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METHOD FOR THE PRODUCTION OF SAMARIUM ALLOYS

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ABSTRACT OF THE DISCLOSURE

Samarium is electrodeposited from a Sm_2O_3 source onto a consumable iron, nickel or cobalt cathode to produce a samarium alloy. The samarium is then separated from the alloy by vacuum sublimation.

This invention, which relates to the preparation of samarium metal and samarium alloys, resulted from work done by the Bureau of Mines in the U.S. Department of the Interior, and domestic title to the invention is in the Government.

Due to expanding metallurgical uses for samarium metal, especially its use as an excellent magnetic material when alloyed with cobalt, the production of high purity samarium metal has become very desirable. However, much difficulty has heretofore been encountered in preparing the metal in a form suitable for such uses. Attempts to electrowin samarium from its oxide have not been successful because reactions between the samarium and electrolyte have occurred. Reduction of samarium halide has met with little success. Some samarium has been produced by reducing the oxide thereof with lanthanum under a vacuum, but this has resulted in the samarium product having undesirable amounts of lanthanum and oxygen.

We have now discovered that high purity samarium metal can be produced by (1) electrodepositing samarium from a Sm_2O_3 source onto an iron, nickel or cobalt cathode to produce a samarium alloy with the cathode metal, and (2) separating samarium from the alloy by vacuum sublimation (distillation). The term sublime (or sublimation), as used throughout the specification and claims, means that the samarium passes from the solid to the gaseous state, and again condenses to solid form, without apparently liquefying.

It is therefore an object of this invention to convert Sm_2O_3 to high purity elemental samarium. Another object is to electrowin samarium from its oxide. A further object is to produce samarium alloys with iron, nickel and cobalt. A still further object is to separate samarium from an alloy of samarium and another metal selected from the group consisting of iron, nickel and cobalt. Other objects and advantages will be obvious from the following detailed description of the invention.

In the practice of the invention, samarium sesquioxide (Sm_2O_3) is dissolved in a molten salt electrolyte while a current is passed therethrough by means of a carbon (graphite) anode and a cathode which is composed of iron, nickel or cobalt. During electrolysis, the molten bath is maintained at a temperature below the melting point of the cathode but above the melting point of the alloy which forms between the samarium and the cathode metal. As a result, the alloy forms in a molten state at the cathode and drips therefrom into a collection vessel. Alternatively, the alloy can be allowed to remain dispersed in the molten bath whereby it is easily separated out as nodules by simple fracturing of the bath after solidification.

Thus, the fast reaction produced by the use of a reactive cathode allows the samarium to be electrowon from its oxide without the samarium having time to react with electrolyte.

An electrolyte composed of SmF_3 and another fluoride selected from the group consisting of LiF, BaF_2, CaF_2, MgF_2 or SrF_2 is particularly suitable for the purposes of invention. In such a mixture, the SmF_3 is preferably present in amounts ranging from about 40 to about 90 weight percent of the electrolyte.

Solidified samarium-cathode metal alloy, which is recovered from the electrodeposition step, is then heated under a vacuum of about 10^{-6} to about 10^{-7} torr to a temperature sufficient to sublime samarium. This temperature is about 800° C. to about 900° C. for a samarium-iron alloy; about 1100° C. to about 1200° C. for samarium-nickel; and about 1100° C. to about 1200° C. for samarium-cobalt. During sublimation samarium vapors are collected in solid form on a cooled surface composed of a material (e.g., tantalum, tungsten or molybdenum) from which the samarium metal may be easily separated by peeling.

The following example specifically illustrates a way in which the invention has been carried out:

A mixture of 81 weight percent SmF_3 and 19 weight percent LiF powders was melted in a graphite crucible inside a chamber having an inert atmosphere. An electrode arrangement consisting of two carbon anodes and one iron cathode was submerged in the fluoride melt. Temperatures in the range of 900° C. to 1,000° C. required for preparing the molten samarium-iron alloy were maintained by internally heating the electrolyte by passing alternating current between the anodes. Samarium sesquioxide was added to the fluoride melt during electrolysis. As the iron cathode was consumed the section thereof external to the bath was slowly immersed in the electrolyte. After completion of electrolysis, the bath was allowed to freeze and the samarium-iron nodules recovered. Operational data during electrolysis are given in the following table.

Sm_2O_3 added to fluoride bath—43 grams
Consumable iron cathode fed to electrolyte—8 grams
Average direct current—52 amp
Average D.C. voltage—23 volt
Average alternating current [1]—69 amp
Average A.C. voltage—41 volt
Initial anode current density (D.C.)—0.5 amp/cm.^{2}
Initial anode current density (A.C.)—1.4 amp/cm.^{2}
Average electrolyte temperature—960° C.
Average cell bottom temperature—580° C.
Duration of electrolysis—1.5 hr.
Sm-Fe alloy recovered—68 grams
Current efficiency—41 percent

[1] Supplemental power applied to the anodes.

The composition of the samarium-iron nodules recovered after electrolysis varied from 12 to 20 weight percent iron. (When cobalt or nickel was used as the cathode under similar operating conditions, the alloy ranged from 20 to 30 weight percent cobalt or nickel.)

Sublimation of the samarium was then accomplished by heating the alloy nodules to a temperature of 800–900° C. in a crucible under a vacuum of 10^{-6} to 10^{-7} torr. Sublimed samarium metal was collected on a tungsten metal cover placed directly above the crucible. The samarium deposit consisted of a substantial layer of metal and was easily separated from the cover by peeling away tungsten. Samarium recovery from the alloy was of the order of 60 percent. Analysis of samarium metal product showed <100 p.p.m. oxygen, <10 p.p.m. carbon, and 10 p.p.m. iron. Other rare-earths, including lanthanum, were not detected by spectrographic or X-ray analysis.

By the present invention, samarium metal is produced in more pure form than that available by standard commercial processes. For example, samarous oxide (SmO), the main source of oxygen contamination in commercial, relatively high temperature reduction processes, does not distill at the temperatures required for vacuum sublimation of samarium in our invention. Further, since lanthanum metal is not necessary in the present invention, lanthanum contamination and a high cost reductant are eliminated. As such, the pure samarium produced by the invention is a desirable alloying element for other metals. Also, the intermediate alloy product, particularly the cobalt alloy, is a valuable material in itself.

Although the particular process herein described is well adapted to carry out the objects of the present invention, it is to be understood that various modifications and changes may be made all coming within the scope of the following claims.

What is claimed is:

1. A proces for treating Sm_2O_3 comprising:

(a) electrodepositing samarium metal from a Sm_2O_3 source onto a cathode selected from the group consisting of iron, nickel and cobalt; said electrodeposition being carried out in a molten electrolyte maintained at a temperature below the melting point of said cathode metal but above the melting point of samarium-cathode metal alloy which forms during electrodeposition on said cathode; and

(b) separating out said alloy.

2. The process of claim **1** in which said molten electrolyte is a mixture of SmF_3 and another fluoride selected from the group consisting of LiF, BaF_2, CaF_2, MgF_2 and SrF_2.

3. The process of claim **2** in which said another fluoride is LiF, and wherein said SmF_3 is present in said electrolyte in an amount of about 40 weight percent to about 90 weight percent of said electrolyte.

References Cited

UNITED STATES PATENTS

3,383,294	5/1968	Wood	204—71
3,298,935	1/1967	Henrie et al.	204—71

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