluminum, and the valve was made of type 316 stainless steel. Neoprene gaskets, 1/4 inch thick, were used between all the flanges. Sealed outlets were provided in the air lock for vacuum, helium, oil bubbler, and a thermocouple vacuum gage tube. A 1/2-inch stainless steel rod served as the cathode lead and was sealed to the lid by thick-walled rubber tubing. Electrically insulated "C" clamps were used to fasten the lid to the air lock. A resistance furnace supplied the heat necessary to melt the electrolyte and to maintain the desired temperature during the experiments. Direct current was supplied by a selenium rectifier. The furnace temperature was measured by a thermocouple connected to a millivolt pyrometer.

Yttrium sponge used in these investigations was produced at Ames Laboratory, Iowa State University, Ames, Iowa. An analysis of this material is presented in table 1. The metals used as alloying constituents consisted of turnings from type A nickel, deoxidized copper, electrolytic iron platelets, small pieces of bar magnesium, and electrolytic manganese platelets. Electrowon yttrium-nickel and yttrium-iron alloys prepared at the Reno Metallurgy Research Center were also used in addition to the alloys prepared by direct melting of the component metals.

TABLE 1. - Analysis of yttrium sponge

Impurity element	Parts per million	Impurity element	Parts per million
Aluminum	50	Magnesium	<10
Boron	(1)	Manganese	150
Calcium	<20	Molybdenum	40
Chromium	(1)	Nickel	1,500
Cobalt	(1)	Silicon	<70
Copper	200		
Iron	100	Oxygen	(2)
Lead	(1)		

[1]Not detected.
[2]0.4 weight-percent.

Reagent-grade halide salts obtained from commercial sources were used directly as electrolyte constituents or for synthesizing certain other bath constituents.

PROCEDURE

Before each series of experiments, the apparatus was thoroughly cleaned, assembled, and evacuated to approximately 10 microns of pressure to permit checking for leaks. The system was considered satisfactorily gastight when the check showed a leak rate of about 1 micron-liter per minute. Vacuum dried LiCl and anode constituents consisting of compacted yttrium plus sufficient alloying metal to provide about 200 grams of the desired composition were placed in the tungsten crucible. The air lock was then removed from the cell enclosure, the crucible was loaded into the enclosure, and the system was reassembled and immediately reevacuated to avoid moisture contamination of the LiCl. The temperature was raised slowly while the cell was kept under vacuum to remove traces of moisture which might contaminate the molten salt by forming oxychlorides. At approximately 400° C, the cell was back-filled with helium and heated to the operating temperature while purging the system with helium.

It was determined by experience that a YCl_3 concentration in the electrolyte of 7 to 12 weight-percent provided the best electrical conductivity and melting point characteristics. This composition range was obtained by reacting anhydrous $NiCl_2$ with yttrium metal as follows:

$$3NiCl_2 + 2Y \rightarrow 2YCl_3 + 3Ni.$$

Stoichiometric amounts of anhydrous $NiCl_2$ and yttrium metal were added to a nickel filter, which consisted of a 3-inch-diameter by 10-inch-long cylinder with a porous closure on one end. The filter was lowered through the air lock into the molten LiCl and held there for several hours to allow the reaction to proceed to completion. It was then slowly removed from the salt and pulled back into the air lock to cool. The nickel formed in this reaction remained in the filter in the form of a mass of entangled, needlelike crystals, and the YCl_3 drained out into the LiCl. Sufficient time was allowed for the molten salts to become homogeneous; then the melt was sampled for YCl_3 analysis. Total weight of the electrolyte was about 1,400 grams.

