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NASA CASE NO. LAR 14448-1

PRINT FIG. 1

**NOTICE**

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Serial No.: 07/912,960  
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LaRC

(NASA-Case-LAR-14448-1)  
MULTI-LAYER LIGHT-WEIGHT PROTECTIVE  
COATING AND METHOD FOR APPLICATION  
Patent Application (NASA) 17 p

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**AWARDS ABSTRACT  
MULTI-LAYER LIGHT-WEIGHT PROTECTIVE COATING  
AND METHOD FOR APPLICATION**

NASA Case No. LAR 14448-1-SB

Metals and their alloys have important structural applications in aircraft and aerospace vehicles. Their application under some conditions, however, is limited by their susceptibility to environmental attack. Titanium and its alloys are particularly attractive for aerospace applications because of their high strength and low density, but titanium reacts vigorously with oxygen and nitrogen at elevated temperatures resulting in serious degradation of mechanical properties.

Previous methods of protecting titanium alloys from environmental attack include the use of coatings applied by painting, physical vapor deposition, chemical vapor deposition, thermal plasma spraying and pack cementation. Limitations to these coatings include the interaction of titanium alloys with the coating materials and the relatively large thickness of coating required, e.g., 25 to 50 micrometers, to provide protection. Interactions of the coating with the alloy may have a deleterious effect on the mechanical properties of the alloy and thick coatings abrogate the advantages of the high strength to weight ratio of titanium alloys.

The present invention is a multi-layer protective coating which overcomes the previous problems by depositing a thin reaction barrier on the metal substrate followed by application of a thin diffusion barrier upon the reaction barrier. A sealant layer may also be applied to the surface of the diffusion barrier. The total thickness of the multi-layer coating is typically about 5 micrometers. An important aspect of the present invention is that the reaction barrier should be non-reactive or passivating with respect to the metal substrate and the diffusion barrier. The diffusion barrier should be non-reactive or passivating with respect to both the reaction barrier and the sealant layer. The sealant should be immiscible with the diffusion barrier. In addition, the sealant should have a softening point lower than the expected use temperature of the metal in order to permit it to flow and fill in any cracks or defects in the diffusion barrier and prevent exposure of the underlying reaction barrier and metal substrate to the environment.

These characteristics of the three layers provide protection to the underlying metal without adding significant weight or degrading mechanical properties.

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LAR 14448-1-SB

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PATENT APPLICATION

MULTI-LAYER LIGHT-WEIGHT PROTECTIVE COATING  
AND METHOD FOR APPLICATION

Origin of the Invention

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The invention described herein was jointly made in the performance of work under a NASA contract and an employee of the United States Government. In accordance with 35 U.S.C. 202, the contractor elected not to retain title.

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Background of the Invention

1. Field of the Invention

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This invention relates generally to protective coatings and more specifically to a coating for the protection of reactive metals and their alloys from environmental attack at high temperatures.

2. Description of the Related Art

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Titanium alloys are critically important to aerospace applications because of their high strength and low density. Their application under some conditions, however, is limited by their susceptibility to environmental attack. Oxygen and nitrogen react vigorously with titanium alloys at elevated temperatures, forming surface oxides and causing solid-solution contamination of the alloy which reduces its ductility. Hydrogen, which may be used as a fuel or as a coolant in certain applications, also reacts with titanium alloys over a broad range of temperatures and pressures, forming hydrides which produce a severe loss in mechanical integrity. Because these reactions occur at elevated temperatures, the use of titanium alloys for long times has been limited to temperatures that

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are several hundred degrees below the temperatures where strength properties are degraded. These limitations in high temperature applications prevent the realization of the maximum mechanical and structural efficiency of the materials. Light-weight protective coatings that shield the materials from the environment can significantly extend their maximum use temperature.

Previous methods of protecting titanium alloys from attack by the environment include use of coatings applied by methods such as painting, physical vapor deposition, chemical vapor deposition, thermal plasma spraying and pack cementation. Many of these coatings, such as  $TiAl_3$ , are heat treated after application, producing a reaction layer between the coating and the base material. Limitations to these coatings include the interaction of titanium alloys with the coating materials utilized and the relatively large thickness of coating required (about 25 to 50 micrometers) to provide a substantial degree of protection for structures using gauges of titanium alloy which may be less than .1 inch. Interactions of the coating with the alloy may have a deleterious effect on the mechanical properties of the alloy and thick coatings abrogate the advantages of the high strength to weight ratio of titanium alloys.

#### Summary of the Invention

It is a primary object of the present invention to provide a thin, light-weight protective coating to protect titanium and other reactive metals and their alloys from attack by the environment when utilized in high-temperature applications. Additional objects and advantages of the present invention are apparent from the specification and drawings which follow.

The foregoing objects are achieved by depositing a thin reaction barrier on the metal substrate followed by application of a thin diffusion barrier layer upon the reaction barrier. A sealant layer may also be applied to the surface of the diffusion barrier.

The reaction barrier should be either non-reactive or passivating with respect to the metal substrate and the diffusion barrier. The diffusion barrier should be non-reactive or passivating with respect to both the reaction barrier and the sealant layer. The sealant should be immiscible and non-reactive with  
5 the diffusion barrier. In addition, the sealant should have a softening point lower than the expected use temperature of the metal in order to permit it to flow and fill in any cracks or defects in the diffusion barrier and prevent exposure of the underlying reaction barrier and metal substrate to the environment.

10 The reaction barrier may be a stable compound such as zirconium silicate, yttrium-stabilized cubic zirconia or barium-titanate. The solid-state-diffusion barrier may be a high viscosity layer such as a silica-rich , i.e., containing more than 50% silica, glass matrix containing a lower softening point magnesium-phosphate glass droplet dispersion. This layer inhibits the solid-  
15 state diffusion of oxygen to the metal substrate. The sealant may be a low viscosity layer such as a magnesium-phosphate glass to prevent direct exposure of the reaction barrier and metal substrate to the atmosphere through interconnected porosity or other flaws.

To prepare and apply the reaction barrier, a solution with controlled  
20 drying and surface tension properties is prepared using alkoxides, hydroxides, salts and oxysalts. The metal alloy is immersed in the solution and then withdrawn at a controlled rate, applying a thin layer of solution on the surface of the metal alloy. The alloy is dried and the deposit is converted to an oxide by thermal decomposition in a furnace.

25 The diffusion barrier layer is composed of compounds with low oxygen diffusivities such as a two-phase glass consisting of a silica-rich glass matrix plus a lower softening point magnesium-phosphate glass droplet dispersion. The droplet phase is soft at the use temperature so that it can promote self-healing of defects and microcracks. To prepare and apply this layer, a solution  
30 with controlled drying and surface tension properties is prepared using

alkoxides, hydroxides, salts and esters. The metal alloy containing the reaction barrier is immersed in the solution and then withdrawn at a controlled rate, applying a thin layer of solution on the reaction barrier surface. The alloy is dried and the deposit is converted to a two-phase glass by thermal decomposition in a furnace.

The sealant layer is composed of a compound such as a magnesium-phosphate glass which has a softening point below the use temperature of the alloy in order to permit flow of the compound to fill in any cracks or defects in the diffusion barrier. To prepare and apply this layer, a solution with controlled drying and surface tension properties is prepared using alkoxides, hydroxides, salts and esters. The metal alloy containing the reaction barrier and diffusion barrier is immersed in the solution and then withdrawn at a controlled rate, applying a thin layer of solution on the diffusion barrier surface. The alloy is dried and the deposit is converted to a glass by thermal decomposition in a furnace.

#### Brief Description of the Drawings

- FIG. 1 is a schematic drawing of the light-weight protective coating.
- FIG. 2 is a photocopy of a scanning electron micrograph of a self-healed microcrack in the protective coating.
- FIG. 3 compares oxidation weight gain at 700°C for a variety of coatings.
- FIG. 4 compares oxidation weight gain at 982°C for a coated and uncoated titanium-aluminide alloy.
- FIG. 5 contains a photocopy of optical micrographs of coated and uncoated titanium alloys after oxidation at 982°C for one hour.

Description of the Preferred Embodiments

Referring to FIG. 1, a reactive metal or alloy such as titanium **10** is coated first with a thin reaction barrier **20** composed of a compound such as zirconium silicate, yttrium-stabilized cubic zirconia or barium-titanate. A diffusion barrier **30**, which consists of a two-phase glass such as a silica-rich glass matrix plus a lower softening point magnesium-phosphate glass droplet dispersion is then deposited on the reaction barrier **20**. The thickness of the reaction barrier **20** is approximately 1 to 2 micrometers and the diffusion barrier layer **30** is approximately 2 to 3 micrometers thick. A further refinement comprises a triplex coating where a sealant layer **35** is applied to the diffusion barrier **30**. The sealant is a low viscosity layer such as a magnesium-phosphate glass to prevent direct exposure of the reaction barrier **20** and the metal substrate **10** to the atmosphere through interconnected porosity or other flaws in the diffusion barrier **30**.

