

# United States Patent

[11] 3,615,885

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 [33] Canada  
 [31] 970,698  
 Pat. 770,080

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[54] **FORMING UNIFORM THICK OXIDE LAYER OF**  
**MATERIAL**  
 3 Claims, 1 Drawing Fig.

[52] U.S. Cl. .... 148/6.3,  
 148/31.5, 148/13.1, 148/133, 23/140, 117/127,  
 117/221, 308/241  
 [51] Int. Cl. .... C23c 11/00  
 [50] Field of Search ..... 148/6.3, 6,  
 31.5, 13.1, 133; 117/221, 127; 23/140

**ABSTRACT:** Several methods of producing a uniform beige oxide layer on Zircaloy-2 have been developed. The oxidized material has excellent wear resistance and should be useful for parts in rubbing contact in water-lubricated mechanisms operating at temperatures up to 500°F.

The oxidation rate of Zircaloy-2 in air is extremely dependent on the surface texture and the treatment given it. A rough surface produced by machining or grit blasting will assure the formation of a uniform beige post-transition oxide layer. A fine surface produced by grit blasting, polishing, machining or grinding will decrease the oxidation rate and will prevent the formation of a uniform beige post-transition oxide. Deep scratches will increase the oxidation rate, not because of contamination from the scratching surface but apparently because of the surface roughness produced.

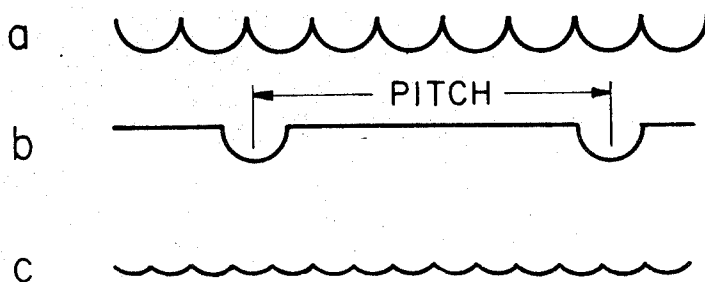


FIG. 1

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# FORMING UNIFORM THICK OXIDE LAYER OF MATERIAL

This invention relates to a method of forming uniform thick oxide layers on a material.

There are various methods of forming tough protective layers on metals but there are various deficiencies in most of them. Tough protective layers which have good wear-resistant properties in corrosive environments are rare and difficult to produce. Layers having good wear and corrosion resistance are especially useful in nuclear reactors where warm fluids such as heavy water at temperatures around 500° F. are present and in intimate contact with the bearing surfaces such as shafts, journals as well as pump parts, etc.

It is common in nuclear reactors to use an alloy of Zirconium known as Zircaloy-2, which is composed of 1.2 to 1.7 percent tin, 0.07 to 0.2 percent iron, 0.05 to 0.15 percent chromium, 0.03 to 0.08 percent nickel and the balance Zirconium. This alloy as well as other allied Zirconium alloys such as Zircaloy-4, are extensively used because of their low neutron capture ratio, relatively high tensile strength and their ability to be machined and welded; however, they have poor wear resistance.

The present invention overcomes these difficulties by achieving a tightly adherent oxide layer on those alloys of Zirconium, which have low neutron capture ratios, such as Zircaloy-2. This oxide layer grows to thicknesses of about 0.008 inch and is beige in color. Chemically it appears to have a formula of  $ZrO_2$  and its characteristic beige color appears to be due to microcracks in the surface of the oxide layer. Such oxide layer is to be contrasted with the distinctive black or blue-black Zirconium dioxide layer which adheres to Zirconium metal as was disclosed in U.S. Pat. No. 2,987,352 issued to the assignee hereof. The beige oxide of the present invention is tightly adherent to alloys of Zirconium to thicknesses of 0.008 inch whereas the blue-black oxide layer on Zirconium metal was not capable of growing to thicknesses in excess of approximately 0.0015 inch without flaking or chipping, and as a result, such layers were of limited usefulness as wear resisting and corrosive resisting surfaces because of their relative thinness.

The present invention provides a method of creating a beige (light brown)-colored Zirconium dioxide layer on the surface of a Zirconium alloy such that it is tightly adherent and uniform in thickness comprising the steps of roughing the surface of the alloy then heating the alloy at elevated temperatures in the presence of oxygen until a beige-colored oxide uniform in thickness forms.

