United States Patent Office

3,736,270

Patented May 29, 1973

3,736,270

SOLID COMPOUND OF RHODIUM AND TUNGSTEN AND MANUFACTURING PROCESS THEREFOR

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No Drawing. Filed July 29, 1971, Ser. No. 167,517
Claims priority, application Belgium, July 29, 1970, 61,435
Int. Cl. C01g *41/00, 55/00;* H01b *1/08*
U.S. Cl. 252—518 3 Claims

ABSTRACT OF THE DISCLOSURE

Rh_2WO_6 crystallized in the tetragonal system under the trirutile form, the parameters a_0 and c_0 being 4.609 and 9.083 A. respectively, having an electrical conductivity of 10^{-4} (ohm·cm.)$^{-1}$ and energy gap of 0.03 e.v.

BACKGROUND OF THE INVENTION

The present invention relates to a new oxygen-containing compound of rhodium and tungsten, Rh_2WO_6, and to a manufacturing process therefor.

SUMMARY OF THE INVENTION

The present invention concerns a compound Rh_2WO_6.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The new compound was prepared from powdered

Rh_2O_3

and WO_3 which were mixed in equimolecular quantities, then comminuted and pelletized.

The starting oxide Rh_2O_3 was obtained by pyrolysis at 500° C. of pure rhodium nitrate supplied by Fluka, whereas the WO_3 was a product supplied by UCB, chemical analysis grade.

In an example, 2.32 g. of the WO_3 and 2.54 g. of the resultant Rh_2O_3 were mixed together. Then during a period of 1 hour, the mixture was comminuted dry in a steel ball mill lined with tungsten carbide and provided with tungsten carbide balls in order to obtain a well homogenized mixture which was then pelletized in the shape of a disc at room temperature under a pressure of 1000 kg./cm.^{2} (6.35 tons per square inch) and heated in air at 950° C., for 24 hours.

The resultant black porous disc of Rh_2WO_6 was then comminuted in the aforesaid ball mill until all particles had a particle size of one micron or below.

An X-ray crystallographic analysis carried out on the thus obtained powder showed that the Rh_2WO_6 crystallizes in the tetragonal system and belongs to the trirutile type. The unit cell has the following parameters:

a_0=4.609 A. and c_0=9.083 A.

The unit cell contains two molecules of Rh_2WO_6.

The intensities of the lines and the observed interplanar

spacings determined in the X-ray crystallographic analysis are given in the following table.

Intensity	Miller indices h	k	l	Interplanar spacing d (A.) Rh_2WO_6
ff	0	0	2	4.54
ff	1	0	1	4.11
TF	1	1	0	3.26
F	1	0	3	2.53
mf	2	0	0	2.305
f	1	1	3	2.218
f	2	0	2	2.06
ff	2	1	1	2.01
ff	1	1	4	1.863
mF	2	1	3	1.704
f	2	2	0	1.629
ff	2	0	4	
f	0	0	6	1.514
f	3	1	0	1.458
mf	3	0	3	1.372
f	2	0	6	1.266

The X-ray crystallographic data show that the thermal treatment of the starting oxides is sufficient to obtain a complete loss of identity of the starting oxides with complete conversion to pure Rh_2WO_6 in a good crystalline state.

In order to measure the electrical conductivity of the obtained Rh_2WO_6, the powder resulting from comminuting the porous disc was again pelletized under the same conditions used for pelletizing the Rh_2O_3-WO_3 mixture. The measured electrical conductivity was in the range of 10^{-4} (ohm·cm.)$^{-1}$. The obtained Rh_2WO_6 is thus really a semiconductor and its forbidden gap, or energy gap, amounts to 0.03 e.v. The terms "forbidden gap" and "energy gap" refer to the distance between the top of the valence band and the bottom of the conduction band; these terms appear, for instance, in "Physics and Technology of Semiconductor Devices" by A. S. Grove, pages 91–95 and 102.

The manufacturing process for the compound of the present invention is very easy and the operative conditions are easily reproducible.

Used as an anodic operative surface in the electrolysis of sodium chloride, the new compound presents very interesting polarization properties and is very resistant to electrochemical attack under cell conditions.

On account of its properties, the compound Rh_2WO_6 of the present invention is very useful for industrial applications not only as an electrode in various electrochemical processes, but also as an oxidation catalyst in organic chemistry or as a component in composite semiconductive devices.

The starting materials were obtained from Fluka, CH–9470 Buchs (Switzerland) and UCB, 33 rue d'Anderlecht, 1620 Drogenbos (Belgium).

The trademark designation of the rhodium nitrate was rhodium (III)-nitrat Dihydrat purissimum No. 83,760. The trademark designation of the WO_3 was anhydride tungstique pour analyse No. 1925. The rhodium nitrate was supplied in a purity grade designated as "purissimum"

which meant a chemical analysis in weight-percent as follows:

31.7% Rh

the WO_3 was supplied in a purity grade designated as: "chemical analysis" which meant a chemical analysis in weight-percent as follows:

	Percent
Insoluble in diluted NaOH	Max. 0.03
Chlorides	Max. 0.0015
Heavy metals (Pb)	Max. 0.002
Iron (Fe)	Max. 0.004
Molybden (Mo)	Max. 0.05
Ammonium (NH_4)	Max. 0.0015
Arsenic (As)	Max. 0.0015
WO_3	Balance

The chemical analysis of the resultant Rh_2WO_6 was in weight-percent as follows:

	Percent
Rh	42.4
W	37.9
O	Balance

The X-ray crystallographic data of the table were obtained by irradiating the comminuted product with a beam of Cu Kα radiation. The intensity designations are according to the ASTM system as follows:

Designation in table	ASTM (relative intensity) 100 I/I_0
TF: Very, very strong	100
mF: Very strong	90
F: Strong	80
	70
m: Medium	60
	50
f: Weak	40
	30
mf: Faint	20
ff: Very faint	10

Demonstrating the utility of the Rh_2WO_6 of the present invention for carrying out the half reaction $2Cl^- \rightarrow Cl_2 + 2e$ is the following example. The comminuted product was spread on a titanium plate and subjected to a pressure of 1000 kg./cm.^{2} at a temperature of 475° C. for 20 minutes to provide a coating of 5 grams/m.^{2} of titanium surface. The coating side of the titanium plate was then subjected, as anode, to two different tests: the first one to measure the overvoltage for the liberation of chlorine under a given anodic current density (10 ka./m.^{2}), the second one to determine the wear or consumption of noble metal as related to the quantity of evolved chlorine. The term "overvoltage" is used herein in the same since as it is used at pages 488–492 of "Physical Chemistry" by Walter J. Moore, Prentice-Hall Inc., second edition. In the overvoltage test the coated plate was used as anode for the electrolysis of a brine containing 250 g. NaCl/kg. of solution saturated with chlorine at 60° C. and at an approximate pH of 2. Under these conditions, the coated plate of this example showed an overvoltage in the range 250 mv. under an anodic current density of 10 ka./m.^{2}. In the wear test, the coated plate was used as anode in a cell with a flowing mercury cathode for the electrolysis of a brine saturated with sodium chloride and chlorine, between 80 and 85° C., under a constant anode-cathode potential difference, the test being stopped when the current density was reduced to one half of its initial value (initial value generally was between 30 and 40 ka./m.^{2}). Under these conditions, the tested plate produced 9 tons of chlorine per square meter of active surface; the rhodium consumption lay below 200 mg. per ton of chlorine produced under an average current density of 20 ka./m.^{2}.

After the 2.32 g. of WO_3 and 2.54 g. of Rh_2O_3 have been comminuted, the well homogenized mixture has a particle size distribution lower than 1μ.

The pelletizing is carried out without any binding additive.

It will be understood that the above description of the present invention is susceptible to various modifications, changes and adaptations, and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.

We claim:

1. Rh_2WO_6 crystallized in the tetragonal system under the trirutile form, the parameters a_0 and c_0 being 4.609 and 9.083 A. respectively, having an electrical conductivity of 10^{-4} (ohm·cm.)$^{-1}$ and an energy gap of 0.03 e.v.

2. Rh_2WO_6 as claimed in claim **1** and having line intensities and interplanar spacing as follows:

Intensity	Miller indices h	k	l	Interplanar spacing d (A.) Rh_2WO_6
ff	0	0	2	4.54
ff	1	0	1	4.11
Tf	1	1	0	3.26
F	1	0	3	2.53
mf	2	0	0	2.305
f	1	1	3	2.218
f	2	0	2	2.06
ff	2	1	1	2.01
ff	1	1	4	1.863
mF	2	1	3	1.704
f	2	2	0	1.629
ff	2	0	4	
f	0	0	6	1.514
f	3	1	0	1.458
mf	3	0	3	1.372
f	2	0	6	1.266

3. A method for making Rh_2WO_6 as claimed in claim **1**, comprising the steps of mixing equimolecular quantities of WO_3 and Rh_2O_3, comminuting the resulting mixture, pelletizing the result of the step of comminuting, and heating the pellets at 950° C. in an oxidizing atmosphere for a period of time sufficient to produce Rh_2WO_6 as claimed in claim **1**.

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U.S. Cl. X.R.

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