The reaction barrier **20** should be either non-reactive or passivating with respect to the metal substrate **10** and the diffusion barrier **30**. The diffusion barrier **30** should be non-reactive or passivating with respect to both the reaction barrier **20** and the sealant layer **35**. The sealant should be immiscible and non-reactive with the diffusion barrier **30**. In addition, the sealant should have a softening point lower than the expected use temperature of the metal in order to permit it to flow and fill in any cracks or defects in the diffusion barrier **30** and prevent exposure of the underlying reaction barrier **20** and metal substrate **10** to the environment.

The following are three illustrative examples of the method for preparing and applying a reaction barrier to the surface of titanium or a titanium alloy:

Example R1. To prepare a zirconium silicate reaction barrier, a solution with controlled drying and surface tension properties was prepared using the following approximate quantities: 1.03 g. water, 0.53 g. HNO<sub>3</sub>, 5.05 g. EtOH and 2.09 g. tetra ethoxy silane. To this solution was added approximately 8.47

EtOH, 0.52 g. HNO<sub>3</sub> and 3.28 g. zirconium n-propoxide. The alloy to be coated was then immersed in the solution and withdrawn at a controlled rate in order to apply a thin layer of solution on the surface of the alloy. The alloy was then dried in the atmosphere, leaving the surfaces covered with a deposit of the prepared solution. The deposit was converted to a stable oxide by thermal decomposition in a furnace at approximately 900°C. This process was repeated as necessary to provide a total reaction barrier layer thickness of approximately 1 to 2 micrometers.

Example R2. To prepare the yttria-stabilized cubic zirconia reaction barrier, a solution with controlled drying and surface tension properties was prepared using the following approximate quantities: 5.53 g. zirconium n-propoxide, 1.15 g. yttrium nitrate, 18.75 g. MeOH and 5.40 g. HNO<sub>3</sub>. To this solution was added approximately 20 ml. MeOH and 20 ml. MEK. The alloy to be coated was then immersed in the solution and withdrawn at a controlled rate in order to apply a thin layer of solution on the surface of the alloy. The alloy was then dried in the atmosphere, leaving the surfaces covered with a deposit of the prepared solution. The deposit was converted to a stable oxide by thermal decomposition in a furnace at approximately 900°C. This process was repeated as necessary to provide a total reaction barrier layer thickness of approximately 1 to 2 micrometers.

Example R3. To prepare a barium titanate reaction barrier, a solution with controlled drying and surface tension properties was prepared using the following approximate quantities: 9.76 g. barium perchlorate, 10.0 g. MeOH, 0.75 g. acetic acid and 8.51 g. titanium butoxide. To this solution was added approximately 100 ml. MEK and 10 ml. MeOH. The alloy to be coated was then immersed in the solution and withdrawn at a controlled rate in order to apply a thin layer of solution on the surface of the alloy. The alloy was then dried in the atmosphere, leaving the surfaces covered with a deposit of the prepared solution. The deposit was converted to a stable oxide by thermal decomposition in a furnace at approximately 900°C. This process was

repeated as necessary to provide a total reaction barrier layer thickness of approximately 1 to 2 micrometers.

The diffusion barrier layer is composed of oxides with low oxygen diffusivities such as a two-phase glass consisting of a silica-rich glass matrix plus a lower softening point magnesium-phosphate glass droplet dispersion. The diffusion barrier layer is tailored so that the droplet phase is soft at the use temperature so that it can promote self-healing of defects and microcracks within the diffusion barrier.

The following are two illustrative examples of the method for preparing and applying a diffusion barrier for use on the preceding reaction barriers applied on titanium or a titanium alloy:

Example D1. To apply a two-phase glass diffusion barrier, a solution with controlled drying and surface tension properties was prepared using the following approximate quantities: 0.61 g. magnesium nitrate, 1.14 g. phosphoric acid, 17.00 g. EtOH and 5.76 g. tetra ethoxy silane. To this solution was then added approximately 2 g. water, 15 ml. MEK and 5 ml. MeOH. The alloy containing the previously applied reaction barrier was immersed in the solution and then withdrawn at a controlled rate, applying a thin layer of solution on the reaction barrier surface. The alloy was dried in the atmosphere, leaving the surfaces covered with a deposit of the prepared solution. The deposit was converted to a two-phase glass by thermal decomposition in a furnace at approximately 700°C.