The invention further contemplates an oxide on the surface of an alloy of Zirconium tightly adherent, beige in color and substantially uniform in thickness and color.

The invention further contemplates that the tightly adherent oxide layer has a thickness of 0.0005 inch to 0.008 inch.

The embodiments of the invention will now be described by way of example reference being had to the accompanying drawing wherein:

FIG. 1 is a cross-sectional representation of different surface profiles produced by machining Zircaloy-2.

## EXAMPLE 1 (M)

As illustrated in table "A" a set of 6 Zircaloy-2 samples were prepared by machining their surface. They were then heated in air at 650° C. for 24 hours.

From the table, it is clear that the surface roughness produced during machining had very pronounced effects on the oxidization characteristics of Zircaloy-2. The depth of cut, crossfeed, and sharpness of the cutting tool determine to a large extent the surface roughness obtained during machining. When the depth of cut and crossfeed are about equal, the surface profile produced with a sharp tool (nose radius 0.0005 inch) will resemble that shown in FIG. 1 a. The oxide layer formed on sample Zr2-12 produced to this configuration was not tightly adherent although it was uniform prior to flaking. This might be due to the fact that the sharp peaks produced during machining were completely oxidized and therefore began to flake.

In specimen Zr2-4 and Zr2-10 the crossfeed was considerably greater than the depth of cut and the surface configuration resembled that illustrated in FIG. 1 b. The oxide layer produced was uniform and tightly adherent and beige (light brown) in color. It was noticed that during the oxidization process the beige (light brown) oxide started forming at the sharp corners produced by the machining and spread rapidly to all parts of the surface. Specimen Zr2-9 was prepared with a cutting tool having a nose radius of about 0.0005 inch and the machining was regulated such that the crossfeed is considerably less than the depth of cut such that a surface profile resembling that of FIG. 1 c was produced; the surface finish produced was exceptionally good however, a beige-colored oxide was not uniformly produced over the surface but a black oxide and beige oxide resulted.

Samples Zr2-9 and Zr2-6 and Zr2-5, however, were too smooth to oxidize uniformly.

TABLE "A"

| Sample No. | Cutting tool material | Nose radius, mil* | Chuck speed, rev./min. | Cross feed, mil/rev. | Approx. depth of cut, mil* | Surface roughness, $\mu$ in. AA | Colour and texture of oxide                                                                           |
|------------|-----------------------|-------------------|------------------------|----------------------|----------------------------|---------------------------------|-------------------------------------------------------------------------------------------------------|
| Zr2-12     | GE 883 carbide        | 0.5               | 375                    | 2.1                  | 1                          | 150                             | Beige, uniform but non-adherent.                                                                      |
| Zr2-4      | do                    | 0.5               | 180                    | 4.5                  | 1                          | 130                             | Beige, uniform and tightly adherent.                                                                  |
| Zr2-10     | do                    | 0.5               | 100                    | 9.0                  | 1                          | 130                             | Do.                                                                                                   |
| Zr2-9      | do                    | 0.5               | 375                    | 0.15                 | 1                          | 8                               | Thin black oxide near centre surrounded by thicker beige oxide.                                       |
| Zr2-6      | High speed steel      | Large             |                        |                      |                            | 21                              | Thin black oxide with light brown spots near centre, surrounded by light brown (beige) thicker oxide. |
| Zr2-5      | Kennametal Carboly    | Large             |                        |                      |                            | 50                              | Do.                                                                                                   |

\* 1 mil=0.001 in

## EXAMPLE 2 (P)

TABLE "B"

|                 | Machined and oxidized for 24 hours at—           |                                                  | Ground and oxidized for 24 hours at—                                         |                                                                                     | Polished and oxidized for 24 hours at—                          |                                              |
|-----------------|--------------------------------------------------|--------------------------------------------------|------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-----------------------------------------------------------------|----------------------------------------------|
|                 | 600° C.                                          | 650° C.                                          | 600° C.                                                                      | 650° C.                                                                             | 600° C.                                                         | 650° C.                                      |
| No pickle       | 5C (150)                                         | CA6 (70)                                         | 13C (28)                                                                     | 7C (40)                                                                             | CA5 (18)                                                        | CA7 (7)                                      |
| Resultant oxide | Continuous uniform tightly adherent beige oxide. | Continuous uniform tightly adherent beige oxide. | Non-continuous streaked adherent beige oxide. Remainder is thin black oxide. | Non-continuous sparse streaked adherent beige oxide. Remainder is thin black oxide. | Mostly thin black oxide with some light brown at circumference. | Speckled, isolated beige oxide mostly black. |

