(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 825 444 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
26.05.2021 Bulletin 2021/21

(51) Int Cl.:
C25D 3/56 *(2006.01)* ***C25D 3/66*** *(2006.01)*

(21) Application number: **20208879.5**

(22) Date of filing: **20.11.2020**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
KH MA MD TN

(30) Priority: **22.11.2019 US 201916691917**

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(54) METALLIC COATING AND METHOD OF APPLICATION

(57) A method of depositing a high entropy metal alloy coating onto a substrate includes mixing metallic salts of one or more elements with a solvent to form a mixture, heating the mixture to form a liquid, such that constituents of the liquid are in a mobile ionic state, and electroplating the metallic salts onto a substrate from the ionic liquid. A solution for electroplating is also disclosed. Preferably, the mixture has a eutectic point that is lower than about 100°C, preferably wherein the eutectic point is between about 10°C and 100°C and the one or more elements includes at least one of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium, and combinations thereof.

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND

[0001] Metallic coatings are applied to substrates to protect the substrate. For instance, the metallic coatings can provide corrosion resistance, high temperature oxidation resistance, protection from mechanical damage (e.g., scratching) or other protections for the substrate. Metallic coatings, and in particular refractory metal coatings that comprise high entropy alloys (HEAs) are typically applied to substrates in a very limited variety of ways, including ball milling and sintering, arc induction plasma melting, plasma spray, or laser cladding. However, it is difficult to apply coatings to non-line-of-sight surfaces, such as internal cooling passages of a component, with these methods. Some metallic coatings can be applied to non-line-of-sight surfaces by electroplating. However, electroplating requires the preparation of a solution containing metallic cations dissolved in a carrier liquid. An electrical current is applied to the solution to deposit the metallic cations into a substrate. Preparing such an aqueous solution for electrodeposition of HEA is difficult and expensive, and leads to poor coating structure and low current efficiencies due to the high rate of hydrogen reduction and evolution at the substrate cathode, which makes electrodepositon of refractory HEA from such an aqueous solution difficult and impractical.

SUMMARY

[0002] A method of depositing a metallic coating onto a substrate according to an example of this disclosure includes or comprises mixing metallic salts of one or more elements with a solvent to form a mixture (e.g. a mixture comprised in a solution for electroplating as disclosed herein), heating the mixture to form a liquid, such that constituents of the mixture are in a mobile ionic state, and electroplating the metallic salts onto a substrate from the liquid.

[0003] In a further example of the foregoing, the mixture has a eutectic point that is lower than about 100°C.

[0004] In a further example of any of the foregoing, the heating is to a temperature at or near the eutectic point.

[0005] In a further example of any of the foregoing, the heating is to a temperature that is between the eutectic point and a temperature 10°C above the eutectic point.

[0006] In a further example of any of the foregoing, the eutectic point is between about 10°C and 100°C.

[0007] In a further example of any of the foregoing, one or more elements include one or more refractory metals.

[0008] In a further example of any of the foregoing, one or more elements includes at least one of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium, and combinations thereof.

[0009] In a further example of any of the foregoing, one or more elements includes at least one metal selected from the group of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium.

[0010] In a further example of any of the foregoing, one or more elements includes at least one of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium.

[0011] In a further example of any of the foregoing, the substrate is a component of a gas turbine engine.

[0012] In a further example of any of the foregoing, the substrate includes at least one non-line-of-sight surface. The electroplating is on the at least one non-line-of-sight-surfaces.

[0013] In a further example of any of the foregoing, the liquid is free from water.

[0014] In a further example of any of the foregoing, the solvent is selected from the group of ionic liquids and deep eutectic solvents.

[0015] In a further example of any of the foregoing, the solvent is a deep eutectic solvent, and incudes at least one of choline chloride with urea, ethylene glycol, glycerol, and malonic acid.

[0016] A solution for electroplating according to an example of this disclosure (e.g. for use in the method of depositing a metallic coating onto a substrate disclosed herein) includes or comprises a mixture of metallic salts of one or more refractory metal elements and a solvent, wherein the mixture has a eutectic point below about 100°C.

[0017] In a further example of the foregoing, the eutectic point is between about 10°C and 100°C.

[0018] In a further example of any of the foregoing, the refractory metal elements include at least one of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium, and combinations thereof.

[0019] In a further example of any of the foregoing, the refractory metal elements include at least one metal selected from the group of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium.

[0020] In a further example of any of the foregoing, the mixture is free from water.

[0021] In a further example of any of the foregoing, the solvent is selected from the group of ionic liquids and deep eutectic solvents.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022]

Figure 1 schematically shows an example component.

Figure 2 schematically shown an example method of electroplating a high entropy refractory alloy onto a substrate.

[0023] The various features and advantages of the disclosed examples will become apparent to those skilled in the art from the following detailed description. The drawings that accompany the detailed description can be briefly described as follows.

DETAILED DESCRIPTION

[0024] Metallic coatings can be applied to substrates in order to protect the substrates from high temperatures, corrosion, mechanical damage, or other conditions. In a particular example, metallic coatings are applied to substrates, such as gas turbine engine components, to provide high temperature resistance for the substrates. Figure 1 shows an example cross section of a substrate 10 having a coating 12. The coating has a thickness t.

[0025] Metallic coatings can be alloys of multiple metals. One example type of metallic coating is a high entropy alloy (HEA). HEAs typically include four or more metallic elements in relatively high proportions, e.g., the four or more metallic elements each comprise higher than trace amounts of the HEA. In a particular example, one or more of the elements is a refractory metal. A refractory metal HEA coating example comprises at least one of niobium, molybdenum, tantalum, tungsten, rhenium, and combinations thereof. Another refractory HEA coating example comprises at least one of zirconium, niobium, titanium, tantalum, hafnium, and combinations thereof. And yet another example of a refractory metals HEA coating comprises at least one of niobium, molybdenum, tantalum, tungsten, rhenium, zirconium, hafnium, titanium, and combinations thereof.

[0026] Electroplating is generally known in the art. Essentially, electroplating includes dissolving metallic cations in a carrier liquid to form a solution. The solution is then applied to the substrate, and an electrical current is applied to the solution and substrate. The electrical current causes the metallic cations to deposit onto the substrate, forming a coating on the substrate. Electroplating can be used to apply coatings to non-line-of-sight surfaces, such as internal cooling passages of a component. For instance, the component can be submerged in the solution, which infiltrates the component to the non-line-of-sight surfaces. The metallic cations can then be electroplated onto the component.

[0027] Figure 2 shows an example method 100 of electroplating a metallic coating 12, such as an HEA metal coating, onto a substrate 10. A refractory metal HEA coating is an exemplary case of the above. In step 102, salts of one or more metallic elements (such as a refractory metals) are mixed with a solvent to form a mixture. The resulting mixture is a low temperature eutectic mixture (i.e., the mixture has a lower melting point than its individual components). Example solvents are deep eutectic solvents (DESs) or ionic liquids. Example ionic liquids are imidazolium, pyridinium, and quaternary ammonium salts. DESs are eutectic mixtures of two or more components, typically consisting of a hydrogen-bond acceptor (HBA), for example a quaternary ammonium halide salt, and a hydrogen-bond donor (HBD). The charge delocalization occurring through hydrogen bonding between hydrogen-bond acceptor anions and hydrogen donor molecules results in a decrease in the melting point of the liquid mixture as compared with the melting points of the individual component of DESs. Examples of DESs include eutectic mixtures of choline chloride with urea, ethylene glycol, glycerol, malonic acid, or other hydrogen bond donor species of amides, alcohols or carboxylic acids, respectively.

[0028] In step 104, the mixture is heated to a temperature at or near its eutectic point to melt it (e.g., form a liquid). For example, the mixture is heated to a temperature between the eutectic point and about 10°C above the eutectic point. In some examples, the eutectic point of the salt mixture is below 100°C. In a more particular example, the eutectic point is between about 10°C and 100°C. Because the eutectic point is on the order of room temperature, the mixture can be heated easily and inexpensively by any known means. The heating causes the constituent chemical species to exist in the liquid in a mobile ionic state (e.g., a liquid that includes ionic assemblies of the metallic salts (cations) and anions).

[0029] In some examples, the liquid mixture is free from water. For instance, the metal salts and solvents from step 102 are selected so that the liquid in step 104 is free from water.

[0030] In step 106, the metal salts (such as refractory metal cations, in one example) in the liquid mixture are electroplated onto the substrate 10 as generally discussed above and known in the art to form the coating 12 on the substrate 10. The electroplating can be any known type of electroplating, including pulsed electroplating and potentiostatic electroplating. In potentiostatic electroplating, the electrical current remains constant through the process. In pulsed electroplating, the electrical current is periodically raised and lowered between high and low values, and the polarity can also be momentarily reversed, to control the composition and thickness t of the resulting coating 12.

[0031] Refractory metals in particular were previously difficult to electroplate because the refractory metals have very high melting points. Creating a low eutectic point liquid with constituents including the desired refractory metals as discussed above greatly reduces the heating required to melt the mixture and form the liquid for electroplating the desired metallic composition onto the substrate 10 of choice, as discussed above. Therefore, the above-described method allows for the relatively simple and inexpensive electro-deposition of metallic coatings such as HEAs containing one or more refractory metals onto substrates, including on non-line-of-sign surfaces.

[0032] Use of the above described method overcomes the barriers involved with electroplating of refractory metals via aqueous electrolyte baths. The reduction half-reaction for refractory metal cations generally involves very high potential as compared to other metals like nickel, zinc, etc. This means that if the carrier liquid includes water, the reaction system will tend towards the electrolysis of water, which reaction has a much lower potential than the electroplating reaction for other metals. This in turn produces hydrogen, which is detrimental to the properties of the substrate metal (e.g. hydrogen embrittlement). In addition, the electroplating efficiency (e.g., amount of metallic coating deposited on the substrate over time) is low. To counteract this, very high voltages would be required to be applied to create the electrical current to drive the electroplating. However, in some examples, the above-described method includes a liquid including refractory metal that is free from water and can be used for electrodeposition. Accordingly, by using the above described method with a water-free liquid, electroplating of refractory metals and metal alloys becomes possible.

[0033] Although a combination of features is shown in the illustrated examples, not all of them need to be combined to realize the benefits of various embodiments of this disclosure. In other words, a system designed according to an embodiment of this disclosure will not necessarily include all of the features shown in any one of the Figures or all of the portions schematically shown in the Figures. Moreover, selected features of one example embodiment may be combined with selected features of other example embodiments.

[0034] In some examples, plasma deposition of refractory metal alloys would create different surface morphologies and potentially compositions compared to electrodeposited coatings via the method described in the present invention.

[0035] The preceding description is exemplary rather than limiting in nature. Variations and modifications to the disclosed examples may become apparent to those skilled in the art that do not necessarily depart from the essence of this disclosure. The scope of legal protection given to this disclosure can be determined by studying the following claims.

Claims

1. A method of depositing a metallic coating onto a substrate, comprising:

mixing metallic salts of one or more elements with a solvent to form a mixture;
heating the mixture to form a liquid, such that constituents of the mixture are in a mobile ionic state; and
electroplating the metallic salts onto a substrate from the liquid.

2. The method of claim 1, wherein the mixture has a eutectic point that is lower than about 100°C, preferably wherein the eutectic point is between about 10°C and 100°C.

3. The method of claim 2, wherein the heating is to a temperature at or near the eutectic point, preferably wherein the heating is to a temperature that is between the eutectic point and a temperature 10°C above the eutectic point.

4. The method of any one of claims 1-3, wherein the one or more elements includes one or more refractory metals.

5. The method of claim 4, wherein the one or more elements includes at least one of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium, and combinations thereof, or wherein the one or more elements includes at least one metal selected from the group of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium.

6. The method of any one of claims 1-3, wherein the one or more elements includes at least one of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium.

7. The method of any one of claims 1-6, wherein the substrate is a component of a gas turbine engine.

8. The method of any one of claims 1-7, wherein the substrate includes at least one non-line-of-sight surface, and the electroplating is on the at least one non-line-of-sight-surfaces.

9. The method of any one of claims 1-8, wherein the liquid is free from water.

10. The method of any one of claims 1-9, wherein the solvent is selected from the group of an ionic liquid and a deep eutectic solvent, preferably wherein the solvent is a deep eutectic solvent, and includes at least one of choline chloride with urea, ethylene glycol, glycerol, and malonic acid.

11. A solution for electroplating, comprising:
a mixture of metallic salts of one or more refractory metal elements and a solvent, wherein the mixture has a eutectic point below about 100°C.

12. The solution of claim 11, wherein the eutectic point is between about 10°C and 100°C.

13. The solution of claim 11 or claim 12, wherein the refractory metal elements include at least one of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium, and combinations thereof, or wherein the refractory metal elements include at least one metal selected from the group of zirconium, niobium, titanium, tantalum, molybdenum, tungsten, rhenium, and hafnium.

14. The solution of any one of claims 11-13, wherein the mixture is free from water.

15. The solution of any one of claims 11-14, wherein the solvent is selected from the group of an ionic liquid and a deep eutectic solvent.

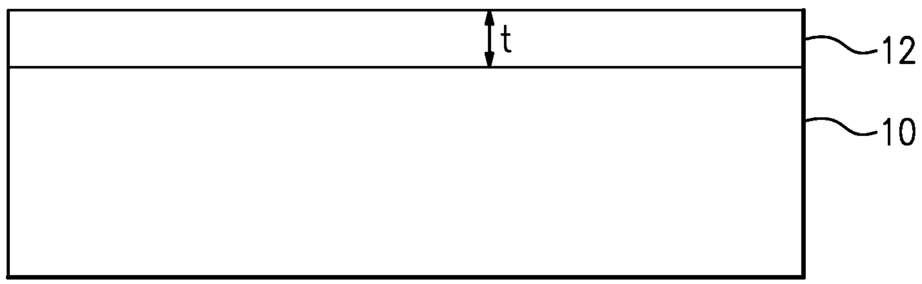
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FIG.1

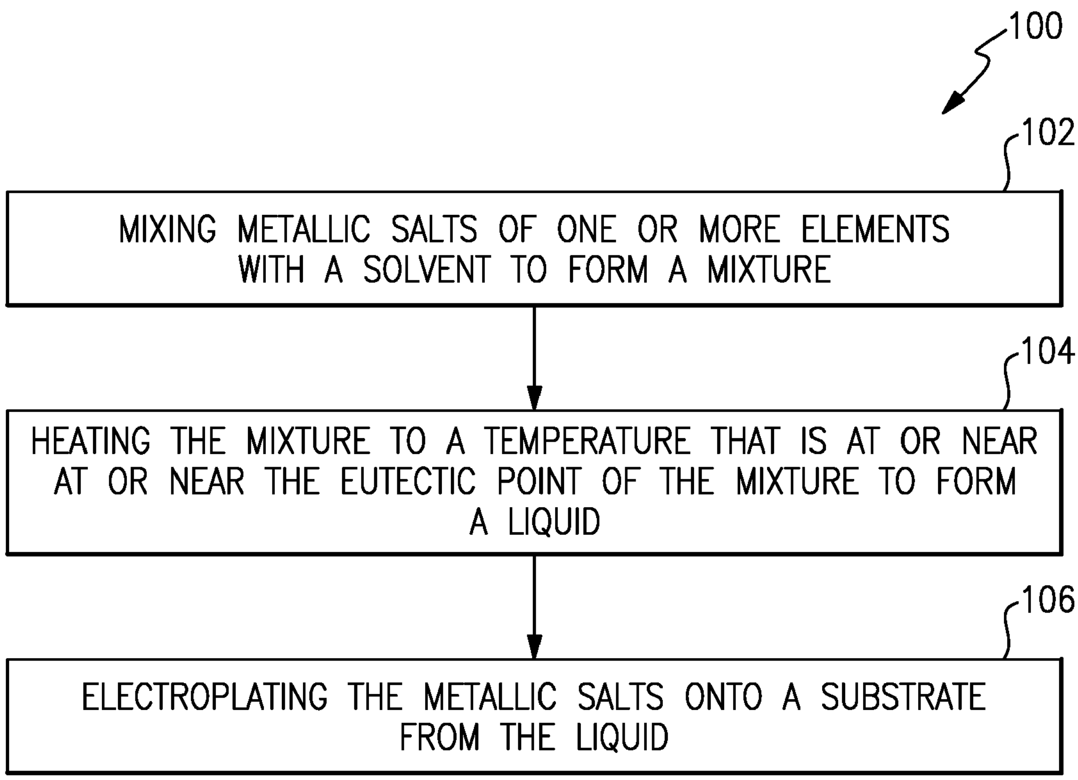
100
102
MIXING METALLIC SALTS OF ONE OR MORE ELEMENTS WITH A SOLVENT TO FORM A MIXTURE
104
HEATING THE MIXTURE TO A TEMPERATURE THAT IS AT OR NEAR AT OR NEAR THE EUTECTIC POINT OF THE MIXTURE TO FORM A LIQUID
106
ELECTROPLATING THE METALLIC SALTS ONTO A SUBSTRATE FROM THE LIQUID

FIG.2

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EUROPEAN SEARCH REPORT

Application Number
EP 20 20 8879

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	9 April 2021	Crottaz, Olivier

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
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