

- [54] **CHEMICAL VAPOR DEPOSITION OF STEEL WITH TANTALUM AND COLUMBIUM**
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- [73] Assignee: **Fonsteel Inc.**, North Chicago, Ill.
- [22] Filed: **Sept. 7, 1971**
- [21] Appl. No.: **177,929**

- [52] U.S. Cl. 117/71 M, 117/93.1 PF, 117/107.2 R, 117/118, 148/6.35, 204/38 S
- [51] Int. Cl. C23c 11/02, C23c 11/04, C23f 17/00
- [58] Field of Search 117/71 M, 107.2 R, 117/107.2 P, 118, 93.1 PF; 148/6.35; 204/38 S; 29/196

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Primary Examiner—Alfred L. Leavitt

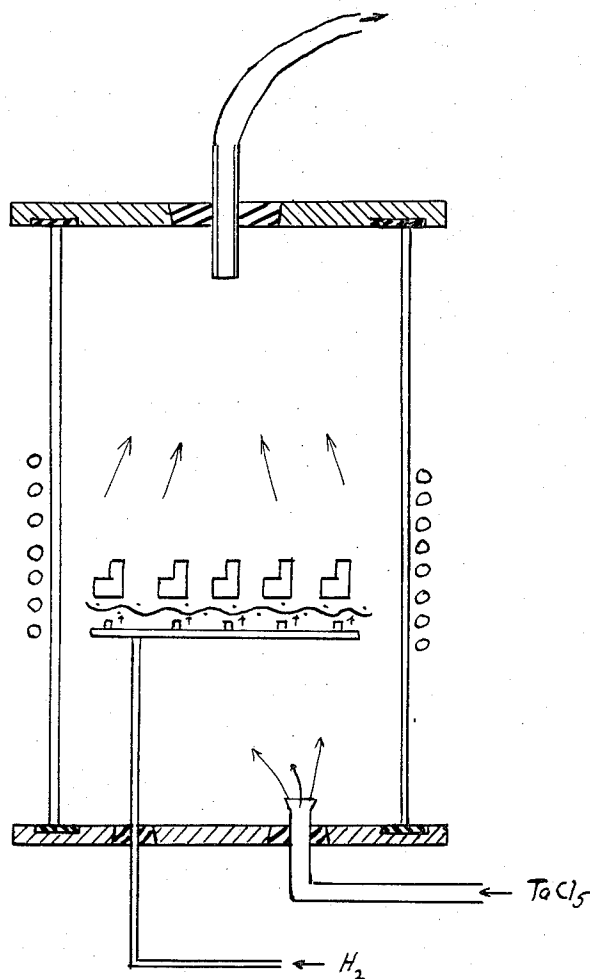
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[57] **ABSTRACT**

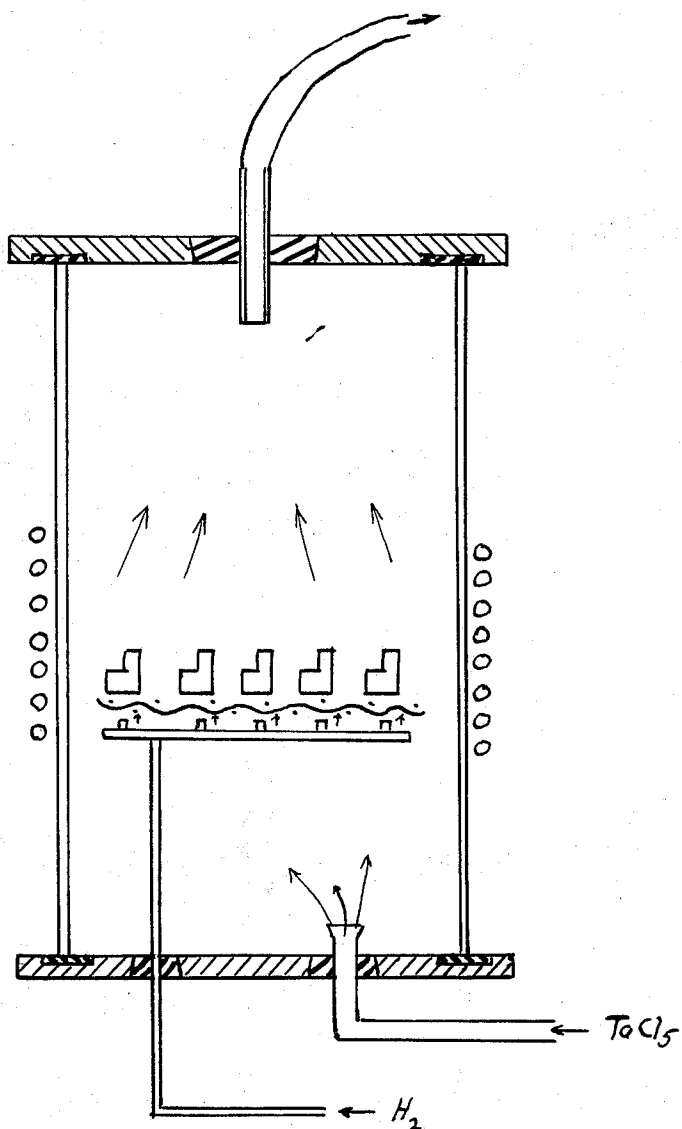
A process for cladding of steels and the resulting product. A consistent and acceptable bond is obtained by providing a containment coating to prevent diffusion of the ingredients of the substrate into the cladding material. A desirable containment coating is one in which one of the constituents is provided by the substrate to provide a composite which is more stable than similar compounds of the cladding coat such as tantalum or columbium. This permits a chemical vapor deposition of the cladding without adverse reaction with surface ingredients. A further step in the process is available in the localizing of flow of gas in the deposition to bring them together just prior to contact with the shape to be coated.