| Light pickle.....  | 11C (80)                                                                       | 10C (140)                                        | 12C (30)                                                                    | 6C (18)                                                        | 8C (19)                                          | 9C (13)                                                         |
|--------------------|--------------------------------------------------------------------------------|--------------------------------------------------|-----------------------------------------------------------------------------|----------------------------------------------------------------|--------------------------------------------------|-----------------------------------------------------------------|
| Resultant oxide... | Continuous uniform tightly adherent beige oxide.                               | Continuous uniform tightly adherent beige oxide. | Almost continuous adherent beige oxide except for several patches of black. | Mostly adherent beige oxide but some patches of thin black.    | Speckled isolated beige oxide mostly thin black. | Non-continuous speckled buff oxide with thin black background.  |
| Heavy pickle.....  | 15C (15)                                                                       | 14C (13)                                         | CA1 (19)                                                                    | CA2 (18)                                                       | CA4 (18)                                         | CA3 (18)                                                        |
| Resultant oxide... | Almost continuous tightly adherent oxide except for very small patch of black. | Continuous uniform tightly adherent beige oxide. | Speckled isolated beige oxide mostly thin black.                            | Non-continuous speckled beige oxide, about half is thin black. | Speckled isolated beige oxide mostly thin black. | Non-continuous speckled beige oxide with thin black background. |

Specimen number is shown followed by surface roughness  $\mu$  in. AA in parentheses.

TABLE "C"

| Purified Si metal | Ottawa silica sand | Pure Al | Norton Crystolon* 280B | Al oxide | SS White* Airbrasive Powder #1 | Exolon Co. Exolon* (alumina) | Cataphote Corp. "Glass shot" (glass bead) | Approx. particle size of grit, in. $\times 10^3$ | Equiv. grit size or mesh |
|-------------------|--------------------|---------|------------------------|----------|--------------------------------|------------------------------|-------------------------------------------|--------------------------------------------------|--------------------------|
|                   |                    | F       |                        |          |                                |                              |                                           | 90-30                                            | -8+20                    |
|                   |                    |         |                        |          |                                |                              | G                                         | 28-14                                            | -25+45                   |
|                   | G                  |         |                        |          |                                |                              |                                           | 20                                               | 32                       |
| G                 |                    |         |                        |          |                                |                              |                                           | 14                                               | 44                       |
|                   |                    |         |                        |          |                                | G                            |                                           | 12-5                                             | -50+1                    |
|                   | G                  |         |                        |          |                                |                              |                                           | 10                                               | 60                       |
|                   |                    |         |                        |          |                                | G                            |                                           | 10-6                                             | -60+100                  |
|                   |                    |         |                        |          |                                |                              |                                           | 6-2                                              | -100+270                 |
|                   | G                  |         |                        |          |                                |                              | G                                         | 5                                                | 120                      |
|                   |                    |         |                        |          |                                |                              |                                           | 4-2                                              | -140+270                 |
|                   |                    |         |                        |          | P                              |                              |                                           | 3.5                                              | 170                      |
|                   |                    |         |                        | P        |                                |                              |                                           | 3                                                | 200                      |
|                   |                    |         |                        |          |                                |                              |                                           | 2                                                | 280                      |
|                   |                    |         |                        |          | P                              |                              |                                           | .9                                               | 600                      |

G=uniform beige oxide forms; F=uniform beige oxide may form; P=uniform beige oxide does not form; All samples oxidized at 650° C. for 24 hr. or less in air.

Various specimens of Zircaloy-2 metal were machined to roughnesses of between 70 and 150  $\mu$  inch AA; ground to finishes of 18 to 40  $\mu$  inch AA; and polished to between 7 and 18  $\mu$  inch AA. The specimens were then placed in a pickle bath for a short time to remove about 0.0003 inch from the surface but this did not change the surface finish a significant amount. Some of the samples were placed in a pickle bath for a longer period of time to remove about 0.003 inch from the surface. This longer pickling reduced the roughness of a rough surface while the longer pickling of smooth surfaces did not change the roughness of the surface to any great extent.

The effects of pickling on the oxidation characteristics of machined, ground and polished Zircaloy are shown in table "B."

As can be seen from this table machined surfaces (roughness of 70-150  $\mu$  inch AA) will normally oxidize to form a uniform layer. Except one small part of one specimen (15C) pickling for long or short periods of time did not appear to affect surface characteristics or oxide formation.

Ground surfaces (roughness of 18-40  $\mu$  inch AA) which have been pickled either for long or short periods of time, will not grow uniform beige oxide layers. A beige oxide layer would not grow on a polished surface of Zircaloy-2 (roughness of 7-18  $\mu$  inch AA). EXAMPLE 3 (A B)

The effect on the oxidizing characteristics of Zircaloy-2 of air blasting with various sizes and types of abrasive grit is shown in table "C." The results have been listed in order of coarseness of grit. The blasting was accomplished in a conventional manner using the various sizes and types of grit listed in the table. All samples were oxidized at 650° C. for about 24 hours in air.

From table "C," it is evident that using a hard grit having particle size at least 0.004 inch will result in a uniform beige oxide. In certain instances, such as where silicon metal is used as the abrasive grit, the resultant oxide covering the blasted area was darker than normal but in areas adjacent to the blasted area where spreading of the oxide layer occurred the oxide layer is a normal beige color.

From table "C" it appears that the composition of grit does not appear to be important except in cases where the grit is softer than the surface being abraded. Pure aluminum did help to promote the formation of a uniform oxide but not to such a degree as to make the oxide useful as a protective layer for the Zircaloy-2.

## EXAMPLE 4 (S)

Scratching helps to promote the formation of an adherent beige oxide layer adjacent to the scratch. The surface of various samples cut from the same block of Zircaloy-2 metal were scratched or scored with various substances such as the elements titanium, cobalt, nickel, copper, lead, molybdenum, graphite (2H pencil), iron, magnesium, tungsten, aluminum and vanadium and then heated at 600° C. for 17 hours or more. The buff oxide formed most readily along the scratches produced by the harder materials such as diamond, tungsten, molybdenum, etc. The effect of the softer materials such as aluminum, copper, iron, lead, graphite, on the oxidation characteristics of Zircaloy-2 was negligible. When a surface of Zircaloy-2 was scored using a vibrating pencil with a diamond tip then heated at 600° C. in air for 24 hours, the resultant oxide was beige in color, uniform and continuous and adherent across the whole of the surface treated.

## WEAR CHARACTERISTICS

Various samples of Zircaloy-2 were oxidized in the manner set out in tables "D" and "E" and the wear resistance properties of the beige oxide layers were tested. In one instance, the wear test was performed by rotating a three-fourths inch outside diameter, 304 stainless steel journal at 77 r.p.m. against the flat samples listed in table "D" under a load of 25 pounds in pH 7 water.

Table "E" illustrates a wear test performed by rotating a journal of "Waukesha88\*" metal of three-fourths inch outside diameter against the flat samples listed in that table, at a load of 200 pounds at a speed of 225 r.p.m. in pH 7 water. The rating characteristics listed in the right-hand column of the tables is an indication of the number of 2-hour runs that could be made under the test condition before the oxide layer wore through.

## CORROSION TEST

Various samples of Zircaloy-2 metal were prepared and oxidized in accordance with the particulars set out in table "F." In all instances, the resulting oxide was continuous uniform and tightly adherent. Coating-types 1 to 6 inclusive were a beige color, coating-types 7, 8 and 9 were a medium brown color. The darker color of the types 7, 8 and 9 was probably

TABLE "D".—WEAR TEST RESULTS WITH 304 STAINLESS STEEL JOURNAL

| Zircaloy-2 sample No. | Surface shot blasted with grit given below | Oxidizing conditions |            | Approx. weight gain of specimen, g./dm. <sup>2</sup> | Equivalent oxide thickness, in. $\times 10^3$ (A) | Length of test min. (C) | Max. depth of wear scar, in. $\times 10^3$ (B) | Rating, $\frac{A}{B} \times \frac{C}{120}$ |
|-----------------------|--------------------------------------------|----------------------|------------|------------------------------------------------------|---------------------------------------------------|-------------------------|------------------------------------------------|--------------------------------------------|
|                       |                                            | Time, hr.            | Temp., °C. |                                                      |                                                   |                         |                                                |                                            |
| Zr2A36                | Silicon metal 0.014 in.                    | 48                   | 650        | Medium brown                                         | 1.33                                              | 3.7                     | 120                                            | 0.39                                       |
| Zr2A29                | Glas-shot 0.002 to 0.004 in.               | 96                   | 650        | Beige                                                | 2.73                                              | 7.3                     | 120                                            | 0.42                                       |
| Zr2A38                | do.                                        | 24                   | 650        | do.                                                  | 0.69                                              | 1.9                     | 120                                            | 0.34                                       |
| Zr2A27                | do.                                        | 48                   | 650        | do.                                                  | 1.55                                              | 4.3                     | 120                                            | 0.49                                       |
| Zr2A11                | Ottawa silica sand 0.005 in.               | 24                   | 650        | do.                                                  | 0.67                                              | 1.9                     | 120                                            | 0.40                                       |
| Pure zirconium        | None                                       | 2                    | 800        | Black                                                | 0.18                                              | 0.5                     | 50                                             | 0.4                                        |

Note.—Wear test performed by rotating a  $\frac{3}{4}$  in. O.D. journal against the flat samples listed above. Journal material, 304 SS. Load, 25 lb. Speed, 77 rev./min. Lubrication, pH 7 water.

TABLE "E".—WEAR TEST RESULTS WITH WAUKESHA 88 JOURNAL

| Zircaloy-2 sample No. | Surface shot blasted with grit given below | Oxidizing conditions |            | Approx. weight gain of specimen, g./dm. <sup>2</sup> | Equivalent oxide thickness, in. $\times 10^3$ (A) | Length of test min. (C) | Max. depth of wear scar, in. $\times 10^3$ (B) | Rating, $\frac{A}{B} \times \frac{C}{120}$ |
|-----------------------|--------------------------------------------|----------------------|------------|------------------------------------------------------|---------------------------------------------------|-------------------------|------------------------------------------------|--------------------------------------------|
|                       |                                            | Time, hr.            | Temp., °C. |                                                      |                                                   |                         |                                                |                                            |
| Zr2A36                | Silicon metal 0.014 in.                    | 48                   | 650        | Medium brown                                         | 1.33                                              | 3.7                     | 120                                            | 0.56                                       |
| Zr2A38                | Glas-shot 0.002 to 0.004 in.               | 24                   | 650        | Beige                                                | 0.69                                              | 1.9                     | 120                                            | 0.58                                       |
| Zr2A28                | do.                                        | 96                   | 650        | do.                                                  | 2.23                                              | 6.2                     | 120                                            | 0.56                                       |
| Zr2A27                | do.                                        | 48                   | 650        | do.                                                  | 1.55                                              | 4.3                     | 120                                            | 0.41                                       |
| Zr2A11                | Ottawa silica sand 0.005 in.               | 24                   | 650        | do.                                                  | 0.68                                              | 1.9                     | 120                                            | 0.64                                       |
| Pure zirconium        | None                                       | 2                    | 800        | Black                                                | 0.18                                              | 0.5                     | 15                                             | 0.1                                        |

Note.—Wear test performed by rotating a  $\frac{3}{4}$  in. O.D. journal against the flat samples listed above. Journal material, Waukesha 88. Load, 200 lb. Speed, 225 rev./min. Lubrication, pH 7 water.

