

[54] **PROCESS FOR THE PREPARATION OF YTTRIUM-SILICON COMPOUNDS OR MASTER ALLOYS BY SILICON CARBIDE REDUCTION OF YTTRIA**

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[58] Field of Search **75/62, 84, 200, 227, 225, 75/152, 134 S, 89**

[56] **References Cited**

UNITED STATES PATENTS

3,104,970 9/1963 Downing 75/84

3,117,175	1/1964	Kohlmeyer.....	75/62 X
3,250,609	5/1966	Bunghardt	75/152 X
3,288,594	11/1966	Smith, Jr.....	75/84
3,364,015	1/1968	Sump	75/152 X
3,440,040	4/1969	Kallenbach	75/152

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[57] **ABSTRACT**

A process for the manufacture of yttrium-silicon master alloys. Using silicon carbide as a reductant, both yttria and silicon carbide are mixed, placed in a crucible and heated for a period of time in a vacuum furnace whereby the mixture is sintered, yielding the desired product and CO and CO₂ gases. The charge is maintained under a dynamic vacuum during heating, holding, and cooling with continuous removal of gaseous reaction products.

5 Claims, No Drawings

PROCESS FOR THE PREPARATION OF YTTRIUM-SILICON COMPOUNDS OR MASTER ALLOYS BY SILICON CARBIDE REDUCTION OF YTTRIA

BACKGROUND

Both yttrium metal and yttrium silicide are useful in the manufacture of nodular cast iron. While magnesium nodulizing agents have been commonly used heretofore, yttrium metal and yttrium silicide possess several advantages over such agents. The use of yttrium metal for producing nodular cast iron is illustrated by Kanter et al. in his U.S. Pat. No. 3,055,756. In producing nodular cast iron employing a yttrium nodulizing agent one finds a lower vapor pressure required and the process enjoys a high recovery rate. Furthermore, yttrium nodulizing agents eliminate the risk of a violent reaction or flash during treatment. However, the present high cost of metallic yttrium makes its use in the manufacture of nodular cast iron prohibitive. The development of a lower cost source of yttrium metal in the form of a yttrium-silicon master alloy would greatly enhance the production and utilization of nodular cast iron containing yttrium.

It is known that yttrium-silicon alloys may be prepared by the chemical reduction of yttrium oxide with silicon metal. However, such prior art processes suffer from the disadvantage that the recovery of yttrium is poor. Furthermore, such processes produce a SiO_2 waste product, of which only part is recoverable from the master alloy by slagging.

Another known means of producing YSi_2 is by silicon reduction of Y_2O_3 under vacuum conditions. However, in order to produce an alloy containing 61 percent yttrium, one must leach the product with sodium hydroxide. While this process involves the generation of waste SiO , which is removed as a gas, the gas condenses to a solid in the cooler part of the reaction vessel.

Misch metal-silicon-iron alloy has been made by reduction of rare-earth oxides and iron scale with calcium silicide. The alloys produced are low in rare-earth metal content (generally less than 30 percent by weight) and the recovery of the rare-earth metal is less than 50 percent.

U.S. Pat. Nos. 3,288,593, 3,116,998 and 3,104,970 illustrate methods for producing certain rare-earth metals by combining the carbon reduction of certain rare-earth oxides with vacuum distillation. These methods effect the production of pure metals. The process involves preparing one rare-earth oxide selected from the group consisting of samarium, neodymium, europium, dysprosium, holmium, erbium and thulium in admixture with a solid carbonaceous reducing agent and furnacing the mixture in vacuo. In U.S. Pat. No. 3,104,970, the useful reducing agents employed are graphite and resistor carbon. U.S. Pat. No. 3,288,593 employs silicon as a preferred reducing agent. These processes however, involve the preparation of pure metals rather than alloys or compounds containing appreciable amounts of reductant or silicon.

Accordingly, it is an object of our invention to prepare yttrium-silicon compounds or master alloys without solid or liquid waste products.

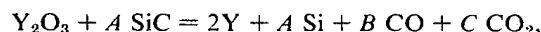
It is also an object of our invention to produce a master alloy high in yttrium.

It is yet a further object of our invention to provide a process for the preparation of yttrium-silicon master alloys by using silicon carbide as a reductant.

THE INVENTION

Our process for the manufacture of yttrium-silicon master alloys involves the use of SiC as a reductant for Y_2O_3 . Measured quantities of silicon carbide and yttria are mixed together thoroughly and placed in a tungsten or other suitable crucible. Preferably the silicon carbide and yttria are in powder form. The crucible and its contents are then placed in a vacuum furnace which is sealed and evacuated. The charge is then heated to the required temperature and held at that temperature for a suitable length of time. As a result the yttria and silicon carbide are sintered whereby the reaction forms the desired product and the waste gases CO and CO_2 . It is essential that the charge be maintained under a dynamic vacuum during the heating, holding, and cooling operations. During the process gaseous waste products CO and CO_2 are continuously removed. The continuous removal of gaseous reaction products tends to drive the reaction to completion.

Our process involves the basic reaction



where

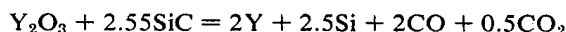
$$A = B + C \text{ and}$$

$$B + 2C = 3.$$

A , B , and C are functions of temperature.

Unlike the processes of the prior art which were concerned with the preparation of pure metals, our invention allows the waste product of the reaction to be removed as CO and CO_2 gases. As a result a higher grade Y-Si product is obtained than that obtained by silicon reduction of Y_2O_3 . In the process of our invention we have found there is no regulus produced containing Y-Si , SiO_2 and silicon with attendant separation problems in order to obtain a Y-Si product. In our process, the recovery of yttrium is high. Unlike the process for reduction of yttria by silicon, there is no SiO or other condensate waste product in the system of our invention. This permits a cleaner and more reliable operation. Using the process of our invention, there is no need to leach the product with NaOH in order to remove excess silicon. While processes involving ferrosilicon reduction of yttria yield products containing approximately 25 percent by weight yttrium silicide, the master alloy produced by the method of our invention using SiC reduction contains more than 90 percent by weight Y-Si .

Considering the basic reaction noted above, at a temperature of $1,750^\circ\text{C}$ the reaction becomes



Thermodynamic calculation show that ΔF° , the standard Gibbs free energy change, is $+148,000$ calories at $2,000^\circ\text{K}$ for the reaction as written. Equilibrium is achieved when the pressure of CO is of the order of 10^{-6} atmospheres and the pressure of CO_2 is of the order of 10^{-7} atmospheres. Thus, the reaction cannot approach completion unless the gaseous waste products are removed. It is necessary that the Y_2O_3 and the SiC have atomic level contact, and this is achieved by sintering during the process.

As one increases the temperature of the reaction, the equilibrium moves to the right. The Y and Si so pro-

duced during the reaction form compounds, and this drives the reaction further to the right.

We have found that the process of our invention may be carried out over a wide range of temperatures from 1,200° to 2,500°C. However, a preferred range is from about 1,600° to 2,500°C. At operating temperatures below 1,200°C the alloying process is poor while at temperatures about 2,500°C, the crucible and furnace materials give poor service. The amount of materials employed in our process is dependant upon the temperatures used during the operation. At a temperature of 1,750°C for example, the molar ratio of Y_2O_3 : SiC would be about 1:2.5.

A number of materials are suitable for use as crucibles to contain the reaction. Materials such as tungsten, silicon carbide, or graphite may be employed. When graphite is used, some yttrium carbide is present in the product material.

The sintering of the component materials may be accomplished in any of a number of standard vacuum furnaces, including the induction and electrical resistance types. The essential requirements of such furnaces is that they be capable of attaining the desired temperatures and supporting a vacuum.

The following examples will serve to more fully illustrate the process of our invention.

EXAMPLE 1

Yttria and silicon carbide were mixed in a molar ratio of 1:3. 11.6 g of this mixture was placed in a silicon carbide crucible and the charge was placed in a vacuum furnace. The system was evacuated to a pressure (dynamic vacuum) of 0.01 torr and the temperature was raised to 1,700°C and maintained at that level for a period of 30 minutes. After cooling and weighing, 7.2 g of Y—Si alloy was recovered. Analysis of the recovered product by means of x-ray diffraction, showed the product to contain major amounts of YSi_2 and a minor amount of YSi.

EXAMPLE 2

9.1 g of a Y_2O_3 :SiC charge mixed in a molar ratio of 1:3 was placed in a graphite crucible and then put in a vacuum furnace in the same manner as Example 1. The pressure of the furnace was reduced to 0.01 torr and the temperature elevated to and maintained at 1,750°C for a period of 10 minutes. Upon cooling, the reaction product was found to weigh 5.8 g. Based on the amount of yttria, the reaction achieved 98% completion. Upon analysis, the product was found to contain: Y—Si = 93.0%, Y_2O_3 = 1.8%, and SiC = 5.0%.

EXAMPLE 3

In the same manner as Example 1, 11.6 g of a Y_2O_3 :SiC charge in a molar ratio of 1:3 was placed in a tungsten crucible. The mixture was ground to a powder state before placing in the crucible. The crucible was then placed in a vacuum furnace and a dynamic vacuum achieved at a pressure of 0.01 torr. The temperature was raised to 2,000°C and held at that level for a period of 20 minutes. 6.4 g of Y—Si alloy was recovered.

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It is also possible to employ mixtures of rare-earth oxides high in yttrium content in the process of our invention. For example, a mixed rare-earth oxide prepared directly from euxenite concentrate may be used in place of Y_2O_3 . Should one desire to prepare a multicomponent master alloy rather than the binary Y—Si, other elements or compounds may be added to the yttria-silicon carbide charge.

It is also within the scope of our invention to employ a mechanical mixture of Si and C in lieu of SiC. However, under these circumstances, generally a large amount of carbon is left in the product.

As illustrated, our invention provides for the use of SiC as a reductant for Y_2O_3 and rare-earth oxides high in yttrium content. Some ores containing yttria in amounts greater than about 30 percent of the total rare-earth oxides are amenable to the process of our invention. Euxenite is an example of such an ore. The process is unique in that it also provides for the removal as CO and CO_2 gases, the waste products of the process in preparing the master alloy Y—Si.

Our invention as described herein may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive.

We claim:

1. A process for the preparation of yttrium-silicon compounds or master alloys by silicon-carbide reduction of yttria comprising the steps:

- mixing a charge consisting essentially of yttria and silicon carbide;
- placing said charge in a vacuum furnace;
- sintering and heating said charge at a temperature of from 1,200° to 2,500°C under dynamic vacuum conditions; [whereby the yttria is reduced and a yttrium-silicon compound is produced];
- cooling said sintered charge under vacuum conditions.

2. The process of claim 1 wherein the sintering temperature is from 1,600° to 2,500°C.

3. The process of claim 2, wherein the charge of yttria and silicon carbide is in a molar ratio of about 1:3.

4. The process according to claim 1, wherein the source of yttria is rare-earth oxides high in Y_2O_3 content.

5. A process for the preparation of yttrium-silicon compounds or master alloys by silicon-carbide reduction of yttria comprising the steps:

- mixing a charge consisting essentially of yttria and silicon carbide in a molar ratio of about 1:3;
- placing said charge in a vacuum furnace;
- sintering and holding said charge at a temperature of from about 1,600° to 2,500°C for a period of time sufficient to reduce the yttria under vacuum conditions; and
- cooling said charge under vacuum conditions whereby a master alloy of Y—Si is produced.

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