



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

November 19, 1970

REPLY TO
ATTN OF: GP

TO: USI/Scientific & Technical Information Division
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for
Patent Matters

SUBJECT: Announcement of NASA-Owned U. S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code USI, the attached NASA-owned U. S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U. S. Patent No. : 3,529,928

Government or : The Boeing Company
Corporate Employee : Seattle, Washington 98124

Supplementary Corporate
Source (if applicable) : _____

NASA Patent Case No. : NPO-10271

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

Yes ☒

No ☐

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of Column No. 1 of the Specification, following the words "... with respect to an invention of . . ."

Elizabeth A. Carter
Elizabeth A. Carter
Enclosure

Copy of Patent cited above

FACILITY FORM 602

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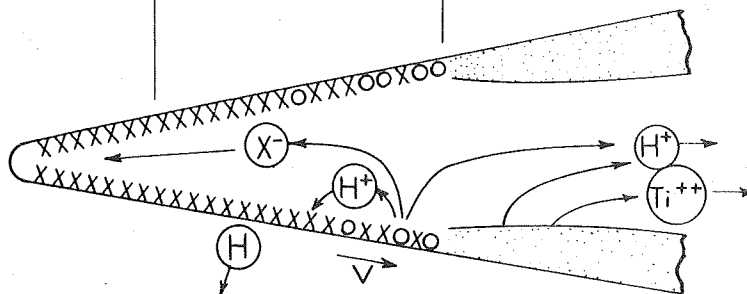
THOMAS O. PAINE, DEPUTY
ADMINISTRATOR OF THE NATIONAL AERONAUTICS
AND SPACE ADMINISTRATION
METHOD OF INHIBITING STRESS CORROSION CRACKS IN TITANIUM ALLOYS
Filed Sept. 30, 1968

3,529,928

TIP
ZONE

MONOLAYER
ZONE

MULTILAYER
ZONE



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3,529,928

METHOD OF INHIBITING STRESS CORROSION CRACKS IN TITANIUM ALLOYS

Thomas O. Paine, Deputy Administrator of the National
Aeronautics and Space Administration, with respect to
an invention of Theodore R. Beck, Seattle, Wash.

Filed Sept. 30, 1968, Ser. No. 763,869

Int. Cl. C23f 11/08

U.S. Cl. 21—2.7

8 Claims

ABSTRACT OF THE DISCLOSURE

Method to prevent stress corrosion cracking of titanium alloys which are subjected to liquids, including pure solvents, comprising adding an oxyanion to the liquids in excess over any chloride, bromide or iodide ions retained in the titanium alloy metal, present in the liquids or obtained from the environment. Further, the addition of the oxyanion prevents stress corrosion cracking of titanium alloys subjected to solutions containing such chloride, bromide and iodide ions in concentrations that are not excessive.

ORIGIN OF INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 83-568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a method for improving the performance of metal alloys. More particularly, the invention relates to a method for preventing stress corrosion cracking of titanium alloys in certain environments.

Description of the prior art

Stress corrosion cracking, SCC, is a severe problem with certain high strength titanium alloys which are exposed to aqueous and other solvent environments.

It is well known that this problem exists, particularly with titanium alloys having a high weight percent aluminum. Titanium alloy tanks, for example, have been known to fail when storing material such as methanol and nitrogen tetroxide. The stress corrosion cracking of titanium in sea water has additionally been reported. Thus, in applications ranging from submarines to supersonic transports, where high strength titanium alloys are particularly desirable, stress corrosion is a problem.

Effort has been directed to developing new alloys resistant to stress corrosion cracking. However, prior to this invention, little effort has been made to evaluate the mechanism of stress corrosion cracking and the reasons therefor in the titanium alloys. In the course of such research a new theoretical model for stress corrosion cracking of titanium alloys and the herein invention was developed. As a result of the development of the model and tests performed, the herein invention was made to inhibit such stress corrosion cracking of titanium alloys exposed to solvents.

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Thus, the object of this invention is to provide a new method for inhibiting stress corrosion cracking of titanium alloys exposed to various fluids.