Example D2. The diffusivity of the diffusion barrier can be decreased by preparing a solution using aluminum nitrate. This solution was made using the following approximate quantities: 0.96 g. magnesium nitrate, 1.88 g. aluminum nitrate, 4.05 g. MeOH and 6.00 g. tetra ethoxy silane. To this solution was added approximately 9.85 g. MEK, 1.44 g. phosphoric acid and 0.50 g. MeOH. The alloy containing the previously applied reaction barrier was immersed in the solution and then withdrawn at a controlled rate, applying a thin layer of solution on the reaction barrier surface. The alloy was dried in the atmosphere, leaving

the surfaces covered with a deposit of the prepared solution. The deposit was converted to a two-phase glass by thermal decomposition in a furnace at approximately 700°C.

To apply the sealant layer to either of the two preceding diffusion  
5 barriers, a solution was prepared using the following approximate quantities:  
0.94 g. aluminum nitrate, 2.69 g. magnesium nitrate, 8.21 g. MeOH and 2.83  
g. tetra ethoxy silane. To this solution was added approximately 2.71 g.  
phosphoric acid, 1.15 g. MeOH and 10.89 g. MEK. The alloy containing the  
previously applied reaction barrier and diffusion barrier was immersed in the  
10 solution and then withdrawn at a controlled rate, applying a thin layer of solution  
on the diffusion barrier surface. The alloy was dried in the atmosphere, leaving  
the surfaces covered with a deposit of the prepared solution. The deposit was  
converted to a glass by thermal decomposition in a furnace at approximately  
700°C.

15 The presence of the magnesium-phosphate dispersion in the diffusion  
barrier layer **30** permits self-healing of microcracks that may form. FIG. 2  
shows a microcrack **40** in the diffusion barrier **30** applied according to Example  
D1 on a titanium sample that has been oxidized at 982°C for one hour. The  
microcrack **40** has been filled by the soft phosphorus-rich dispersion **50**,  
20 thereby preventing attack of the metal substrate by oxygen and nitrogen in the  
environment.

Tests of oxidation weight gain at 700°C and 982°C were conducted on  
a variety of coated and uncoated titanium samples to determine the relative  
effectiveness of the multi-layer protective coating. FIG. 3 shows that a  
25 commercial purity titanium alloy protected with diffusion barriers prepared  
according to Example D1 combined with yttrium-stabilized cubic zirconia and  
barium titanate reaction barriers showed significantly less weight increase due  
to attack by oxygen and nitrogen in the environment than the uncoated titanium  
alloy when tested at 700°C. Embrittlement of the metal occurs when weight  
30 gain due to oxidation reaches approximately .25 mg/cm<sup>2</sup>. A comparison of the

time required to obtain a weight change of .25 mg./cm<sup>2</sup> indicates that titanium protected with the present invention takes over 100 times as long to become embrittled as uncoated specimens of titanium.

FIG. 4 indicates that the 5 micrometer thick, multi-layer protective coating with a sealant layer, a diffusion barrier prepared according to Example D2 and a zirconium silicate reaction barrier applied on a Ti-14Al-21Nb alloy provides improved protection from environmental attack when tested at 982°C compared to that obtained with a 40 micrometer thick coating of Sermalloy J. Sermalloy J is a trademark for a proprietary, aluminum-based coating available from Sermatech of Limerick, Pennsylvania. The triplex coating with the zirconium silicate reaction barrier and a diffusion barrier prepared according to Example D2 also resulted in improved oxidation resistance when compared to a 5 micrometer thick proprietary coating of Al-SiB<sub>x</sub> which is available from Lockheed Corporation.

FIG. 5 shows the severe oxidation that occurs on an uncoated specimen of commercial purity titanium alloy that was oxidized one hour at 982°C. In comparison, the alloy protected with a multi-layer coating, consisting of an yttrium stabilized cubic zirconia reaction barrier and a diffusion barrier prepared according to Example D1, and exposed to the same oxidizing environment as the uncoated specimen showed significantly reduced oxidation of the titanium alloy.

Although the present invention has been described in detail with respect to certain preferred embodiments thereof, it is understood by those of skill in the art that variations and modifications in this detail may be made without any departure from the spirit and scope of the present invention, as defined in the hereto-appended claims.

What is claimed is:

MULTI-LAYER LIGHT-WEIGHT PROTECTIVE COATING  
AND METHOD FOR APPLICATION

Abstract of the Disclosure

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A thin, light-weight, multi-layer coating is provided for protecting metals and their alloys from environmental attack at high temperatures. A reaction barrier is applied to the metal substrate and a diffusion barrier is then applied to the reaction barrier. A sealant layer may also be applied to the diffusion barrier if desired. The reaction barrier is either non-reactive or passivating with respect to the metal substrate and the diffusion barrier. The diffusion barrier is either non-reactive or passivating with respect to the reaction barrier and the sealant layer. The sealant layer is immiscible with the diffusion barrier and has a softening point below the expected use temperature of the metal.

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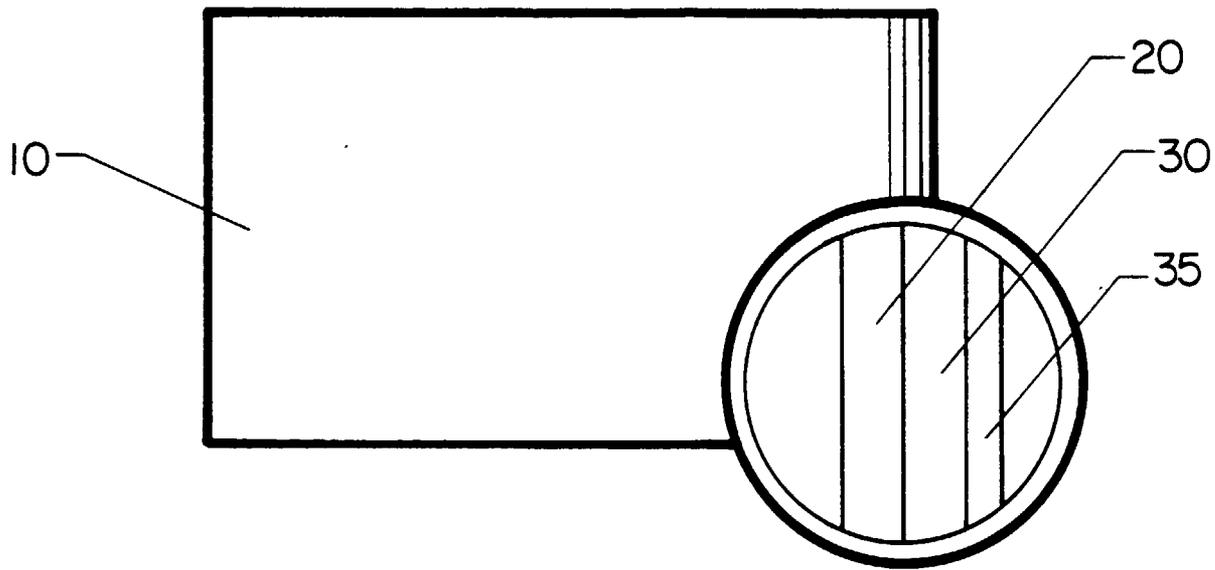


FIG. 1

NASA CASE NO. LAR14148-1-5D  
INVENTOR: KARL E. WIEDEMANN et al  
SHEET 1 OF 5

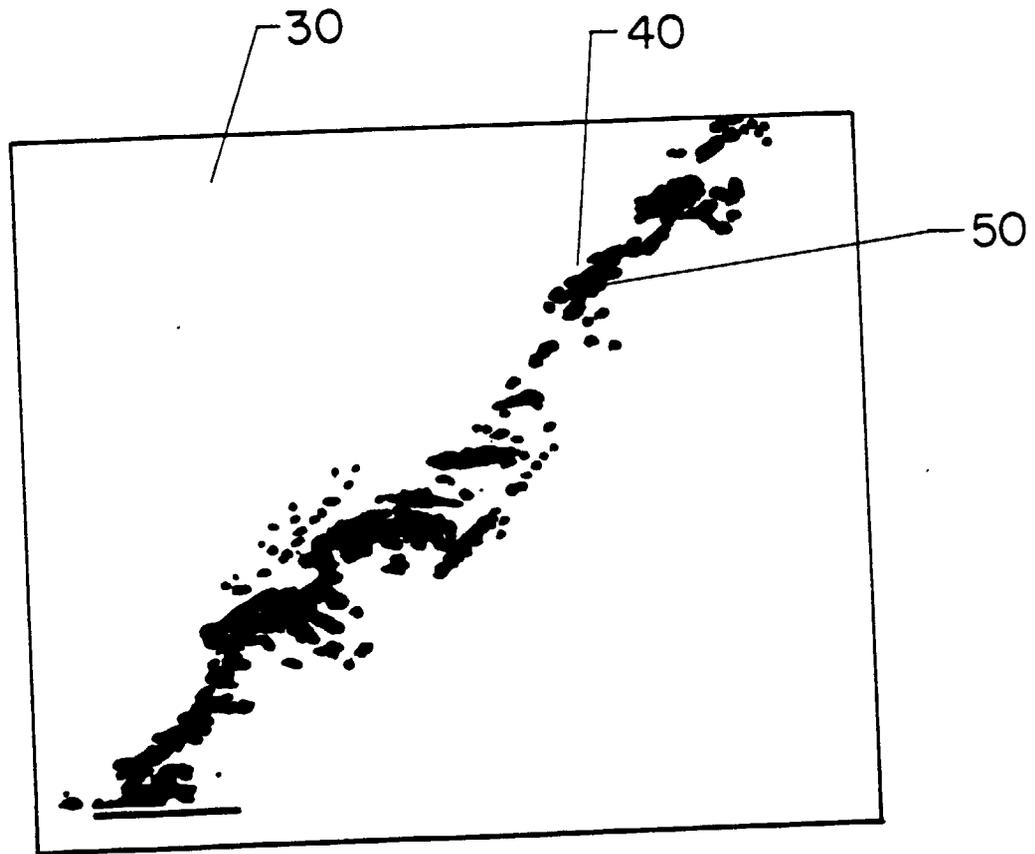


FIG. 2

MYSA CASE NO. LAR14448-1-38  
INVENTOR: KARL E. WIEDEMANN et al  
SHEET 2 OF 5

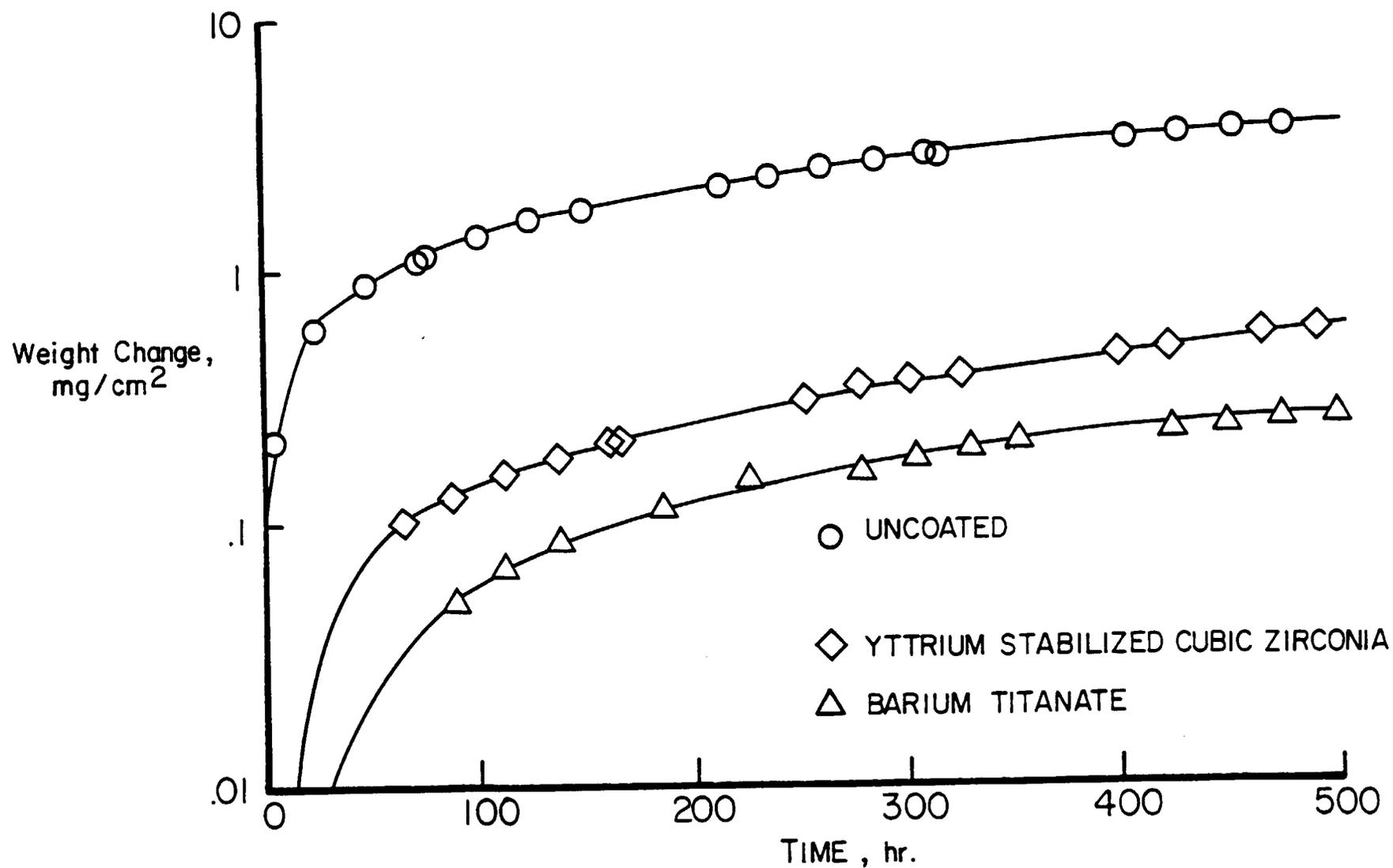


FIG. 3

NASA CASE NO. LAR14446-1-00  
INVENTOR: KARL E. WIEDENMANN et al  
SHEET 3 OF 5

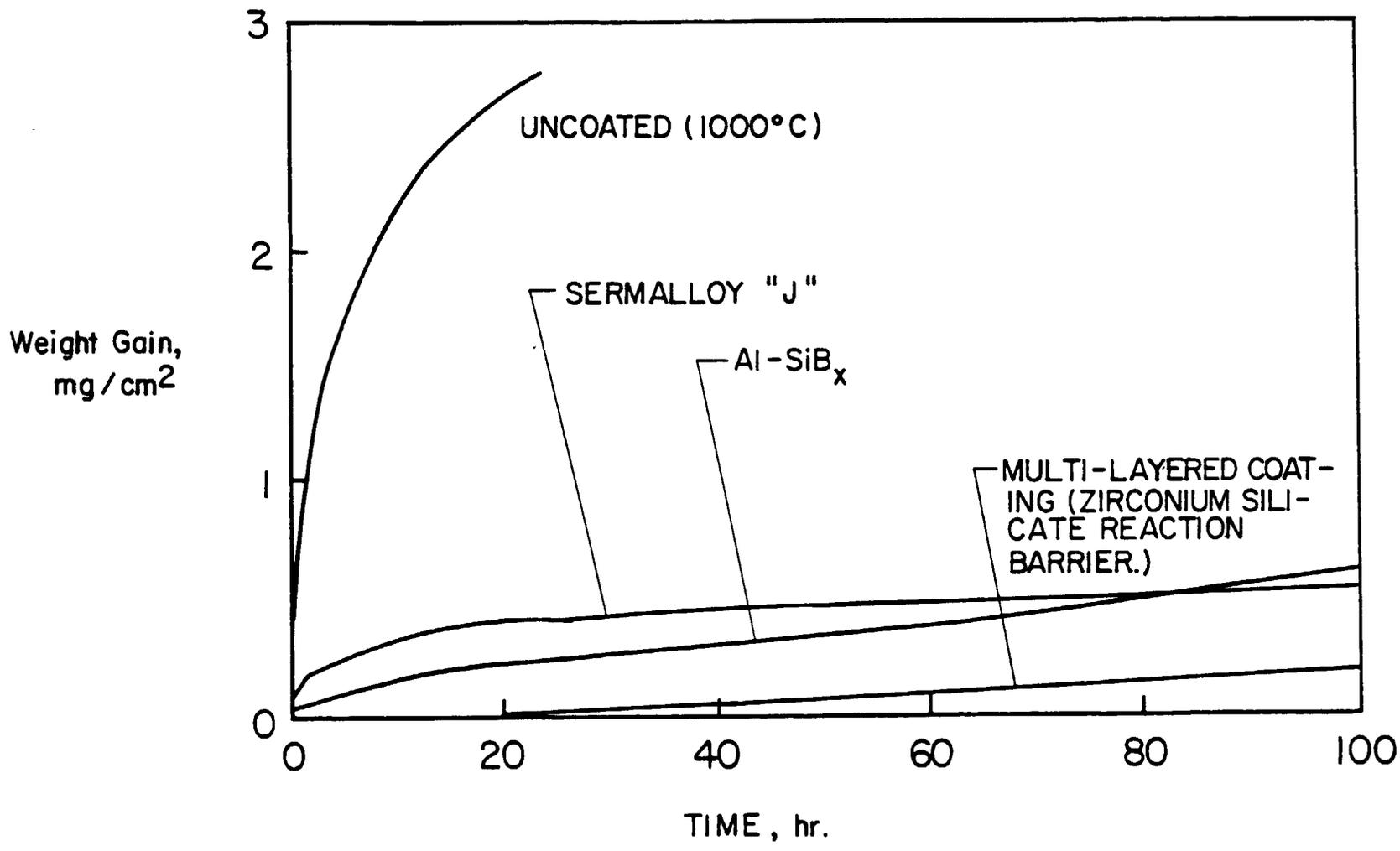


FIG. 4

NASA CASE NO. LAR1444B 1-28  
