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Honma et al.

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[54] **PROCESS FOR THE PRODUCTION OF ALLOY SPONGE OF TITANIUM OR ZIRCONIUM BASE METAL BY MIXING A HALIDE OF THE ALLOYING METAL WITH TITANIUM OR ZIRCONIUM TETRACHLORIDE AND SIMULTANEOUSLY REDUCING**

[75] Inventors: **Shunzo Honma; Minoru Harada,** both of Takaoka, Japan

[73] Assignee: **Nippon Soda Company, Ltd.,** Tokyo, Japan

[*] Notice: The portion of the term of this patent subsequent to June 13, 1989, has been disclaimed.

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[58] **Field of Search** 75/84.5

[56] **References Cited**

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Primary Examiner—Leland A. Sebastian
Assistant Examiner—R. E. Schafer
Attorney, Agent, or Firm—Oblon, Fisher, Spivak, McClelland & Maier

[57] **ABSTRACT**

An alloy sponge of titanium or a zirconium base metal is produced by admixing a halide of an additive alloy element with titanium tetrachloride or zirconium tetrachloride, and thereafter reducing both simultaneously with a metallic alkali to produce said alloy of titanium or zirconium.

3 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF ALLOY SPONGE OF TITANIUM OR ZIRCONIUM BASE METAL BY MIXING A HALIDE OF THE ALLOYING METAL WITH TITANIUM OR ZIRCONIUM TETRACHLORIDE AND SIMULTANEOUSLY REDUCING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process of producing an alloy sponge of a titanium or zirconium base metal, and more particularly to a process of producing a titanium or zirconium alloy sponge, containing alloy elements such as, for example, aluminum, tin, tantalum, molybdenum, vanadium, etc.

2. Description of Prior Art

Heretofore, industrial manufacturers of titanium or zirconium sponge have generally concentrated their efforts on achieving high lelves of purity, and very little attention has been directed toward solving those problems attendant in the inclusion of impurity additives into the pure metal sponge. In producing titanium or zirconium alloys, it has been usual to melt a mixture of the pure titanium or zirconium sponge with an appropriate quantity of an additive metal. Usually, the predetermined quantity of the additive is mechanically combined with the pure titanium, or zirconium sponge, such as by mechanically mixing the sponge metal with the additive, or by coating the additive onto the sponge metal. The mixture is then pressed into briquettes and the briquettes are connected to form bars of predetermined dimensions. The thus-formed bars are then subjected to arc melting in a vacuum or in an inert atmosphere, whereby the bars are used as consumable electrodes, in order to form the necessary alloy melt. Such conventional processes, however, have not been considered to be entirely satisfactory from the point of view of efficient manufacturing production, since the steps necessary to integrate the pure titanium sponge or pure zirconium sponge, with the additive metal, in the formation of the briquettes, is quite complicated. Moreover, under certain conditions of additive metal distribution in the briquettes, significant amounts of segregation could occur in the product alloy. For instance, it has been found that due to the very great difference between the melting points of titanium or zirconium and certain additive elements, such as tantalum, tungsten, molybdenum, etc., it has not been possible to obtain complete alloying of the additive metal with the titanium. In some instances, no alloying at all is obtained, and in other instances, only small amounts of alloying is obtained, which can cause quite serious segregation effects to occur. Likewise, if the additive metal has a melting point which is significantly lower than titanium, such as is the case with aluminum, tin, etc., it has been found that serious segregation can occur, or low additive metal yields will be obtained, because of the extremely high vapor pressures these additives have at the titanium melting temperature.

In order to alleviate these problems, it has been suggested to introduce the additive element in the form of a mother alloy, such as an alloy of the type of aluminum-vanadium, aluminum-molybdenum, aluminum-chromium-vanadium, etc., but even this expedient has not proven entirely satisfactory. For example, in the case of titanium-tantalum type alloys, or titanium-molybdenum type alloys, alloying of the mother alloy with titanium or zirconium is quite difficult and is generally not considered to be an effective solution to the problem.

A need exists, therefore, for a commercially suitable technique for alloying any of a variety of additive elements with titanium or zirconium, which is economically efficient and which will produce a uniform, highly pure alloy sponge.

SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide a process for the production of an alloy sponge of titanium or zirconium, whereby a highly uniform alloy ingot may be obtained efficiently and economically.

Another object of the present invention is to provide a process of producing an alloy sponge of titanium or zirconium base metal of good uniformity and high purity.

Still another object of this invention is to provide a process of producing an alloy sponge of a titanium or zirconium base metal whereby the titanium or zirconium alloy ingots can be easily produced.

These and other objects have now herein been attained, in one aspect, by providing a process wherein a halide of an additive alloy element is admixed with titanium tetrachloride or zirconium tetrachloride, and with a metallic alkali, and thereafter simultaneously reducing the additive halide and the titanium or zirconium tetrachloride to produce metallic titanium or zirconium.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

According to the present invention, a titanium or zirconium sponge material is produced by admixing titanium tetrachloride or zirconium tetrachloride with a halide of an additive element. The mixture is then simultaneously reduced by contact with an alkali metal.

Suitable alkali metals useful in this process include sodium and potassium, although sodium is most preferred from an industrial point of view.

The additive halide may be in the form of a chloride, fluoride, iodide or bromide, but most preferred are the chlorides or fluorides. Suitable additive halides usable in the present invention may be, for example:

Al	Aluminum chloride	$AlCl_3$
Si	Silicon tetrachloride	$SiCl_4$
V	Vanadium tetrachloride	VCl_4
Mo	Molybdenum pentachloride	$MoCl_5$
Cr	Chromium trichloride	$CrCl_3$
Sn	Tin tetrachloride	$SnCl_4$
Ta	Tantalum pentachloride	$TaCl_5$
	(Potassium heptafluorotantalate)	K_2TaF_7
Fe	Ferric chloride	$FeCl_2$
Mn	Manganese chloride	$MnCl_2$
Hf	Hafnium tetrachloride	$HfCl_4$
Zr	Zirconium tetrachloride	$ZrCl_4$
W	Tungsten pentachloride	WCl_5
Nb	Niobium pentachloride	$NbCl_5$
Co	Cobalt chloride	$CoCl_2$
Ni	Nickel chloride	$NiCl_2$
Cu	Cuprous chloride	$CuCl$
P	Phosphorus pentachloride	PCl_5
S	Sulphur dichloride	SCl_2
C	Carbon tetrachloride	CCl_4
Zn	Zinc tetrachloride	$ZnCl_4$
Be	Beryllium chloride	$BeCl_2$
Y	Yttrium chloride	YCl_2
Pd	Palladic chloride	$PdCl_2$
Pt	Platinic chloride	$PtCl_2$

The additive halide may be used in the physical form of a solid or liquid. If the additive halide is liquid, it is preferable that it be premixed with liquid titanium tetrachloride before adding it thereto. On the other hand, if the additive halide is solid, it may be added in the form of fine powder or as a suspension in the titanium tetrachloride.

When the additive element is being added to zirconium tetrachloride, which is solid at room temperatures, the zirconium tetrachloride may be gassified into the reactor through a sublimation furnace and the additive element may be simultaneously reduced with the gaseous zirconium tetrachloride in either a solid or liquid form.

In the subject reaction, the alkali metal may be used in stoichiometric or less than stoichiometric amounts, although if the total of the titanium or zirconium tetrachloride and the additive halide is 0.5 or preferably 1 to 2 percent more than the stoichiometric amounts, with respect to the metallic alkali, the alloy sponge obtained thereby may have a beautiful metallic gloss, and a lower Brinell hardness than the gloss and hardness of similar alloys prepared by conventional methods.

One of the unique aspects of the present invention is that the relatively large quantity of heat generated during the reduction of the titanium or zirconium tetrachloride to a lower chloride or free metal state, is advantageously used to reduce the difficulty reduceable additive halide. For this reason, it has been found that if the additive halide is added to a lower chloride of titanium or zirconium, and simultaneously reduced with the metallic alkali, reduction is quite difficult and a high quality alloy sponge cannot ordinarily be obtained. However, various types of suitable alloys may be obtained according to the process of the present invention.

In the preferred practice of the present invention, the titanium or zirconium tetrachloride, and the halide of the additive alloy element is simultaneously partially reduced with metallic alkali at a temperature of between 600° to 800°C., so as to reduce most of the titanium or zirconium tetrachloride to the elemental metal form and to its lower chloride form, and to reduce most of the additive alloy to its elemental metal form. The reaction temperature should then be increased to about 900° to 950°C. for 1 to 10 hours. This technique provides a titanium or zirconium alloy which is characterized by large crystals having a relatively stable surface, which can be easily purified by leaching, and which is essentially devoid of surface impurities. This alloy also contains only a negligible quantity of hydrogen gas absorbed on its surface. Accordingly, the present invention results in a higher quality alloy sponge than heretofore obtainable, except by extraordinary procedures.

After the atmosphere in the reduction reactor is sufficiently replaced with an inert gas, such as argon, the predetermined amount of metallic alkali is charged to the reactor. The reactor is then heated and maintained at a temperature of 600° to 800°C., preferably 600° to 700°C. while the titanium or zirconium tetrachloride and the additive halide are gradually charged to the reactor in a predetermined ratio. An air cooled reactor jacket which is also heatable, may be provided to maintain the reaction conditions within the required range. The total charge of metallic alkali may be introduced at one time to the reactor, or it may be charged simultaneously or sequentially with the tetrachloride and the additive halide. When the tetrachloride is titanium tetrachloride, the rate of introduction of the tetrachloride and the additive halide may be adjusted by a flowmeter, and a feeder may be provided with a vibrator or the like. After the reactants are completely charged to the reactor, the reactor is further heated to a temperature of above 900°C. for 1 to 10 hours in order to complete the reaction. The product is then cooled, removed and washed with water, with dilute mineral acid solution, or with hydrochloric acid. A high purity titanium or zirconium alloy sponge of uniform composition may then be obtained. This alloy sponge may be pressed into briquette form and arc melted in an inert atmosphere or in vacuo. Ingots of titanium or zirconium alloy having an evenly distributed composition, can be produced by pressing into the briquettes after crushing and mixing the sponge of titanium or zirconium base metal, even if the ratio of the admixed base metal halide and the additive element varies, or segregation in the composition of sponge causes, because of the total amount of both halide of base metal and additive elements is predetermined desirably.

Having now generally described the invention, a further understanding of the invention can be obtained by reference to certain specific Examples which are presented herein for purposes of illustration only, and are not intended to be limiting unless otherwise specified.

EXAMPLE (Ti-Al-Sn)

96.2 kg of metallic sodium, filtered and refined under an argon atmosphere, was charged into an iron reactor of 640 × 1600 mm. in size. The reactor was heated to 600°C. in an electric furnace. Then, 186 kg. of titanium tetrachloride containing 2.74 kg. of tin tetrachloride was charged into a raw material weighing tank, and 12.4 kg. of aluminum chloride crystals were charged into a powder charging tank. Both were then charged into the reactor vessel in such a manner that the ratio of both materials were held at a predetermined rate. The reaction temperature was maintained at 630° to 750°C. to effect the primary reaction. The aluminum chloride was continuously charged in such a manner that the charging amount thereof was adjusted by using a vibrator. After approximately 12 hours, the aluminum chloride was fully introduced. The reactor was heated to 950°C. for 5 hours to complete the secondary reaction, and the reacted product was cooled and discharged. After the reacted product had been leached with 1,000 liters of 1 percent hydrochloric acid and had then been washed, the product was dried in vacuo at 60°C. The alloy sponge thus obtained had a grain size of 2–60 meshes and was black in color. A yield, or available percentage, of 85 percent was obtained. In examining a dispersion of the constituents of the additive alloy in a specimen, it was found that it contained 4.6 to 5.1% Al and 2.4 to 2.7% Sn indicating the composition as Ti–5Al–2.5 Sn. A hydrogen content of 0.0022 to 0.0026 percent was also found. Thus, a uniform and superior titanium alloy sponge containing only a slight amount of hydrogen was obtained. This specimen was formed into a briquette which was arc melted to form an ingot button. The Brinell hardness of the button was 276 to 283.

EXAMPLE 2 (Ti-Al-Sn)

Using the iron reactor described in Example 1, 305 kg. of titanium tetrachloride containing 4.8 kg. of tin tetrachloride and 26.8 kg. of aluminum crystals were charged into the reactor, together with 160 kg. of metallic sodium. The reactor was heated to 640° to 730°C. and maintained at this temperature. The other steps described in Example 1 were performed. The product thus obtained was a black sponge and its yield percentage was 87 percent. Analysis of this product showed that it was a titanium alloy sponge containing 5.0% Al and 2.4% Sn, and 0.0022 percent hydrogen. This sponge product was formed into briquettes which were arc melted to form a button ingot. The Brinell hardness of the button was 282.

EXAMPLE 3 (Ti-Al-V)

97.9 kg. of metal sodium was filtered and refined under an argon atmosphere and was charged into the iron reactor used in Example 1. The reactor was heated to 600°C. by an electric furnace, and 185.8 kg. of titanium tetrachloride containing 7.6 kg. of vanadium tetrachloride and 14.8 kg. of aluminum chloride crystals were charged into the iron reactor vessel such that the ratio of the reactants corresponded to predetermined ratios. The reactants were then heated to 620° to 750°C. After the reactants had been completely charged to the reactor within 5 hours, the reactor was further heated to 930° to 960°C. for 5 hours to complete the reaction. The product was cooled and discharged, and was leached with 1,000 liters of 1 percent hydrochloric acid and washed. It was then dried in vacuo at 60°C. The product obtained had a grain size of 2 to 60 meshes and was black in color. Its yield percentage was 85 percent. The constituents of the alloy sponge were found to be 5.9% Al and 4.0% V. Thus, a titanium alloy sponge having the composition of Ti-6Al-4V of commercial titanium alloy, was obtained. Its hydrogen content was 0.0030 percent. This sponge was formed into a briquette which was melted to form an ingot button. The Brinell hardness of the button was found to be 310.

EXAMPLE 4 (Ti-Ta)

Using the iron reactor vessel described in Example 1, 188.1 kg. of titanium tetrachloride was charged into the raw material weighing tank, and 5.42 kg. of potassium fluoric tantalum crystal was charged into the reactor charging tank. 92.8 kg. of metallic sodium was charged into the reactor and was heated at 650°C. under an argon atmosphere. Thereafter, titanium tetrachloride and potassium fluoric tantalum were charged into the reactor at a predetermined ratio for 8 hours. The reactor was heated at 720° to 780°C. The materials in the reactor were then heated to 930° to 960°C. for 5 hours to complete the reaction. The product obtained was cooled and discharged and leached with 800 liters of 1 percent hydrochloric acid and then washed. It was dried in vacuo at 65°C. and it was found to be black in color with a yield percentage of 84 percent. The product was identified as a titanium alloy containing 5.2% Ta and 0.0030 percent hydrogen. It was subjected to arc melting to form a button ingot which was found to have a Brinell hardness of 140.

EXAMPLE 5 (Ti-Al)

Using the iron reactor described in Example 1, 192 kg. of titanium tetrachloride was charged into a raw material weighing tank, and 7.4 kg. of finely crushed aluminum chloride was added thereto. The mixture was agitated continuously. 96.9 kg. of metallic sodium was charged into the reactor vessel and it was heated to 600°C. under an argon atmosphere. Thereafter, aluminum chloride suspended in titanium tetrachloride was gradually dropped into the reactor over an 8 hour period and then reacted at 640° to 725°C. The reaction was then further heated to 920° to 950°C. for 5 hours in order to complete the reaction. The product so obtained was cooled and discharged and leached with 1,000 liters of 1 percent hydrochloric acid solution. After washing and drying in vacuo at 60°C., the black sponge product was found to be a titanium alloy containing 3.0% Al and 0.0024 percent hydrogen. Similarly, products containing 7.0% Al and 10.0% Al were produced. The aluminum content in the alloy sponge may be freely adjusted as desired.

EXAMPLE 6 (Zr-Sn)

503 kg. of metallic sodium, filtered and refined under an argon atmosphere, was charged into the iron reactor described in Example 1 which was heated to 700°C. in an electric furnace. A mixture of gaseous zirconium tetrachloride and tin tetrachloride in a ratio of 125.8 kg. of zirconium tetrachloride to 1.650 kg. of tin tetrachloride, corresponding to 98.5% Zr to 1.5% Sn, was heated to 350°C. and charged into the reactor. The temperature of the reaction was held at 720° to 780°C. After the raw materials were completely charged to the reactor over a period of approximately 12 hours, the materials were heated to 900° to 950°C. for 6 hours to complete the reaction. The product obtained was leached with 1,200 liters of 1 percent hydrochloric acid, and then was washed and thereafter dried in vacuo at 65° C. The product thus obtained was a gray sponge and its yield percentage was found to be 83 percent. As a result of analysis of the additive alloy constituents, the product was found to contain 1.3 to 1.6% Sn showing the composition of 1.5Sn-Zr alloy. The alloy also was found to contain 0.0032 percent hydrogen. This sponge was formed into briquettes which were arc melted to form button ingots having a Brinell hardness of 135.

EXAMPLE 7 (Zr-Nb)

608 kg. of metallic sodium was filtered and refined under an argon atmosphere, heated at 650°C., in an electric furnace and charged into the iron reactor described in Example 1. A mixture of gaseous zirconium tetrachloride and niobium pentachloride of a predetermined ratio of 150.1 kg. of zirconium tetrachloride to 3.64 kg. of niobium pentachloride, corresponding to 97.5% Zr to 2.5% Nb, was heated at 350°C. and charged into the reactor. The reaction was effected at 700° to 760°C. After the reactants were completely charged into the reactor over a period of approximately 10 hours, the materials were then heated to 920° to 960°C. for 6 hours to complete the reaction. The product was cooled and discharged and leached with 1,000 liters of 1 percent hydrochloric acid. It was then washed and dried in vacuo at 60°C. to obtain a gray sponge. The yield percentage of the sponge was 82 per-

cent and the alloy constituents were found to be 2.2 to 2.4% Nb and 0.0035 percent hydrogen.

All of the button ingots obtained by arc melting the titanium or zirconium alloy sponge, as described in the above Examples, had glossy metal skins and had similar hardness to that produced by conventional processes. This clearly indicates that the process of this invention is suitable for providing a high quality alloy sponge.

In addition to the alloy compositions described in the above Examples, the process of the present invention may also be equally applied to obtaining alloy compositions such as, for example: Ti-8Al-1Mo-1V, Ti-5Al-2Cr-1Fe, Ti-6Al-6V-2Sn, Ti-8Mn, Ti-4Al-3Mo-1V, Ti-13V-11Cr-3Al, Ti-15Mo-5Zr, Ti-5Al-5Sn-5Zr-2Cr-1Fe, Ti-0.2Pd, Ti-11Sn-5Zr-2.5Al-0.25Si, in case of titanium Zr-Sn-Fe-Cr (Ni)-Nb base metal, series Zr-Cr-Mo-(Fe) series, in case of zirconium base metal.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention. Accordingly,

What is claimed as new and intended to be covered by Letters Patent of the United States is:

1. A process of producing an alloy sponge of a titanium or zirconium base metal, which comprises;

introducing titanium tetrachloride or zirconium tetrachloride, one or more alloy element metal halides selected from the group consisting of $AlCl_3$, $SiCl_4$, VCl_4, $MoCl_5$, $SnCl_4$, $TaCl_5$, K_2TaF_7, $FeCl_2$, $MnCl_2$, $CrCl_3$, $HfCl_4$, $ZrCl_4$, WCl_5, $NbCl_5$, $CoCl_2$, $NiCl_2$, CuCl, PCl_5, SCl_2, CCl_4, $ZnCl_4$, $BeCl_2$, YCl_2, $PbCl_2$, and $PtCl_2$, and a metallic alkali as a reducing agent into a reactor vessel having no mixing means,

maintaining the mixture at a temperature within the range of 600° to 800° C., then completing the reduction reaction in the same reactor at a temperature range of 900° to 950° C. for 1 to 10 hours,

washing the reaction product with a dilute mineral acid aqueous solution.

2. A process of claim **1**, wherein the total amount of titanium or zirconium tetrachloride and the halide of additive alloy element is 0.5 to 2.0 percent greater than the stoichiometrical amount with respect to the metallic alkali.

3. A process of claim **1**, wherein the metallic alkali is metallic sodium.

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