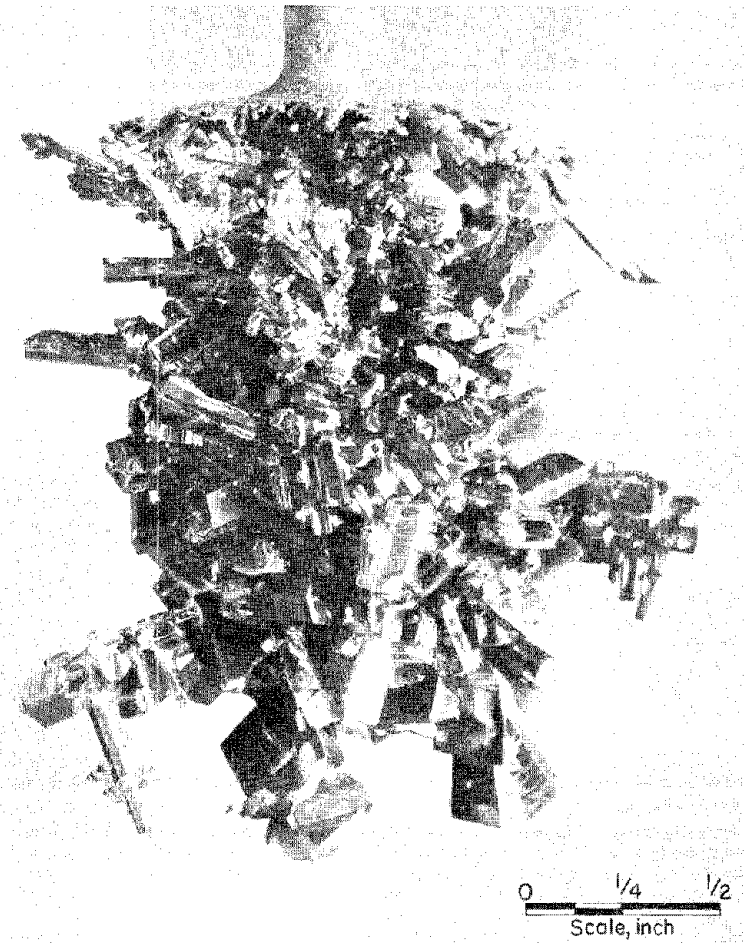

FIGURE 2. - Electrodeposited Yttrium Crystals.

After the electrolyte was sampled, a tungsten cathode was fastened to the cathode lead and the air lock lid was replaced. An inert atmosphere was established by evacuating and refilling the air lock with helium. The slide valve was then opened to the cell enclosure, and the cathode was lowered into the salt. After a 5-minute holding period to establish thermal equilibrium, electrolysis was initiated.

To terminate electrolysis, the cathode was removed and suspended just above the electrolyte for 5 minutes to allow most of the adhering salt to drain from the deposit. The deposit was then pulled into the air lock to cool and the slide valve was closed. After a 30-minute cooling period, the cathode and deposit were removed from the air lock. Figure 2 depicts a typical cathode product. Several deposition cycles (runs) were made from each batch of anode starting material to determine the effect of prolonged electrolysis on the degree of transfer of metallic elements from the anode to the cathode.

Following each deposition cycle during the metal transfer investigations, the crystals were stripped from the cathode and leached in anhydrous methyl alcohol. Samples of the leached crystals were analyzed for metallic impurities by atomic absorption and optical emission spectrographic methods. In the oxygen transfer studies, representative crystals from different areas of the deposit were selected for oxygen analysis by the inert gas fusion method.

RESULTS

Initial investigations on metallic transfer consisted of experiments on four different yttrium-nickel and yttrium-iron alloys. The experiments were conducted at 900° to 1,000° C in LiCl-YCl_3 electrolytes in which the initial YCl_3 content ranged from 7.4 to 8.5 weight-percent.

To evaluate the effect of cathode current density on the degree of impurity transfer, a series of experiments was performed on the refining of an 80-weight-percent yttrium, 20-weight-percent nickel alloy in which the electrolysis current was varied from 1 to 10 amperes. This corresponded to an initial cathode current density of 100 to 1,000 amp/ft^2. The resulting cell voltage ranged from about 0.2 to 1.1 volts. Finer crystals were obtained at the higher current densities; however, there was no apparent difference in the transport of metallic impurities to the cathode that could be related to current density, and a majority of the succeeding experiments on the different alloy systems were performed at an initial cathode current density of 250 amp/ft^2.

In the subsequent experiments on the 80-weight-percent yttrium-nickel alloy at an initial cathode current density of 250 amp/ft^2, about 95 percent of the yttrium in the anode had been electrotransported to the cathode after 15 deposition cycles. Cathode current efficiencies per deposition cycle ranged from 98 to 69 percent. Analytical data on the transfer of metallic elements to the cathode are presented in table 2. (In this and succeeding tables, except where noted, data are given for the initial and final runs, and for two representative intermediate runs.)