SUMMARY OF THE INVENTION

The above and other objects of this invention are accomplished by adding to the liquids to be in contact with the titanium alloy extremely small amounts, generally in parts per million, of oxyanions, generally in the form of soluble salts. The oxyanions can include for example, phosphates, chromates, nitrates, carbonate. The cation portion of the salt does not affect the results of the invention and thus could include potassium, sodium, lithium and the like. In addition to the foregoing inorganic oxyanions, organic compounds also containing oxyanion groups such as nitromethane and the like are contemplated.

The addition of these compounds to the fluid material serves to completely inhibit the stress corrosion of the titanium alloys. The amount of the additive is generally determined by the amount of residual chloride in the titanium metals and/or any amount of chloride, bromide or iodide ions present in the fluid composition. As will be shown, a significant excess of the oxyanions should be present relative to the estimated amount of the chloride or other deleterious ions present. Generally, this is from 10 to 100 times the amount of the halide ions on a molar basis.

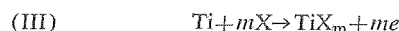
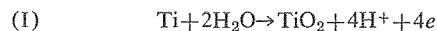
It is believed that the invention will be better understood from the following detailed description and drawing in which:

The figure is a pictorial representation of proposed electrochemical events in a propagating stress corrosion crack in titanium.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The development involved in this invention was made from studies on a prevalent titanium alloy known as Ti-8-1-1. This alloy contains 8 weight percent aluminum, 1 weight percent molybdenum, and 1 weight percent vanadium. It had been previously established and was known in the art that this particular alloy was quite susceptible to stress corrosion cracking, hereinafter referred to as SCC. It should be pointed out, however, that any titanium alloy susceptible to stress corrosion cracking will behave in essentially the same manner, and thus this invention is applicable to a wide spectrum of such alloys.

In order to understand the invention, attention should first be directed to the electrochemical mechanism for stress corrosion crack propagation under potentiostatic conditions in salt solutions. This mechanism has been previously described by the invention in various publications. The analysis is based on three electrochemical reactions that are likely to occur in a propagating crack, as follows:



where X=chloride, bromide or iodide ions.

It is pointed out that only the reactions of titanium are considered since it is the major constituent of the alloy.

Reaction I above is the formation of an oxide film on a newly exposed titanium surface on the walls of a propagating crack. Reaction II is a reduction of hydrogen ions to hydrogen atoms which may dissolve in the metal electrolyte or form gas bubbles. Reaction III is a combination of halide ions X^- with titanium to form a halide.

It has been found that stress corrosion cracking in aqueous environments at room temperature is very specific to three anions and no others. The anions are chloride, bromide and iodide. Other anions that were investigated included fluoride, hydroxide, sulfide, sulfate, nitrate, perchlorate, cyanide and thiocyanate. The reason for only the three halide ions contributing to such corrosion is not known. Precracked alloy specimens were used to study this stress corrosion cracking in pure liquids and solvents with very low salt concentrations. The fatigue cracks were made in notched tensile specimens by flexing them at the midsection with four point loading. This was sufficient to cause small quarter-circle fatigue crack zones on each side of a .001 inch radius machined notch in a .060 inch thick specimen. The propagation of the precracked notched tensile specimen was then studied in the various solvent materials.

The specimens were initially disposed in various solvents which included distilled water, methanol, carbon tetrachloride, methylene chloride, and trichloroethylene. Stress corrosion cracking occurred in all of these solvents. However, there was considerable variation in the crack propagation velocities. Since the SCC was observed in methanol and distilled water it was believed that it was caused by traces of chloride from some source. As a result a series of experiments was made to determine the effect of added chloride to distilled water and methanol. The specimens were handled with rubber gloves after washing with acetone and methanol to avoid any chloride contamination from the hands. The crack propagation velocities were increased with added chloride concentration in both the distilled water and the methanol.

