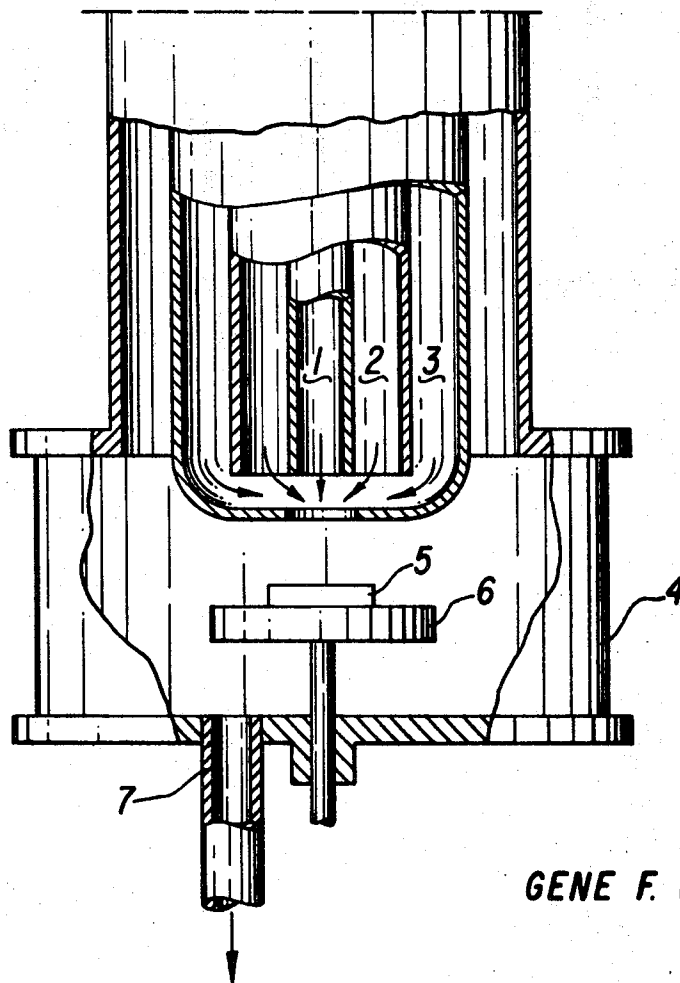


Nov. 17, 1970

G. F. WAKEFIELD
PROCESS OF SIMULTANEOUSLY VAPOR DEPOSITING SILICIDES
OF CHROMIUM AND TITANIUM
Filed Aug. 24, 1967

3,540,920



GENE F. WAKEFIELD
INVENTOR

BY

Robert F. Wakefield

ATTORNEY

1

3,540,920

PROCESS OF SIMULTANEOUSLY VAPOR DEPOSITING SILICIDES OF CHROMIUM AND TITANIUM

Gene F. Wakefield, Richardson, Tex., assignor to Texas Instruments Incorporated, Dallas, Tex., a corporation of Delaware

Filed Aug. 24, 1967, Ser. No. 662,923

Int. Cl. C23c 11/08

U.S. Cl. 117—106

3 Claims 10

ABSTRACT OF THE DISCLOSURE

Process for chemically vapor depositing silicides of titanium and chromium upon a heated substrate by the reduction of silicon, chromium and titanium halides with hydrogen.

Related patent application: Ser. No. 579,963, filed Sept. 16, 1966.

This invention relates to the deposition of metal silicides upon a substrate by the reduction of silicon and metal halides with hydrogen.

Refractory metals, such as tantalum, molybdenum, columbium (niobium) and tungsten, by way of examples, are especially desirable for applications requiring high strength at elevated temperatures, particularly where ease of fabrication and ductility are needed. However, before any of these metals can satisfy a wide range of requirements, they must receive an oxidation resistant coating. Silicides of metals such as titanium and chromium, being metallurgically compatible with refractory metals, form a good coating which protects these refractory metals against oxidation.

While many techniques can be employed to prepare such silicide coatings, several features make the vapor streaming technique of chemical vapor deposition especially desirable. Process parameters may be individually and accurately controlled, allowing high reproducibility. Also, the chemical vapor deposition process possesses the inherent property of forming an overlay coating, that is, a coating which can be applied to a substrate with minimum interaction.