11 Claims, 1 Drawing Figure



PATENTED OCT 23 1973

3,767,456



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CHEMICAL VAPOR DEPOSITION OF STEEL WITH TANTALUM AND COLUMBIUM

This invention relates to a process for cladding steels with tantalum or columbium and to the resulting product.

There are certain applications of steel in which the product would be much enhanced by a cladding of tantalum on the surface to increase resistance to corrosion. The problem is to find an acceptable and reproducible bond between the tantalum and the steel and, secondly, to achieve uniformity over all the surfaces of a complex shape or a batch of complex-shaped hardware.

An attempt to deposit tantalum directly on steel containing carbon results in a poor bonding inasmuch as the tantalum combines with the carbon of the steel at an excessive rate leaving Kirkendall type porosity in the steel. It is possible to provide an excellent bond between tantalum and pure metals such as molybdenum, chromium and iron; but as the carbon content of the steel increases, the bond becomes less satisfactory. In steels such as the stainless variety the carbon content may be reduced to the point of not causing objectionable combining with tantalum, but the high nickel content creates the problem here. In a CVD process, the nickel will diffuse rapidly into tantalum leaving again the objectionable porosity.

The present invention contemplates a coating on steel which will protect the surface against the deterioration when tantalum is deposited by chemical vapor deposition. It is, therefore, an object of the invention to provide a process for cladding steel with tantalum or possibly columbium which is consistently successful and uniform.

It is a further object to provide a product of a tantalum clad steel resulting from the process and to provide a process which insures uniform results on complicated shapes.

Other objects and features of the invention relating to details of the process and the product will be apparent in the following description and claims in which the principles of the invention are set forth in connection with the best mode presently contemplated for the practice of the invention.

A DRAWING accompanies the disclosure and a single view thereof may be described as a diagrammatic illustration of an apparatus for accomplishing the present invention.

In connection with the problem of tantalum cladding of carbon containing steel, I propose to establish a containment surface on the steel which will prevent carbon diffusion from the steel substrate to the tantalum being deposited thereon.

By way of definition, an "overcoat" on a particular substrate is defined as the deposition of a measurable thickness of material on a surface. All electroplated coatings are overcoats; and, similarly, hydrogen-reduced refractory metal halides in a chemical vapor deposition process results in an overcoat. In these depositions, all the components of the coating are provided by the plating bath or the plating gas and none are provided by the substrate.

I propose a containment surface on a substrate which might be defined as a "displacement diffusion" coating in which at least one of the constituents of the coating is provided by the substrate. In this process, the coating does not build up on the surface to any appreciable ex-

tent but rather grows into the surface. For example, when titanium is used, this may be referred to as a "titanizing process." The "-izing" or "-ized" suffix placed on the end of the name of the element deposited from the gas denotes such a reaction.

In connection with titanizing, there is a reaction of the titanium with the carbon in an atmosphere of $TiCl_4$ in the temperature range of 900° – $1100^{\circ}C$, which forms a thin diffusion barrier of titanium carbide. The $TiCl_4$ reacts with the surface carbon on the carbon steel substrate to form TiC and once all surface carbon is reacted, the titanium deposition ceases. Thus, there is a definite limitation on the thickness of the displacement diffusion coating. Since titanium carbide is thermodynamically more stable than TaC , the pure tantalum may be deposited without further carbon diffusion from the substrate. In the preparation of the displacement diffusion coating, there may be a reaction with free carbon on the surface with the $TiCl_4$ but, in general, the carbon is available primarily from metal carbides in the substrate which are less stable than TiC . Nearly all the metal carbides normally occurring in carbon steel and low alloy carbon steel are less stable than TaC and thus displacement diffusion coating is required.

While titanium has been mentioned above, it is possible to use a containment coating of a metal selected from Groups IVb and VIb of the Periodic Table iron and cobalt. Of this group, for example, titanium carbide and ZrC are both more stable than tantalum carbide. After this containment coating is applied, it is possible to overcoat with pure tantalum in a CVD process without further carbon diffusion from the substrate.

In connection with stainless steels which are high in chromium and nickel, the problem with carbon diffusion is reduced since the carbide with chromium, namely, Cr_7C_3 , is very stable. On the other hand, the nickel content of the stainless steel will diffuse uncontrollably into a tantalum clad coat. Thus, for these steels, an overcoat of the pure metal to which tantalum may be bonded in a CVD process must be used. In some instances, a plating process may be used and in other instances a plasma spray can provide a coating to which tantalum may successfully bond. In each case, care must be used to obtain a good bond between the substrate and the overcoat. With electroplating, careful pre-plating procedures must be observed in the cleaning of the part and well controlled plating steps must be utilized. In the plasma spraying, a coating of pure iron, chromium, cobalt, molybdenum or tungsten may be applied; in fact, any of the metals from Group IVb and Group VIb as well as iron or cobalt can be practically applied in this way.

Once the pure metal overcoat is applied to the stainless steel, the nickel diffusion is blocked and the CVD coating or clad of tantalum can be readily applied using conventional procedures.

It will be appreciated that carbon steel can also be plated or plasma sprayed with pure metals as above described to block carbon diffusion. With steel casting for example, they are sometimes ground out and plasma coated with iron to remove the surface porosity and then titanized to stabilize any carbon that may have diffused into the plasma coat. Then the tantalum clad may proceed with a resulting good quality and uniform coat.

With respect to the use of plasma spray of iron on stainless steel, the carbon diffusion is not as critical a problem since the iron interlayer remains pure iron and the bonding of the CVD tantalum readily occurs without titanizing.

It has also been noted in tantalum cladding that deposition has occurred preferentially on certain areas of exposed parts rather than uniformly or in the areas where it is most generally desired. Tantalum cladding has been much improved by a control of the mixing of the tantalum Cl_5 and the hydrogen reactant gases.

In the chemical vapor deposition process which otherwise proceeds in accordance with accepted procedures in a reduction reaction, better results have been obtained when the TaCl_5 is introduced to the chamber in the normal manner as indicated in the drawing. However, the hydrogen is introduced through a separate feed line or a plurality of feed lines which terminate immediately upstream of the object to be coated. In other words, the gases are intentionally separated until they impinge on the objects to be coated. This provides excellent control in putting the tantalum deposit where it is desired. Utilizing this technique, uniform tantalum claddings have been obtained on batches of cast valve bodies, for example, during a 45-minute deposition period in a system that formerly could not generate tantalum coverage over all areas of the valve bodies during a 5-hour period of deposition. Thus, there is a great savings in materials and expense in performing the process as well as a much more desirable and uniform result. In some instances, a control of this combined flow which is brought together immediately upstream of the area to be plated can be improved by using multiple exhaust ports which are balanced to direct the flow to certain areas of the parts to be exposed.

While the above description has referred to tantalum cladding, it will be appreciated that columbium (niobium) is chemically similar and may be applied as a cladding coat in the same way as has been described in connection with tantalum. The same problems which require a containment coat for tantalum exist in relation to columbium. There is a considerable savings in the use of columbium since it is a less expensive metal but, on the other hand, tantalum has a broader applicability as a corrosion resistant material.

I claim:

1. A process of depositing tantalum on steel shapes which comprises:

coating a steel shape with a containment coat of a metal selected from Groups IVb and VIb of the Periodic Table, Fe and Co, and

b. depositing on said containment coat a layer of tantalum by chemical vapor deposition.

2. A process of depositing a cladding coat of tantalum on a carbon bearing steel shape which comprises:

a. titanizing a surface of said shape in an atmosphere of TiCl_4 in a temperature range of 900° – 1100°C , and

b. depositing a layer of tantalum on said titanized surface by chemical vapor deposition of TaCl_5 and hydrogen in a reduction reaction.

3. A process of depositing a cladding on steel shapes which comprises:

a. coating a steel shape with a containment coat of a metal selected from Groups IVb and VIb of the Periodic Table, Fe and Co, and

b. depositing on said containment coat a layer of metal selected from the group consisting of tantalum and columbium by chemical vapor deposition.

4. A process of depositing a cladding coat on a carbon bearing steel shape which comprises:

a. titanizing a surface of said shape in an atmosphere of TiCl_4 in a temperature range of 900° – 1100°C , and

b. depositing a layer of metal selected from the group consisting of tantalum and columbium on said titanized surface by chemical vapor deposition of a pentachloride of a metal in said group and hydrogen in a reduction reaction.

5. A process of depositing a cladding coat on a carbon bearing steel shape which comprises:

a. chromizing a surface of said shape in an atmosphere of chromium chloride in a temperature range of 900° – 1100°C , and

b. depositing a layer of metal selected from the group consisting of tantalum and columbium on said chromized surface by chemical vapor deposition of a pentachloride of a metal in said group and hydrogen in a reduction reaction.

6. A process of depositing a cladding coat on a carbon bearing steel shape which comprises:

a. electroplating chromium onto a surface of said shape, and

b. depositing a layer of a metal selected from the group consisting of tantalum and columbium on said plated surface by chemical vapor deposition of a pentachloride of a metal in said group and hydrogen in a reduction reaction.

7. A process of depositing a cladding coat on a stainless steel shape which comprises:

a. electroplating chromium onto a surface of said shape, and

b. depositing a layer of metal selected from the group consisting of tantalum and columbium on said plated surface by chemical vapor deposition of a pentachloride of a metal in said group and hydrogen in a reduction reaction.

8. A process of depositing a cladding coat on a stainless steel shape which comprises:

a. plasma spray coating iron onto a surface of said shape, and

b. depositing a layer of metal selected from the group consisting of tantalum and columbium on said plated surface by chemical vapor deposition of a pentachloride of a metal in said group and hydrogen in a reduction reaction.

9. A process of depositing a cladding coat on steel shape which comprises:

a. coating a steel shape with a containment coat of metal selected from groups IVb and VIb of the Periodic Table, Fe and Co., and

b. depositing a layer of metal selected from the group consisting of tantalum and columbium on said surface in a reduction reaction in a chamber at temperatures from 900° to $1,100^\circ\text{C}$. by introducing a pentachloride of a metal in said group consisting of tantalum and columbium into the chamber in a stream moving toward a part to be clad, and introducing hydrogen through separate feed lines at one or more points immediately upstream of the surface of a part to be coated.

10. A process of depositing tantalum on steel shapes which comprises:

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- a. coating the surface of a steel shape with a metal selected from Groups IVb of the Periodic Table under conditions to transform the surface carbon of the shape into a carbide having greater stability than tantalum carbide, and
 - b. depositing on said treated surface a layer of tantalum by chemical vapor deposition.
11. A process of depositing columbium on steel shapes which comprises:

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- a. coating the surface of a steel shape with a metal selected from Groups IVb of the Periodic Table under conditions to transform the surface carbon of the shape into a carbide having greater stability than columbium carbide, and
- b. depositing on said treated surface a layer of columbium by chemical vapor deposition.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,767,456 Dated October 23, 1973

Inventor(s) FREDERICK A. GLASKI

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the title page:

The Assignee "Fonsteel" should be --Fansteel--.

Column 3, line 46: Insert the following paragraph at the end of specification:

The term "coating" or "coat" as used in the specification and claims has reference to the application, by CVD, plating, or plasma spray, to a substrate surface of a metal in an extremely thin layer under conditions as above described in which the metal unites with the surface carbon of the substrate to form a carbide having greater stability than tantalum carbide. The surface is thus prepared for the application of tantalum by chemical vapor deposition to the extent that there will be no perceptible formation of tantalum carbide at the bonding face. The above description of coating relates to metals from Group IVb and the coating may also include metals from Group VIb, iron and cobalt applied as a pure metal to reduce the carbon diffusion during the tantalum coating.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,767,456 Dated October 23, 1973

Inventor(s) FREDERICK A. GLASKI

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Page 2, continued:

Column 4, line 55 (Claim 9):

After "CO" delete ---.

Column 5, line 2 (Claim 10):

"Groups" should be --Group--.

Column 6, line 2 (Claim 11):

"Groups" should be --Group--.

Signed and sealed this 2nd day of April 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents