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PREPARATION OF ZIRCONIUM FOR COLD WORKING

Kenneth H. Dale, Louisville, Ky., assignor to Olin Mathieson Chemical Corporation, East Alton, Ill., a corporation of Virginia

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This invention relates generally to metal treating and more particularly to zirconium and to methods for placing a metallic coating thereon and to a process for cold working zirconium.

Zirconium, because of its low neutron absorption, is particularly advantageous for making containers and other metallic parts to be used in conjunction with atomic engines and for the transportation of radioactive material. A layer of an adherent abrasive scale is formed on zirconium when it is exposed to the air and zirconium has a rapid work hardening rate. Consequently, it is extremely difficult to cold work the metal and a special treatment is required before it can be elongated without fracturing by cold rolling, deep drawing, extruding and similar cold working processes. One method for removing the scale from zirconium available heretofore involves removing the scale by abrasive polishing, such as wire brushing and grit blasting. Then to improve the cold working properties of the metal, the freshly brushed surface is deeply etched in a chemical solution and coated with a layer of nickel by an electroplating process. The plated metal must next be hardened to bring about diffusion and alloying of the nickel with the zirconium. Such a process is laborious, requires the use of specialized expensive equipment and, in order to recover a zirconium surface, the alloy must be machined from the surface. Zirconium has the additional undesirable characteristic of readily reacting with hydrogen, nitrogen and oxygen when heated and as a result it has been necessary heretofore to anneal the zirconium in vacuo.

It is, therefore, an object of this invention to provide an improved method for cold working zirconium. Another object of this invention is to provide a process for preparing zirconium for cold working. A further object of the invention is to provide a method for placing on zirconium a protective coating of another metal. A still further object of this invention is to provide a method for annealing zirconium in air; i.e., without evacuating the annealing furnace. Still another object of the invention is to provide a solution and process for removing scale from the surface of zirconium. A still further object of the invention is to provide a solution for coating zirconium with a ductile metal. Another object of the invention is to provide a process for lubricating zirconium while cold working. Another object of the invention is to provide a means for coating zirconium articles with an adherent and smooth deposit of a ductile material adapted to be removed by chemical means without etching the surface of the zirconium article.

The foregoing objects as well as others are achieved in accordance with this invention, generally speaking, by providing a solution for removing the scale from zirconium by chemical means and a means for coating the cleaned zirconium surfaces with a coating of a ductile metal. In accordance with this invention, the scale is removed from the zirconium by immersing the zirconium article in an aqueous solution of nickel sulfate, fluoride ions and an oxidizing agent such as hydrogen peroxide.

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The cleaning is improved by including a minor amount of a wetting agent in the solution. The cleaned zirconium surface is first coated by chemical reduction with a layer of tin or zinc by immersing it in an aqueous solution of a soluble zinc or tin salt and fluoride ions and leaving it therein until the zinc or tin is deposited in a smooth adherent film on the zirconium. It has been found that zirconium coated with either tin or zinc has improved cold working properties over uncoated zirconium and that in some instances the cold working characteristics of zirconium may be further improved by coating the tin or zinc coating zirconium with another ductile metal. When additional coatings are desired, the tin or zinc coated zirconium is first coated with a very thin film of copper. Such a film of copper is commonly known in the industry as a copper strike. The copper surface may then be coated with a ductile metal by electroplating it in a suitable bath for electroplating copper with copper or for plating copper with any other ductile metal such as brass, iron, tin, lead and the like or by means of a suitable chemical reduction process. A more adherent coating is obtained when a copper strike is used even if the final coating is to be copper. A preferred solution from which copper may be electrolytically deposited over the copper strike is an alkaline cyanide copper solution. This solution may be used also for placing the copper strike on the article.

The total thickness of the coating or coatings of metal on zirconium must be within the range of from about 0.001 inch to about 0.002 inch for satisfactory cold working. If the thickness is greater than this, the coating peels from the metal during the cold working operation and the zirconium is not properly protected if the thickness is less than 0.0008 inch.

It has been found that the scale appearing on the surface of metallic zirconium after exposure to the atmosphere may be removed rapidly without etching the metal by immersing the zirconium in an aqueous solution of from about 300 grams to about 700 grams of nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) per liter and fluoride ions in a concentration equivalent to from about 15 milliliters to about 30 milliliters of 48% hydrofluoric acid per liter at a temperature of from about 200° F. to about 210° F. Fifteen to thirty milliliters of hydrofluoric acid contain from about 7.75 grams to about 15.5 grams fluoride ions.

Zirconium may be coated with zinc by immersing it in an aqueous solution of from about 800 grams to about 1600 grams per liter zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), about 15 milliliters to about 30 milliliters 48% hydrofluoric acid (0.516 gram fluoride ion per milliliter) and from about 15 grams to about 30 grams per liter aluminum sulfate ($\text{Al}_2\text{SO}_4 \cdot 3$). Zinc is deposited upon the zirconium by chemical reduction in such a solution. Any suitable zinc salt may be substituted for zinc sulfate, such as, for example, zinc chloride, but the amount of zinc ion utilized in the solution should be substantially equivalent to the zinc ion concentration of the solution specified above. The fluoride ion may be supplied to the solution used to remove the scale from the zirconium and to the zinc coating solution by dissolving therein sodium fluoride, ammonium fluoride, ammonium bifluoride, potassium fluoride or potassium bifluoride or any other suitable fluoride salt provided the amount thereof is within the fluoride ion concentration obtained by the use of the above amounts of hydrofluoric acid. The plating solution will deposit a suitable coating of zinc on a properly cleaned zirconium surface by chemical reduction in from one-half to one minute while the solution is at room temperature, or in other words, within the neighborhood of about 20° C.

A suitable coating of tin may be applied to the properly cleaned zirconium article by immersing it in an aqueous solution of a tin salt and fluoride ions. A preferred

solution for plating the zirconium from an aqueous solution by chemical reduction contains a soluble tin salt in quantities equivalent to about 54 grams per liter stannous sulfate (SnSO_4) or 100 grams per liter stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), about 9 milliliters per liter 48% hydrofluoric acid, about 2 grams per liter gelatin and about one gram per liter of a suitable wetting agent such as beta naphthol. The article should be immersed in the solution for from about 5 to about 10 minutes while the solution is at room temperature. The tin deposit resulting from immersion in such a solution has been found particularly well suited for lubricating zirconium in cold working operations so the zirconium may be provided with a coating of from about 0.001 inch to about 0.002 inch tin and cold worked without any other coating of ductile metal. In some instances, it may be necessary to immerse the article longer than 10 minutes in order to obtain a coating of about .002 inch. If the metal is to be annealed, however, it is advisable to place a coating of copper or brass as described in more detail hereinafter over the tin. In those instances where other metals are to be placed over the tin, the tin coating may be from about 0.0005 to about 0.001 inch in thickness. Furthermore, if the amount of reduction in thickness of the metal during cold working is relatively great the added protection of the copper, brass, or the like over the tin is sometimes desirable.

An aqueous solution found particularly well suited for placing a thin film of copper over a zinc or tin coating on zirconium contains about 165 grams per liter copper cyanide, about 195 grams per liter sodium cyanide, about 120 grams per liter sodium carbonate and about 10 grams Rochelle salt. The solution should be at a temperature of between about 120° F. and about 140° F. and the article should be electroplated for about two minutes at a current density of about 24 amperes per square foot after which time the current should be turned off. The current should then be turned on and the article plated for about 5 minutes at about 12 amperes per square foot, to complete the copper strike. The film of copper obtained is about 0.00001 inch to about 0.00002 inch. If no other metal is to be placed on the copper, the thickness of the copper may be increased until the total thickness of the base coating of tin or zinc, the copper strike and the final copper plate is about 0.002 inch by continuing the plating treatment.

As stated above, zirconium having a thin copper strike coating may be plated with a thicker coating of a ductile material such as, for example, copper, brass, tin, iron or the like in order to further improve the zirconium cold working characteristics. Any suitable electroplating solution for plating over copper may be utilized for this purpose. The coating of these metals should be from about 0.0005 to about 0.0010 inch or of sufficient thickness that the total thickness of the coating on the zirconium is within the range of about 0.001 to about 0.002 inch if the metal is to be cold worked such as by drawing or rolling.

A solution suitable for placing a brass coating on copper has the following composition:

9 to 12 grams per liter zinc cyanide
19 to 25 grams per liter copper cyanide
12 to 16 grams per liter sodium carbonate
28 to 35 grams per liter sodium cyanite
Temperature, 75° F.-100° F.
Current density, 2.5-15 amperes per square foot
Voltage, 1.5-2

A solution particularly well suited for immersion plating zirconium having a film of tin or zinc and a film of copper thereon with iron has about the following composition:

Ferrous sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ --- 660 grams per liter.
Hydrofluoric acid (48%) HF --- 30 milliliters per liter.
Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$ --- 5 grams per liter.

Manganese sulfate, MnSO_4 ----- 5 grams per liter.
Sodium alkyl aryl sulfonate ----- .2 gram per liter.
Temperature ----- 150° F.
Time ----- 5 to 10 minutes.

As an example of a process for cold working zirconium, a zirconium strip about 0.104 inch thick is cleaned by immersing it in a suitable alkaline cleaner container from about 2 to 4 ounces per gallon sodium orthosilicate or other suitable alkali such as, for example, sodium carbonate or trisodium phosphate at a temperature of about 150° F. to 180° F., rinsed in warm water and then immersed in an aqueous solution of about 10 percent by weight nitric acid and about 0.5 percent hydrofluoric acid for about 15 seconds at room temperature. The strip is then rinsed in water at about 20° C. and is immediately immersed in a solution containing from about 300 to about 700 grams per liter nickel sulfate, 15 to 30 milliliters per liter 48 percent hydrofluoric acid, 0.1 to 0.2 gram per liter sodium alkyl aryl sulfonate or other suitable wetting agent and about 0.5 to 1 milliliter per liter hydrogen peroxide at a temperature of between about 200° F. and 210° F. until the scale on the surface of the zirconium has been removed.

The cleaned zirconium article is coated with a layer of zinc from about 0.0005 to about 0.001 inch thick by immersing it in a zinc plating solution having the composition specified hereinbefore at room temperature. The zinc plating solution is rinsed from the article with water and a film of copper from about 0.00001 to about 0.00002 inch thickness is placed over the zinc by electroplating as described above. After the copper strike has been placed on the metal, the current is turned off the second time. The copper coated zirconium may then be coated with one of the ductile metals until the total thickness of coatings on the zirconium is within the range of about 0.001 inch to about 0.002 inch. The zirconium is then coated with glycerine and cylindrical blanks are cut therefrom and the blanks are drawn and shaped into a cup by conventional cold working methods with a punch and die. It has been found that the coating adheres to the zirconium and elongates with it as it is cold worked and acts as a barrier between the cold working tools and the zirconium if its thickness is within the range specified above and the coating thus materially increases the life of the tools without scratching or otherwise marring the surface of the zirconium.

As indicated hereinbefore zirconium cleaned and coated in accordance with this invention may be heated to annealing temperatures without evacuating the annealing furnaces. Also annealing the coated metal is cleaned and pickled in a suitable aqueous solution and is then cold worked by rolling, drawing or similar process. The metallic coating of tin or zinc or the coating of one of these metals with another ductile metal such as iron, tin, copper and the like may be removed from the zirconium by immersing the article in a suitable solvent for the coating which is not a solvent for the zirconium. After the coating has been removed, a bright zirconium finish is obtained without any etching or other marring of the surface.

Although the invention has been described in considerable detail in the foregoing, it is to be understood that such detail is solely for the purpose of clarifying the invention and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it is limited by the appended claims.

I claim:

1. The process for preparing zirconium for cold working which comprises removing the oxide scale in an aqueous solution of about 300 to about 700 grams nickel sulfate per liter, fluoride ions in a concentration equivalent to from about 15 to about 30 milliliters of 48 percent hydrofluoric acid per liter and hydrogen peroxide, coating the thus cleaned zirconium with a

metal selected from the group consisting of tin and zinc by immersing it in an aqueous solution selected from the group consisting of solutions of tin ions at least equivalent to about 54 grams per liter of stannous sulfate with from about 15 to about 30 milliliters of 48% hydrofluoric acid per liter and solutions of zinc ions containing from about 800 grams to about 1600 grams per liter of zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), about 15 to 30 milliliters of 48% hydrofluoric acid per liter and from about 15 to about 30 grams per liter of aluminum sulfate, electrolytically depositing a film of copper on the resulting surface, and thereafter depositing a coating of a ductile metal over the copper film.

2. The process of claim 1 wherein the zirconium is plated with zinc after cleaning.

3. The process of claim 1 wherein the zirconium is plated with tin after cleaning.

4. The process of claim 1 wherein the final coating is copper.

5. The process of claim 1 wherein the final coating is brass.

6. The process of claim 1 wherein the final coating is iron.

7. The process for preparing zirconium for cold working which comprises removing the oxide scale therefrom in an aqueous solution of from about 300 to about 700 grams nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) per liter, and from about 15 to about 30 milliliters of 48% hydrofluoric acid per liter at a temperature of from about 200° F. to about 210° F., coating the zirconium with zinc by immersing it in a solution of from about 800 to about 1600 grams per liter zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), about 15 to about 30 milliliters 48% hydrofluoric acid per liter, from about 15 to about 30 grams per liter aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) in an aqueous solution, depositing a coating of copper over the zinc by electroplating with a current density of at least about 15 amperes per square foot in a solution containing about 165 grams per liter copper cyanide, about 195 grams per liter sodium cyanide, about 120 grams per liter sodium carbonate and about 10 grams per liter Rochelle salt at a temperature of from about 120° F. to 140° F., and thereafter depositing a coating of a ductile metal over the copper strike.

8. The process for removing the oxide scale from zirconium which comprises immersing the zirconium in an aqueous solution consisting essentially of from 30 percent to 70 percent nickel sulfate, 1 percent to 3 percent hydrofluoric acid and minor amounts of hydrogen peroxide and a compatible wetting agent.

9. A process for producing zirconium having an adherent, ductile electrodeposit of a metal on the surface thereof which comprises first depositing on the clean zirconium a coating of tin by chemical reduction in a solution consisting essentially of tin ions at least equivalent to about 54 grams per liter of stannous sulfate with from about 15 to about 30 milliliters of 48 percent hydrofluoric

acid per liter, and thereafter coating the zirconium with a ductile metal.

10. A solution for coating zirconium with zinc by chemical reduction which consists essentially of from 800 grams to 1600 grams per liter zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), about 15 milliliters to about 30 milliliters 48 percent hydrofluoric acid per liter, from about 15 grams to about 30 grams per liter aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$).

11. A method of coating zirconium articles with an adherent and smooth deposit of a ductile metal which comprises cleaning the zirconium article to remove substantially all of the surface oxide film, coating the cleaned article by immersing it in a solution selected from the group consisting of solutions of tin ions at least equivalent to about 54 grams per liter of stannous sulfate with from about 15 to about 30 milliliters of 48% hydrofluoric acid per liter and solutions of zinc ions containing from about 800 grams to about 1600 grams per liter of zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), about 15 to about 30 milliliters of 48% hydrofluoric acid per liter, and from about 15 to about 30 grams per liter of aluminum sulfate, and thereafter electrolytically depositing a coating of a ductile metal thereon.

12. A process for improving the cold working properties of zirconium which comprises coating the zirconium with a film of ductile metal from about 0.001 to about 0.002 inch thick, said film being composed of a layer of tin adjacent the zirconium, a copper strike adjacent the tin, and an electrodeposited layer adjacent the copper strike of a ductile metal selected from the group consisting of copper, brass, tin, iron and lead.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,938,841

May 31, 1960

Kenneth H. Dale

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 12, for "coating" read -- coated --; column 4, line 7, for "container" read -- containing --; line 13, for "ofi" read -- of --; same column 4, line 50, for "Also" read -- After --.

Signed and sealed this 8th day of November 1960.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents