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(54) Title: COMPOSITE STRUCTURE AND METHOD OF PREPARING THE SAME

(57) Abstract: Provided are a composite structure and a method of preparing the same. The composite structure may comprise: a substrate; a decoration coating formed on the substrate which is made from the material selected from the group consisting of titanium carbonitride, titanium aluminum nitride, and tungsten nitride; and a metallization coating formed on the decoration coating, which is made from the material selected from the group consisting of tungsten, aluminum, titanium, chromium, and stainless steel. Also provided is an electronic device with at least a part thereof being made of the composite structure.



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COMPOSITE STRUCTURE AND METHOD OF PREPARING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims priority to and benefits of Chinese Patent Application
5 No. 201010216447.4, filed with the State Intellectual Property Office of the People's
Republic of China (SIPO) on Jun. 28, 2010, the entire content of which is hereby
incorporated by reference.

FIELD

10 The present disclosure relates to composite structures, more particularly to a
composite structure and a method of preparing the same.

BACKGROUND

15 The composite structures were widely used in aviation, aerospace, chemical,
shipbuilding, communication, electronic, auto and other industries. Especially for
electronic products, the composite structures may increase the external attraction and
sensation of these products as well as the value thereof.

At present, physical vapor deposition (PVD), especially magnetron sputtering is the
most popular coating process currently in use, which may provide good performance on
20 bonding, wear and corrosion resistance. However, this process can only bring bald or
monotonous decoration colors.

SUMMARY

In viewing thereof, the present disclosure is directed to solve at least one of the
25 problems existing in the prior art. Therefore, a composite structure is needed, which may
present a coating surface which is more colorful, even with metal quality and sensation.
Further, a method of preparing the same may also need to be provided.

According to an embodiment of the present disclosure, a composite structure is
provided, comprising: a substrate; a decoration coating formed on the substrate which is
30 made from the material selected from the group consisting of titanium carbonitride,
titanium aluminum nitride, and tungsten nitride; and a metallization coating formed on the
decoration coating, which is made from the material selected from the group consisting of
tungsten, aluminum, titanium, chromium, and stainless steel.

According to another embodiment of the present disclosure, a method of preparing a
35 composite structure is provided, comprising the steps of: coating a decoration coating on

a substrate, the decoration coating being made from the material selected from the group consisting of titanium carbonitride, titanium aluminum nitride, and tungsten nitride; and coating a metallization coating on the decoration coating, the metallization coating being made from the material selected from the group consisting of tungsten, aluminum, titanium, chromium, and stainless steel.

With the composite structure of the present disclosure, the coating is colorful, and has metal quality and sensation with high bonding force, good wear resistance and good corrosion resistance.

Additional aspects and advantages of the embodiments of the present disclosure will be given in part in the following descriptions, become apparent in part from the following descriptions, or be learned from the practice of the embodiments of the present disclosure.

DETAILED DESCRIPTION

It will be appreciated by those of ordinary skill in the art that the disclosure may be embodied in other specific forms without departing from the spirit or essential character thereof. The presently disclosed embodiments are therefore considered in all respects to be illustrative and not restrictive.

In some embodiments, a composite structure comprises a substrate, a decoration coating formed on the substrate, and a metallization coating formed on the decoration coating. In some embodiments, the decoration coating is made from the material selected from the group consisting of titanium carbonitride, titanium aluminum nitride, and tungsten nitride. In some embodiments, the metallization coating is made from the material selected from the group consisting of tungsten, aluminum, titanium, chromium, and stainless steel.

In the present disclosure, the composite structure may also be known or termed as a decoration material, which may be applied to different application fields, such as electric devices etc.

In one embodiment, the decoration coating is made from titanium carbonitride, and the metallization coating is made from stainless steel.

In another embodiment, the decoration coating is made from titanium aluminum nitride, and the metallization coating is made from stainless steel.

The thickness of the decoration coating or the metallization coating may be adjusted according to the required colors. In one embodiment, the thickness of the decoration coating may be about 0.8-2 μ m, and the thickness of the metallization coating may be

about 2-8nm. In another embodiment, the thickness of the decoration coating may be about 1.0-1.5 μ m, and the thickness of the metallization coating may be about 3-6nm.

In some embodiments, the composite structure further comprises a transition coating between the substrate and the decoration coating to increase the bonding force between the substrate and the decoration coating. In some embodiments, the transition coating is made from the material selected from the group consisting of tungsten, aluminum, titanium, chromium, and stainless steel. In one embodiment, the transition coating is made from the same material as that of the decoration coating.

In some embodiments, the substrate is made from the material selected from the group consisting of stainless steel, titanium, chromium, aluminum, magnesium, zinc, titanium alloy, magnesium alloy and aluminum alloy.

In some embodiments, a method of preparing the composite structure is provided. The method comprises the steps of: coating a decoration coating on a substrate by magnetron sputtering; and coating a metallization coating on the decoration coating by magnetron sputtering. In some embodiments, the decoration coating is made from the material selected from the group consisting of titanium carbonitride, titanium aluminum nitride, and tungsten nitride. In some embodiments, the metallization coating is made from the material selected from the group consisting of tungsten, aluminum, titanium, chromium, and stainless steel. In some embodiments, target materials during the magnetron sputtering are at least one material selected from the group consisting of titanium, titanium-aluminum, tungsten, chromium, and stainless steel.

In some embodiments, one or more pairs of magnetron targets may be used during the magnetron sputtering, each pair of magnetron targets are powered by one power supply, two targets are each independently connected to one terminal of the power supply, and the targets were insulated from the vacuum chamber.

In some embodiments, a support for holding work pieces may clockwise or counterclockwise rotate around the central axis of the vacuum chamber. In one embodiment, the rotating rate is about 0.5-10 rpm. In another embodiment, the rotating rate is about 2-6 rpm.

In some embodiments, the target for coating the decoration coating has a flat shape; and the target for coating the metallization coating has a cylindrical shape. In some embodiments, the target materials have a purity of above 99.9%. In one embodiment, the target materials have a purity of above 99.99%.

In some embodiments, a bias power supply is used for bombarding the coatings during the magnetron sputtering. The ion bombardment may increase the binding force and the densification of the coatings.

5 In some embodiments, the thickness of the decoration coating is controlled to be about 0.8-2 μ m under a first magnetron sputtering condition; and the thickness of the metallization coating is controlled to be about 2-8nm under a second magnetron sputtering condition. In one embodiment, the thickness of the decoration coating is controlled to be about 1-1.5 μ m under the first magnetron sputtering condition, and the thickness of the metallization coating is controlled about 3-6nm under the second
10 magnetron sputtering condition.

In one embodiment, the first magnetron sputtering condition is as follows: a power of the power supply is about 5-10 KW; a vacuum degree is about 0.3-0.8Pa; a time period is about 35-120 min; a working gas is an inert gas; a reactive gas is nitrogen or a mixed gas of nitrogen and acetylene; and a bias voltage is about 50-200V with a duty cycle of about
15 15%-75%.

In some embodiments, the flow rate of the reactive gas is progressively increased, and:

when the reactive gas is nitrogen, the initial flow rate of nitrogen is about 30-80 standard milliliters per minute, and the final flow rate of nitrogen is about 90-260 standard
20 milliliters per minute; and

when the reactive gas is a mixed gas of nitrogen and acetylene, the initial flow rate of nitrogen is about 10-40 standard milliliters per minute, and the final flow rate of nitrogen is about 50-100 standard milliliters per minute; and acetylene is supplied constantly with a flow rate of about 1-20 standard milliliters per minute; or acetylene is supplied with a
25 progressively increased flow rate with an initial flow rate of about 8-20 standard milliliters per minute and a final flow rate of about 20-60 standard milliliters per minute.

In one embodiment, the second magnetron sputtering condition is as follows: a power of the power supply is about 1-8 KW; a vacuum degree is about 0.1 - 1.0 Pa; a time period is about 1-6 min; a working gas is an inert gas; and a bias voltage is about 100-200
30 V with a duty cycle of about 15%-50%.

In another embodiment, the first magnetron sputtering condition is as follows: a power of the power supply is about 7-9 KW; a vacuum degree is about 0.4-0.7 Pa; a time period is about 40-70 min; a working gas is an inert gas; a reactive gas is nitrogen or a mixed gas of nitrogen and acetylene; and a bias voltage is about 150-200 V with a duty
35 cycle of about 30%-50%.

In some embodiments, the flow rate of the reactive gas is progressively increased, and:

when the reactive gas is nitrogen, the initial flow rate of nitrogen is about 40-60 standard milliliters per minute, and the final flow rate of nitrogen is about 100-150 standard milliliters per minute; and

when the reactive gas is a mixed gas of nitrogen and acetylene, the initial flow rate of nitrogen is about 20-30 standard milliliters per minute, and the final flow rate of nitrogen is about 50-80 standard milliliters per minute; and acetylene is supplied constantly with a flow rate of about 1-20 standard milliliters per minute; or acetylene is supplied with a progressively increased flow rate with an initial flow rate of about 8-20 standard milliliters per minute and a final flow rate of about 20-60 standard milliliters per minute.

In one embodiment, the second magnetron sputtering condition is as follows: a power of the power supply is about 2-4 KW; a vacuum degree is about 0.4-0.7 Pa; a time period is about 3-5 min; a working gas is an inert gas; and a bias voltage is about 150-200 V with a duty cycle of about 30%-50%.

In some embodiments, the inert gas may be helium or argon. In one embodiment, the purity of the inert gas is greater than 99.9%. In another embodiment, the purity of the inert gas is greater than 99.99%.

In some embodiments, in order to increase the bonding force between the substrate and the decoration coating, the method further comprises coating a transition coating on the substrate by magnetron sputtering before coating a decoration coating. The condition for forming the transition coating is as follows: a power of the power supply is a constant power in a range of about 8 KW to 10 KW; a vacuum degree is about 0.4-0.7 Pa; a time period is about 5-15 min; a working gas is an inert gas; and a bias voltage is about 150-200 V with a duty cycle of about 50%-75%. The target material is at least one material selected from the group consisting of titanium, titanium-aluminum, tungsten, chromium, and stainless steel.

In some embodiments, the substrate is made from the material selected from the group consisting of stainless steel, titanium, chromium, aluminum, magnesium, zinc, titanium alloy, magnesium alloy and aluminum alloy.

In some embodiments, in order to increase the bonding force between the substrate and the transition coating, the method further comprises plasma cleaning the substrate before coating the transition coating by magnetron sputtering. The plasma cleaning step comprises using the positive ion of the glow discharge plasma to bombard the substrate under the following condition. A vacuum degree is about 0.8-1.2 Pa; a time period is about

25-30 min; a working gas is an inert gas; and a bias voltage is about 900-1150 V with a duty cycle of about 50%-75%.

In some embodiments, the method further comprises pre-treating the substrate before plasma cleaning the substrate. The pretreatment step comprises mechanical
5 polishing, sand grinding, or wire drawing the substrate, and then ultrasonic cleaning the substrate.

The following examples provide additional details of the composite structure according to embodiments of the present disclosure.

10 EXAMPLE 1

The substrate is made from stainless steel #316L.

(1) Pretreatment

a) Mechanical polishing

Using a JM-101 polisher available from DongGuan JingMi Machinery Equipment Co.,
15 Ltd., the substrate was rough polished with a SBT-600 yellow rough polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min; and then fine polished with a SBW-804 white fine polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min.

20 b) Ultrasonic cleaning

The polished substrate was immersed in a wax removing agent, an oil removal agent, and deionized water in turn, and subjected to ultrasonic cleaning for 5min, 5min, and 10min in turn.

The wax removing agent and the oil removal agent are available from MacDermid Inc.
25 The temperature of the deionized water was about 70°C during the ultrasonic cleaning.

(2) Preparing composite structure

The magnetron sputtering coating equipment available from Beijing Powertech Co., Ltd. was used for coating.

The target material was titanium with a purity of 99.9%, and two pairs of flat
30 magnetron targets were disposed symmetrically in a magnetron sputtering region.

a) Plasma cleaning

The substrate was placed onto the support in the vacuum chamber, and the support was rotated at a rotating rate of about 3 rpm. The vacuum chamber was rough evacuated using the rotary vane vacuum pump and the Roots pump. When the vacuum degree in
35 the vacuum chamber was about 5Pa, the vacuum chamber was fine evacuated using a

molecular pump until the vacuum degree or pressure was 0.08Pa. Then, the vacuum chamber was heated and evacuated until the vacuum degree was 6×10^{-3} Pa. Argon was introduced into the vacuum chamber until the vacuum degree was about 1Pa, and then the substrate was subjected to plasma cleaning at a bias voltage of 1100V with a duty cycle of 75% for 30min.

b) Coating transition coating

The titanium target power supply was turned on, the pressure was adjusted to about 0.5Pa, a power of the power supply was 9 KW, and then magnetron sputtering was performed at a bias voltage of about 200 V with a duty cycle of about 75% for 10 min to form the transition coating on the substrate.

c) Coating decoration coating

The power of the power supply was about 9KW, and at a bias voltage of about 150 V with a duty cycle of about 50%, acetylene and nitrogen were introduced into the vacuum chamber. The flow rate of acetylene was about 10sccm, the flow rate of nitrogen was progressively increased from 20sccm to 50sccm, and then magnetron sputtering was performed for 40 min to form the composite structure.

The titanium target power supply was turned off, the introduction of acetylene and nitrogen was stopped, and the composite structure was cooled for 10min to form a decoration coating with a thickness of about 1.2um on the transition coating. The decoration coating is golden yellow and a bit red and has metal quality.

d) Coating metallization coating

The magnetron sputtering coating equipment available from Beijing Powertech Co., Ltd. was used for coating.

The target material was stainless steel with a purity of 99.9%, and two pairs of cylindrical magnetron targets were disposed in a magnetron sputtering region.

The vacuum chamber was rough evacuated using a rough vacuum pumping system. When the vacuum degree in the vacuum chamber was about 5Pa, the vacuum chamber was fine evacuated using a molecular pump until the pressure (or vacuum degree) was 0.08Pa. Then, the vacuum chamber was heated and evacuated until the pressure (or vacuum degree) was 6×10^{-3} Pa. Argon was introduced into the vacuum chamber until the pressure (or vacuum degree) was about 0.5Pa. The flow rate of argon was about 350sccm, the target power supply was turned on, a power of the power supply was 1.5 KW, and then magnetron sputtering was performed at a bias voltage of about 200 V with a duty cycle of about 50% for 4 min.

The target power supply and the bias power were turned off, the introduction of argon was stopped, and the composite structure was cooled for 10min to form a metallization coating with a thickness of about 4nm on the decoration coating. The metallization coating is light pink and has metal quality and sensation.

5 EXAMPLE 2

The substrate was made from titanium alloy #TA2.

(1) Pretreatment

a) Mechanical polishing

Using a JM-101 polisher available from DongGuan JingMi Machinery Equipment Co.,
10 Ltd., the substrate was rough polished with a SBT-600 yellow rough polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min; and then fine polished with a SBW-804 white fine polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min.

15 b) Wire drawing

The substrate was fine polished using a JM-101 polisher available from DongGuan JingMi Machinery Equipment Co., Ltd. with a red fine polishing ointment 555-10 available from Shenzhen Hongfang Guanhua Science and Technology Co., Ltd. at a rotating rate of 1420 rpm for 10 min.

20 c) Cleaning

The substrate was immersed in a wax removing agent, an oil removal agent, and deionized water in turn, and subjected to ultrasonic cleaning for 5min, 5min, and 10min in turn.

The wax removing agent and the oil removal agent were available from MacDermid
25 Incorporated. The temperature of the deionized water was about 70 °C during the ultrasonic cleaning.

(2) Preparing a composite structure

The magnetron sputtering coating equipment available from Beijing Powertech Co., Ltd. was used for coating.

30 The target material was titanium with a purity of 99.9%, and two pairs of flat magnetron targets were disposed symmetrically in a magnetron sputtering region.

a) Plasma cleaning

The substrate was placed onto the support in the vacuum chamber, and the support was rotated at a rotating rate of about 3 rpm. The vacuum chamber was rough evacuated
35 using the rotary vane vacuum pump and the Roots pump. When the vacuum degree in

the vacuum chamber was about 5Pa, the vacuum chamber was fine evacuated using a molecular pump until the pressure (or vacuum degree) was 0.08Pa. Then, the vacuum chamber was heated and evacuated until the pressure (or vacuum degree) was 6×10^{-3} Pa. Argon was introduced into the vacuum chamber until the pressure (or vacuum degree) was about 1Pa, and then the substrate was subjected to plasma cleaning at a bias voltage of 1100V with a duty cycle of 75% for 30min.

b) Coating transition coating

The titanium target power supply was turned on, the pressure was adjusted to about 0.5Pa, a power of the power supply was 9 KW, and then magnetron sputtering was performed at a bias voltage of about 200 V with a duty cycle of about 75% for 10 min to form the transition coating on the substrate.

c) Coating decoration coating

The power of the power supply was adjusted to about 7KW, and at a bias voltage of about 170 V with a duty cycle of about 75%, acetylene and nitrogen were introduced into the vacuum chamber. The flow rate of acetylene was about 20sccm, the flow rate of nitrogen was progressively increased from 10sccm to 80sccm, and then magnetron sputtering was performed for 35 min to form a composite structure.

The titanium target power supply was turned off, the introduction of acetylene and nitrogen was stopped, and the composite structure was cooled for 10min to form a decoration coating with a thickness of about 1.2um on the transition coating. The decoration coating is golden yellow and a bit red and has metal quality and sensation.

d) Coating metallization coating

The magnetron sputtering coating equipment available from Beijing Powertech Co., Ltd. was used for coating.

The target material was stainless steel with a purity of 99.9%, and two pairs of cylindrical magnetron targets were disposed in a magnetron sputtering region.

The vacuum chamber was rough evacuated using a rough vacuum pumping system. When the vacuum degree in the vacuum chamber was about 5Pa, the vacuum chamber was fine evacuated using a molecular pump until the pressure (or vacuum degree) was 0.08Pa. Then, the vacuum chamber was heated and evacuated until the pressure (or vacuum degree) was 6×10^{-3} Pa. Argon was introduced into the vacuum chamber until the pressure (or vacuum degree) was about 0.5Pa. The flow rate of argon was about 350sccm, the target power supply was turned on, a power of the power supply was 3 KW, and then magnetron sputtering was performed at a bias voltage of about 150 V with a duty cycle of about 30% for 3 min.

The target power supply and the bias power were turned off, the introduction of argon was stopped, and the composite structure was cooled for 10min to form a metallization coating with a thickness of about 3nm on the decoration coating. The metallization coating is light pink and has metal quality and sensation.

EXAMPLE 3

The substrate is made from stainless steel #31 6L.

(1) Pretreatment

a) Mechanical polishing

Using a JM-101 polisher available from DongGuan JingMi Machinery Equipment Co., Ltd., the substrate was rough polished with a SBT-600 yellow rough polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min; and then fine polished with a SBW-804 white fine polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min.

b) Ultrasonic cleaning

The polished substrate was immersed in a wax removing agent, an oil removal agent, and deionized water in turn, and subjected to ultrasonic cleaning for 5min, 5min, and 10min in turn.

The wax removing agent and the oil removal agent were available from MacDermid Incorporated. The temperature of the deionized water was about 70 °C during the ultrasonic cleaning.

(2) Preparing a composite structure

The magnetron sputtering coating equipment available from Beijing Powertech Co., Ltd. was used for coating.

The target material was titanium-aluminum with a molar ratio of 5:5, and two pairs of flat magnetron targets were disposed in a magnetron sputtering region.

a) Plasma cleaning

The substrate was placed onto the support in the vacuum chamber, and the support was rotated at a rotating rate of about 3 rpm. The vacuum chamber was rough evacuated using the rotary vane vacuum pump and the Roots pump. When the vacuum degree in the vacuum chamber was about 5Pa, the vacuum chamber was fine evacuated using a molecular pump until the pressure (or vacuum degree) was 0.08Pa. Then, the vacuum chamber was heated and evacuated until the pressure (or vacuum degree) was 6×10^{-3} Pa. Argon was introduced into the vacuum chamber until the pressure (or vacuum

degree) was about 1Pa, and then the substrate was subjected to plasma cleaning at a bias voltage of 1100V with a duty cycle of 75% for 30min.

b) Coating transition coating

The pressure was adjusted to about 0.5Pa, the target power supply was turned on, a power of the power supply was 5 KW, the flow rate of argon was 280sccm, and then magnetron sputtering was performed at a bias voltage of about 200 V with a duty cycle of about 75% for 10 min to form the transition coating on the substrate.

c) Coating decoration coating

The power of the power supply was about 5KW, and at a bias voltage of about 200 V with a duty cycle of about 30%, nitrogen was introduced into the vacuum chamber. The flow rate of nitrogen was progressively increased from 40sccm to 150sccm, and then magnetron sputtering was performed for 50 min to form a composite structure.

The target power supply was turned off, the introduction of nitrogen was stopped, and the composite structure was cooled for 10min to form a decoration coating with a thickness of about 1.5um on the transition coating. The decoration coating is blue-purple and has metal quality and sensation.

d) Coating metallization coating

The magnetron sputtering coating equipment available from Beijing Powertech Co., Ltd. was used for coating.

The target material was stainless steel with a purity of 99.9%, and two pairs of cylindrical magnetron targets were disposed in a magnetron sputtering region.

The vacuum chamber was rough evacuated using a rough vacuum pumping system. When the vacuum degree in the vacuum chamber was about 5Pa, the vacuum chamber was fine evacuated using a molecular pump until the pressure (or vacuum degree) was 0.08Pa. Then, the vacuum chamber was heated and evacuated until the pressure (or vacuum degree) was 6×10^{-3} Pa. Argon was introduced into the vacuum chamber until the pressure (or vacuum degree) was about 0.5Pa. The flow rate of argon was about 280sccm, the target power supply was turned on, a power of the power supply was 2 KW, and then magnetron sputtering was performed at a bias voltage of about 100 V with a duty cycle of about 15% for 4 min.

The target power supply and the bias power were turned off, the introduction of argon was stopped, and the composite structure was cooled for 10min to form a metallization coating with a thickness of about 5nm on the decoration coating. The metallization coating is light blue and has metal quality and sensation.

EXAMPLE 4

The substrate is made from stainless steel #31 6L.

(1) Pretreatment

a) Mechanical polishing

Using a JM-101 polisher available from DongGuan JingMi Machinery Equipment Co., Ltd., the substrate was rough polished with a SBT-600 yellow rough polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min; and then fine polished with a SBW-804 white fine polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min.

b) Ultrasonic cleaning

The polished substrate was immersed in a wax removing agent, an oil removal agent, and deionized water in turn, and subjected to ultrasonic cleaning for 5min, 5min, and 10min in turn.

The wax removing agent and the oil removal agent were available from MacDermid Incorporated. The temperature of the deionized water was about 70 °C during the ultrasonic cleaning.

(2) Preparing composite structure

The magnetron sputtering coating equipment available from Beijing Powertech Co., Ltd. was used for coating.

The target material was titanium-aluminum with a molar ratio of 5:5, and two pairs of flat magnetron targets were disposed in a magnetron sputtering region.

a) Plasma cleaning

The substrate was placed onto the support in the vacuum chamber, and the support was rotated at a rotating rate of about 3 rpm. The vacuum chamber was rough evacuated using the rotary vane vacuum pump and the Roots pump. When the vacuum degree in the vacuum chamber was about 5Pa, the vacuum chamber was fine evacuated using a molecular pump until the pressure (or vacuum degree) was 0.08Pa. Then, the vacuum chamber was heated and evacuated until the pressure (or vacuum degree) was 6×10^{-3} Pa. Argon was introduced into the vacuum chamber until the pressure (or vacuum degree) was about 1Pa, and then the substrate was subjected to plasma cleaning at a bias voltage of 1100V with a duty cycle of 75% for 30min.

b) Coating decoration coating

The pressure was adjusted to 0.5Pa, the target power supply was turned on, the power of the power supply was adjusted to about 5KW, and at a bias voltage of about 100 V with a duty cycle of about 15%, nitrogen was introduced into the vacuum chamber. The

flow rate of nitrogen was progressively increased from 80sccm to 200sccm, and then magnetron sputtering was performed for 60 min to form a composite structure.

The target power supply was turned off, the introduction of acetylene and nitrogen was stopped, and the composite structure was cooled for 10min to form a decoration coating with a thickness of about 1.6 μ m on the transition coating. The decoration coating is blue-green and has metal quality and sensation.

c) Coating metallization coating

The magnetron sputtering coating equipment available from Beijing Powertech Co., Ltd. was used for coating.

The target material was stainless steel with a purity of 99.9%, and two pairs of cylindrical magnetron targets were disposed in a magnetron sputtering region.

The vacuum chamber was rough evacuated using a rough vacuum pumping system. When the vacuum degree in the vacuum chamber was about 5Pa, the vacuum chamber was fine evacuated using a molecular pump until the pressure (or vacuum degree) was 0.08Pa. Then, the vacuum chamber was heated and evacuated until the pressure (or vacuum degree) was 6×10^{-3} Pa. Argon was introduced into the vacuum chamber until the pressure (or vacuum degree) was about 0.5Pa. The flow rate of argon was about 280sccm, the target power supply was turned on, a power of the power supply was 1 KW, and then magnetron sputtering was performed at a bias voltage of about 100 V with a duty cycle of about 15% for 4 min.

The target power supply and the bias power were turned off, the introduction of argon was stopped, and the composite structure was cooled for 10min to form a metallization coating with a thickness of about 3nm on the decoration coating. The metallization coating is light blue and has metal quality and sensation.

COMPARATIVE EXAMPLE 1

The substrate is made from stainless steel #316L.

(1) Pretreatment

a) Mechanical polishing

Using a JM-101 polisher available from DongGuan JingMi Machinery Equipment Co., Ltd., the substrate was rough polished with a SBT-600 yellow rough polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min; and then fine polished with a SBW-804 white fine polishing ointment available from JacksonLea (Jiangmen) Polishing Materials Co., Ltd. at a rotating rate of 2840 rpm for 10 min.

b) Cleaning

The polished substrate was immersed in a wax removing agent, an oil removal agent, and deionized water in turn, and subjected to ultrasonic cleaning for 5min, 5min, and 10min in turn.

The wax removing agent and the oil removal agent were available from MacDermid Incorporated. The temperature of the deionized water was about 70 °C during the ultrasonic cleaning.

(2) Preparing composite structure

The magnetron sputtering coating equipment available from Beijing Powertech Co., Ltd. was used for coating.

The target material was titanium with a purity of 99.9%, and two pairs of flat magnetron targets were disposed symmetrically in a magnetron sputtering region.

a) Plasma cleaning

The substrate was placed onto the support in the vacuum chamber, and the support was rotated at a rotating rate of about 3 rpm. The vacuum chamber was rough evacuated using the rotary vane vacuum pump and the Roots pump. When the vacuum degree in the vacuum chamber was about 5Pa, the vacuum chamber was fine evacuated using a molecular pump until the pressure (or vacuum degree) was 0.08Pa. Then, the vacuum chamber was heated and evacuated until the pressure (or vacuum degree) was 6×10^{-3} Pa. Argon was introduced into the vacuum chamber until the pressure (or vacuum degree) was about 1Pa, and then the substrate was subjected to plasma cleaning at a bias voltage of 1100V with a duty cycle of 75% for 30min.

b) Coating transition coating

The titanium target power supply was turned on, the pressure was adjusted to about 0.5Pa, a power of the power supply was 9 KW, and then magnetron sputtering was performed at a bias voltage of about 200 V with a duty cycle of about 75% for 10 min to form the transition coating on the substrate.

c) Coating decoration coating

The power of the power supply was about 9KW, and at a bias voltage of about 150 V with a duty cycle of about 50%, acetylene and nitrogen were introduced into the vacuum chamber. The flow rate of acetylene was progressively increased from 10sccm to 22sccm, the flow rate of nitrogen was progressively increased from 20sccm to 70sccm, and then magnetron sputtering was performed for 45 min to form a composite structure.

The titanium target power supply was turned off, the introduction of acetylene and nitrogen was stopped, and the composite structure was cooled for 10min to form a

decoration coating with a thickness of about $H \mu\text{m}$ on the transition coating. The decoration coating has metal quality and sensation.

TESTING

(1) Chroma value

5 The chroma values L , a , and b of the composite structures according to EXAMPLES 1-4 and COMPARATIVE EXAMPLE 1 were tested by a chromameter respectively, where "L" represents luminance, a represents colors ranging from green to red and the b represents colors ranging from blue to yellow..

(2) Bonding force

10 The coating surface of the composite structure was cut into $100 \text{ } 1\text{mm} \times 1\text{mm}$ square grids, and a #600 tape available from 3M Co., Ltd., U.S. was applied onto the surface. The tape was adhered tightly to the surface, and lifted and removed quickly. If 0-5%, by area, of the coating was peeled off, the quality of the composite structure was ranked as 5B; if 5-10%, by area, of the coating was peeled off, the quality of the composite structure
15 was ranked as 4B; if 10-20%, by area, of the coating was peeled off, the quality of the composite structure was ranked as 3B; if 20-30%, by area, of the coating was peeled off, the quality of the composite structure was ranked as 2B; if 30-50%, by area, of the coating was peeled off, the quality of the composite structure was ranked as 1B; and if more than 50%, by area, of the coating was peeled off, the quality of the composite structure was
20 ranked as 0B.

(3) Wear resistance

The composite structures according to EXAMPLES 1-4 and COMPARATIVE EXAMPLE 1 were placed into a tank in a Rosier vibratory wear machine respectively. The abrasives comprise yellow cone particles, green pyramid particles, and Rosier cleaning
25 agent FC1 20.

During the test, the worn out area was measured every half an hour. If the worn out area was less than or equal to $1 \times 1 \text{ mm}$, the test was continued until the worn out area was greater than $1 \times 1 \text{ mm}$. The test time was recorded.

The composite structures are acceptable if the worn out area was less than or equal
30 to $1 \times 1 \text{ mm}$ after the composite structures were tested for 2 hours.

(4) Corrosion resistance

A salt mist box was used for testing. The salt mist comprises 5% NaCl, CuCl_2 and glacial acetic acid. $\text{PH}=3.1-3.3$. The temperature in a testing room was 50°C , the temperature in the box was about 63°C , and the testing time was 8 hours.

The appearances of the composite structures were evaluated according to standard GB6461 -86.

The test results of the composite structures according to EXAMPLES 1-4 and COMPARATIVE EXAMPLE 1 were recorded in table 1.

5

Table 1

		EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4	COMPARATIVE EXAMPLE 1
Chroma value	Decorative coating	L:69.93 a:7.07 b:22.25	L:68.51 a:7.81 b:23.24	L:48.35 a:2.52 b:-10.61	L:48.93 a:-2.95 b:-17.13	L:48.05 a:5.05 b:4.6
	Metallization coating	L:65.79 a:4.12 b:2.80	L:61.45 a:5.63 b:4.6	L:65.57 a:-3.16 b:-3.74	L:68.89 a:-3.10 b:-4.68	
Bonding force		5B	5B	5B	5B	5B
Wear resistance		5 hours	5 hours	5 hours	5 hours	4.5 hours
Corrosion resistance		No corrosion	No corrosion	No corrosion	No corrosion	Slight corrosion

As may be seen from Table 1 that, with the composite structures according to EXAMPLES 1-4, the coating is colorful, and has metal quality and sensation, high bonding force, good wear resistance and good corrosion resistance.

Many modifications and other embodiments of the present disclosure will come to mind to one skilled in the art to which the present disclosure pertains having the benefit of the teachings presented in the foregoing description. It will be apparent to those skilled in the art that variations and modifications of the present disclosure may be made without departing from the scope or spirit of the present disclosure. Therefore, it is to be understood that the disclosure is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A composite structure, comprising:

a substrate;

5 a decoration coating formed on the substrate which is made from the material selected from the group consisting of titanium carbonitride, titanium aluminum nitride, and tungsten nitride; and

10 a metallization coating formed on the decoration coating, which is made from the material selected from the group consisting of tungsten, aluminum, titanium, chromium, and stainless steel.

2. The composite structure of claim 1, wherein the thickness of the decoration coating is about 0.8-2 μ m, and the thickness of the metallization coating is about 2-8nm.

15 3. The composite structure of claim 2, wherein the thickness of the decoration coating is about 1-1.5 μ m, and the thickness of the metallization coating is about 3-6nm.

20 4. The composite structure of claim 1, wherein the substrate is made from the material selected from the group consisting of stainless steel, titanium, chromium, aluminum, magnesium, zinc, titanium alloy, magnesium alloy and aluminum alloy.

5. The composite structure of claim 1 or 4, further comprising:

25 a transition coating between the substrate and the decoration layer which is made from the material selected from the group consisting of tungsten, aluminum, titanium, chromium, and stainless steel.

6. The composite structure of claim 5, wherein the transition coating is made from the same material as that of the decoration coating.

30 7. A method of preparing a composite structure, comprising the steps of:

coating a decoration coating on a substrate, the decoration coating being made from the material selected from the group consisting of titanium carbonitride, titanium aluminum nitride, and tungsten nitride; and

coating a metallization coating on the decoration coating, the metallization coating being made from the material selected from the group consisting of tungsten, aluminum, titanium, chromium, and stainless steel.

5 8. The method of claim 7, wherein the decoration coating is formed on the substrate by magnetron sputtering, and the metallization coating is coated on the decoration coating by magnetron sputtering.

10 9. The method of claim 8, wherein target materials during the magnetron sputtering are at least one material selected from the group consisting of titanium, titanium-aluminum, tungsten, chromium, and stainless steel.

15 10. The method of claim 9, wherein a target for coating the decoration coating has a flat shape, and a target for coating the metallization coating has a cylindrical shape.

11. The method of claim 8, wherein a bias power supply is used for bombarding during the magnetron sputtering.

20 12. The method of claim 11, wherein the thickness of the decoration coating is controlled to be about 0.8-2 μ m under a first magnetron sputtering condition with a power of about 5 to 10 Kw, a vacuum degree of about 0.3 to 0.8Pa, a time period of about 35-120min under an inert gas atmosphere using a reactive gas of nitrogen or a mixed gas of nitrogen and acetylene with a bias power voltage of about 50-200V having a duty cycle of about 15%-75%.

25 13. The method of claim 12, wherein the reactive gas is supplied with a progressively increased flow rate, and wherein:

when the reactive gas is nitrogen,

30 the initial flow rate of nitrogen is about 30 standard milliliters per minute to about 80 standard milliliters per minute, and the final flow rate of nitrogen is about 90 standard milliliters per minute to about 260 standard milliliters per minute; and

when the reactive gas is a mixed gas of nitrogen and acetylene,

35 the initial flow rate of nitrogen is about 10 standard milliliters per minute to about 40 standard milliliters per minute, and the final flow rate of nitrogen is about 50 standard milliliters per minute to about 100 standard milliliters per minute; and

acetylene is supplied constantly with a flow rate of about 1 standard milliliter per minute to about 20 standard milliliters per minute; or acetylene is supplied with a progressively increased flow rate with an initial flow rate of about 8 standard milliliters per minute to about 20 standard milliliters per minute and a final flow rate of about 20 standard milliliters per minute to about 60 standard milliliters per minute.

14. The method of claim 12, wherein the thickness of the metallization coating is controlled to be about 2-8nm under a second magnetron sputtering condition with a power of about 1KW to about 8KW, a vacuum degree of about 0.1 Pa to about 1.0Pa, a time period of about 1-6 min under an inert gas atmosphere, and a bias power voltage of about 100-200V having a duty cycle of about 15%-50%.

15. The method of claim 7, wherein the substrate is made from the material selected from the group consisting of stainless steel, titanium, chromium, aluminum, magnesium, zinc, titanium alloy, magnesium alloy and aluminum alloy.

16. An electronic device with at least a part thereof being made of the composite structure according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/076164

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C23C, B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,CNKI, WPI, EPODOC: decorat+, titanium carbonitride, TICN, titanium aluminum nitride, tungsten nitride, WC, aluminum, chromium, stainless steel, Ti, Al, Cr

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category [*]	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP1577416A1 (SEIKO EPSON CORP), 21 Sep. 2005 (21.09.2005), paragraphs 31-111, abstract	1-16
A	WO2010033799A1 (ACME UNITED CORP, et al.), 25 Mar. 2010 (25.03.2010), the whole document	1-16
A	CN101468538A (BYD CO LTD), 01 Jul. 2009 (01.07.2009), the whole document	1-16
A	CN1055957A (INST OF ELECTROTECHNICS CHINESEACAD), 06 Nov. 1991 (06.11.1991), the whole document	1-16

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 16 Sep. 2011 (16.09.2011)	Date of mailing of the international search report 13 Oct. 2011 (13.10.2011)
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer ZHANG Li Telephone No. (86-10)62085009

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN201 1/076164

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN201 1/076164

Continuation of: the second sheet **A. CLASSIFICATION OF SUBJECT MATTER**

C23C 14/35 (2006.01) i

C23C 14/16 (2006.01) i

B32B 15/01 (2006.01) i