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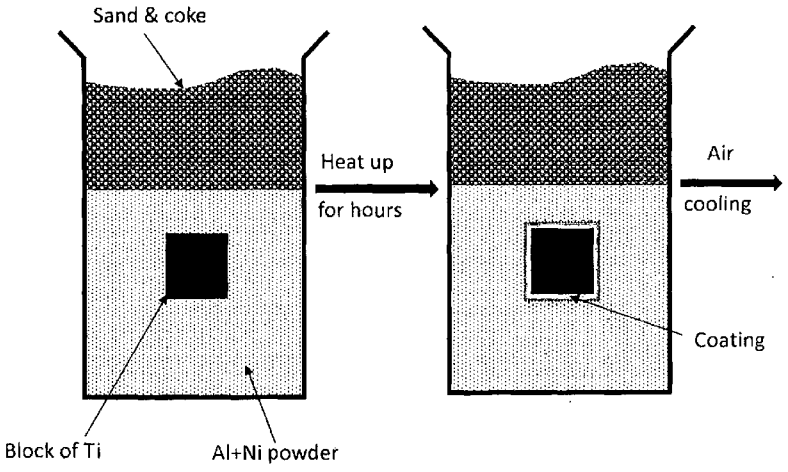

Figure 1: Packed powder diffusion coating process.

(57) **Abstract**: A method of treating a titanium or titanium alloy substrate to provide increased high temperature oxidation resistance and wear resistance, which method comprises: providing on the substrate a composition comprising aluminium particles, another metal powder selected from nickel, copper and zinc powder and an activator; and heating to an elevated temperature until an inter-metallic coating forms on the substrate.

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METHOD OF TREATMENT

Field of the Invention

The present invention relates to the treatment of titanium and titanium alloys to provide increased high temperature oxidation resistance and wear resistance.

Background to the Invention

Titanium and titanium-based alloys are used in a variety of applications that take advantage of their lightness, high strength and excellent corrosion resistance. The aerospace industry in particular may be mentioned here.

However, these materials tend to exhibit poor oxidation resistance due to their relatively high chemical reactivity in high temperature environments. The materials can also show low wear resistance. These shortfalls can limit the range of usage of titanium and titanium-based alloys, and their service life when used in applications associated with high temperature and heavy (abrasive) wear. Thus, currently the most used Ti alloys tend to be used at lower temperatures, such as Ti6Al4V (only used up to about 300°C) and Ti 1100 and IMI834 (only used up to about 600°C).

Efforts to address these limitations have focussed on the development of new alloys, but this tends to increase production costs and can impair other desirable properties such as ductility and toughness. With this in mind a variety of surface coating technologies have been employed with the aim of manipulating surface properties of the material rather than bulk properties. By way of example, mention may be made of PVD, CVD, thermal spray and cold spray methodologies. These approaches seek to provide a coating layer over a substrate with the coating layer having desirable properties in terms of oxidation and wear resistance. However, such coating technologies can suffer poor bond strength between the coating layer and the underlying substrate. In particular, differences in thermal expansion

coefficient mean that the coating layer does not typically adhere well to the substrate at elevated temperature.

With this background in mind, the present invention seeks to provide an alternative methodology for treating a titanium or titanium alloy substrate in order to achieve enhanced high temperature oxidation resistance and wear resistance.

Summary of the Invention

Accordingly, the present invention provides a method of treating a titanium or titanium alloy substrate to provide increased high temperature oxidation resistance and wear resistance, which method comprises:

providing on the substrate a composition comprising aluminium powder, another metal powder selected from nickel, copper and zinc powder and an activator; and

heating to an elevated temperature until an intermetallic coating forms on the substrate.

In one embodiment, the present invention provides a method of treating a titanium or titanium alloy substrate to provide increased high temperature oxidation resistance and wear resistance, which method comprises:

providing on the substrate a composition comprising aluminium powder, another metal powder selected from nickel, copper and zinc powder and a halide activator; and

heating to an elevated temperature until an intermetallic coating forms on the substrate.

The present invention also provides a titanium or titanium alloy substrate that has been treated in accordance with the present invention to provide increased high temperature oxidation resistance and wear resistance to a surface of the substrate.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

Brief description of the drawings

Embodiments of the present invention are illustrated with reference to the accompanying non-limiting figures in which:

Figure 1 is a schematic illustrating implementation of the method of the present invention;

Figure 2 illustrates certain physical properties of a coating formed in accordance with the present invention;

Figure 3 is a schematic illustrating an apparatus for implementing the method of the present invention together with a photograph of the same;

Figure 4 shows photographs of specimens for use in a bonding force test and a lug shear tester;

Figure 5 is a plot of wear resistance of coating produced using the invention compared to plain Ti and Ti6Al4V;

Figure 6 is a plot of weight gain of coated and uncoated titanium compared to Superni 75 superalloy at 900°C;

Figure 7 shows photographs of samples including Ti, Ti6Al4V, Al-Ni coating on Ti and Ti6Al4V after oxidation at 900°C and 800°C for 24h;

Figure 8 includes optical micrographs on the cross-sections of coatings produced using the present invention on pure Ti substrate treated at 650°C for different times: (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h, (e) 15 hours;

Figure 9 is a plot showing the variation of the thickness of coatings produced using the present invention on pure Ti and Ti6Al4Vsubstrates with treatment time at 650°C;

Figure 10 shows optical micrographs on the cross-sections of coatings produced using the present invention on pure Ti6Al4V substrate treated at 650°C for different time: (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h, (e) 15h

Figure 11 includes SEM back scattered electron micrographs of the coatings produced on (a) Ti-10Cr-2Fe-3Al and (b) Ti-6554 substrates;

Figure 12 includes SEM back-scattered electron micrographs of coatings produced using the present invention on pure Ti substrate produced at 650°C for 15 hours;

Figure 13 includes X-ray diffraction patterns on the topmost surface and on the layer that is close the interface of coatings produced using the present invention on pure Ti substrate at 650°C for 15 hours;

Figure 14 shows the cyclic oxidation behaviors of the coatings produced using the present invention on pure Ti and Ti6Al4Vsubstrate compared with those of pure Ti, Ti6Al4V and Superni 75 alloys (oxidation was undertaken at 800°C and 900°C for 24 hours);

Figure 15 shows cyclic oxidation behaviors of the coatings produced using the present invention on pure Ti and Ti6Al4V substrate compared with those of pure Ti and Ti6Al4V alloys (oxidation was undertaken at 1000°C for 24 hours);

Figure 16 shows the coefficient of friction (COF) of a coating produced using the present invention on Ti6Al4V substrate measured at different loads for 30 minutes and compared to the Ti6Al4V alloy;

Figure 17 shows the wear resistance, indicated by the wear volume, of a coating produced using the present invention on Ti6Al4V substrate measured at different loads for 30 minutes and compared to the Ti6Al4V alloy; and

Figure 18 includes SEM micrographs showing the morphology on worn surfaces after wear testing at a load of 50N: (a) Ti6Al4V,(b) coating produced using the invention at 650°C.

Detailed Description of the Invention

The present invention relies on forming a coating on a titanium or titanium alloy substrate by heating the substrate in contact with a mixture of aluminium powder, Ni or Zn or Cu powder, and activator/catalyst. The coating comprises intermetallic species and is believed to be formed by a diffusion-based mechanism. Specifically, it is believed that during heating titanium atoms diffuse from the substrate to the powder mixture surrounding the substrate and react with the aluminium in the mixture to form Al-Ti intermetallics. When nickel is present in the powder mixture the aluminium may also react with it to form Al-Ni intermetallics. When copper and zinc are present in the powder mixture, these species are not believed to react with the aluminium (or titanium). Aluminium atoms in the powder mixture are also believed to diffuse from the powder mixture into the substrate, thereby forming Al-Ti intermetallics within surface regions of the substrate. This is believed to lead to the formation of sub-micrometre or even nanometre-scaled structures within the substrate close to the original surface of the substrate.

This diffusion-based mechanism leads to the formation of a coating that has very good adhesion to the underlying substrate. As the coating is formed by diffusion there is no hard boundary as such between it and the substrate, and this means that the thermal expansion coefficient varies gradually rather than abruptly. Provision of a coating in accordance with the present invention can provide increased surface hardness (and thus increased wear resistance) and a surprisingly high increase in oxidation resistance at elevated temperature. In fact, by employing the present invention it may be possible to produce coated titanium and titanium alloys substrates that exhibit high temperature oxidation resistance that is at least comparable to some nickel-based superalloys. The present invention may therefore increase the range of applications in which titanium and titanium alloys may be used.

In accordance with the present invention a composition comprising a mixture of aluminium powder, one of nickel powder, copper powder and zinc powder, and an activator is provided on (the parts of) the substrate to be coated. The present invention must use aluminium powder since formation of Al-Ti intermetallics is important to formation of a coating having desirable properties. The other metal used (nickel, copper or zinc) is believed to play some beneficial role in allowing/facilitating diffusion of aluminium and titanium atoms as necessary, although the precise details of this are not clearly understood.

In accordance with a preferred embodiment of the invention it is preferred to use a powder mixture of aluminium and nickel powder. In this regard the formation of Al-Ni intermetallics may be desirable to achieving a coating with desirable properties. In other embodiments the composition includes particles aluminium and copper powders or aluminium and zinc powders.

The present invention is described with reference to using aluminium in combination with another metal, namely nickel, copper or zinc. It may be possible to employ aluminium in combination with other metals but in this case such (other) metal must not impede or

interfere with diffusion of aluminium and titanium atoms and reactions to form Al-Ti intermetallics.

The composition should be in intimate contact with the substrate surface and the composition may be consolidated/pressed onto and around the substrate to facilitate this. It is preferred that there minimal no voids and air gaps at the interface between the substrate surface to ensure good contact between the substrate and the composition. The composition should be in dry form. The composition should be provided as a relatively thick layer enough to cover the surface of the substrate, for example at least about 5mm thick. In an embodiment, the composition is packed around the substrate in a suitable container. This embodiment may be regarded as a packed powder diffusion coating technique. The packing process includes burying the substrate in the composition in a container, shaking to ensure intimate contact between the substrate and composition and compaction of the composition around the substrate. Then, a layer of a mixture of sand and coke may be provided on top of the coating composition to prevent ingress of air and to provide a reducing environment

Prior to providing the composition on the substrate the relevant surface(s) of the substrate may be cleaned (e.g. de-greased). It may also be desirable to prepare the surface(s) by machining or grinding as this may enhance coating formation.

The present invention has been found to give advantageous results in terms of high temperature oxidation resistance and wear resistance by using a mixture of aluminium powder in combination with nickel powder, copper powder or zinc powder in the composition. The efficacy of combining in the composition aluminium and one or more of these other metals may be assessed by experiment.

Generally, the average particle size of the aluminium powder used is from 10 to 50 μm. The nickel, copper and zinc are used at an average particle size of from 5 to 15 μm. Useful metal particles are commercially available.

Typically, the composition contains up to 80% by weight of aluminium particles based on the total weight of the composition. The other metals may each be used in an amount up to 40% by weight based on the total weight of the composition.

The activator (catalyst) used is one that promotes formation of the Al-Ti intermetallic coating layer by diffusion of metallic species, and possibly formation of the Al-Ni intermetallics when nickel is used in combination with aluminium. The activator may be a halide activator such as ammonium chloride, aluminum chloride or zinc chloride. Aluminium chloride has been found to work well but can be unstable. The use of ammonium chloride is therefore preferred. Generally, the activator (catalyst) is used in an amount of up to 5% by weight based on the total weight of the composition.

In accordance with an embodiment of the invention the composition may also include a small amount of a refractory material, such as alumina (particles), that is inert at the temperature at which heating takes place. It has been found that this kind of material allows the coated substrate to be more readily released from the coating composition after heating has taken place and the coating has been formed as required. Generally, the refractory material has an average particle size of 10 to 50 μm and is present in an amount of up to 30% by weight based on the total weight of the composition.

The composition is formed by intimate blending of the individual components to form a uniform mixture. This is desirable in terms of ensuring formation of a uniform and homogeneous coating on the substrate.

Once provided the composition has been provided in intimate contact with the substrate heating is undertaken. The temperature should be sufficiently high to allow the coating to form by diffusion of active metal species. Generally, the temperature will be from 500 to 900°C. Heating is generally carried out for a number of hours, for example up to 15 hours. It has been found that the coating generally develops more rapidly at higher temperatures than at lower temperatures. It may be beneficial to carry out heating in an inert atmosphere.

To be useful the coating developed in accordance with the present invention should have a thickness of at least 100 μm, for example from 100 to 2000 μm. The thickness depends upon the coating parameters used, primarily on the temperature and time of heating, and these may be manipulated and optimized as necessary. The optimum coating thickness for a given application may also be determined.

After heating the substrate is allowed to cool before removal from excess coating composition. The coating on the substrate may then be subjected to surface finishing as may be required, for example to maintain dimensional tolerances. Grinding, machining and/or polishing may be applied to the coated substrate. Coated substrates may be assessed for coating quality and analysed using a variety of techniques, such as optical microscopy, electron microscopy and X-ray diffraction.

The present invention may be used to treat a titanium or titanium alloy substrate. Various grades of pure titanium may be used, such as Grade 2. Examples of titanium alloys that may be treated include Ti6Al4V, Ti10V2Fe3Al, Ti6Cr5Mo5V4Al, Ti1100 and IMI834. This list is not exhaustive however and the usefulness of the present invention in relation to other grades of titanium and other titanium alloys may be assessed by experiment.

The present invention may be used to coat the entire exterior surface of a substrate or only a part of the exterior surface. Surfaces not to be coated may be masked or otherwise prevented from being in contact with the composition that is used in the method.

It is believed that the present invention will enable titanium and titanium alloys to be more widely used in applications where their high temperature oxidation resistance and/or wear resistance might previously have been an impediment to use. Total world titanium mill product shipments in 2006 were over 75,000 tons. Approximately 40% of that titanium demand comes from the aerospace industry. Modern aircraft include many tons of titanium per unit and it is commonly used for structural components as well as in engine components at temperatures less than 550°C. It is also used extensively in military aircraft

with titanium contributing a significant percentage of the structural weight per unit. In view of this, a significant commercial application of the present invention is likely to be in using coated titanium alloys instead of parts made of superalloys for use at high temperatures. Superalloys are expensive alloys that exhibit high mechanical strength and creep resistance at high temperatures. Commonly, these alloys are nickel-based. Superalloys are used primarily in the high temperature sections of gas turbine engines (both aerospace and land-based turbines) where titanium and titanium alloys have not been used due to problems of high temperature oxidation. It would be advantageous to provide an alternative to these superalloys for use in this context, and the present invention may permit this.

The invention may also be applied to provide wear resistant coatings on titanium machine components such as on drill bits and cutting tools. Conventionally, surface hardening of such components is undertaken by using gas nitriding, chemical/physical vapour deposition, thermal spraying or laser gas alloying in cases where components are subject to sliding forces or friction.

The present invention may also find use in providing wear resistant coatings on medical implants.

Embodiments of the present invention are illustrated with reference to the following non-limiting examples.

Example 1

Apure titanium piece was placed in a stainless steel container, and buried in a packed powder mixture. The container was placed in a tube furnace with argon protection and heated to temperatures of between 600 and 900 °C for around 12 hours. The argon pressure was kept at 0.04~0.06 MPa with a gas flow rate of 0.1~0.3 ml/min during the whole process.

The arrangement is shown schematically in Figure 1. The figure shows a substrate block (Ti) with dimension of 15×15×15mm embedded and completely surrounded in a composition comprising aluminium (average size ~45 μm, 63.2 wt.%) and nickel (1~5 μm, 15.8 wt.%) powders as metals, ammonium chloride (1 wt.%) as catalyst to activate the metallic particles, and alumina (average size ~45 μm, 20 wt.%) particles as inert filler to avoid sintering. This powder mixture is thoroughly mixed for 60 minutes in a mechanical powder-mixer before use. A layer of sand and coke is provided over the upper surface of the composition to prevent oxidation of metallic powders and titanium substrate by atmospheric oxygen. Heating was undertaken at a rate of 5°C/min to the desired temperature. A composite coating consisting of Al, Al_3Ti and Al_3Ni waa found to have been formed on the surface of the titanium alloy (see Figure 2).

A modified arrangement was employed to produce coatings on titanium alloys without argon protection. This arrangement is shown in Figure 3. At the bottom of the container, a small amount of pure alumina (average particle size: ~45 μm) was pre-filled, in order to facilitate easy removal of the samples after heating. The container was then filled with a powder mixture to completely cover the specimen substrate. The remaining part of the container was topped up with pure alumina powder to evacuate air in order to reduce oxidation of the packed powder. The container was sealed by a combination of compact mechanical contact and high temperature aluminide-base cement to achieve a strong sealing effect. Heating was carried out in a box furnace (exposure to air directly).

Bonding force test

Coatings up to 1000 μm thick have been found to have a bonding force stronger than sprayed coatings. The bond strength of the coating can be determined under shear conditions using a lug shear tester (see Figure 4). A coating strip of 10×10mm^2 with a thickness of 1 mm was produced on a 40×10×10 mm substrate lug, which covers the middle of the substrate as shown in Figure 4. Using an instrumented load frame, the lug with a coated strip was forced through a steel die with a 10×10 mm square opening and with sharp edges, and the coatings were sheared off. The nominal shear strength was

calculated as the peak load divided by the area of the coating/substrate interface. Since no adhesive is required, this testing method overcomes the problem associated with the adhesive failing before the coating. Three tests were performed for the coating, and the average bond strength was found to be 50 MPa. This is believed to be higher than the bond strength that can be achieved by spray coating methodologies, such as cold spray.

The initial goal of the coating was to provide increased surface hardness, and this was achieved with wear resistance over plain Ti being increased by a factor of >3. Figure 5 shows a comparison of volume loss for a Al-Ni coated material produced in accordance with the invention compared to plain Ti and Ti6Al4V. Two-body abrasive wear tests were conducted on the pin-on-disc TABER® Rotary platform abrasion tester (Model 5135), where the coatings and the comparison titanium alloys slides over SiC abrasive paper (#600) adhered on a rotating disc. The wear testing parameters are: specimen size 10×10×10 mm, axial load 5-30 N, and disc rotation speed 60cycles/min.During the tests the surface of SiC paper was cleaned by vacuum. The volume loss of the specimen was utilized to evaluate the wear resistance of materials under two-body abrasive conditions.

Surprisingly it was also found that the coating produced in accordance with the present invention prevented high temperature oxidation of the underlying titanium substrates up to 1000°C. Oxidation is major barrier that prevents the use of titanium in high temperature environments as titanium oxide is brittle. What is also surprising is that at these elevated temperatures the aluminium in the coating should melt. However, the material structure of the coating prevents this from happening. The high temperature resistance of the new, coated material is similar to a superalloy. Advantageously, however the coated material can be created at a much lower cost due to the significantly lower nickel content.

Figure 6 shows weight gain (a measure of the amount of oxidation) versus time at 900 °C. The uncoated materials show significant oxidation, while the coated Ti6Al4V and Ti show comparable performance to the Superni-75 superalloy. The photographs of the corresponding samples after oxidation are given in Figure 7.

Example 2

As received commercial Ti alloys plates and rods, including pure Ti (Grade 2), Ti-6Al-4V, Ti-10V-2Fe-3Al and Ti-6Cr-5Mo-5V-4Al, were cut into 10×10×10 mm blocks. All faces of the blocks were ground on silicon carbide (SiC) paper up to grade 600, followed by ultrasonic cleaning and drying. The packed powder mixture used was the same as that in Example 1 (Al: ~45 μm, 63.2 wt.%; Ni: 1~5 μm, 15.8 wt.%; NH_4Cl: 1 wt.%; Al_2O_3: ~45 μm, 20 wt.%). An optimized treatment temperature of 650°C was chosen to produce coatings with different thickness on Ti alloys for various heating times of 3-15 hours, followed by air cooling down to room temperature.

Microstructure analysis

The thickness of coatings produced on was measured on optical micrographs. The microstructure and chemical compositions of the coatings was also examined using scanning electron microscopy (SEM) together with energy-dispersive spectroscopy (EDS) on JEOL 6460LA. X-ray diffraction of Cu *Kα* radiation was used to characterize the phase structures of coatings.

Oxidation test

In order to evaluate the oxidation resistance of the coatings, thermal cyclic oxidation tests were conducted in static air at temperature ranging from 800 to 1000°C for 24 cycles. Each cycle consisted of one hour immersion in static air in the box furnace, followed by a 30 minutes air cooling down to room temperature. The coated samples were subjected to oxidation together with pure Ti and a commercial Ti-6Al-4V alloy for comparison. These specimens were placed in a quartz tube with both ends closed through a 20 mm hole on the cylinder wall. An electronic balance was used to measure weight change. The sample weights were measured to 0.0001g. The oxidation kinetics were monitored by measuring the weight gain as a function of oxidation time and also by measuring the total scale thickness after oxidation.

Friction and wear tests

Dry sliding wear tests on the coatings were performed on an Optimol SRVIII oscillating friction and wear tester at room temperature (25°C) in air with a relative humidity of 40-50%. The machine was equipped with a ball-on-disc contact configuration, which uses WC-Co balls with a hardness of HV-1750 as the counter friction pair. Prior to testing, all specimens were cut into 3mm thick plates and mechanically polished through a level of #1200 grit paper, followed by ultrasonic cleaning and drying. Detailed testing parameters are as follows: 2 mm oscillating stroke with a frequency of 5 Hz, and a load ranging from 10 to 50 N were applied for 30 minutes; wear volume loss were determined by formula proposed by Qu *et al* [An efficient method for accurately determining the wear volumes of sliders with non-flat wear scars and compound curvatures; Wear, **261** (7-8) (2006): 848-855. For comparison, the tribological behaviour of Ti-6Al-4V samples was explored under the same conditions.

Results and Discussion

Microstructure and thickness

The cross-sectional optical micrographs of coatings produced on pure Ti substrates in the powder mixture at 650 °C for 3-15 hours are shown in Figure 8. All coatings produced for different times are integrated very well with the substrates and no cracks, gaps and pores are observed along the interface, indicating a high level of bonding. One can also see that as the treatment time increases from 3 hours to 12 hours, not only does the coating thickness increase, but it also becomes more compacted. In the coating produced in 3 hours as shown in Fig. 8(a), tiny pores can be observed. However, fully compact coatings without noticeable pores or cracks are obtained after treatment over 6 hours. Figure 8(b)–(e) show dense coatings. The variation of coating thickness on pure Ti substrates with the treatment time is plotted in Figure 9. The thickest coating is obtained after 12 hours

treatment. Treatment for longer time up to 16 hours reduces the thickness. The actual reason for this reduction in thickness is not clear.

To validate the technique in Ti alloys, the methodology of the present invention was also carried out on Ti6Al4V alloy, which is a typical Ti alloy. The cross-sectional optical micrographs of PPDC coatings on Ti6Al4V substrates produced at 650°C for 3-15 hours are shown in Figure 10. Similar to pure Ti, all coatings exhibit a high level of bonding with the substrates without cracks, pore and gaps. However, dense coatings are obtained when the heat treatment is over 6 hours. Variation of the coating thickness with treatment time is also shown in Figure 10. Compared to the coatings on pure Ti, the coatings produced on Ti6Al4V substrates are slightly thinner. It is believed that the existence of aluminium in Ti6Al4V may suppress aluminium atom diffusion from the source powder into the substrate.

In order to further validate the methodology of the present invention, coatings were produced on Ti-10Cr-2Fe-3Al and Ti-6Cr-5Mo-5V-4Al alloy substrates. As shown in Figure 11, thick and dense coatings were also successfully produced on both Ti alloys. Therefore, it is reasonable to conclude that the newly developed technique can be used on various Ti alloys and the thickness of the coating can be varied from 100 μm to 2000 μm depending on the treatment temperature and time.

Phase structure in the coating

To explore the phase structure of the coatings, backscattered electron micrographs on the cross-sections of the coatings were examined in SEM. Figure 12 shows a typical example of such micrographs, taken from the coating on pure Ti produced at 650°C for 15hours. It can be seen that the coating consists of two different phases, i.e. it is a composite coating. The "white" phase uniformly distributes in the "dark" matrix phase. Subsequent EDS analysis revealed that the "white" phase is an Al-Ni intermetallic compound and the "dark" phase is an Al-T intermetallic compounds.

To further identify the phases in the coating, X-ray diffraction analysis was performed on both the topmost surface and on the coating layer close to the interface between the coating and substrate. The latter was explored through mechanical removal of material outer layers from the substrate. The X-ray diffraction spectra are shown in Figure 13. Indexing the spectra indicates that the coating contains Al_3Ni and Al_3Ti intermetallic compounds and Al solid solution.

Compared to the monolayer of intermetallic, this composite coating could provide much more volume tolerance avoiding the formation of cracks during heating or cooling.

Oxidation resistance

Figure 14 shows the kinetic curves of cyclic oxidation of coatings, pure Ti and Ti6Al4V in static air at 800 and 900°C for 24 cycles, respectively. It can be seen that the weight gains of coated samples are much lower than that of pure Ti and Ti6Al4V at both temperatures. Compared to a Ni-based superalloy (Superni 75), the coatings show comparable, or even better, oxidation resistance than the Ni-based superalloy. This implies that some Ni-based superalloys could possibly be replaced with coated Ti alloys in industrial applications, significantly reducing the cost.

In order to investigate the effects of coatings with different thicknesses on oxidation resistance, the weight gains of coatings produced at 650°C for different times ranging from 3 to 15 hours were measured at 1000°C for 24 cycles and the results are shown in Figure 15. Compared to pure Ti and Ti6Al4V, the coatings exhibit excellent oxidation resistance, and the thickness of coating has no obvious effects on their oxidation behavior.

Friction and wear

Figure 16 shows the average friction coefficients of the coatings measured at different loads. At each load, the coatings show lower friction coefficient than Ti6Al4V substrates. In addition, the coatings also exhibit higher wear resistance under dry sliding conditions, as shown in Figure 17. This is attributed to the hardening effect of Al_3Ti in the coating. After

the dry sliding tests on both coating and Ti6Al4V substrate, examination of the worn surface shows the same abrasive wear, and shallower grooves can be observed on the worn surface of the coating than that on surface of worn Ti6Al4V substrate, as shown in Figure 18.

Example 3

The process uses a powder mixture of commercial Al powder with average particles size ranged from 10 μm to 40 μm, 10 to 40 wt% Ni powder with particle size ranged from 5 μm to 15 μm, and 10 to 30% Al_2O_3, together with 0.5 to 4 % NH_4Cl as catalyst. After burying a titanium substrate in the powder mixture in a container, heat treatment is carried out at temperature between 550°C to 800°C for various times depending on the thickness of the coating required. The optimised parameters of treatment to achieve thick coatings are a coating composition of approx. 60wt%Al, approx. 20wt%Ni, approx. 20wt%Al_2O_3 and approx. 1wt%NH_4Cl, treated at 650°C for 1 to 12 hours.

The thickness of the coating produced varies from 100 μm to 2000 μm depending on the treatment parameters. Electron microscopy and X-ray diffraction analysis indicates that the coating consists of Al, $TiAl_3$ and $NiAl_3$ phases forming a composite coating. The hardness of the coating has been found to be 2 to 3 times higher than the substrate with significantly increased wear resistance. More importantly, the oxidation resistance provided by the coating has been found to be comparable to Ni-based superalloys at temperature as high as 1000°C.

Raw materials and equipment:

Substrate: pure Ti, Ti alloys and Ti-based composites. Surface finish as machined or ground.

Powders: Commercial pure Al powder with average particle size between 10 and 40 μm.

Commercial pure Ni powder with average particle size between 1 and 20 μm.

Commercial NH_4Cl as catalyst.

Furnace: Any open air heat treatment furnaces.

Container: stainless steel or ceramic container. Dimension of the container depends on the size of Ti components.

Mixing of powders:

50-80%Al, 10-40%Ni, 10-30%Al_2O_3, and extra 1-4%NH_4Cl (all in weight percentage)

Mixing: using any mechanical mixer.

Treatment regime:

Temperature: 550°C to 800°C

Time: 3 to 12 hours

Heating: In furnace

Cooling: In furnace or in air

Procedure:

1. Prepare surface of the Ti components as machined or ground
2. Mixing the powders and catalyst in a proper proportion in the mechanical mixer
3. Place a layer of Al_2O_3 powder (~5 mm thick) on the bottom of the container.
4. Bury the Ti components in the powder mixture in the container
5. Top up the container with pure Al_2O_3 powder
6. Seal the container by a combination of compact mechanical contact and high temperature aluminide-based cement to achieve a better sealing effect
7. Heat the container in the furnace to the designed temperature and isothermally holding for various times, followed by furnace cooling or air cooling.
8. At room temperature take the components out of the powder and mechanically clean the surface using metal brush.
6. Further machining or grinding to achieve the required surface finish.

Properties:

- Improved hardness compared with the substrate

- Improved wear resistance compared with the substrate
- Significantly improved oxidation resistance compared with the substrate. After PPDC treatment, the oxidation resistance of TI alloys is comparable to the Ni-based superalloys.

5

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of treating a titanium or titanium alloy substrate to provide increased high temperature oxidation resistance and wear resistance, which method comprises:

providing on the substrate a composition comprising aluminium particles, another metal powder selected from nickel, copper and zinc powder and an activator; and

heating to an elevated temperature until an intermetallic coating forms on the substrate.

2. The method of claim 1, wherein the composition comprises aluminium and nickel powders.

3. The method of claim 1, wherein the composition comprises aluminium and copper powders.

4. The method of claim 1, wherein the composition comprises aluminium and zinc powders.

5. The method of any one of the preceding claims, wherein the activator is a halide activator.

6. The method of claim 5, wherein the halide activator is selected from ammonium chloride, aluminium chloride and zinc chloride.

7. The method of any one of the preceding claims, wherein the composition further comprises particles of a refractory material.

8. The method of claim 7, wherein the refractory material is alumina.

9. The method of any one of the preceding claims, wherein the elevated temperature is from 500 to 900°C.

10. The method of claim 9, wherein heating takes place for a period of up to 15 hours.

11. The method of any one of the preceding claims, wherein the intermetallic coating has a thickness of at least 100 μm.

12. The method of any one of the preceding claims, wherein the titanium or titanium alloy is selected from Grade 2 titanium, Ti6Al4V, Ti10V2Fe3Al, Ti6Cr5Mo5V4Al, Ti1100 and IMI834.

13. The method of claim 1, wherein the substrate is a drill bit or cutting tool.

14. A titanium or titanium alloy substrate treated in accordance with the method of any one of claims 1 to 13.

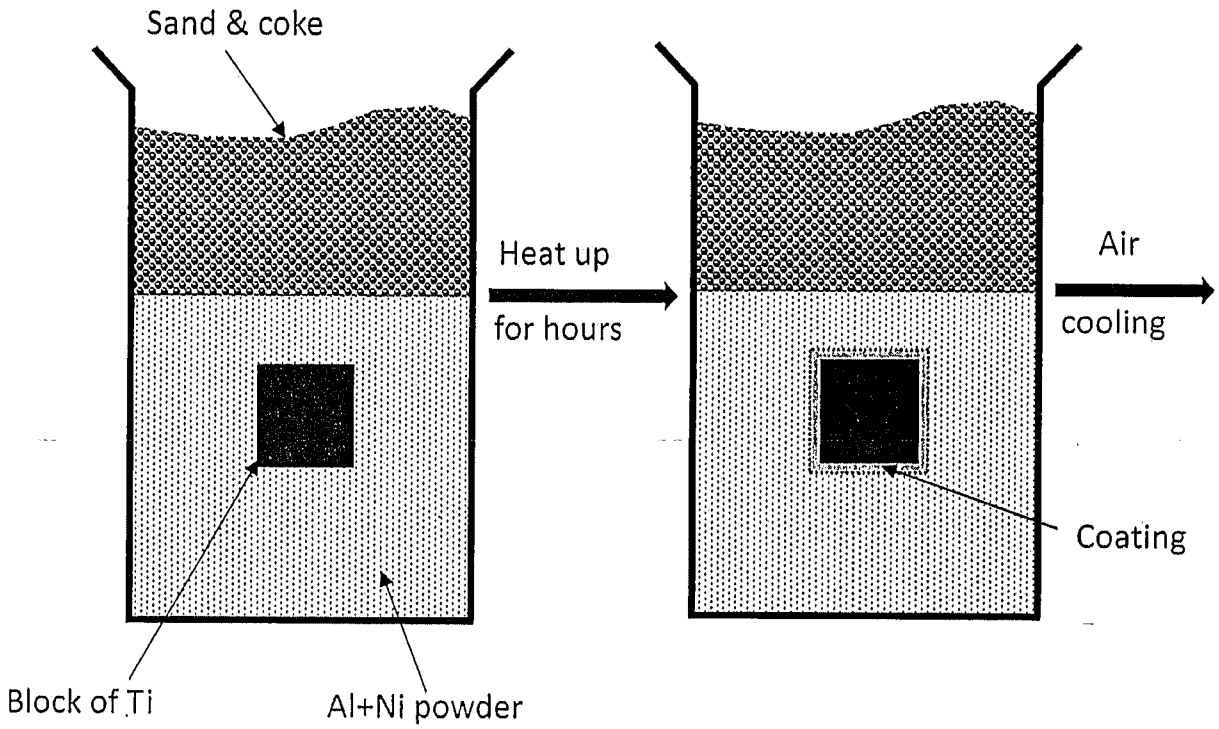


Figure 1: Packed powder diffusion coating process.

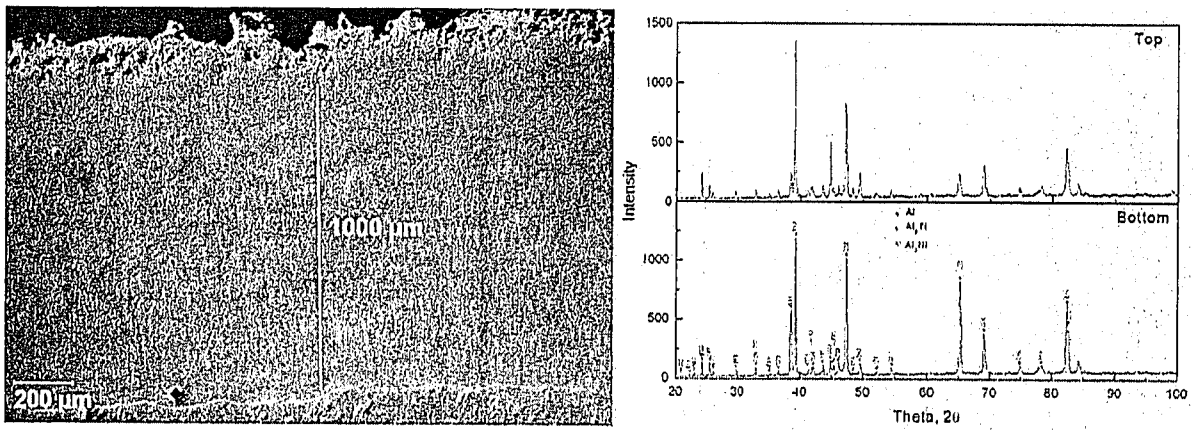


Figure 2: Physical properties of the coating.

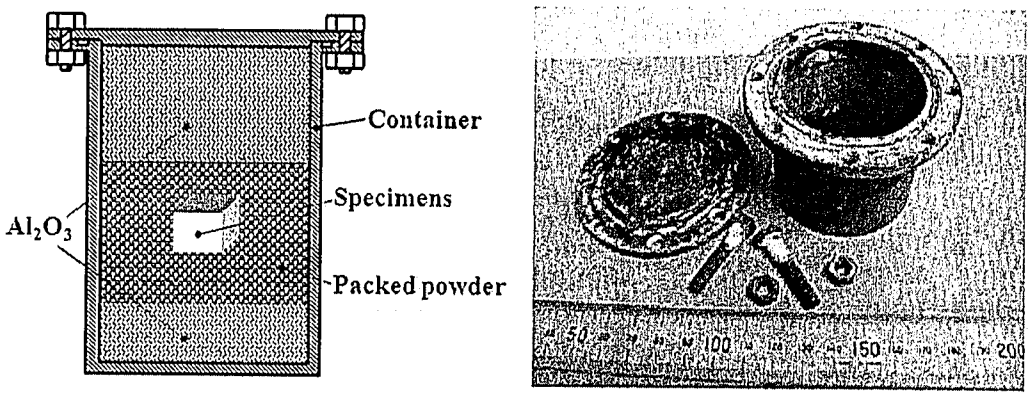


Figure 3: Schematic configuration of modified facility for packed powder diffusion process

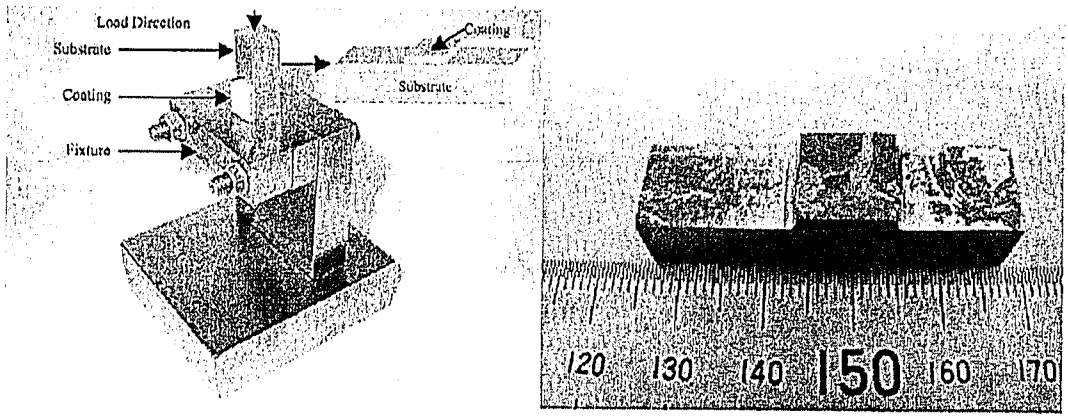


Figure 4 Photograph of lug shear tester and specimen

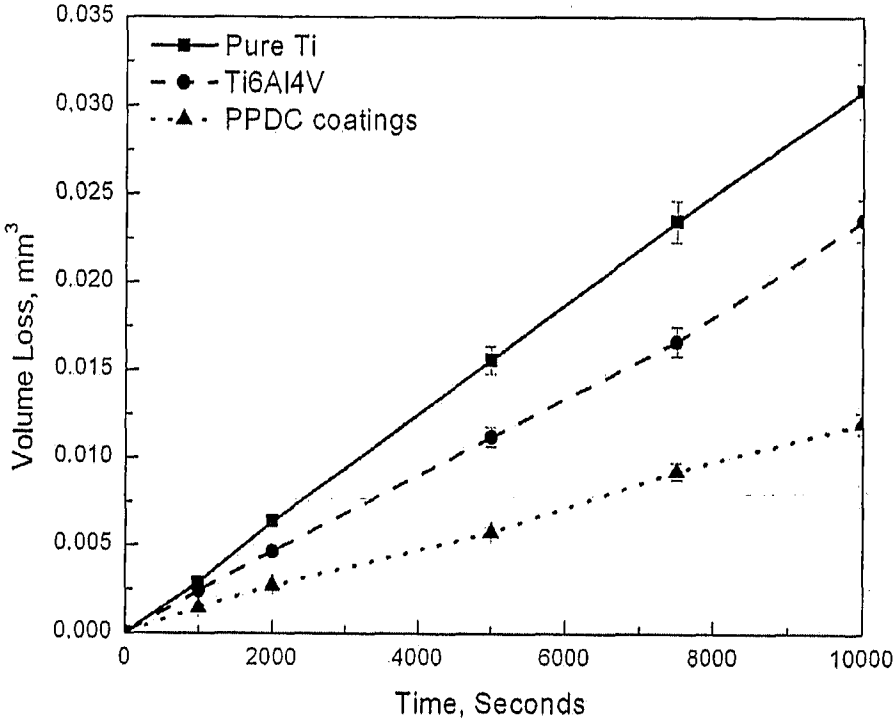


Figure 5: Wear resistance of new coating compared to plain Ti and Ti6Al4V

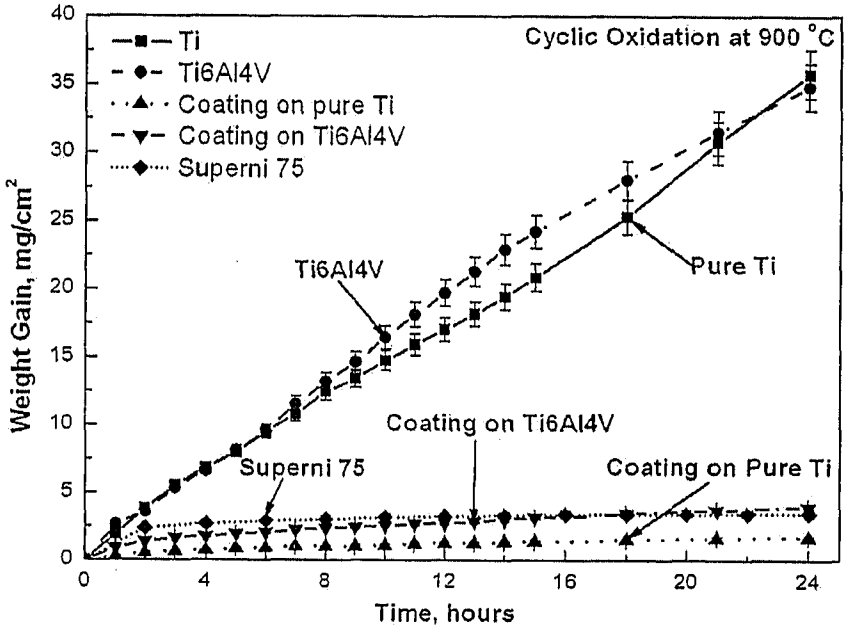


Figure 6: Weight gain of coated and uncoated titanium compared to Superni 75 superalloy at 900 °C

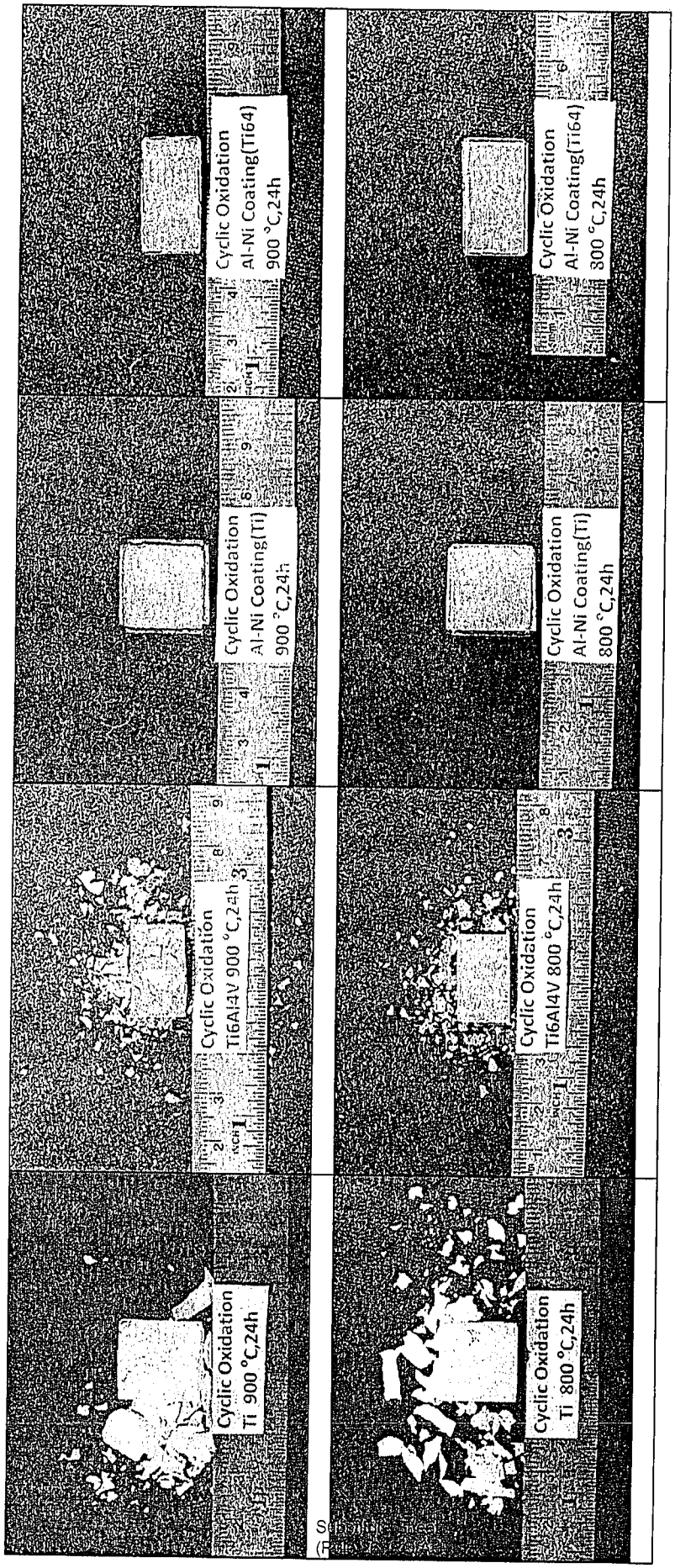
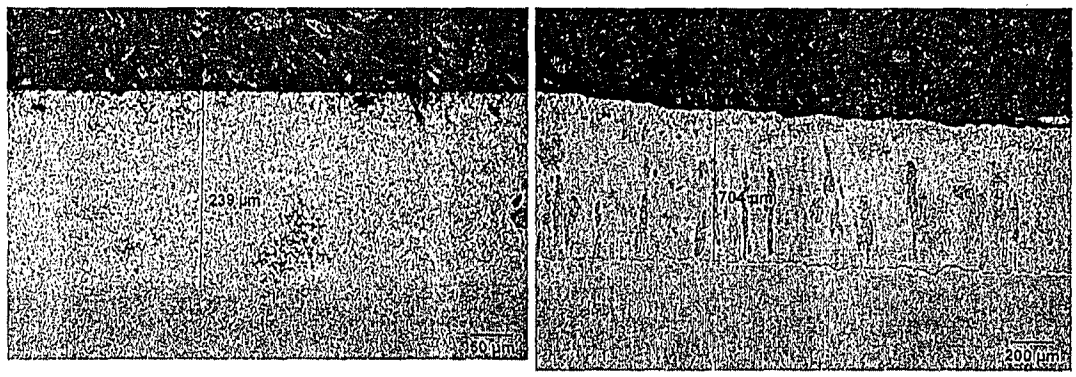
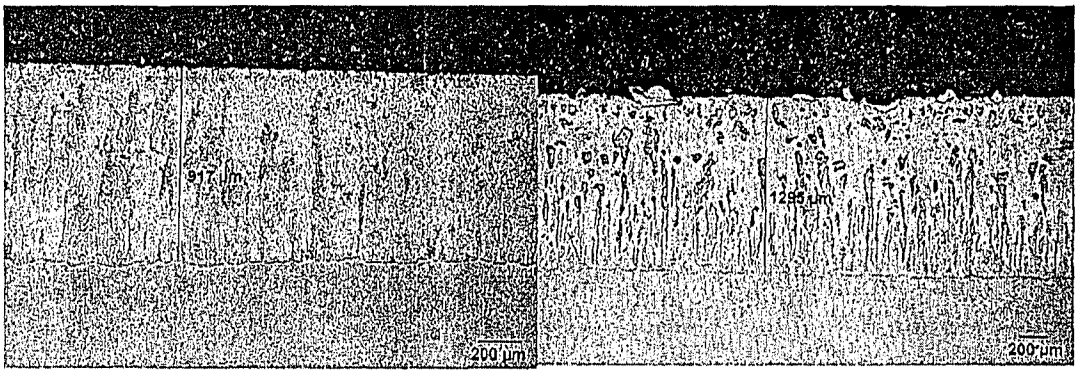


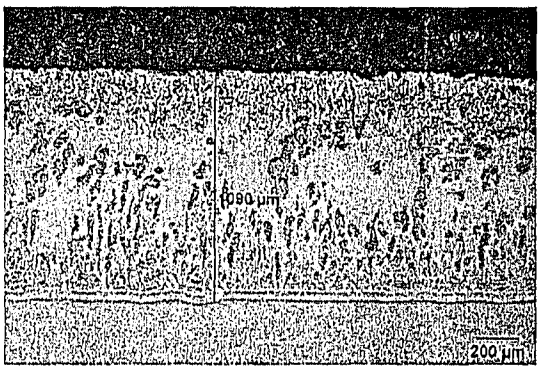
Figure 7: Photographs of samples after oxidation at 900 °C and 800 °C for 24 hours



(a) 650 °C, 3 h (b) 650 °C, 6 h



(c) 650 °C, 9 h (d) 650 °C, 12 h



(e) 650 °C, 15 h

Figure 8: Optical micrographs on the cross-sections of PPDC coatings on pure Ti substrate treated at 650°C for different time: (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h, and (e) 15h

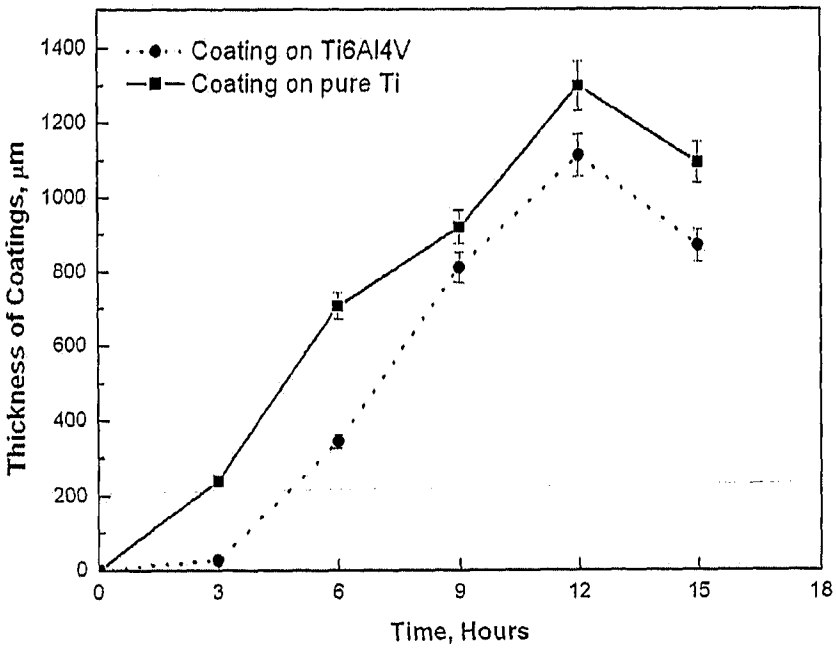
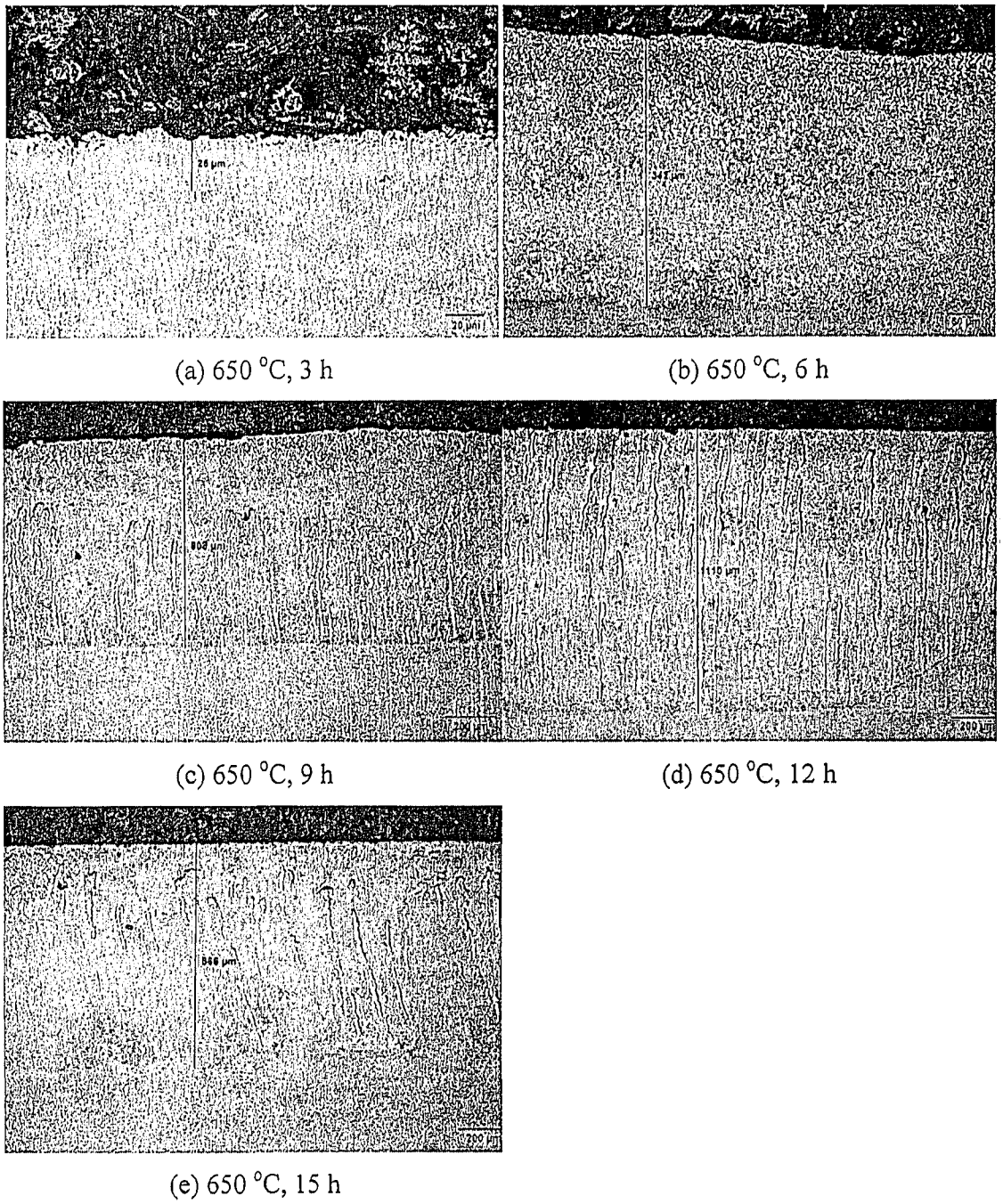


Figure 9: Variation of the thickness of PPDC coatings on pure Ti and Ti6Al4Vsubstrates with PPDC treatment time at 650°C.

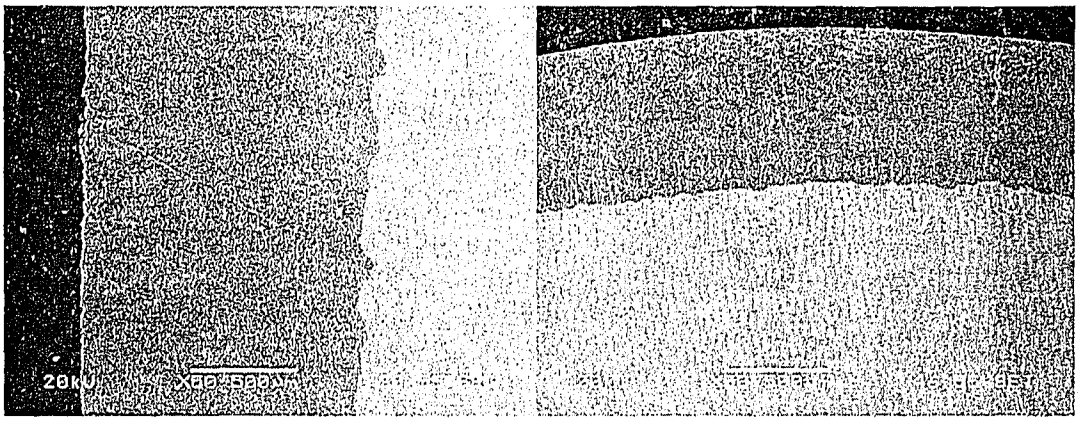


(a) 650 °C, 3 h (b) 650 °C, 6 h

(c) 650 °C, 9 h (d) 650 °C, 12 h

(e) 650 °C, 15 h

Figure 10: Optical micrographs on the cross-sections of PPDC coatings on pure Ti6Al4V substrate treated at 650 °C for different time: (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h, and (e) 15h



(a) PPDC coatings on Ti-10V-2Fe-3Al (b) PPDC coatings on Ti-6Cr-5Mo-5V-4Al

Figure 11: SEM back scattered electron micrographs of the PPDC coatings produced on (a) Ti-10V-2Fe-3Al and (b) Ti-6Cr-5Mo-5V-4Al substrates

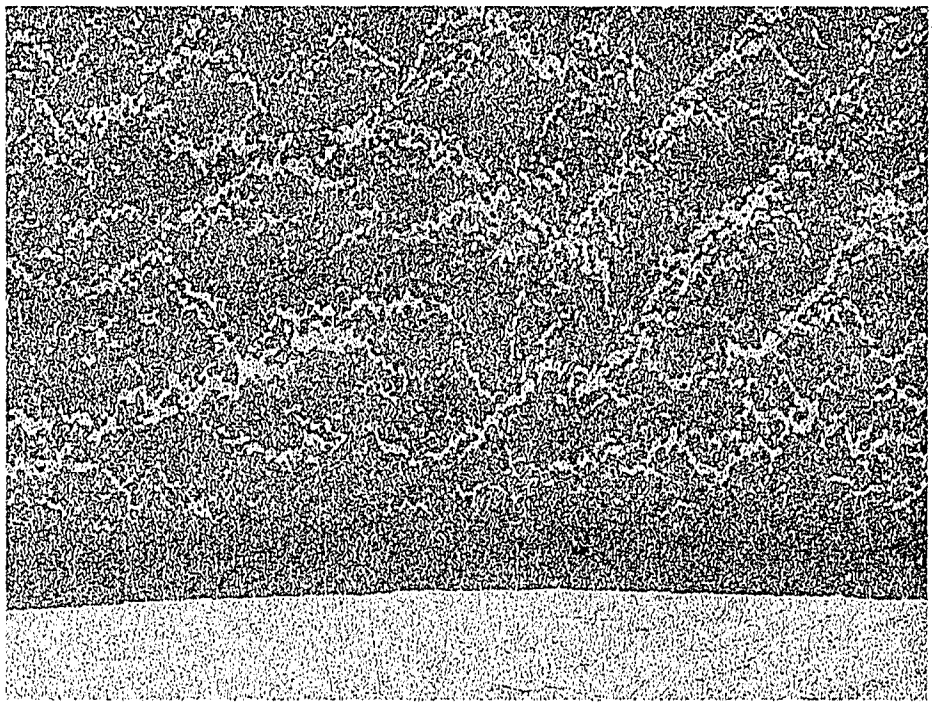


Figure 12: SEM Back-scattered electron micrographs of coatings produced on pure Ti substrate produced at 650°C for 15 hours.

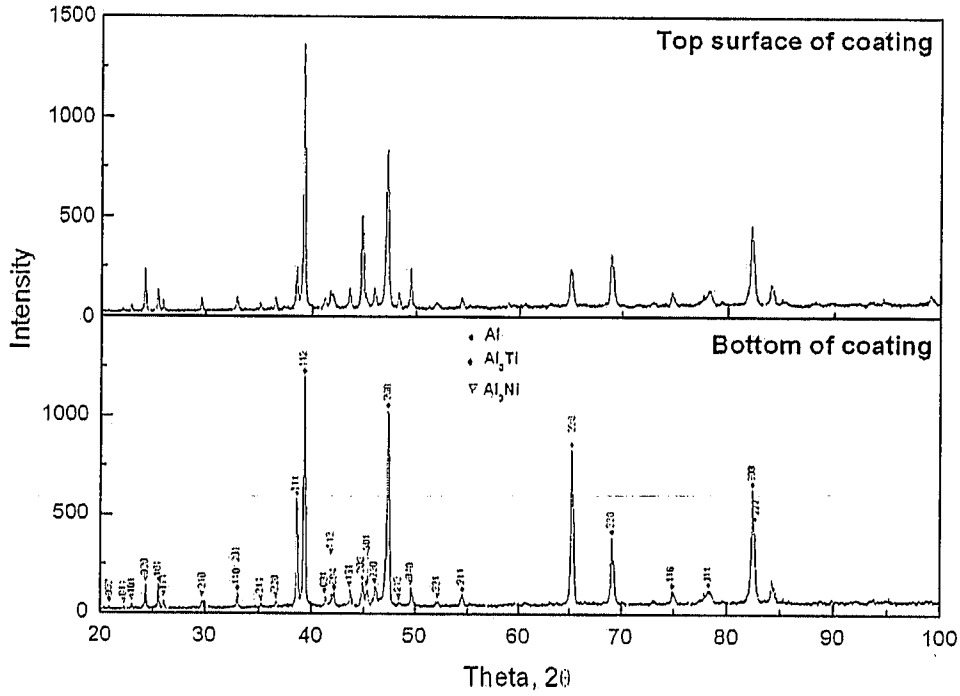


Figure 13: X-ray diffraction patterns on the topmost surface and on the layer that is close the interface of PPDC coatings produced on pure Ti substrate at 650°C for 15 hours

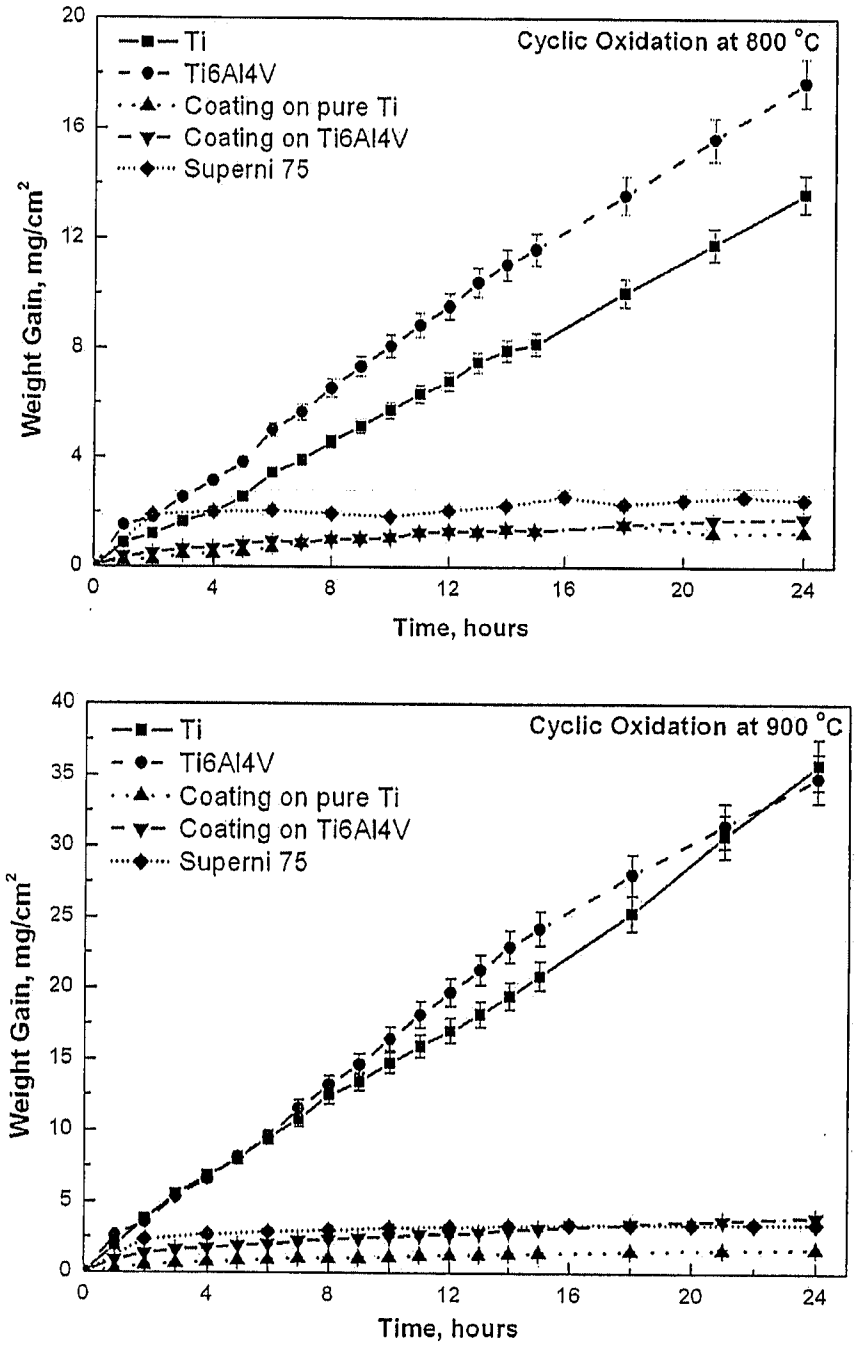


Figure 14: Cyclic oxidation behaviors of the PPDC coatings on pure Ti and Ti6Al4Vsubstrate compared with those of pure Ti, Ti6Al4V and Superni 75 alloys. Oxidation was undertaken at at800°C and 900°C for 24 hours.

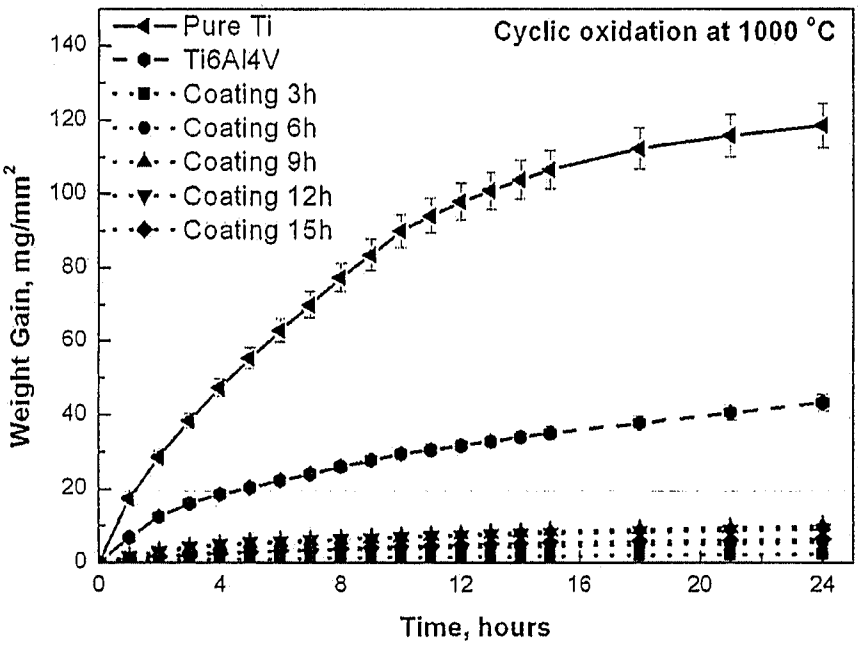


Figure 15: Cyclic oxidation behaviors of the PPDC coatings on pure Ti and Ti6Al4V substrate compared with those of pure Ti and Ti6Al4V alloys. Oxidation was undertaken at 1000°C for 24 hours.

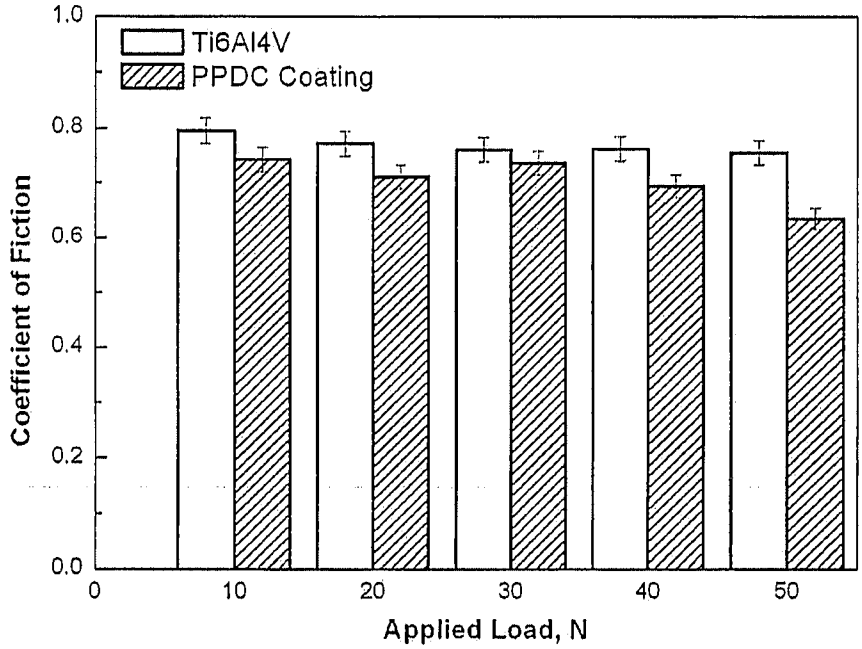


Figure 16: Coefficient of friction (COF) of the PPDC coating on Ti6Al4V substrate measured at different loads for 30 minutes and compared to the Ti6Al4V alloy.

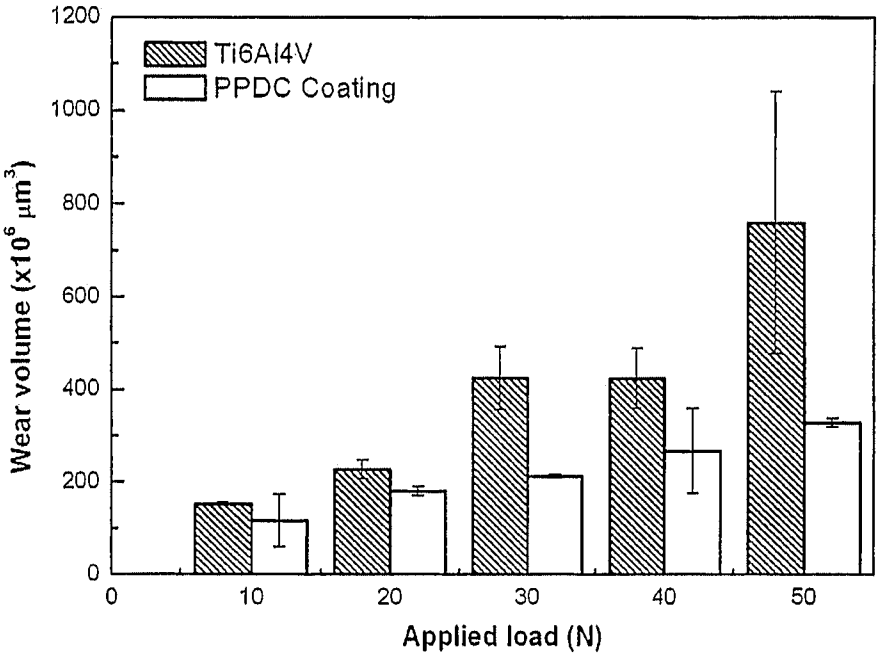
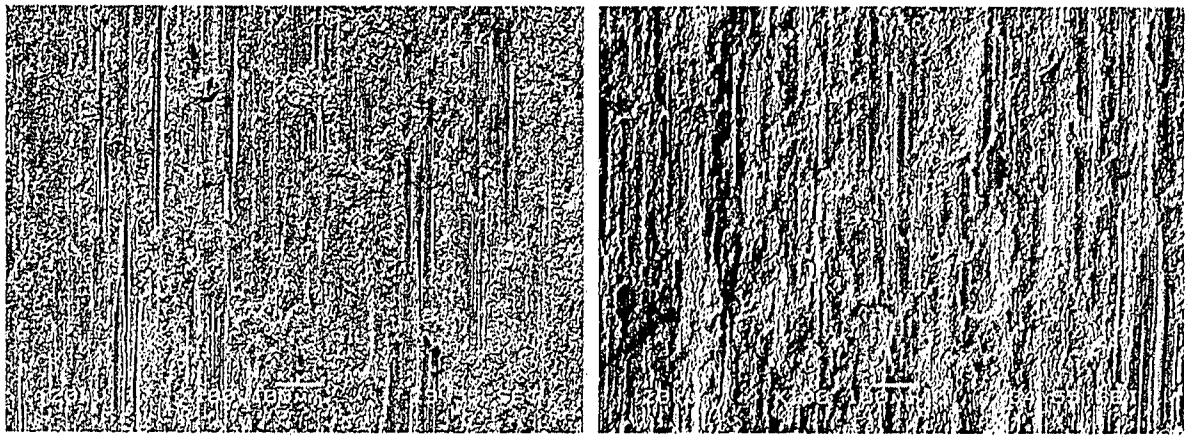


Figure 17: Wear resistance, indicated by the wear volume, of the PPDC coating on Ti6Al4V substrate measured at different loads for 30 minutes and compared to the Ti6Al4V alloy.



(a) Ti6Al4V (b) PPDC coating

Figure 18: SEM micrographs showing the morphology on worn surfaces after wear testing at a load of 50N: (a) Ti6Al4V, (b) PPDC coating at 650°C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2012/001209

A. CLASSIFICATION OF SUBJECT MATTER

C23C 10/48 (2006.01)

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)

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)

WPI & EPODOC - IPC & EC: C23C 10/28/low, C23C 24/-, B22F 7/04, B22F 2/08, C01G 23/-, C22B 34/12 & Keywords (titan+, ti, alumin+, al, nickel, ni, copper, cu, zinc, zn); Google Patents - Keywords (pack cementation, pack dispersion, aluminide, aluminizing, titanium, titanium substrate, copper, zinc, nickel)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

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"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

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Date of the actual completion of the international search	Date of mailing of the international search report
10 January 2013	10 January 2013

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INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2012/001209**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3589935 A (BRILL-EDWARDS et al.) 29 June 1971 See column 3 lines 4-10, column 7 lines 31-38, column 9 line 12 to column 10 line 34, claim 1	1, 4-14
X	US 4141760 A (BALDI) 27 February 1979 See column 3 lines 35-38, column 10 line 40 to column 11 line 3	1, 2, 5, 6, 11-14
X	SU 1135799 A (BELORUSSIAN POLY) 23 January 1985 English abstract obtained from WPI database - Accession Number 1985-202135	1, 3, 5, 7-14
A	US 5334417 A (RAFFERTY et al.) 02 August 1994 See whole document, in particular column 1 lines 54-66	
A	WO 2010135144 A1 (SIFCO INDUSTRIES, INC.) 25 November 2010 See whole document, in particular page 4 lines 5-15, page 8 lines 3-18, page 16 lines 9-32	
A	US 5077140 A (LUTHRA et al.) 31 December 1991	
P,A	KR 10-2012-0054239 A (DAMUL E&C CO., LTD) 30 May 2012 English Abstract and translation obtained from South Korean Intellectual Property Office website	

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2012/001209**

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2012/001209**

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2012/001209**

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2012/001209**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		Patent Family Member/s	
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