TABLE 2. - Metallic element transfer during electrorefining of 80-weight-percent yttrium-nickel alloy, ppm

Element	Anode analysis	Cathode product analysis			
		Initial run	Intermediate run A	Intermediate run B	Final run
Aluminum	70	22	24	51	<20
Calcium	<20	([1])	([1])	([1])	([1])
Chromium	150	<3	3	<3	3
Cobalt	<30	([1])	([1])	([1])	([1])
Copper	240	27	34	<10	25
Iron	220	<15	<15	<15	<15
Magnesium	14	14	36	<10	<10
Manganese	740	<6	<6	<6	21
Molybdenum	30	<7	<7	<7	<7
Nickel	([2])	<10	<10	<10	20
Silicon	120	<45	<45	<45	<45

[1] Not detected.
[2] 20 weight-percent.

A similar experiment was conducted on an impure electrowon Y-Ni alloy containing 51.2-weight-percent yttrium and 46.2-weight-percent nickel as the major constituents. In this experiment, nine deposition cycles were performed, and about 90 percent of the yttrium was electrorefined from the anode at current efficiencies per deposition cycle of 87 to 65 percent. Results in table 3 show that a greater degree of transfer of cobalt, copper, iron, and nickel occurred than in the previous experiment.

TABLE 3. - Metallic element transfer during electrorefining of a low-grade electrowon yttrium-nickel alloy, ppm

Element	Anode analysis	Cathode product analysis			
		Initial run	Intermediate run A	Intermediate run B	Final run
Aluminum	250	<15	<15	<15	<15
Boron	100	([1])	([1])	([1])	5
Calcium	1,000	<20	<20	<20	<20
Cobalt	500	([1])	([1])	([1])	100
Copper	500	<10	([1])	<10	500
Iron	1,800	([1])	([1])	([1])	180
Magnesium	<10	15	15	15	15
Manganese	1,000	20	<10	30	<10
Molybdenum	120	([1])	([1])	([1])	([1])
Nickel	([2])	50	<20	<20	500
Silicon	130	<20	<20	20	<20
Yttrium	([3])	([4])	([4])	([4])	([4])

[1]Not detected.
[2]46.2 weight-percent.
[3]51.2 weight-percent.
[4]Major constituent.

Two experiments were conducted on the yttrium-iron system, using a synthesized 80 yttrium-iron alloy and a low-grade electrowon alloy containing 81.3-weight-percent yttrium and 14.7-weight-percent iron as anode starting materials. In studies on the 80-weight-percent yttrium-iron system, 11 deposition cycles were performed, during which about 70 percent of the yttrium was electrorefined from the anode at current efficiencies per run of 99 to 70 percent. After 15 runs using the electrowon alloy, more than 95 percent of the yttrium was electrotransported to the cathodes at current efficiencies of 99 to 60 percent. Transfer of metallic elements in both systems was negligible (tables 4-5).

TABLE 4. - Metallic element transfer during electrorefining of 80-weight-percent yttrium-iron alloy, ppm

Element	Anode analysis	Cathode product analysis			
		Initial run	Intermediate run A	Intermediate run B	Final run
Aluminum	40	<20	<20	<20	<20
Calcium	<20	([1])	([1])	([1])	([1])
Chromium	<3	<3	<3	<3	<3
Cobalt	<30	([1])	([1])	([1])	([1])
Copper	180	18	35	18	21
Iron	([2])	<15	<15	19	18
Magnesium	<10	<10	<10	<10	<10
Manganese	120	<6	<6	<6	<6
Molybdenum	30	<7	<7	<7	<7
Nickel	1,200	<10	<10	<10	<10
Silicon	50	<45	<45	<45	<45

[1]Not detected.
[2]20 weight-percent.

TABLE 5. - Metallic element transfer during electrorefining of a low-grade electrowon yttrium-iron alloy, ppm

Element	Anode analysis	Cathode product analysis			
		Initial run	Intermediate run A	Intermediate run B	Final run
Aluminum	1,000	<10	<10	<10	<10
Calcium	4	4	5	3	3
Chromium	110	9	8	10	7
Copper	500	3	3	3	4
Iron	(1)	10	7	12	2
Lead	120	<25	<25	<25	25
Magnesium	<10	<10	<10	<10	<10
Manganese	430	2	2	2	2
Molybdenum	120	<15	<15	<15	<15
Nickel	300	4	2	3	9
Silicon	<20	<20	<20	<20	<20
Yttrium	(2)	(3)	(3)	(3)	(3)

[1] 14.7 weight-percent.
[2] 81.3 weight-percent.
[3] Major constituent.