INVENTOR: KARL E. WIEDERHANN et al  
SHEET 4 OF 5

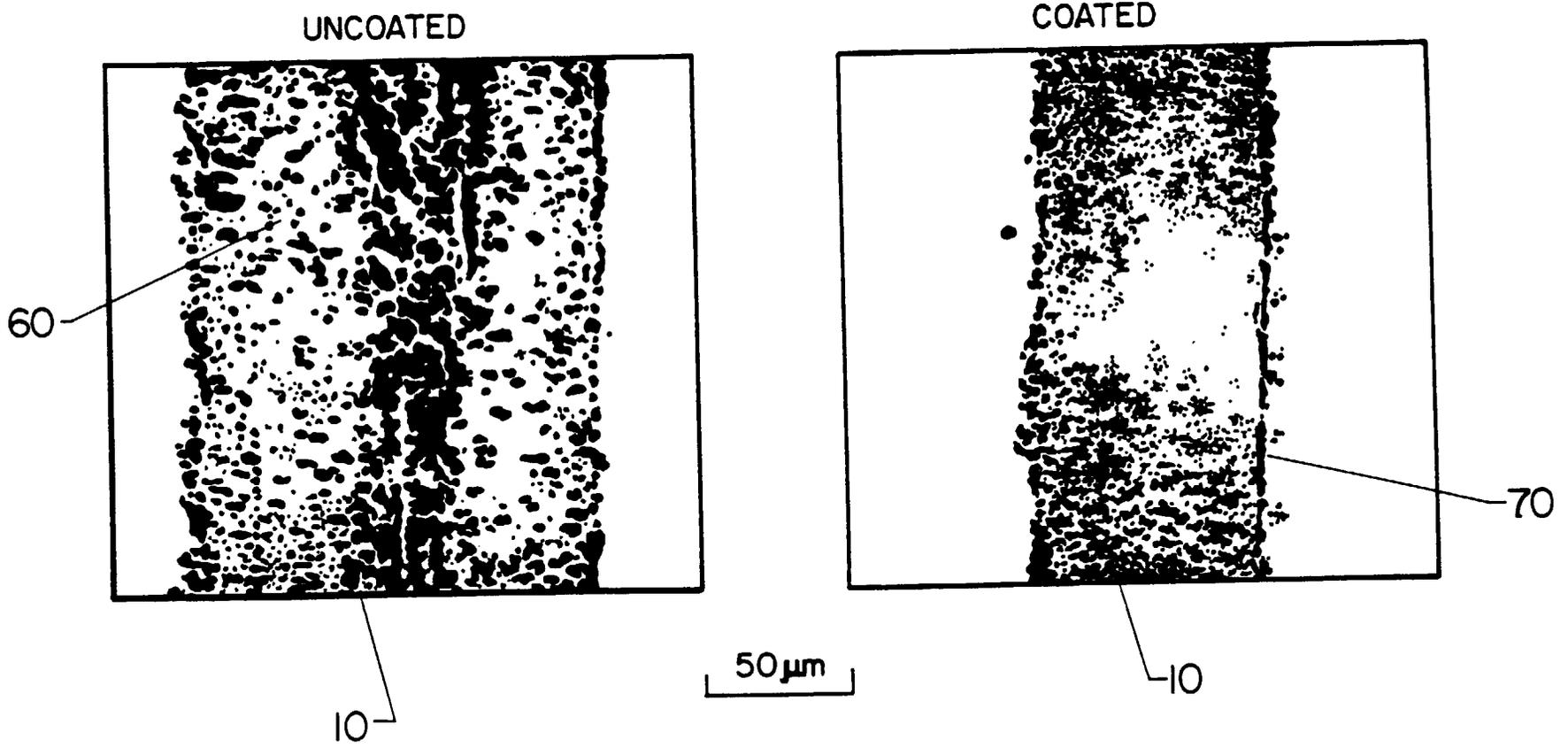


FIG. 5

NASA CASE NO. LAR14442-1 SD  
INVENTOR: KARL E. WIEDEHANN et al  
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