Since it was observed that chloride concentration increased the SCC, a small amount of silver nitrate was next added to the distilled water and methanol solutions in various runs in order to precipitate any chloride contamination that might be present. There was no evidence of any precipitate. However, SCC was completely inhibited in these runs at a concentration of 100 p.p.m. of silver nitrate. At this point, it was felt that the inhibition of SCC could have been due to precipitation of traces of chloride or to the effect of the nitrate ion. Thus, runs were made utilizing an equivalent molar concentration of potassium nitrate. It was observed that the potassium nitrate was only slightly less effective in inhibiting stress corrosion cracking. Further, it was found that a concentration of only 10 p.p.m. potassium nitrate sufficiently inhibited SCC in methanol. Additionally, sodium sulfate was found to be an effective inhibitor at a concentration of 10 p.p.m. in methanol. As a result, it was concluded that the inhibition of SCC was due to the presence of an oxyanion.

In attempting to explain the effect of the oxyanion, attention is again directed to the Reaction I-III above. Data has been obtained on the rates of Reactions I and II. Calculations using kinetic data for oxidation by Reaction I indicate that the oxide forms too slowly to produce wedging of the crack at the velocities that have been observed.

Attention is now directed to the figure, where a model of a wedge-shaped crack is seen. O represents oxide and X represents halide ions. At the tip zone, there is a monolayer of halide ions with no oxide present. Outside of the tip zone is the monolayer zone where the halide is displaced by a monolayer of oxide. Within this monolayer zone, Reaction II can occur, but once again it appears that the rate is too low to produce sufficient hydrogen to cause embrittlement. Reaction II is suppressed on oxide covered walls. It is believed that the halide ion reaction

with the highly stressed apex metal atoms occurs at the crack tip and causes the crack propagation in accord with Reaction III.

In moderately concentrated electrolytes, the anodic current for Reaction I on the walls can be supplied from a source exterior to the crack. Such current may come from cathodic reactions on the exterior of the specimen, or electrically connected structures. With pure solvents or solvents with very low concentrations of dissolved salts in the crack, as generally in the case of the herein invention, the resistivity is so high that the monolayer zone is electrically isolated from the environment. It is proposed, as shown in the figure, that a current of halide ions X^- flows into the tip zone where they are instrumental in the cleavage process, either through chemical or surface forces. In the monolayer zone the halide is displaced by oxide and recycles to the tip. Some simultaneous hydrogen ion reduction occurs at the negative potential of the tip zone with the hydrogen presumably entering the metal. The hydrogen ion reduction current density becomes small at the positive potential of the multilayer zone where formation of oxide and soluble titanium species occur in parallel. The electrical current is carried out of the crack by titanium ions and hydrogen ions produced by oxide formation. The net generation of hydrogen ions in the crack causes the solution to become acid in respect to the bulk solution outside of the crack.

As can be seen from the foregoing discussion, and as represented in the schematic figure, it is believed that the chloride or other halide ion is responsible for SCC in distilled water and methanol. In these two solvents the question then arises as to the source of the halide ion. It is believed that the most probable source would appear to be the metal alloy itself. The concentration of chloride in commercially pure metal has been reported as being on the order of 10 to 20 p.p.m. This level is sufficient to provide enough chloride ions by extraction from newly exposed surfaces from a few microns of ductile yielding at the root of a notch to start SCC. The effect of the oxyanions such as the nitrate or sulfate inhibitors is to swamp the incipient crack front or tip with ions that do not cause SCC before sufficient chloride can be accumulated from the metal. This accounts for the low level of inhibitor required.

As indicated, from the foregoing experiments performed, it was found that oxyanion concentrations in excess of 10 p.p.m. in the methanol solvent solution would effectively inhibit stress corrosion cracking where the solvents were essentially free from chloride, bromide or iodide ions. However, the amount of oxyanion required would appear to be dependent upon the amount of the chloride or other two halide ions present in the metal or solvent or obtained from the environment. Environmental halide ions can come from perspiration, salt mist from the sea and the like. Recent analysis of titanium alloys have indicated chloride concentrations from less than .5 p.p.m. atomic by wet chemistry technique to over 10 p.p.m. atomic by mass spectrograph. Such analyses are being further continued by these and other techniques to resolve the differences.

In order to estimate the length of crack required to make available from the metal enough chloride to form an adsorbed monolayer in the tip zone a means concentration of 10 p.p.m. atomic will be assumed.

