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(54) Prebaked zirconium for electron beam melted barrier tube shell material.

(57) Process for producing purified zirconium by baking a distilled sponge of zirconium for at least one-half hour at 120-400°C and then EB melting the vacuum baked sponge, preferably in a multiple swept beam electron beam furnace. Preferably a rotary feeder type EB furnace is used such that the sponge can be baked and melted without being consolidated into an electrode and preferably the distilled sponge is tested and sponge having more than the desired oxygen level is rejected and only sponge having less oxygen is selected for use as the distilled sponge to be baked and EB melted.

PROCESS FOR PRODUCING PURIFIED ZIRCONIUM

This invention relates to the production of purified zirconium.

The conventional process for making zirconium metal utilizes a fluidized bed process in which the ore is subjected to a chlorination step which produces a relatively impure, hafnium-containing zirconium tetrachloride and by-product silicon tetrachloride (which by-product is relatively easily separated). The hafnium and zirconium containing material is then subjected to a number of purifying operations and also a complex hafnium separation operation. These operations result in purified oxides of zirconium and hafnium, which, of course, are maintained separate. The purified oxides are separately chlorinated. Zirconium and hafnium are commonly reduced from the chloride by means of a reducing metal, typically magnesium. At the present time, the commercial processes are batched-type processes. U.S. Patent Specification No. 3,966,460, for example, describes a process of introducing zirconium tetrachloride vapor onto molten magnesium, with the zirconium being reduced and traveling down through the magnesium layer to the bottom of the reactor and forming a metallic sponge. The metallic sponge (containing remaining chloride and some remaining excess reducing metal) is then placed in a distillation vessel for removal of the remaining salt and reducing metal by high temperature vacuum distillation. The sponge material is generally crushed, screened and pressed into electrodes for vacuum arc melting. Particularly, the material is multiple (typical double or triple) vacuum arc melted to provide ingots which are then further fabricated into various shapes. Most of the zirconium currently is used to produce Zircaloy.

Commercial nuclear reactors generally have used Zircaloy tubes as cladding material to contain the uranium dioxide fuel. Generally a Zircaloy ingot is processed into a so-called "trex" and pilgering operations are used to reduce the trex inside diameter and wall thickness to size. Ultra-pure zirconium has been proposed for a liner for the inside surface of Zircaloy tubing which is used as a cladding for nuclear fuel and is described in, for example, U.S. Patent Specification No. 4,372,817 (Armijo et al.). A similar use of moderate purity material is proposed in U.S. Patent Specification No. 4,200,492 (Armijo et al.). The ultra-pure zirconium material described has been purified by iodide cells to produce so called "crystal bar" material. This rather expensive crystal bar processing is performed after reduction and is described, for example, in U.S. Patent Specification No. 4,368,072 (Siddal).

EB (electron beam) melting of materials, including zirconium has been discussed in a number of U.S. patent specifications. EB melting has been used to consolidate crushed particles or chips in so called hearth furnaces and to separate impurities by either overflowing floating inclusions (U.S. Patent Specification No. 4,190,404 (Drs et al.) or to produce an electrode for arc melting (U.S. Patent Specification No. 4,108,644 (Walberg et al.). A number of U.S. patent specifications have used EB melting of powders or granules, often producing an ingot in a chilled mold. These powder melting EB patent specifications include U.S. Patent Specification Nos. 2,942,098 (Smith); 2,960,331 (Hanks); 2,963,530 (Hanks et al.); 2,997,760 (Hanks et al); 2,935,395 (Smith); and 4,482,376 (Tarasescu et al.). Electron beam zone refining using multiple passes is described in U.S. Patent Specification No. 3,615,345 (King).

EB melting using a consumable feed "electrode" to produce an ingot collected in a chilled mold has also been discussed in a number of U.S. patent specifications, including 3,087,211 (Howe); 3,226,223 (Bussard et al.); 2,880,483 (Hanks et al.); and 4,130,416 (Zaboronok et al.). U.S. Patent Specification No. 3,219,435 (Gruber et al.) shows a commercial type EB furnace utilizing multiple beams. Typically the beams are directed to the surface of the molten pool and are continually swept across the pool surface to avoid overheating of any single portion of the pool surface. U.S. Patent Specification No. 3,091,525 to (D. A. Hunt) describes adding a small amount of zirconium, for example, to hafnium, for example and melting in an EB furnace to deoxidize the hafnium. Japanese application 1979-144789 Kawakita, published as patent publication 1981-67788 describes the use of a very small ingot with a high power density and ultra slow melting to produce a deep molten pool to produce a high purity ingot directly usable for lining of Zircaloy tubing for nuclear reactor applications. Such laboratory sized apparatus with its high powered consumption and very low throughput is, of course, not practical for commercial production.

Accordingly, a process for producing zirconium in purified form comprises reducing zirconium tetrachloride to produce a sponge of metallic zirconium which is distilled to generally remove residual magnesium and residual magnesium chloride, and melting the distilled sponge to produce an ingot, characterized by vacuum baking the distilled sponge for at least one-half hour at 120-400°C; and electron beam melting said vacuum baked sponge.

This is a process for making a very pure material for use in the lining of the interior of zirconium alloy fuel element cladding, and having, in particular, exceptionally low oxygen. Generally this process provides material much purer than the so-called sponge material and almost as good as the crystal bar material, at a fraction of the cost of crystal bar material. Generally purified zirconium produced according to the present invention has oxygen in the 250-350 ppm range and iron in the 50-300 ppm range. Total impurities are generally in the 500-1000 ppm range (total impurities for these purposes generally comprise the elements listed in the afore-mentioned U.S. Patent Specification No. 4,200,492).
Vacuum baking in the temperature range of 120-400°C generally removes moisture absorbed on the surface of the sponge (it is felt that the moisture generally is in the form of absorbed moisture on small amounts of residual magnesium chloride salt which still may remain after distillation). The EB melting generally removes iron from the zirconium. The combined baked and EB melted material provides high purity material approaching the quality of crystal bar.

Preferably, the vacuum baked material is generally maintained in an inert atmosphere between the vacuum baking and EB melting to avoid moisture pick up. The vacuum baking can be performed within the EB furnace prior to the start of melting and the vacuum maintained until melting is begun, thus generally avoiding the regaining of moisture. Preferably, also the distilled sponge is tested and only sponge having less than about 600 ppm of oxygen is selected for use in the instant process.

It has been found that moisture has heretofore been a significant contributor of oxygen to zirconium during the normal processing. Further, our experiments have shown that only by vacuum baking within a relatively narrow temperature range can this oxygen contamination be generally avoided. This moisture, if not generally eliminated prior to melting, results in oxidizing of zirconium and magnesium, which zirconium oxide can then only be eliminated by very expensive processing (i.e., by the crystal bar process or by extremely slow and extremely high temperature EB melting as described in the afore-mentioned Japanese Patent Report 1981-67788). In addition, vacuum melting at below 250°C generally requires longer times for moisture reduction and baking at above 400°C causes the oxidation of zirconium and hydrolized $MgCl_2$ (to MgO), thus affixing the oxygen, rather than removing it.

It has generally been found that the iron impurity level is reduced by about a factor of 2 on each pass through the EB furnace (that is, when the intermediate ingot form during the first EB melting pass is used as the consumable electrode for a second EB melting, the iron level is reduced by another factor of approximately 2). As compared with copending United States patent application S.N. 871,183, filed June 5, 1986, this process makes the speed of the first EB melting less critical, and provides for a more controlled and more complete moisture removal, and thus a lower oxygen content product for a given oxygen level in the distilled sponge. Thus, generally this process gives oxygen levels in the 250-350 ppm range (which, of course, are preferred in any event, but are much more controllably obtained in the instant invention). These two inventions are desirably combinable such that the material can be prebaked, EB melted, and then vacuum arc melted for optimum properties.

Generally virgin material (as opposed to recycled scrap or turnings) is selected, generally for low oxygen content, at the sponge stage to obtain the best product. While generally low oxygen sponge material is desirable, reliably measuring such oxygen levels at the sponge stage is difficult.

While the baking at 120-400°C for at least one-half hour (and preferably for several hours including, for example, 12 to 16 hours), is most desirably done within the EB furnace such that the material can be maintained under vacuum until melting, the material can be baked in any vacuum chamber, including the EB welding chambers which are sometimes used to weld end stubs on electrodes which have been fabricated by pressing sponge material.

Conversely, the crushed sponge can be baked prior to pressing (again preferably generally keeping the material in a dry, inert atmosphere) and then pressed and possibly subjected to a second baking cycle.

Another alternative is for vacuum baking directly in a EB melter without pressing into an electrode in a furnace of the type where granules can be fed as in the aforementioned "powder melting EB patent specifications" (e.g., U.S. Patent Specification Nos. 2,942,098; 4,482,376, etc.). Some such EB furnaces are referred to as "rotary feeder" EB furnaces.

Although it is desirable to avoid exposure to the atmosphere between the vacuum baking and EB melting, the moisture pick up is apparently not extremely rapid and exposures of less than one hour to the atmosphere will generally give good results. Multiple passes through the EB furnace can, of course, be used, and may be necessary, especially if the starting material is high in iron. Multiple passes through a vacuum arc melting can, of course, follow the EB melting and, as mentioned in the aforementioned copending application, provides homogenous distribution of impurities and avoids localized impurity concentrations.

Thus, the product of this process has low total impurities, and especially a low oxygen and low iron (the iron level generally being controlled by the number of passes through the EB furnace). The process is relatively inexpensive and, being compatible with existing production processes, requires little additional capital investment.

Claims

1. A process for producing zirconium in purified form which comprises reducing zirconium tetrachloride to produce a sponge of metallic zirconium which is distilled to generally remove residual magnesium and residual magnesium chloride, and melting the distilled sponge to produce an ingot, characterized by vacuum baking the distilled sponge for at least one-half hour at 120-400°C; and electron beam melting said vacuum baked sponge.

2. A process according to claim 1, characterized in that the vacuum baked sponge is generally maintained in an inert atmosphere between vacuum baking and EB melting.

3. A process according to claim 2, characterized in that vacuum baking is performed in an EB furnace prior to melting and the EB melting is then performed without breaking vacuum.

4. A process according to claim 3, characterized in that a rotary feeder EB furnace is utilized and the sponge is melted without being consolidated into an electrode.

5. A process according to claim 3 or 4, characterized in that the EB furnace has multiple swept beams.

6. A process according to claim 3, 4 or 5, characterized in that the EB melted sponge is melted by multiple passes through a vacuum arc.

7. A process according to claim 1, characterized in that the vacuum baked sponge is exposed to the atmo sphere for less than one hour between the vacuum baking and the EB melting.

8. A process according to any of claims 1 to 7, characterized in that the distilled sponge is tested and sponge having 600 ppm or more of oxygen is rejected.