A readily apparent advantage of the vapor streaming technique of chemical vapor deposition is the possibility of depositing silicide coatings of successively different materials by varying the chemicals in the reactant gas phase. In addition, coatings of varying or graded composition (as compared to multi-layered composites) can be obtained by varying the relative concentrations of the reactants as the deposition takes place. As a result, multi-component coatings of controlled composition can be deposited in a single coating operation.

The advantages of the vapor streaming technique of chemical vapor deposition are emphasized by comparison with the alternative processes for the formation of metal silicide coatings for oxidation protection of refractory metals. Such coatings are conventionally applied by one of three processes. One is the "pack" or "vacuum pack" process which involves the heating of the articles to be coated in a granular mixture consisting of reactive materials and inert particles. See for example, Pat. No. 3,293,068 granted to E. F. Bradley et al. Dec. 20, 1966. During a relatively long cycle of several hours, a metal coating can be diffused into the surface of the article. This process is then repeated using reactive silicon materials to transfer silicon into the coating. Again, the time required is several hours. This type of coating process necessarily results in considerable interdiffusion of the coating and the substrate, and therefore will contain ele-

2

ments of the substrate dissolved in the coating, thus limiting the composition of the coatings that can be obtained.

A second process is the fluidized bed process wherein the materials to be coated are heated in a fluid bed reactor. Such a reactor lessens the time required to form a coating but nevertheless results in the same type of diffused coating. A third method for the formation of the silicide coating is the "slurry" method, whereby powders of the elements to be included in the coating are painted on the surface to be coated, and then the coated article is heated in a furnace to react and form the coating. Such a process will, in general, include in the coating impurities acquired during the handling of the metal and the silicon powders.

In accordance with the method of this invention, coatings of metal silicides are formed upon a substrate by the reduction of silicon and metal halides with hydrogen.

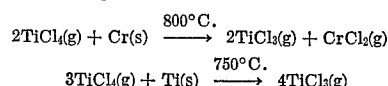
Accordingly, it is an object of the invention to provide a method of chemically vapor depositing metal silicides upon a substrate. Further objects are to provide a method of depositing multicomponent coatings and of forming graded composition coatings.

These and other objects, features and advantages of the invention may be better understood by reference to the following description taken in conjunction with the accompanying drawing which shows apparatus suitable for practicing the method of the invention.

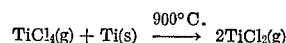
Although the method of the present invention is described with reference to chlorides of metals, it is to be understood that, by selection of the appropriate apparatus, reactants, flow rates, and temperatures, other halides may also be utilized in accordance with the principles of the invention. Accordingly, the following detailed description is to be taken as exemplary.

For the formation of silicides of titanium and chromium, reactive materials comprising titanium and chromium halides, and a halide of silicon are mixed with hydrogen and brought into contact with the heated surface of the substrate to be coated.

Controlled mixtures of titanium trichloride ($TiCl_3$) and chromium dichloride ($CrCl_2$) may be obtained by flowing titanium tetrachloride ($TiCl_4$) in a stream of inert gas such as argon or helium over heated chromium and titanium metals contained within a reaction chamber. The following reactions are believed to occur:



or

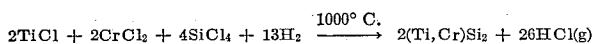


The metals are preferably maintained at a temperature between $750^\circ C.$ and $900^\circ C.$

The relative concentration of halides in the reactant gas stream may be controlled by placing an alloy or mixture of titanium and chromium in the chamber. The composition of the materials placed in the chamber determines the composition of the resulting halide reactant gas stream. Alternatively, a two compartment halide generating chamber may be used. Variation of the proportion of titanium tetrachloride gas passed through each of the compartments and the selection of the composition of the metals placed in either compartment determine the relative concentration of halides in the reactant gas stream. This technique is described in greater detail in copending and commonly assigned patent application, Ser. No. 579,693, filed Sept. 16, 1966.

Suitable conventional means are provided for combining silicon tetrachloride ($SiCl_4$) with the titanium and chromium chlorides and hydrogen. These gases then

mix in the vicinity of the substrate to produce silicides of titanium and chromium substantially in accordance with the following reaction.



One appropriate manner of combining the reactants in the vicinity of the substrate is shown in the drawing. The apparatus comprises three concentric tubes, 1, 2 and 3 for conveying gaseous reactants to the substrate, a reaction chamber 4, a substrate holder 5, provided with suitable heating means 6 and an exhaust 7. A vapor stream 1 comprising an inert carrier gas such as helium and chromium and titanium halides, such as TiCl_3 and CrCl_3 , the preparation of which has been described above, a vapor stream 2 comprising an inert carrier gas such as helium and a silicon halide, such as SiCl_4 , and a stream of hydrogen 3 are separately conveyed to the vicinity of the heated substrate where they combine and react to form a deposit of chromium and titanium silicides.

Typical flow rates and reaction conditions are indicated in the following table:

PARAMETERS AND RESULTS OF CHROMIUM-TITANIUM-SILICON DEPOSITIONS

Run No.	H_2 flow (l./min.)	He Flows (liters/minute)				Cr and Ti temperature ($^\circ\text{C.}$)	Reactor temperature ($^\circ\text{C.}$)	Increase in weight (mg./cm. ²)
		TiCl_4 bubbler	TiCl_4 dilutant	SiCl_4 bubbler	SiCl_4 dilutant			
1.....	7.0	1.25	1.25	0.10	1.25	910	1,350	21.1
2.....	7.0	4.0	2.5	0.05	1.25	910	1,350	21.6
3.....	7.0	4.0	2.5	0.05	1.25	910	1,350	21.1
4.....	7.0	4.0	2.5	0.05	1.25	910	1,350	21.3
5.....	7.0	4.0	2.5	0.05	1.25	910	1,350	20.4
6.....	7.0	4.0	2.5	0.05	1.25	910	1,350	17.3
7.....	7.0	4.0	2.5	0.05	1.25	910	1,350	20.1
8.....	7.0	1.5	4.0	0.03	1.25	880	1,250	12.4
9.....	7.0	0.0	5.0	0.03	1.25	880	1,250	5.8
10.....	7.0	1.5	4.0	0.03	1.25	880	1,250	11.0
11.....	7.0	1.5	4.0	0.03	1.25	880	1,250	19.0
12.....	7.0	1.5	4.0	0.03	1.25	880	1,250	17.7
13.....	7.0	1.5	4.0	0.03	1.25	880	1,250	23.0
14.....	7.0	1.5	4.0	0.03	1.25	880	1,250	16.4
15.....	7.0	1.5	4.0	0.03	1.25	880	1,250	19.6
16.....	7.0	1.5	4.0	0.03	1.25	880	1,250	14.9
17.....	7.0	1.5	4.0	0.03	1.25	880	1,250	18.8
18.....	7.0	1.5	4.0	0.03	1.25	880	1,250	19.4
19.....	7.0	1.5	4.0	0.03	1.25	880	1,250	12.7
20.....	7.0	1.5	4.0	0.03	1.25	880	1,250	10.1
21.....	7.0	1.5	4.0	0.03	1.25	880	1,250	14.2

NOTE: The base metal, or substrate, for each run was a columbium alloy.

The coating rate was observed to be quite rapid (2-3 mils/10 minutes of deposition). Also the corners and edges of the sample were coated as well as the flat sur-

to introduce impurities into the interface boundary. The following example will further serve to illustrate the multicomponent coating described above.

EXAMPLE

	Hydrogen flow (liters/min.)	Helium flow (liters/min.)	WCl_5 (milliliters/min.)	SiCl_4 (milliliters/min.)
Tungsten deposition (substrate temp. 800°C. , time 10 min.).....	5.5	5	16	-----
Silicide deposition (substrate temp. $1,300^\circ\text{C.}$, time 20 min.).....	5	5	-----	25
Total deposition, mg./cm. ²	40	-----	-----	-----

faces. The process has the "throwing power" to coat hidden or faying surfaces. Examination of the coating by metallographic analysis showed the deposit to be fine grained and revealed a sharp demarcation line between the coating and the substrate. The coatings obtained in run No. 12 and run No. 3 are quite uniform and have a relatively smooth top surface.

The method of the invention has also been successfully employed to produce coatings of tungsten silicide. A tungsten halide, such as tungsten chloride, WCl_6 , which is available commercially or which may be made by the reaction of chlorine and tungsten metal, is combined with silicon tetrachloride and hydrogen by suitable appropriate means such as that shown in the drawing.

Typical flow rates and reaction conditions are indicated by the following example.

EXAMPLE

A columbium alloy substrate was heated to 1300°C. and tungsten chloride (WCl_6) and silicon tetrachloride reduced with hydrogen at the surface of the substrate using the following flow rates: H_2 , 5 liters/minute; He, as a carrier gas for the halide reactants 5 liters/minute; WCl_6 , 16 milliliters/minute; and SiCl_4 , 25 milliliters/minute. The deposit forms a continuous coating having a relatively smooth top surface.

The oxidation protection of tantalum or columbium alloys with a tungsten diffusion barrier layer overlaid with a coating of tungsten silicide is an example of a multicomponent coating which may be formed by the method of the invention. Tungsten metal is initially deposited by the reduction of a tungsten halide (WCl_6). Thereafter, addition of a silicon halide (SiCl_4) to the gas composition causes the deposition of tungsten silicide. The coating is rapidly formed in accordance with this method. Moreover, there is no cooling or handling of the substrate between coating stages. Hence, bonding between the tungsten and tungsten silicide is particularly good because of the elimination of operations which might tend

The layers obtained are continuous and well bonded to one another.

A further modification of the method of the invention is the formation of graded composition coatings, by which is meant a coating of a first composition initially deposited on the substrate; the composition of the reactant gas stream is then gradually changed to produce a coating of a second composition at the outer surface of the first. Such coatings are desirable to achieve greater metallurgical compatibility or to match the thermal expansion coefficients of substrate and coating to produce improved adhesion. For example, the first composition may be selected for its compatibility with the substrate, e.g. chromium silicide, and the second composition may be selected for its resistance to oxidation, e.g. chromium-titanium silicide. Such a coating may be formed by de-

5

positing upon the heated substrate chromium silicide by the reduction of, for example, chromium chloride and silicon chloride with hydrogen as described above. After a layer of chromium silicide has been formed, titanium chloride is introduced into the reactant gas stream to produce a deposit of silicides of both chromium and titanium.

It is understood that the above described applications of the method of the invention are merely illustrative of its principles. Various other modifications may be devised by those skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. A method for depositing a coating of chromium and titanium silicides on a refractory metal substrate comprising:

forming a gaseous or vaporous reactant stream including a titanium halide, a chromium halide, a silicon halide, and hydrogen;

heating the substrate to a temperature of at least 1000° C.; and

passing said reactant stream in contact with the heated substrate to deposit said coating thereon.

2. The method according to claim 1 wherein said

6

halides are chromium dichloride (CrCl_2), titanium trichloride (TiCl_3) and silicon tetrachloride (SiCl_4).

3. The product produced by the method according to claim 1.

References Cited

UNITED STATES PATENTS

2,884,894	5/1959	Ruppert et al. -----	117—106 X
3,047,419	7/1962	Yntema et al.	
3,307,964	3/1967	Jacobson -----	117—106 X
3,409,459	11/1968	Jacobson -----	117—106 X

OTHER REFERENCES

Campbell, I. E. et al. The Vapor-Phase Deposition of Refractory Materials, in Journal Electrochemical Society, 96(5): pp. 325, 326, November 1949. 117—106.

Moers, K. Z.: Anorg. U. Allgem. Chem., vol. 198, p. 261, 1931. 117—106.

ALFRED L. LEAVITT, Primary Examiner

J. R. BATTEN, Jr., Assistant Examiner

U.S. Cl. X.R.

117—69, 71, 135.1; 148—6.3