Copper transfer from an anode containing 20-weight-percent copper and 80-weight-percent yttrium was similarly studied in an $LiCl-YCl_3$ bath at 925° C. This experiment consisted of nine deposition cycles and resulted in the electrotransport of almost 80 percent of the yttrium from the anode. Analyses showed that the copper content of the cathode products remained below 20 ppm until the copper concentration in the anode had increased to 43 weight-percent. At greater copper concentrations, transfer of copper to the cathode increased rapidly to 2,100 ppm (table 6). Cathode current efficiency in the initial experiment was 88 percent, and decreased to 65 percent in the final run.

TABLE 6. - Metallic element transfer during electrorefining of 80-weight-percent yttrium-copper alloy, ppm

Element	Anode analysis	Cathode product analysis			
		Initial run	Intermediate run A	Intermediate run B	Final run
Aluminum	40	<15	<15	<15	15
Calcium	<20	(1)	(1)	(1)	(1)
Copper	(2)	7	6	14	2,100
Iron	110	<20	<20	<20	<20
Lead	20	(1)	(1)	(1)	(1)
Magnesium	10	25	25	80	160
Manganese	120	<10	<10	<10	15
Molybdenum	35	(1)	(1)	(1)	(1)
Nickel	1,200	(1)	(1)	500	500
Silicon	50	<10	<10	<10	<10

[1] Not detected.
[2] 20 weight-percent.

An LiCl-YCl_3 electrolyte at 950° C was used in an experiment to determine the transfer of manganese and iron from an alloy containing the following, in weight-percent: Mn, 5; Fe, 20; and Y, 75. During a series of 11 runs, 90 percent of the yttrium was removed from the anode material. Cathode current efficiency per deposition cycle ranged from 97 to 72 percent. As shown in table 7, iron and manganese concentrations in the cathode products were less than 30 ppm throughout the series.

TABLE 7. - Metallic element transfer during electrorefining of a 75-20-5 yttrium-iron-manganese alloy, ppm

Element	Anode analysis	Cathode product analysis			
		Initial run	Intermediate run A	Intermediate run B	Final run
Aluminum	40	15	<15	<15	<15
Calcium	20	([1])	([1])	([1])	([1])
Cobalt	<20	20	([1])	400	1,000
Copper	150	10	20	<10	50
Iron	([2])	8	5	5	28
Magnesium	<10	20	60	200	30
Manganese	([3])	<2	5	6	12
Molybdenum	30	<10	<10	10	20
Nickel	1,100	([1])	([1])	([1])	([1])
Silicon	60	<30	<30	<30	<30

[1] Not detected.
[2] 20 weight-percent.
[3] 5 weight-percent.

Refining of an yttrium-magnesium alloy containing 40-weight-percent magnesium resulted in a high degree of magnesium transfer. The deposition cycles were conducted at 825° C in an LiCl-YCl_3 bath. Analytical data presented in table 8 show that the magnesium content of the cathode products increased to 11 percent after only three runs. The cathode current efficiencies ranged from 68 to 13 percent.

TABLE 8. - Metallic element transfer during electrorefining of a 60-weight-percent yttrium-magnesium alloy, ppm

Element	Anode analysis	Cathode product analysis		
		Run 1	Run 2	Run 3
Aluminum	60	<15	<15	<15
Calcium	<20	([1])	([1])	([1])
Cobalt	30	50	([1])	([1])
Copper	120	<20	<20	<20
Iron	180	1,800	500	1,800
Magnesium	([2])	1,000	4,000	([3])
Manganese	200	160	20	400
Molybdenum	20	10	10	10
Nickel	900	([1])	([1])	([1])
Silicon	50	<20	<20	<20

[1] Not detected.
[2] 40 weight-percent.
[3] 11 weight-percent.

Data obtained during the refining of yttrium alloys in LiCl-YCl_3 melts showed that the oxygen contents of the anode and the cathode products were nearly identical. A study was made of the effect of other halide systems on decreasing the degree of oxygen transfer. Initial efforts in this phase of the research were directed toward an evaluation of various halides to obtain approximate melting point and electrical conductivity data, and to determine whether they would react with yttrium to form an yttrium halide. Iodides and bromides of sodium and potassium, and lithium chloride and fluoride were found to be substantially nonreactive at 700° to 900° C. Based on this evaluation, various binary and ternary systems composed of one or two of these salts plus an yttrium halide were arbitrarily selected for use as electrolytes in this study. The yttrium halide was made in situ for each series of experiments, with exception of the YF_3-LiF series, by reacting yttrium metal with nickel halide. In the YF_3-LiF series, the YF_3 was obtained from a commercial source.

The electrolyte studied first was evaluated at 750° to 850° C and contained the following, in weight-percent: NaI, 46.7; KI, 34.4; and YI_3, 18.9. Fifteen deposition cycles were performed at initial cathode current densities of 50 to 400 amp/ft^2. The resulting cathode deposits contained large quantities of nonremovable adhering salts, making the crystals unsuitable for obtaining valid analytical results.

Evaluation of a bromide system was made in an electrolyte containing the following, in weight-percent: KBr, 50.9; NaBr, 29.3; and YBr_3, 19.8. The experiment consisted of 10 deposition cycles conducted at 750° and 800° C at initial cathode current densities ranging from 25 to 300 amp/ft^2. At the lower cathode current densities, the crystals were large and cubic; at the higher current densities, they were smaller and bayonet-shaped. The adhering salts could not be completely separated from the metal. However, these salts were present as a very thin layer giving a high metal to salt ratio. Analysis of the deposits prepared in this series indicated, with a good degree of accuracy, that the oxygen content of the metal was nearly the same as the anode material.

An electrolyte containing 65 weight-percent YF_3 and 35 weight-percent LiF was studied at 825°, 875°, and 925° C, in an experiment consisting of 12 runs. Initial cathode current densities were 25 and 100 amp/ft^2. Current efficiencies were not determined for this system, owing to the problem of separating the adhering fluoride salts from the metal. Small crystals containing large amounts of adhering salts were formed at a current density of 100 amp/ft^2. However, crystals formed at 25 amp/ft^2 were much larger and had a relatively small amount of adhering salts. The oxygen content of these crystals ranged from 72 to 97 percent less than the anode starting material.

An electrolyte containing 70 weight-percent LiCl, 14 weight-percent LiF, and 16 weight-percent YF_3 was evaluated at 725° to 825° C. This experiment consisted of 28 deposition cycles conducted at initial cathode current densities of 25 to 100 amp/ft^2. Current efficiencies ranged from 94 to 76 percent. Crystals made in this electrolyte were larger but similar in shape to those produced in the all fluoride system, and could be cleaned of adhering salts by prolonged leaching in cold methanol and a final water leach. The oxygen

content of these crystals was 70 to 85 percent less than the anode material. More bath fuming was observed, and more sublimate was collected in the cool portion of the cell compared with the fluoride experiments at the same temperatures.

Data on the oxygen content of metal refined in the various electrolytes are shown in table 9. Spectrographic analyses for metallic impurities were also obtained on cathode products made in the LiCl-LiF-YF_3 electrolyte. A typical analysis showed the following metallic impurities, in parts per million: Al, <15; Ca, <20; Cu, <5; Fe, -15; Mg, <10; Mn, <15; Mo, -10; and Si, <<40. Because it was impossible with most electrolytes to completely remove adhering salts from the metal crystals, the halide content of the metal was not determined. The results cited compared favorably with data obtained on crystals formed in the LiCl-YCl_3 system during electrorefining of the yttrium-base alloys.

TABLE 9. - Oxygen content of cathode products prepared in different electrolytes from anode material containing 0.4 weight-percent oxygen

Electrolyte system	Cathode product oxygen analysis, weight-percent			
	Initial run	Intermediate run A	Intermediate run B	Final run
LiCl-YCl_3	0.38	0.37	0.34	0.52
NaBr-YBr_3	.36	.33	.42	.36
LiF-YF_3	.01	.05	.11	.11
LiCl-LiF-YF_3	.12	.07	.07	.06

CONCLUSIONS

Investigations on electrorefining of yttrium from selected yttrium-base alloys in LiCl-YCl_3 electrolytes showed that metallic impurities in the cathode products were substantially less than in the anode material when yttrium was refined from alloys containing Fe, Ni, and Mn. These studies also demonstrated that yttrium-copper and yttrium-magnesium alloys were not practical starting materials, because the copper and magnesium transferred to the cathode products in appreciable quantities. Variation of initial cathode current density did not substantially affect the purity of the electrorefined metal.

Studies on the electrotransport of oxygen from unalloyed yttrium showed that no refining with respect to oxygen occurred in metal treated in LiCl-YCl_3, and NaBr-KBr-YBr_3 electrolytes. For metal refined in LiF-YF_3 and LiCl-LiF-YF_3 systems, the oxygen content was significantly reduced. The metallic impurity content of products made in electrolytes containing fluorides was comparable with those prepared in the all chloride system.

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INT.-BU.OF MINES,PGH.,PA. 18060