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METHOD FOR EVALUATING COATING DISCONTINUITIES

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Fig. 1.

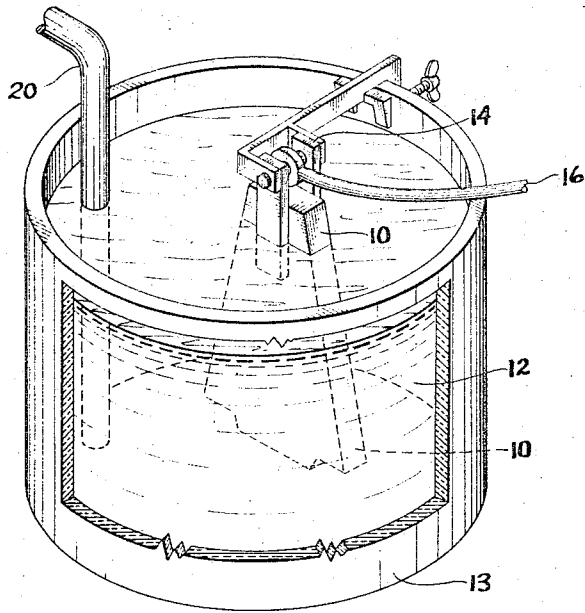
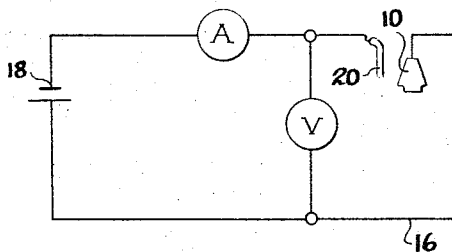


Fig. 2.



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3,366,554 METHOD FOR EVALUATING COATING DISCONTINUITIES

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ABSTRACT OF THE DISCLOSURE

An electrochemical method is disclosed providing accurate detection of defects in non-metallic coatings which have been applied to molybdenum alloys. An electrical conducting material having a non-metallic coating, such as a disilicide coated molybdenum alloy, is wetted with an electrolyte and made the anode in a direct current circuit. Electrolytic chemical action attacks any molybdenum metal exposed by flaws in the disilicide coating. A colored reaction product of electrolyte and molybdenum ions indicate the presence of flaws in the disilicide coating.

Prior attempts to solve the problem of flaw detection in non-metallic coatings have been: (a) the use of X-ray, ultrasonic, eddy current or radiochemical techniques; (b) the use of a nitric-phosphoric acid etchant with phenylhydrazine indicator.

The methods mentioned in (a) have proven insensitive in detecting non-metallic coating flaws in the present state of the art.

Method (b) is not even suitable for those flaws readily visible to the unaided eye, and seldom does it provide a positive test when applied to flaws which are not large enough to be readily seen at a magnification of one power.

A flaw-free, protective coating is required to prevent electron loss (i.e., oxidation) of structures fabricated from the series of refractory alloys based on molybdenum. Alloys in which molybdenum is the major constituent may be used as a structural material for many critical applications because of the metal's high melting point. However, molybdenum loses lattice electrons rapidly in air at temperatures much lower than melting.

In the present state of the art, the disilicide diffusion coating (MoSi_2) is the most successful oxidation-resistant coating known. In the application of this coating to a metal surface, however, surface cracks and pinholes often develop within the coating. If these coating discontinuities extend to base metal, structural failure may occur as the result of extensive base metal electron loss at high temperatures.

Since flaw detection by X-ray, ultra-sonic, eddy current or radiochemical techniques have proved insensitive, some form of chemical test providing flaw detection by color change was necessary.

The teachings of this invention overcome the limitations of the aforementioned prior art. In accordance with this invention, the surface of the test specimen is wet with an electrolyte and made the anode in a substantially non-variable direct-current circuit. Electrolytic chemical action will attack any metal exposed by flaws in the disilicide coating with concomitant formation between metal ions and electrolyte of a colored reaction product.

This colored reaction product may be observed by transferring it onto an absorbent paper strip lying directly over the test specimen. When the paper strip is removed, an exact outline of any coating flaw is imprinted on its surface by the colored ion complex formed by the dissolved metal and electrolyte. If the colored ion is water-soluble, the anode may be wetted or immersed in an elec-

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trolyte in a clear, glass container. Disilicide coating flaws which penetrate to base metal are outlined on the surface of the specimen by virtue of the colored reaction product. The last mentioned method provides a more accurate and readily observable detection means than any others heretofore developed, since it provides overall flaw detection of an entire part or specimen in a single step.

Therefore, it is an object of the teachings of this invention to provide for the detection of microscopic flaws in non-metallic coatings of metals which extend to base metal.

Another object of the teachings of this invention is to provide flaw detection in non-metallic coatings which permits complete specimen investigation with a single step simple test.

Still another object of the teachings of this invention is to establish a correlation between the size of imperfections in disilicide coatings of molybdenum alloys and the likelihood of failure of the alloys due to air oxidation at elevated temperatures.

A fourth object of the teachings of this invention is to evaluate suspected flaws in non-metallic coatings which are visible but which are of unknown extent.

Other objects of this invention will become apparent from the following description in which:

FIG. 1 is an illustration of test apparatus embodied in the teachings of this invention wherein a test specimen of disilicide coated molybdenum alloy forms the anode in an electrolytic chemical reaction.

FIG. 2 is an illustration of the direct current circuit providing energy for the electrolytic chemical reaction.

Referring to FIG. 1, a test specimen 10 comprising a molybdenum alloy having a disilicide coating is suspended in an electrolyte 12 within a clear container 13 by a clamp 14. As a preferred example we find an electrolyte composed as follows satisfactory for an illustrative purpose of the invention: stannous chloride (SnCl_2) 0.2%; potassium thiocyanate (KCNS) 5-10%; and hydrochloric acid (HCl) 0.1 N, balance to give a solution of pH 1. The preferred electrolyte as herein above described provides a rapidly forming red color complex with molybdenum which gives good flaw definition and long color duration with little or no residue. Any alkali metal or ammonium salt of thiocyanate will suffice as well as potassium thiocyanate.

Other electrolyte solutions providing fair to good electrochemical determinations include:

(a) 0.1 N hydrochloric acid and saturated phenylhydrazine indicator, also providing a red color complex with molybdenum;

(b) 2% acetic acid and pyrogallol, providing a yellow color complex with molybdenum;

(c) 0.1 N hydrochloric acid, 0.01% 1,10-phenanthroline, and 1% stannous chloride, giving a blue-black color complex with molybdenum;

(d) 0.1 N hydrochloric acid, and 0.1% potassium xanthate, providing a red-blue color complex with molybdenum; and,

(e) 0.1 N hydrochloric acid and 1% hydrogen peroxide, providing a yellow color complex with molybdenum.

The teachings of this invention are not to be restricted to the electrolyte solutions mentioned above which serve simply as illustrative of possible combinations.

In general, any acid other than a strong oxidizing acid will serve in combination with any of the metal halides as an electrolyte, as long as the pH of the solution is low enough to prevent precipitation of reactants from solution. The presence of halogen ion in a pH of acidic nature provides the necessary corrosive environment for reaction with the base metal of a test specimen. As noted in the

preferred embodiment of the teachings of this invention, a pH of 1 for this particular embodiment is the preferred acidic environment; the embodiment, however, is not restricted to use of hydrochloric acid as the source of hydrogen ion.

Considering now FIG. 2 in conjunction with FIG. 1, by means of a flexible wire connection 16 the test specimen is caused to receive electric current from a substantially non-variable direct-current source 18. A cathode 20, comprising, for example, sixteen gage copper wire, is connected to the negative pole of the substantially non-variable direct-current source 18. The cathode 20 is maintained a nominal distance of 1 inch or more, in the electrolyte solution 12, from the test specimen 10.

Immediately following the application of voltage from the substantially non-variable direct-current source 18, and using the preferred electrolyte above, a red film is formed on the surface of the test specimen 10 indicating a molybdenum surface contamination on the disilicide coating. This surface color is dispersed by agitation of the solution by any energy source such as sonic waves directed at the solution or any number of mechanical agitation means. Thereafter, any appearance of a steady red line on the surface of test specimen 10 or a flow of red color from the line, indicates a positive test for exposed base metal. The appearance of such a colored reaction product can be detected by use of any number of electro-mechanical systems, or detected visually. The ionizing base metal, in the presence of the stannous chloride reducing agent, is stabilized as Mo^{+5} . Reaction with thiocyanate ion CNS^- forms the vivid, water soluble red complex ion of general composition $(\text{Mo}^{+5}\text{R})(\text{SCN}^-)_n$. Metal ions which normally interfere with colorimetric determination of molybdenum, such as vanadium, tungsten, chromium and copper, are not a problem because the high molybdenum concentration overshadows their reaction in this invention.

By maintaining the voltage supply from the substantially non-variable direct-current source 18 between 0.5 to 2.0 volts, in the preferred embodiment, cathode gassing is minimized. The current density in this preferred embodiment, across the test specimen 10, is approximately 1 milliamperes per square centimeter of the test specimen.

These parameters are not to be taken in the restrictive sense but merely reflect the most efficient conditions for the particular electrolyte illustrated. In general, the voltage need only be within those boundary conditions which give satisfactory results within a particular situation. Too high a voltage will result in cathode gassing; too low a voltage results in too slow a reaction period.

Because there is a direct relationship between flaw size in test specimen 10 and the volume of the colored reaction product which flows out of the flaw during test, a severity rating can be approximated to flaws as follows:

(1) The flaw is outlined on the surface of test specimen 10 but no colored reaction product can be seen flowing out into the electrolyte 12.

(2) The flaw is outlined on the surface of test specimen 10 and the colored reaction product oozes slowly out into the electrolyte 12.

(3) The flaw is outlined on the surface of test specimen 10 and a strong stream of the colored reaction product flows out into the electrolyte 12.

Using this classification it has been determined that where a flaw is found as in (1) above, a majority of test specimens do not fail due to oxidation at $1480^\circ \pm 25^\circ \text{C}$. and 760 mm. of pressure. A flaw present in disilicide coatings providing test results as in (2) above signifies a likelihood that a majority of those specimens yielding such a test will fail. And all specimens, yielding a flaw determination test result as in (3) above, will fail under these elevated temperature oxidation conditions.

By probing those areas of predicted oxidation which have been outlined by the above procedure, the extent of undercoating attack of base metal can be determined. By measuring the width of disilicide flaws and correlating

width of flaw with electro-chemical testing results, a direct relationship between flaw width and oxidation resistance was recognized.

It was found that with a flaw width in the disilicide coating of molybdenum alloys of less than 3 microns, a majority of specimens did not fail under oxidation at $1480^\circ \pm 25^\circ \text{C}$. and 760 mm. of pressure. Where flaw width ranges from 3 to 6 microns a majority of specimens failed; and where flaw width ranges 7 microns and more, all specimens failed due to oxidation of base metal molybdenum alloy under conditions of $1480^\circ \pm 25^\circ \text{C}$. and 760 mm. pressure.

Since numerous changes may be made in the above apparatus and different embodiments may be made without departing from the spirit thereof, it is intended that all matter contained in the foregoing description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. The method of detecting defects in disilicide coatings applied to an electrical conducting part containing molybdenum in major proportion comprising the steps:

(a) wetting the part with a electrolyte solution which comprises in composition:

- (1) a reducing agent;
- (2) hydrogen ion of a concentration to maintain an acidic medium; and,
- (3) an indicator responsive within acidic limits and giving a colored reaction product with ions of said electrical conducting part in a reduced state;

(b) making the part anodic in the presence of a cathode by passing a direct current of known density through the part; and,

(c) detecting for appearance of a colored reaction product.

2. The method defined in claim 1 wherein the reducing agent provides a metal corrosive ion.

3. The method defined in claim 1 wherein the color indicator is an alkali metal thiocyanate.

4. The method defined in claim 1 wherein the source of hydrogen ion is any acid other than a strong oxidizing acid.

5. The method defined in claim 1 wherein the reducing agent is a metal halide.

6. The method of detecting defects in a molybdenum disilicide coating for a part comprising a molybdenum alloy in major proportion comprising the steps:

(a) wetting the part with an electrolyte solution which comprises substantially in composition:

- (1) a metal halide;
- (2) a color indicator responsive, within acidic limits, to molybdenum ion in a reduced state; and,
- (3) a source of hydrogen ion;

(b) making the part anodic in the presence of a cathode by passing direct current of known density through the part; and,

(c) detecting for appearance of a colored reaction product.

7. The method defined in claim 6 wherein the color indicator is an alkali metal thiocyanate.

8. The method defined in claim 6 wherein the source of hydrogen ion is any acid other than a strong oxidizing acid.

9. The method of testing a specimen of molybdenum disilicide coated molybdenum alloy for flaws and defects in the molybdenum disilicide coating comprising the steps:

(a) immersing the specimen and a cathode in an electrolyte solution which comprises in composition:

- (1) a reducing agent;
- (2) hydrogen ion of a concentration to maintain an acidic medium; and,
- (3) an indicator responsive within acidic limits and giving a colored reaction product with molybdenum ion in a reduced state;

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- (b) making the specimen anodic in the presence of the cathode by passing direct current of known density through the specimen; and,
- (c) detecting for appearance of a colored reaction product.

10. The method defined in claim 9 wherein premature colored reaction products are dissipated by agitating the solution with an energy source.

11. The method of testing a specimen of molybdenum disilicide coated molybdenum alloy for flaws and defects in the molybdenum disilicide coating comprising the steps:

- (a) immersing the specimen and a cathode in an electrolyte solution comprising substantially:

- (1) 0.2% stannous chloride;
- (2) 5-10% potassium thiocyanate; and,
- (3) 0.1 N hydrochloric acid, balance to a pH of 1.0;

- (b) making the specimen anodic by passing a direct current of known density through the specimen; and,

- (c) detecting for appearance of a colored reaction product.

12. The method defined in claim 11 wherein the direct current has a density across the specimen of at least 1

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milliampere per square centimeter of the specimen surface area.

13. The method defined in claim 11 wherein a substantially non-variable voltage between 0.5 and 2.0 volts is applied to the specimen.

14. The method defined in claim 11 wherein the electrolyte solution comprises substantially:

- (1) 0.2% stannous chloride;
- (2) 5-10% ammonium thiocyanate; and,
- (3) 0.1 N hydrochloric acid, balance to a pH of 1.0.

15. The method defined in claim 11 wherein the electrolyte solution comprises substantially:

- (1) 0.2% stannous chloride;
- (2) 5-10% sodium thiocyanate; and,
- (3) 0.1 N hydrochloric acid, balance to a pH of 1.0.

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