

SPECIFICATION

Method for stripping tungsten carbide from titanium or titanium alloy substrates

The present invention relates to a process for stripping tungsten carbide from a titanium or titanium alloy substrate.

Various aircraft components and engine components are today manufactured from titanium or titanium base alloys. The surfaces of such articles which are subject to wear are frequently coated with a wear-resistant material such as tungsten carbide. In the recovery of titanium metal or titanium base alloy for reworking from scrap or salvage parts or the resurfacing of otherwise sound parts, it is necessary to remove the carbide coating prior to reworking the metal. Coatings of various kinds have been applied to titanium substrates for various purposes. These coatings have included plated material, such as nickel and chromium, or scale as a result of oxidation of the surface due to high temperature heat treatment, or the like.

U.S. Patent 2316579 describes an electrolytic process for removing metal coatings from titanium or titanium alloy substrates, using as the electrolyte an aqueous solution of chromium trioxide (CrO_3). The workpiece is made the anode and the cell is operated at a current density of between 100 and 250 amperes per square foot. The temperature of the electrolyte is in the range of from 155° to 185°F. The results are improved by the inclusion of boric acid (H_3BO_3).

U.S. Patent 3632490 describes the removal of oxide coatings from titanium and titanium base alloys by a two step process. Two separate electrolytes are provided in separate tanks. In the first tank, the workpiece is the cathode of the cell and, in the second tank, the workpiece is the anode of the cell. In this case, the electrolyte is a solution of sodium dichromate and hydrofluoric acid. The temperature of the electrolyte solutions is about 185°F and the voltage from 6 to 17 volts of 20 amperes. The current density in the cathodic cycle is from 100 to 1000 amperes per square foot and in the anodic cycle should be from 80 to 1000 amperes per square foot. The treatment time is approximately 5 minutes at 200 amperes per square foot.

Another electrolytic stripping process for titanium base substrates is described in U.S. Patent 3,793,172; this process is concerned with the stripping of copper-nickel-chromium deposits from titanium. The stripping bath consists of an aqueous solution containing fluoboric acid (HBF_4) and phosphoric acid (H_3PO_4). In use, the current density is about 16 amperes per square inch with an operating voltage of 7.5 volts DC. The stripping time is generally less than about 3 minutes.

In general, these prior art processes have depended upon deplating or mechanically loosening scale by electrolytically generated hydrogen gas using the workpiece as one of the electrodes in a predetermined electrolyte composition. In deplating, the materials which are deplated are elemental metals.

We have now developed a method in which the material removed or stripped from the titanium or titanium alloy substrate is tungsten carbide.

According to the present invention, there is provided a method of electrochemically stripping tungsten carbide from a titanium or titanium alloy substrate in an electrolytic cell, which comprises immersing a titanium workpiece having a tungsten carbide coating thereon as an anode in an aqueous solution containing from 4 to 40% by weight of CrO_3 , which solution has a temperature of at least 100°F, together with a metallic cathode inert to the aqueous CrO_3 solution, and imposing a direct current voltage across the anode and cathode of from 6 to 50 volts at a current density of from 3.6 to 40 amperes per square foot for a period of at least 30 minutes.

The substrate is not deleteriously affected by this treatment. The tungsten carbide coating is completely removed without effect on the base metal. The method according to the invention is faster than prior art methods and requires no surveillance or additional handling until coating removal is attained. Stripping is accomplished in a wide range of solution concentrations and parts may be fully or partially immersed without any surface effects. A surface discoloration may form which is easily removed by immersing the part in nitric-hydrofluoric acid solution for a few seconds. Another advantage of the present process is that the stripping process actually cleans all immersed surfaces and removes any other coatings which may be present.

In the following description, reference will be made, by way of example, to the single Figure of the accompanying drawing which is a diagrammatic representation of an electrolytic cell suitable for carrying out the method according to the invention. The workpiece illustrated is a gas turbine blade having tungsten carbide as a hard surfacing material applied to titanium midspan surfaces for wear resistance. This coating needs to be removed when it is faulty or worn and the workpiece is to be reconditioned.

The tungsten carbide coatings which are applied by various means, for example by plasma flame spray application techniques, have a thickness of from 0.010 to 0.015 inch to provide a hard surface for long life wear characteristics. If the coating is faulty, for example incomplete, or is worn so as to require replacement, the previous coating must be stripped from the surface. Moreover, the stripping must be done without any attack

on the titanium or titanium alloy substrate. Although pure titanium metal may be used as the material from which jet engine airfoil or blade elements may be fabricated, the usual material used is an alloy. A typical example of a titanium alloy useful in the fabrication of aircraft parts is known as Ti-6Al-4V (AMS 4928) titanium alloy.

When shaped in the manner shown in the annexed drawing, the midspan surface 12 and 14 are coated at their distal extremities as shown at 16 with tungsten carbide. This coating provides a hard surface having excellent wear characteristics and is the surface which must be stripped of the tungsten carbide prior to recovering or reclamation of titanium or titanium alloy substrate for reworking.

As shown in drawing, the titanium or titanium alloy workpiece 10 is supported in an electrolytic cell 11, and connected by a suitable supporting fixture 13 into a direct current circuit as the anode. The cathode may be any suitable conductor which is not attacked by the electrolyte, for example lead, carbon, titanium or other conductor inert to the electrolyte.

The electrolyte is an aqueous solution of chromic oxide (CrO_3) or any other material capable of producing chromate ions in solution. Thus, instead of chromic acid, soluble chromates and bichromates may be used therefor and are to be considered the equivalent of chromic acid on a stoichiometric basis. The term "chromic acid equivalent" as used herein is intended to include chromic acid itself (CrO_3) and stoichiometrically equivalent weights of soluble chromates and bichromates. Commercial CrO_3 contains a small amount of sulphate which is believed to be beneficial, although not essential, to the present process.

The composition of the electrolyte may vary quite widely. In general, the electrolyte is an aqueous solution, that is a tap water or distilled water solution of chromic acid or an equivalent chromate ion-producing material, for example sodium bichromate in a stoichiometrically equivalent amount, containing from 4 to 40% by weight of CrO_3 . The electrolyte may optionally contain from 0.03 to 1.0% by weight of sulphate ion, suitably added as sulphuric acid. It should be noted that commercial CrO_3 may contain a small amount of SO_4 .

The following Table I gives typical examples of aqueous electrolyte solutions useful in accordance with the present invention. The numerical values are parts by weight.

ELECTROLYTE SOLUTIONS

Ex. No.	H ₂ O	CrO ₃	H ₂ SO ₄ (Total SO ₄ -)
1	128	6	—
2	128	17	0.045
3	128	28	1.5
4	128	33	1.0
5	128	40	0.3
6	128	50	1.8
7	128	80	0.045

Best results have been obtained with Example 4 above at a temperature of 130°F to 140°F for 60 to 80 minutes at a current density of from 4 to 8 amperes per square foot. The electrolyte was contained in a glass vessel and lead cathodes were used. Complete stripping of a tungsten carbide coating on midspan portions of a titanium alloy blade, as illustrated in the accompanying drawing, was obtained.

In use, the concentration of the chromate ion gradually decreases because of reaction with the tungsten carbide. A precipitate is formed which settles to the bottom of the cell and which may be removed from time to time as desired. Under such conditions, the treatment time will tend to increase with use. Thus at lower concentrations of CrO_3 , the required treatment time will be longer than for higher concentrations. The presence of sulphate ion apparently aids in catalyzing the removal of the tungsten carbide from the workpiece surface. It is also found that the thicker the tungsten carbide coating, the longer will complete stripping of the workpiece surface take. When stripping of the tungsten carbide is complete, further residence in the electrolyte bath will cause no damage to the base material. Accordingly there is no upper limit on the time of exposure to stripping conditions.

The temperature of the electrolyte in the electrolytic cell during operation may range from 100°F up to about 180°F. For most purposes, a preferred temperature is from 120° to 140°F. Higher temperatures tend to reduce the required treatment time. The voltage which is applied to the cell across the electrodes may be from 6 to 50 volts. In general, faster stripping is achieved at the higher voltages.

The current density is relatively low and ranges from 0.025 to 0.27 amperes per square inch, or 3.6 to 40 amperes per square foot. In the voltage range of 6 to 9 volts, from 25 to 50 amperes may be drawn in treating an area of approximately 6 square feet. The time of residence in the electrolytic bath depends upon the thickness of the coating to be removed and the other conditions mentioned above. In a fresh electrolyte solution, the time

- required to strip 0.008 to 0.010 inch of tungsten carbide is from 60 to 80 minutes at a voltage of from 6 to 9 volts and a current density of from 3.6 to 10 amperes per square foot. Voltage and current may be varied during a given stripping operation. Agitation of the bath improves the rate of removal of the tungsten carbide coating. To this end, a stirring device is preferably provided for the electrolytic bath and vigorous, boiling agitation created. To maintain the temperature of the bath within the desired range, heating coils or electric resistance heaters may be provided. When higher voltages are used, the treatment time may be reduced. For example at 40 volts, about 30 minutes is found satisfactory.

To illustrate commercially unacceptably long residence time at or near marginal conditions, a 5% electrolyte solution at 95°F at 40 volts and a current density of about 5 a.p.s.f. without agitation failed to strip tungsten carbide completely from blade midspan portions in three 30 minute cycles. Removal of some tungsten carbide was, however, evident. Residence time may be improved in this case by adjusting upwardly one or more of the operating parameters, that is CrO_3 concentration, temperature, and current density.

CLAIMS

1. A method for electrochemically stripping tungsten carbide from a titanium or titanium alloy substrate in an electrolytic cell, which comprises immersing a titanium work-piece having a tungsten carbide coating thereon as an anode in an aqueous solution containing from 4 to 40% by weight of CrO_3 , which solution has a temperature of at least 100°F, together with a metallic cathode inert to the aqueous CrO_3 solution, and imposing a direct current voltage across the anode and cathode of from 6 to 50 volts at a current density of from 3.6 to 40 amperes per square foot for a period of at least 30 minutes.

2. A method according to claim 1, in which the aqueous solution also contains a small amount of sulphate ion.

3. A method according to claim 2, in which the concentration of sulphate ion is from 0.03 to 1.0% by weight.

4. A method according to any of claims 1 to 3, in which the metallic cathode is lead.

5. A method according to any of claims 1 to 4, in which the solution contains from 5 to 40% by weight of CrO_3 .

6. A method according to any of claims 1 to 5, in which the aqueous solution is agitated during the stripping operation.

7. A method according to any of claims 1 to 6, in which the period of treatment in the solution is from 60 to 80 minutes.

8. A method according to any of claims 1 to 7, in which the temperature of the solution is from 120 to 140°F.

9. A method according to claim 1, in which the aqueous solution contains, by weight, about 20% of CrO_3 and from 0.03 to 0.75% of sulphate ion, the voltage is from 6 to 9 volts, the current density is from 4 to 8 amperes per square foot, the period of treatment is from 60 to 80 minutes and the temperature is from 130 to 140°F.

10. A method for electrochemically stripping tungsten carbide from a titanium or titanium alloy substrate in an electrolytic cell substantially as herein described with reference to the accompanying drawing.

11. A titanium or titanium alloy substrate electrochemically stripped of tungsten carbide by a method in accordance with any of the preceding claims.

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