United States Patent Office 2,894,320
Patented July 14, 1959

2,894,320

COATING URANIUM FROM CARBONYLS

David H. Gurinsky, Center Morulus, N.Y., and Samuel Steingiser, Storrs, Conn., assignors to the United States of America as represented by the United States Atomic Energy Commission

No Drawing. Application May 9, 1949
Serial No. 92,250

18 Claims. (Cl. 29—198)

This invention relates to adherent corrosion resistant coatings for uranium metal and to methods of making same. More particularly this invention pertains to a chemical method of plating adherent corrosion resistant material on uranium bodies.

An object of this invention is to provide a process for the application of uniform adherent protective metal coatings to uranium bodies.

A further object of this invention is to provide a method for the preparation of a uranium body or a uranium alloy body having a minimal carbon content.

A further object of this invention is to provide uranium metal bodies having a uniform adherent protective metal coating diffusion bonded thereto, said metal coating improving the corrosion resistance of the body.

A still further object of this invention is to provide a method for the application of a molybdenum coating to uranium metal and further to provide a uranium body having an adherent molybdenum coating diffusion bonded thereto.

A still further object of the present invention is to provide a means for the preparation of corrosion resistant uranium alloy materials.

Other objects and advantages will be apparent upon further examination of this specification.

The present invention is concerned with a chemical method of applying metal coatings to uranium metal bodies by dry plating thereon the metal obtained by thermal decomposition of organometallic compounds.

We have discovered a method for coating uranium metal which comprises heating a uranium body in the presence of and in contact with an organometallic compound such as the carbonyls of nickel, molybdenum, chromium, columbium, tungsten and copper. After suitable treatment by methods well known in the art for the preparation of metals prior to plating, the prepared uranium metal is heated in contact with the metal carbonyl compound to a temperature sufficient to decompose the metal carbonyl thereby dry plating the resultant free metal on the surface of the uranium metal body, and said metal-coated body is further heated to a higher temperature in order to diffuse at least part of the metal coating within said uranium body. The coated uranium body is heated at a temperature preferably higher than the coating temperature in order to thermally diffuse the coating metal within the uranium body. Apparently the diffused metal in some cases forms an alloy of the eutectic type with uranium.

The initial temperature for the deposition of metal from the carbonyl is above the decomposition temperature of the metal carbonyl and is usually of the order of 300° to 400° C. The temperature for the diffusion of the deposited metal is of the order of 300° to 800° C. and

preferably 600° C. It can readily be seen that the temperatures selected for the plating operation are dependent upon the specific metal carbonyl used in plating. A suitable heating means is selected on the basis of ease of temperature control and the temperature range desired. Because induction heating tends to cause fusion locally between uranium and the metal being plated thereon, particularly such metals as nickel, resistance heating has been found to be better adapted to the process of this invention and is the preferred means on account of the ease with which temperature control is maintained.

A preferred method employs the use of gaseous carriers for the metal carbonyl vapors during the plating step. Hydrogen, carbon dioxide, carbon monoxide and inert gases, such as argon are the usual ones employed as carriers for the metal carbonyl vapors. The concentration of the metal carbonyl in the gaseous carrier during the plating step is controlled by the temperature in the metal carbonyl supply chamber and the rate of flow of the carrier gas. It can readily be seen that the rate of deposition of the metal coating from the carbonyl and the depth of the layer of metal deposited thereby is dependent upon the rate of flow for the metal carbonyl vapor and the period of exposure of the uranium metal to this vapor.

The product formed by this embodiment of the present invention consists of a uranium metal body alloyed with minor proportions of an alloying metal such as nickel or chromium which is diffused therein from the surface coating wherein said metal coating is joined to the resultant binary-uranium alloy by means of a bond effected between the uranium and the coating metal by the diffusion process.

The diffusion process is preferably carried out in the presence of inert gases such as those which serve as carriers for the metal carbonyl vapor during the plating process.

A further embodiment of this invention comprises the application of a metal coat to a uranium body and the subsequent thermal diffusion of said metal coating into the uranium body to form an alloy thereby and the application of a second alloying metal to the previously coated uranium body followed by diffusion bonding of said second metal coat into the previously treated uranium body. The application of either or both coatings may be by the metal carbonyl treatment described above in the first embodiment. In some instances the second alloying metal which is plated on a previously metal coated uranium body and thermally diffused therein, follows the path of the alloying metal initially diffused within the uranium body. The product formed by the second embodiment of this invention consists of a ternary uranium alloy containing minor percentages of the coating metals alloyed and at least partially diffused therein so that, depending upon the extent of said diffusion, the ternary alloy is coated with one or more layers of metal or metals which have been dry plated thereon.

Heretofore the formation of molybdenum-uranium alloys and the coating of uranium with such metals as molybdenum, particularly in minor amounts, has not easily been achieved since molybdenum is bonded to or diffused into uranium only with considerable difficulty. The use of only small amounts of molybdenum in conjunction with uranium has been found to be particularly desirable since stabilization of uranium in certain desirable phases, e.g., the gamma phase, can best be achieved by the addition of only small amounts, of the order of about 5 weight percent of molybdenum.

In carrying out the process of this invention we have discovered that when a uranium body is dry plated with a metal such as nickel derived from the decomposition of the organometallic nickel carbonyl, the resultant coating and diffusion of said nickel coating into a uranium body apparently conditions the uranium for the subsequent reception of molybdenum therein. Therefore, when nickel is bonded and diffused into uranium in this manner, and a coating of molybdenum is subsequently applied on a uranium body thus treated, the molybdenum readily diffuses into the uranium, usually along the same path and in the pattern of the eutectic previously formed by nickel with uranium.

This effect described in the preceding paragraph is not produced if the carbonyls of nickel and molybdenum are applied simultaneously, and, in fact, the presence of molybdenum simultaneously with nickel prior to thermal diffusion appears to retard the thermal diffusion of nickel into uranium.

A further interesting effect on the uranium metal itself is obtained by the application of coatings such as the nickel-molybdenum diffusion bonded coating applied according to the process of this invention. A normal uranium slug contains approximately 1200 p.p.m. of carbon. After coating with nickel and molybdenum joined by a diffusion bond by the process of this invention, the carbon content of the uranium slug is thereby reduced to approximately 300 to 400 p.p.m. Such decarburization of a uranium slug is especially desirable when such a slug is to be used in a neutronic reactor wherein the presence of an additional moderator material such as carbon is particularly undesirable.

In general, the products formed by the process of this invention are well adapted for use in neutronic reactors wherein it is desired to keep the addition of corrosion resistant elements at a certain minimum in order to avoid the introduction of materials having a high neutron capture cross sections, as the introduction of such high neutron capture cross section materials tends to reduce the efficiency of a neutronic reactor by increasing the amount of nonfissionable material present. The amount of nonfissionable alloy material added to the uranium by the process of this invention suitably ranges from the order of 300–600 p.p.m. to a value of 5 to 10 percent by weight. The deposition of protective coatings using the 5 to 10 percent alloy material produces layers of alloy metal of possibly .05" thickness on uranium slugs measuring ½" x 1".

The coated uranium alloys formed by the process of this invention are superior to those products having substantially the same components and formed by other methods wherein the coatings are applied by electroplating methods or techniques of powder metallurgy such as cementation processes.

Coatings applied by electroplating, for example contained surface warts and pits while carbonyl coated specimens could be uniformly coated with one or more layers of metal. While the formation of blisters occurs infrequently in the carbonyl method, these blisters could be pressed down easily without causing fissures in the coatings whereas in specimens plated by other methods the formation of blisters is the rule rather than the exception and these blisters are more permanent in character.

In addition to being more strongly adherent to the base metal, the metal carbonyl treated uranium body shows improved resistance to such corrosive effects as those caused by moisture and air. Comparison of Tables I and II shows the superior corrosion resistance for metal carbonyl treated specimens as compared with electroplated specimens in terms of weight gain when specimens are subjected to air corrosion at 200° C. without any attempt to control the moisture and oil content in the air. Of course, there is a greater difference in corrosion resistance between uncoated uranium and uranium coated by the process of this invention.

TABLE I

Nickel carbonyl coating (diffused 4 hours at 640° C. in argon)

Base Material	Total Hrs. at 200° C.	Type Failure of Plating	Total Wt. Gain, Mg.	Gain, Mg./cm.²/hr.
Uranium	528	Cracking on radii	18.6	.0026
Do	1,022	do	650.0	.0468
Uranium alloy containing 2% Cb and 1% Zr.	64	One single crack around each end of cylinder.	45.0	.0517

TABLE II

Nickel electroplating (diffused 4 hours at 640° C. in argon)

Base Material	Total Hrs. at 200° C.	Type Failure of Plating	Total Wt. Gain, Mg.	Gain, Mg./cm.²/hr.
Uranium	64	Cracking on radii	60.6	.0696
Do	256	do	186.7	.536
Uranium alloy containing 2% Cb and 1% Zr.	64	Cracking on radii and on sides.	179.5	.2062
Do	64	Cracking on radii, complete separation.	340.1	.3907

Moreover, the coating applied by the carbonyl diffusion process outlined herein appears to be mechanically stronger than the coatings applied by electroplating or powder metallurgy techniques and the resultant product shows greater shear strength and improved ductility.

To illustrate the chief embodiments of this invention, the following description of the process and apparatus used in this process is herein set forth. However, the scope of the process of this invention is not to be limited other than by the limitations set forth in the accompanying claims.

In accordance with the process of this invention, the surface of the uranium body is prepared for the coating operation by conventional methods of mechanical or electrolytic polishing which are well known to those skilled in the art. The prepared billet is then placed in an evacuated reaction chamber and the uranium billet is degassed by heating. The system is then flushed with carbon monoxide or other inert carrier gas used in the process. A manifold arrangement is used to permit the passage of any one gas or a combination of gases into the system, which gases may be passed through or around a glass reservoir containing the metal carbonyl and from there to the reaction chamber. The mixture of carbonyl and carrier gas in the reaction chamber is maintained at a suitable pressure of about 10^{-2} mm. or even as much as one atmosphere by controlling the rate of input and exhaust rate for the carbonyl and carrier gas mixture. Low pressures are maintained by means of vacuum pumps or metal and oil diffusion pumps. The molybdenum carbonyl, which is solid at room temperature, is contained in a thermostatically controlled supply chamber maintained at a temperature of 35° C. and fed to a condenser type chamber held at 25° C. in order to furnish a constant vapor pressure of molybdenum carbonyl to the reaction system. The mixture of metal carbonyl with the carrier gas is passed into the reaction chamber through a water-cooled, spiral-shaped copper tube in which tiny orifices have been drilled in order to furnish points of exit for the carbonyl vapor from the supply source.

The reaction chamber consists of a double-walled glass bell jar, water-cooled between the two walls and sealed to a brass base. This bell jar can be evacuated through a trap, an oil diffusion pump and a high vacuum pump. Within the bell jar is a central platform or preferably a rotating turntable to support and rotate the slug at about

2 r.p.m. thereby providing for the deposition of a more uniform metal coating. It was found that unless the uranium body is rotated, there is a tendency for incrustations of metal to form on the uranium body opposite the points of exit of the metal carbonyl-carrier gas mixture from the supply orifices.

The temperature of the uranium billet is preferably maintained at 300° to 400° C. for the plating operation, and is controlled by a thermocouple mechanism which records temperature and initiates the necessary response

mately 0.080" and the concentration of the nickel in the uranium falls to 150 p.p.m. only at a depth of 0.180" from the surface. The molybdenum concentration was approximately 7500 p.p.m. in the first .005" depth cut examined. In the second .005" depth cut, molybdenum was present only to the extent of 150 p.p.m. in contrast to the presence of 1,000 p.p.m. nickel at this same level. Below the second 0.005" depth cut, the amount of molybdenum present decreased generally and was thereafter not in excess of 100 p.p.m.

TABLE III

Experiment Number	Surface Preparation	Initial Pressure, mm.	Degassing Temperature, ° C.	Initial Treatment		Carrier	Carbonyl Schedule	
				Temp., ° C.	Reducing Agent		Temperature of Uranium Billet, ° C.	Plating Operation
1	Electrolytic	3×10^{-6}	700	700	CO	Argon at 6×10^{-2} mm	700	Mo for 2½ hrs.
2	do	1×10^{-5}	700	700	None	Argon at 8×10^{-2} mm	700	Mo for 6 hrs.
3	Mechanical	3×10^{-5}	300	300	H_2	do	400	Ni at .08 mm. for ½ hr.
				300	CO		600	Mo for 6¾ hrs.
4	Electrolytic	5×10^{-5}	700	600	H_2	CO_2 at .1 mm	450	Ni at .08 mm. for 3.4 hrs.
				600	CO and CO_2		6–700	
5	Mechanical	3×10^{-5}	800	600	CO	CO for Ni; argon for Mo.	600	Ni for 1 hr.
							6–700	Mo for 7½ hrs.

in the induction of resistance heater. It can be readily seen that the rate of the plating reaction is controlled by the rate of input of metal carbonyl and the extent of dilution of said metal carbonyl with the carrier gas. The speed of rotation of the uranium billet and the efficiency of the arrangement of supply nozzles also affect the reaction rate. In such an apparatus and under the controlled conditions outlined above, a metal coating derived from metal carbonyl measuring about 0.003" to 0.004" can be applied within about five or six hours to uranium cylinders measuring ½" x 1" and ¾" x 3".

Experiments 1 and 2 in Table III illustrate the first embodiment of the process.

The second embodiment of this invention is illustrated by the data for experiments 3, 4 and 5 in Table III which shows the process wherein uranium metal is precoated with a conditioning metal which is diffused therein in the preparation of the uranium metal body in order to effectively apply and diffuse a second metal coating therein. Ordinarily such metals as molybdenum or columbium do not readily combine with uranium. For example, a coating of nickel from the decomposition of nickel carbonyl is dry plated upon uranium metal heated to a temperature between 300–400° C. Within the same vessel and preferably in the continued presence of the carrier gas, the nickel coated uranium is then further heated to about 600–900° C. in order to diffuse the nickel. At 750° C. the thermal diffusion of nickel in uranium is very rapid. While still in the same reaction vessel and in the presence of an inert atmosphere, a molybdenum coating is then dry plated from molybdenum carbonyl on the nickel treated uranium and further heating, preferably to at least about 600° C., diffuses the molybdenum into the uranium along substantially the same eutectic pattern formed previously by the nickel diffused in the uranium. There is some indication that the shear strength of the uranium-molybdenum diffusion bond formed at temperatures in the vicinity of 600° C. is superior (ca. 10,000 p.s.i.) to that formed at higher temperatures e.g., about 700–800° C.

Metallographic examination of successive 0.005" cuts taken from these specimens reveals that the uranium body forms a uranium nickel eutectic alloy (M.P. 738° C.) with the nickel which has been dry plated and diffused therein. The nickel is distributed by the diffusion process with apparent uniformity beneath the surface of the uranium body and the resultant concentration of nickel is about 1,000 p.p.m. up to a depth of approxi-

The products formed by the preceding experiments can be described as consisting of uranium billets coated with one or more metals, such as Ni, Cr, Mo, Cb, and W, wherein said coatings are diffusion bonded to the uranium body thereby forming a binary or ternary alloy with the uranium base metal depending upon the coating metal or metals involved. The size of the coating will obviously depend upon the amount initially deposited upon the uranium body and the extent of the subsequent thermal diffusion treatment. Moreover the distribution of the minor alloy metals in the uranium treated by this process likewise depends upon the thermal diffusion treatment. As previously described, the concentration of the elements diffused within the uranium body gradually decreases with the increase in distance from the body surface and coating from which coating the minor alloy metal (or metals) is derived.

All the specific compositions and embodiments of the processes disclosed in the present application are illustrative rather than limiting in scope and therefore the numerous equivalents and modifications apparent to those skilled in the art are included within the scope of the present invention. The appended claims are intended to cover all features of novelty as broadly as possible in view of the prior art.

What is claimed is:

1. An article of manufacture which comprises a uranium metal billet, an adherent coating of a protective metal plate around said billet, and an alloy of uranium and said protective metal, said alloy being between and bonded to said plate and said billet.

2. An article of manufacture which comprises a uranium metal billet, an adherent coating of nickel metal plate around said billet, and an alloy of uranium and nickel between and bonded to said nickel plate and said uranium billet.

3. An article of manufacture comprising a uranium metal billet, an adherent coating of chromium plate around said billet, and an alloy of uranium and chromium between and bonded to said chromium plate and said billet.

4. An article of manufacture which comprises a billet of uranium metal, a molybdenum coat around said billet, a ternary alloy of molybdenum, uranium and nickel, said ternary alloy layer being interposed between and adherently bonded to said molybdenum coat and said uranium billet.

5. An article of manufacture which comprises a billet of uranium metal, a ternary alloy of uranium, molybdenum and nickel surrounding and bonded to said billet, a binary alloy of molybdenum and nickel surrounding and bonded to said ternary alloy, a molybdenum coat around said binary alloy and bonded to said uranium billet through said alloys.

6. A process for the diffusion of molybdenum in a billet or the like of uranium comprising applying a conditioning coating of a molybdenum-carrier metal to said uranium billet, heating to diffuse at least part of said metal-carrier coating therein to form an alloy of uranium and carrier metal, subsequently applying a molybdenum coating on said treated uranium billet, and heating to diffuse part of said molybdenum coating within said alloy of uranium and carrier metal.

7. The process of claim 6 wherein said carrier metal for molybdenum is nickel.

8. A method for improving the resistance of uranium to corrosion comprising heating a uranium metal body in the presence of a metal carbonyl compound in the vapor state, thereby plating the metal from the metal carbonyl vapor on the surface of the uranium body to form a coating thereon, and continuing the heating of said metal-coated uranium body, thereby diffusing at least part of said metal coating through said uranium metal.

9. The process of claim 8 wherein said metal carbonyl is molybdenum carbonyl.

10. The process of claim 8 wherein said metal carbonyl is nickel carbonyl.

11. A method for improving the resistance of uranium to corrosion comprising heating a uranium metal body in the presence of a mixture consisting of a metal carbonyl compound in the vapor state and a carrier gas inert with respect to uranium metal, thereby plating the metal from said metal carbonyl vapor on the surface of a uranium body to form a coating, and continuing the heating of said metal-coated uranium body to form a diffusion bond between said metal coating and said uranium body.

12. The process of claim 11 wherein said metal carbonyl is nickel carbonyl.

13. The process of claim 11 wherein said metal carbonyl is chromium carbonyl.

14. A process for dry plating an adherent metal on a uranium metal body comprising heating a uranium metal body in the presence of a carbonyl of an alloying metal at a temperature above the decomposition temperature of said metal carbonyl to produce a metal plated uranium body, and further heating said metal-plated body thereby forming a diffusion bond between said plated alloying metal coating and said uranium body.

15. A process for dry plating an adherent metal on a uranium metal body comprising heating a uranium metal body in the presence of a mixture of an inert gas and a carbonyl of an alloying metal at a temperature above the decomposition temperature of said metal carbonyl to dry plate said alloying metal on said uranium body, and further heating in the presence of an inert gas said metal-coated body thereby forming a diffusion bond between said plated alloying metal coating and said uranium body.

16. A process comprising heating a uranium metal body in the presence of a carbonyl of a metal carrier for molybdenum to provide a plated coating of said carrier metal, heating to diffuse at least part of said coating therein to form an alloy of uranium and carrier metal, subsequently heating the resulting body in the presence of molybdenum carbonyl to provide a molybdenum coating, and heating to diffuse part of said molybdenum coating within said alloy of uranium and carrier metal.

17. A method for the preparation of a uranium body having a nickel-molybdenum coating diffusion bonded thereto comprising heating a uranium metal body in the presence of nickel carbonyl in the vapor state to plate nickel from said nickel carbonyl vapor on the surface of said uranium body, continuing heating of said nickel-plated uranium body in order to diffuse at least part of said nickel plating through said uranium metal body, heating the resultant uranium-nickel alloy coated uranium body formed thereby in the presence of molybdenum carbonyl in the vapor state to plate molybdenum thereon, and further heating the resultant molybdenum coated nickel-uranium alloy body to a temperature sufficient to diffuse part of said molybdenum coating within the uranium-nickel alloy.

18. The process of claim 17 wherein said metal carbonyl vapors are admixed with an inert gaseous carrier for said metal carbonyls in the vapor state.

References Cited in the file of this patent

UNITED STATES PATENTS

945,504	Farkas	Jan. 4, 1910
1,228,194	Fahrenwald	May 29, 1917
1,650,979	Brace	Nov. 29, 1927
1,902,503	Howe	Mar. 21, 1933
2,475,601	Fink	July 12, 1949
2,653,879	Fink	Sept. 29, 1953

FOREIGN PATENTS

861,390	France	Oct. 28, 1940
233,011	Switzerland	Oct. 2, 1944