It will be further assumed that all of the chloride required for stress corrosion cracking comes from the metal in a distilled water environment and that, once extracted, the chloride is conserved in the tip zone and the monolayer zone. It will be assumed that the chloride is extracted from only the exposed surface atomic layer of metal, i.e., no diffusion from the bulk metal. Chloride is probably extracted from more than a monatomic layer and more than a monolayer of adsorbed ions are required for SCC but these two corrections are compensating. The calculation is to obtain an order-of-magnitude length only.

Consider a unit square array of metal atoms on the surface with dimensions of $10^3 \times 10^3$ atoms. This square would contain 10^6 metal atoms and, statistically, 10 chlorine atoms. To obtain one 10^3 atom row of chlorine atoms would require crack advancement of $10^3/10=100$ unit square arrays. For a tip zone of 10^{-6} cm. length, the number of rows of adsorbed chloride ions in a square array is $10^{-6}/d$, where d is the chloride ion diameter. Assuming a one-to-one correspondence of adsorbed chloride ions to surface metal atoms, the length of crack required to gather sufficient chloride ions is:

$$L = \left(\frac{100 \text{ units}}{\text{row Cl}^-} \right) \left(\frac{10^3 \text{ Ti atoms}}{\text{unit}} \right) \left(\frac{d \text{ cm.}}{\text{Ti atom}} \right) \left(\frac{10^{-6} \text{ cm.}}{d \text{ cm./row Cl}^-} \right) = 10^{-1} \text{ cm.}$$

This is about the length of the fatigue crack put in the metal. Thus if the distilled water entering the crack sweeps the surface chloride to the tip by migration the crack could initiate immediately. Without a fatigue crack, an induction period would be required to gather chloride from the surface of the metal deformed plastically and breaking the surface oxide at the root of a notch. If there is some additional chloride, bromide, or iodide in the solvent the SCC, of course, would be enhanced.

In order to roughly determine the amount of oxyanion required based on 10 to 100 times the amount of chloride present in the solvent on a molar basis (as determined from more concentrated salt solutions), calculations can be made as follows: For each p.p.m. of sodium chloride in the solvent the amount of sodium nitrate needed is as follows:

$$1 \text{ p.p.m. NaCl} \times \frac{\text{NaNO}_3}{\text{NaCl}} \times 10 = 14.5 \text{ p.p.m. NaNO}_3$$

or

$$1 \text{ p.p.m. NaCl} \times \frac{\text{NaNO}_3}{\text{NaCl}} \times 100 = 145 \text{ p.p.m. NaNO}_3$$

where

$$\frac{\text{NaNO}_3}{\text{NaCl}} = \frac{85}{58.5} = 1.45$$

The above calculations are for approximate amounts and are used to illustrate only an order of magnitude.

As pointed out above, this invention is particularly concerned with the problem of residual chloride, bromide or iodide ions in the titanium metal alloys which are exposed to inert solvents and to traces of those halogen ions

in the solvents, whatever the source. It should be quite apparent that solutions or solvents containing the same halide ions will cause stress corrosion cracking in the alloys. Where high concentration of the halide ions on the order of one molar are present in the solvents, little can be done to prevent SCC. However, where small or trace amounts in the form of impurity are present, this invention is equally applicable in that the small amounts of oxyanion required should not affect the performance or chemistry of the solvents exposed to the alloy, thus inhibiting the material from SCC.

What is claimed is:

1. A method of inhibiting stress corrosion cracking in titanium alloys in contact with liquids comprising:

adding to said liquids prior to contact with said alloys an oxyanion in molar excess of the predicted amount of halide ions present in contact with said metal.

2. The method of claim 1 wherein said oxyanion is selected from the class consisting of phosphate, chromate, nitrate, carbonate, and sulfate oxyanions.

3. The method of claim 1 wherein said oxyanion is in the form of a soluble salt.

4. The method of claim 1 wherein the amount of oxyanion is at least 10 to 100 times the amount of halide ions present.

5. The method of claim 1 wherein said liquids are free of halide ions prior to contact with said titanium alloys.

6. The method of claim 2 wherein said oxyanion is selected from the class consisting of silver nitrate, potassium nitrate and sodium sulfate.

7. The method of claim 1 wherein said halide ions are selected from the class consisting of iodide, bromide and chloride.

8. The method of claim 7 wherein said halide is chloride.

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