TABLE "F".—RESULTS OF CORROSION TESTS

| Coating type | Surface preparation                                         | Air oxidation treatment |            | Weight gain, g./dm. <sup>2</sup> | Equivalent oxide thickness, in. $\times 10^3$ | Corrosion testing in water |                |      |              |                                              |
|--------------|-------------------------------------------------------------|-------------------------|------------|----------------------------------|-----------------------------------------------|----------------------------|----------------|------|--------------|----------------------------------------------|
|              |                                                             | Time, hr.               | Temp., °C. |                                  |                                               | Temp., °C. $\pm 5^\circ$   | Oxygen, p.p.m. | pH   | Time, months | Weight change, g./dm. <sup>2</sup> per month |
| 1            | Sand-blasted with glassshot 0.0041 to 0.0021 in. size.      | 96                      | 650        | 2.63                             | 7.3                                           | 254                        | <.01           | 10.0 | 2            | -20                                          |
| 2            | do.                                                         | 48                      | 650        | 1.56                             | 4.3                                           | 254                        | <.01           | 10.0 | 2            | +6                                           |
| 3            | do.                                                         | 24                      | 650        | 0.67                             | 1.9                                           | 254                        | <.01           | 10.0 | 2            | +9                                           |
| 4            | Sand-blasted with Ottawa silica sand about 0.0049 in. size. | 69                      | 650        | 2.38                             | 6.6                                           | 254                        | <.01           | 10.0 | 2            | -22                                          |
| 5            | do.                                                         | 48                      | 650        | 1.16                             | 3.2                                           | 254                        | <.01           | 10.0 | 2            | -7                                           |
| 6            | do.                                                         | 24                      | 650        | 0.71                             | 2.0                                           | 254                        | <.01           | 10.0 | 2            | -6                                           |
| 6            | do.                                                         | 24                      | 650        | 0.57                             | 1.6                                           | 77                         | (2)            | 9.8  | 1            | -2                                           |
| 6            | do.                                                         | 24                      | 650        | 0.58                             | 1.6                                           | 77                         | (2)            | 9.9  | 2            | <1                                           |
| 7            | Sand-blasted with silicon metal about 0.014 in. size.       | 24                      | 650        | 0.64                             | 1.5                                           | 177                        | <.01           | 10.0 | 1            | -31                                          |
| 8            | do.                                                         | 96                      | 650        | 2.85                             | 7.9                                           | 254                        | <.01           | 10.0 | 2            | -105                                         |
| 9            | do.                                                         | 48                      | 650        | 1.35                             | 3.7                                           | 254                        | <.01           | 10.0 | 2            | -37                                          |
| 9            | do.                                                         | 24                      | 650        | 0.77                             | 2.1                                           | 254                        | <.01           | 10.0 | 2            | -19                                          |

<sup>1</sup> pH controlled with ammonia.

<sup>2</sup> Air in contact with water surface.

<sup>3</sup> pH controlled with LiOH.

due to the effect of silicon on Zircaloy-2. The different coatings were then subjected to corrosion tests at the conditions shown in table "F." The oxide layers of types 2, 3, 5 and 6 had the lowest weight change and were considered most desirable. The type 1 and 4 oxide layers were the thickest (around 0.007 inch) and some of the relatively large weight changes during the corrosion test may have been due to spalling at the sharp corners of the specimens.

Crytolon is the trade mark of Norton Company; Exolon is the registered trade mark of the Exolon Company; S. S. White is the registered trade mark of S. S. White Dental Manufacturing Company; and Waukesha 88 is the registered trade mark of an alloy produced by Waukesha Foundry Company. Throughout the application these registered trade marks have been indicated by an asterisk (\*).

In this specification the abbreviation "AA" means arithmetical average deviation from mean.

What we claim is:

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1. A method of forming an oxide layer from a surface layer of an article of an alloy of zirconium having a low-neutron capture cross section, which includes the steps of roughening the surface of the surface layer to a depth of between 70 $\mu$  inches AA and 150 $\mu$  inches AA to make the surface more receptive to oxidation and heating the surface layer between 600° C. to 800° C. for between 24 hours and 96 hours with the roughened surface exposed to oxygen to form from the surface layer an oxidized coherent layer, which is substantially uniform in thickness and is beige colored in appearance.

2. A method according to claim 1, wherein the alloy of zirconium comprises by weight 1.2 to 1.7 percent tin, 0.07 to 0.2 percent iron, 0.5 to 0.15 percent chromium, 0.03 to 0.08 percent nickel, balance zirconium except for impurities. AA and 150 $\mu$  inches AA in the surface layer.

3. A method according to claim 1, wherein the surface layer is between 0.0005 inch and 0.008 inch in thickness.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,615,885 Dated October 26, 1971

Inventor(s) Robert Douglas Watson et al.

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

On the cover sheet insert -- [73] Assignee: Atomic Energy of Canada Limited, Ottawa, Ontario, Canada --.

Signed and sealed this 12th day of September 1972.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents