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(54) A METHOD OF PREPARING NITRIDES, OXIDES OR OXYNITRIDES OF REFRACTORY METALS AND SOLID SOLUTIONS OF SAID COMPOUNDS

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The invention relates to a method of preparing nitrides, oxides and oxynitrides of refractory metals and solid solutions of said compounds.

These compounds are used as highly refractory and corrosion-resistant materials, e.g., in the production of monocrystals, as elements in microelectronics, laser engineering and as alloying additives.

Previously proposed methods for preparing nitrides of refractory metals include nitriding metal hydrides, e.g., titanium nitride is produced at 1800—1900°C, by reacting titanium hydride and ammonia in an arc discharge. The application of these methods to the industrial scale manufacture of chemically and granulometrically homogeneous products is very difficult.

There are various chemical methods of preparing individual oxides of refractory metals, but it is difficult to obtain products of a uniformly fine particle size by such techniques.

No industrial methods of producing oxynitrides as individual compounds are described in literature.

Methods are known for preparing solid solutions of nitrides and oxides of refractory metals which are based on prolonged sintering of mixtures of starting compounds or oxidizing or nitriding sintered metal alloys at high temperatures. The products obtained

by these methods are then subjected to grinding to the required degree of fineness. The above-said methods, however, are disadvantageous in that the products are chemically and physically non-homogeneous.

An object of the present invention is to obviate or mitigate the aforesaid disadvantages.

According to the present invention there is provided a method of preparing nitrides, oxides and oxynitrides of refractory metals and solid solutions thereof comprising evaporating a metal or an alloy thereof in the form of a consumable electrode in an electric arc, in a gaseous medium of nitrogen and/or oxygen at a pressure of from 2 to 7 atmospheres, wherein the arc is an alternating current arc operating at a current of from 5 to 15 Amps per cm² of the electrode working surface, an electrode voltage of from 10 to 20 kW and an arc length of from 10 to 15 mm.

The term "refractory metal" as used herein and in the claims is intended to include silicon.

Solid solutions of the nitrides, oxides and oxynitrides of more than one metal may be produced by either of two methods. Each of the pair of electrodes may be made of a different metal or alternatively the electrodes may be made of alloys.

The process may be carried out in an airtight apparatus with coaxial and axially movable cooled conductors. The conductors may be provided with a device for attachment of electrodes made of metals which are used in preparing the aforesaid compounds or their solid solutions (the connection of an electrode with a conductor can be effected, e.g., by screwing, and therefore the conductors and electrodes in such a case are threaded). The electrodes may be cylindrical or prismatic rods whose end faces must be parallel since they are the electrode working surfaces.

The apparatus on the inside surface of

which the compound or the solid solution deposits is preferably made of a stainless steel or titanium and provided with a water jacket. The specific volume of the apparatus is preferably about 25 litres per kg of the product formed per cycle.

The apparatus is preferably evacuated before filling with purified nitrogen and/or oxygen. It is also possible to introduce into the mixture a gas which is inert to the starting metals and products. The inert gas is preferably argon. The pressure of the gas is established and maintained during the process within a range from 2 to 7 atm. The electrodes are drawn closer to one another until a 10—15 mm distance between the parallel working surfaces is reached.

An electric arc is struck and is maintained between the electrodes by using a high-voltage high-frequency generator. The current density is from 5 to 15 A per cm² of the working surface of the electrode with the electrode voltage being from 10 to 20 kW. As the electrodes are consumed, they are drawn closer together so that the distance between them remains in the range of from 10 to 15 mm.

Under these conditions the metal vapours react quantitatively with nitrogen and/or oxygen to form compounds which condense from the gaseous phase into homogeneous microaggregates and precipitate on to the cooled inside surface of the apparatus.

Advantages of the proposed method are that the compounds or solid solutions are obtained directly as particles having chemical, physical and granulometric homogeneity in a yield of practically 100 per cent. There is no contamination of the product with by products or with materials of the apparatus, since the metals showing reactivity in the vaporous state contact only the gaseous reactant.

The present invention will now be described, by way of illustration, in the following Examples.

Example 1

Titanium nitride was prepared by the method of the invention in a 10 litre apparatus made of stainless steel. The metallic titanium used was of more than 99% purity and the nitrogen contained about 0.005 vol.% of oxygen. The electrodes were rods of metallic titanium, each 100 g in weight, 60 mm long and 3 cm² in cross section of the working surface.

The apparatus was evacuated to 0.05 mm Hg pressure and filled with nitrogen to a pressure of 4 atm. The process was carried out at a current of 10 A per cm² of the electrode working surface and an electrode voltage of 20 kW. The nitrogen pressure was maintained between 4 and 7 atm. and the arc length was from 10 to 15 mm. The reaction was allowed to proceed for 38 hrs.

There were obtained 195 g of titanium nitride which contained 22.4% of nitrogen (TiN_{0.99}, where 0.99 is the number of nitrogen gram atoms per gram atom of titanium).

According to X-ray analysis the product contained one phase: titanium nitride of a face-centered cubic lattice. The grain size of the titanium nitride powder was 0.001—0.01 μ. The yield of the final product was 97% by weight of the metal used. The residues of the electrodes were butted and reused. Their total weight was 45 g.

Example 2

In the apparatus as described in Example 1 there was prepared the solid solution: ZrNb₂O₇, that is, ZrO₂.Nb₂O₇. The starting metals were of more than 98% purity. The electrodes were rods: one of metallic niobium, 120 g in weight, 3 cm² in cross section, 4.75 cm in length; and the other of metallic zirconium: 60 g in weight, 2 cm² in cross section and 3.0 cm in length.

The apparatus was evacuated to 0.05 mm Hg and filled with oxygen to a pressure of 3 atm. The process was carried out for 6 hours at a 10 A current density per cm² of the electrode working surface and an electrode voltage of 20 kW. During the process the arc length was kept between 10 and 15 mm and the oxygen pressure between 2 and 4 atmospheres.

There were obtained 150 g of powder that was a theoretical 98% yield by weight of the metals used. According to chemical analysis the composition of the substance was ZrNb_{2.10}O_{7.23}. X-ray analysis confirmed the presence of the solid solution ZrO₂.Nb₂O₇. The residues of the electrodes were Zr, 12.5 g and Nb, 17.0 g. The grain size of the powdered solid solution was 0.001—0.01 μ.

Example 3

To obtain a solid solution of the formula TiNbN₂ or TiN · NbN there were used metals of a 98% purity.

The electrodes were rods; one was made of metallic niobium, 100 g in weight, 3 cm² in cross section, and 3.9 cm in length and the other was metallic titanium 55 g in weight, 3 cm² in cross section and 4.0 cm in length.

The apparatus was evacuated to 0.05 mm Hg and filled with nitrogen to a pressure of 3 atm. The process was carried out for 20 hours at a 10 A current per cm² of the electrode working surface and an electrode voltage of 20 kW. During the process the arc length was kept between 10 and 15 mm and the oxygen pressure from 3 to 6 atm.

There were obtained 140 g of the powder (98% of theoretical yield) with a grain size of 0.001—0.01 μ. According to chemical analysis, the composition of the substance was TiNb_{0.997}N_{1.997} or TiN · (NbN)_{0.997}. X-ray

analysis confirmed the presence of a single phase of the solid solution $TiN \cdot NbN$. The residues of the electrodes were Ti, 15 g and Nb, 23 g.

Example 4

To obtain titanium oxide of the formula TiO_2 , there was used metallic titanium of higher than 98% purity. The electrodes were rods, each 50 g in weight, 3 cm^2 in cross section and 3.75 cm in length. The apparatus was evacuated to 0.05 mm Hg and filled with oxygen and argon (at a volume ratio of 1:1) up to a total pressure of 4 atm. The process was carried out for 15 hours at a 10 A current per cm^2 of the electrode working surface and an electrode voltage of 20 kW. During the arc length was kept between 10 and 15 mm and the total gas pressure from 3 to 5 atm. The gas pressure was maintained by introducing oxygen.

These were obtained 131 g of powder that amounted to a 98% yield. Its grain size was 0.001—0.01 $m\mu$. The composition of the substance according to chemical analysis was $TiO_{2.00}$. X-ray analysis confirmed a single TiO_2 phase.

The residues of the electrodes came to 20 g.

Example 5

To obtain niobium oxide of the formula Nb_2O_5 , there was used metallic niobium of a purity higher than 98%. The electrodes were niobium rods, each 110 g in weight, 3 cm^2 in cross section and 4 cm in length.

The apparatus was evacuated to 0.05 mm Hg and filled with oxygen and argon (at a volumetric ratio of 1:1) up to 4 atm. pressure. The process was carried out for 20 hours at 10 A current per cm^2 of the electrode working surface and an electrode voltage of 20 kW. During the process the arc length was kept between 10 and 15 mm and total gas pressure from 3 to 5 atm. The gas pressure was maintained by introducing oxygen.

There were obtained 277 g of powder with a grain size of 0.001—0.01 $m\mu$. Chemical analysis showed the composition of the substance as being $Nb_2O_{5.00}$. X-ray analysis confirmed a single Nb_2O_5 phase. The residues of the electrodes came to 22 g. The yield of the final product was 98%.

Example 6

To obtain niobium oxynitride of the formula $Nb_2O_5N_2$ (or $Nb_2O_5 \cdot 2NbN$) there was used metallic niobium of a purity higher than 98%. The electrodes were rods, each 110 g in weight, 3 cm^2 in cross section and 4 cm in length.

The apparatus was evacuated to 0.05 mm Hg and filled with a mixture of oxygen and nitrogen (at a volumetric ratio of 1:1) up

to 3 atm. pressure. The process was carried out for 25 hours at 10 A current per cm^2 of the electrode working surface and an electrode voltage of 20 kW. During the process the arc length was kept between 10 and 15 mm and the pressure of the gas mixture from 2 to 4 atm. The pressure was maintained by introducing a mixture of O_2 and N_2 in a volumetric ratio of 5:2.

There were obtained 250 g of the powder (indicative of a 98% yield) with a grain size of 0.001—0.01 $m\mu$. Chemical analysis showed the composition of the substance to be $Nb_2O_5N_2$. X-ray analysis confirmed only a $Nb_2O_5N_2$ phase. The residues of the electrodes came to 22 g.

Example 7

To obtain titanium oxynitride of the formula Ti_2ON_2 , there was used metallic titanium of a purity higher than 98%. The electrodes were rods, each of them being 50 g in weight, 3 cm^2 in cross section and 3.75 cm in length. The apparatus was evacuated to 0.05 mm Hg and filled with oxygen and nitrogen (at a volumetric ratio of 1:2) to 3 atm. pressure. The process was carried out for 10 hours at a 10 A current density per cm^2 of the electrode working surface and an electrode voltage of 20 kW. During the process the arc length was kept between 10 and 15 mm and the pressure of the gas mixture from 2 to 4 atm. The pressure was maintained by introducing a mixture of O_2 and N_2 in a volumetric ratio of 1:2. There were obtained 102 g of the powder (a 98% yield) with a grain size being 0.001—0.01 $m\mu$.

Example 8

To obtain silicon nitride of the formula Si_3N_4 there was used elementary silicon with n-type conductivity and of a purity higher than 98%.

The electrodes were rods, each of them being 85 g in weight, 4.5 cm^2 in cross section and 4.5 cm in length.

The apparatus was evacuated to 0.05 mm Hg and filled with nitrogen up to 3 atm. pressure. The process was carried out at 8 A current per cm^2 of the electrode working surface and an electrode voltage being 20 kW. During the process the arc length was kept between 10 and 15 mm and the nitrogen pressure from 2 to 4 atm.

There were obtained 166 g of the powder (a 98% yield). Its grain size was 0.001—0.01 $m\mu$. Chemical analysis showed the composition of the substance as being Si_3N_4 . X-ray analysis confirmed a single phase of Si_3N_4 . The residues of the electrodes came to 25 g.

Example 9

To obtain silicon nitride of the formula Si_3N_4 , there was used elementary silicon (of

a purity higher than 98%) with n-type conductivity.

5 The electrodes were rods, each 85 g in weight, 4.5 cm² in its cross section and 4.5 cm in length.

10 The apparatus was evacuated to 0.05 mm Hg and filled with nitrogen up to 6 atm. pressure. The process was carried out at 8 A current per cm² of the electrode working surface and an electrode voltage of 20 kW. During the process the arc length was kept between 10 and 15 mm and the nitrogen pressure from 6 to 7 atm.

15 There was obtained 244 g of the powder (a 98% yield). Its grain size was 0.001—0.01 m μ . Chemical analysis showed the composition of the substance as being Si₃N₄. The residues of the electrodes came to 20 g.

WHAT WE CLAIM IS:—

20 1. A method of preparing nitrides, oxides and oxynitrides of refractory metals and solid solutions thereof comprising evaporating a metal or an alloy thereof in the form of a consumable electrode in an electric arc, in a
25 gaseous medium of nitrogen and/or oxygen at a pressure of from 2 to 7 atmosphere, wherein the arc is an alternating current arc operating at a current of 5 to 15 Amps per cm² of the electrode working surface, an electrode voltage of from 10 to 20 kW
30 and an arc length of from 10 to 15 mm.

2. A method according to claim 1 where-

in the nitrogen and/or oxygen is diluted with a gas which is inert both to the starting metals and to the final product.

3. A method according to claim 2 where- 35 in the inert gas is argon.

4. A method according to claim 1 or 2 or 3 wherein solid solutions of the products are obtained by the use of electrodes each made 40 of a different metal.

5. A method according to claim 1 or 2 or 3 wherein solid solutions of the products are obtained by the use of electrodes made 45 of alloys.

6. A method of preparing nitrides, oxynitrides and oxides of refractory metals and solid solutions of said compounds substantially as hereinbefore described in Ex- 50 amples 1 to 9.

7. Nitrides, oxides and oxynitrides of refractory metals and solid solutions of said compounds whenever prepared by the method claimed in any of claims 1 to 6.

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