Effect of different pretreatment processes on the properties of copper plating on titanium alloy tubing surface

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This paper investigated on the non-cyanide copper plating processes on titanium alloy tubing surface. The properties of copper plating on titanium alloy surface were studied under different pretreatment processes, adhesion strength of copper plating was tested by using scratch and tensile method, the coating microstructures were analyze by scanning electron microscopy (SEM) and EDS. Comparing the performance of the copper coating on titanium alloy surface under different pretreatment processes, the best pretreatment process of copper plating method was optimized, the full-size titanium alloy tubing thread samples with copper coating were also tested by make-up/break-out experiment. Based on the systematic analysis it can be concluded that the copper coating on titanium alloy surface with activation and nickel plated pretreatment had advantages of high adhesion strength, compact coating and low porosity, this non-cyanide copper plating process can solve thread galling problem of titanium alloy tubing and promote large-scale application of titanium alloy materials in petrochemical industry.

KEYWORDS: TITANIUM ALLOY TUBING - COPPER PLATING - PRETREATMENT PROCESSES - ADHESION STRENGTH - THREAD GALLING

INTRODUCTION

With increasing exploration and development of high sulfurous gas fields in China, the demand for high performance of oil country tubular goods (OCTG) is becoming more and more pressing [1-5]. A lot of work on research and development of high performance OCTG had been done recently in China, such as application of 13Cr and super 13Cr tubing used for Tarim oilfield in northwest of China, and development of nickel-base alloy tubing used in southwest of China [6,7]. But by virtue of the performance limitations of material itself, these tubes still unable to meet the growing challenges of the critical well conditions.

Titanium alloy OCTG with excellent corrosion resistance and good mechanical properties has great potential applications in petrochemical industry and is becoming one of the main development directions of OCTG. Due to poor wear resistance and low thermal conductivity of titanium alloy, the surface of OCTG made by Ti-6Al-4V titanium alloy is easy to scratch, the thread connection of titanium alloy OCTG is prone to occur galling in make-up and break-out operation, which greatly restrict the use of titanium material in the petrochemical industry. Recently, varied surface modification has been widely applied in Ti-6Al-4V to obtain wear and corrosion resistant surfaces, such as plasma treatment, ion implantation, and PVD etc. [8-12] Copper has advantages of good thermal conductivity and good ductility, using copper plating process can effectively improve the wear resistance and thermal conductivity on the surface of Ti-6Al-4V titanium alloy under the condition of high temperature and heavy load, the friction coefficient can also be reduced [13].

Research reports about copper plating on titanium alloy surface were rare, it is because that activity of titanium element is high and the surface of titanium alloy is easy to generate a dense layer of oxide film, which cause it is difficult to obtain the plating with good binding force on the surface of titanium alloy [14-16].

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The copper sulfate cyanide-free technology is employed in the preparation of copper plating on Ti-6Al-4V titanium alloy surface was studied in this paper; the effect of different pretreatment process (including activation and pre-coating) on coating structure, composition and film-substrate adhesion stress was investigated in this study. The copper plating thread samples of full-size titanium alloy tubing with optimized pretreatment process was tested by make-up and break-out experiment at last.

EXPERIMENTAL

The titanium alloy tubing tested in this paper was made by Ti-6Al-4V titanium alloy, which was produced by Xi'an Sanhuan Science & Technology Development Corporation in China. Chemical compositions of materials was shown in Tab.1, microstructure was widmanstatten structure, the hardness of materials was 29.5HRC. Φ30mm×5mm test specimens were cut from titanium alloy tubing, all the faces of specimens were mechanically polished with 1000Cw SiC abrasive paper and were cleaned by acetone solution in Ultrasonic cleaning machine.

Tab. 1 - Chemical composition of the tested sample (in wt.%)

Fe	C	N	H	O	Al	V	Ti
0.25	0.09	0.05	0.013	0.20	6.1	4.1	balance

In order to investigate into the effect of different pretreatment processes on the properties of copper plating layer, all test specimens were divided into four groups according to different pretreatment. Specimens of group A were prepared by copper plating without any pretreatment, specimens of group B were prepared by nickel pre-coating then copper plating, surfaces of group C specimens were activated with galvanostatic etching and then electroplated copper, specimens of group D were prepared by copper plating after the activation and pre-coating of nickel. All the Cu electroplating was conducted with a current density of 2.5Adm^{-2} to obtain about a 25μm-thick Cu plating on the four groups test specimen.

In order to study adhesion strength of copper plating, one end of specimens with copper plating was bonded with the same size stainless column prepared by shot penning, as shown in Fig.1. According to ASTM 633-01 standard the tensile tests were carried out at a speed of 1mm/min until the coating damaged.

The microstructure and the surface of coating were analyzed by an optical microscope (OLYMPUS BH2-HLSH) and a scanning electron microscope (SEM, TESCAN-VEGAII) equipped with energy dispersive spectrometer (EDS, OXFORD -INCA350). Hardness of coating were tested by HSV-20 hardness test machine, the make-up and break-out test of full-size titanium alloy tubing thread connection were carried out at torque test system in Tubular Goods Research Centre of China National Petroleum Corporation.

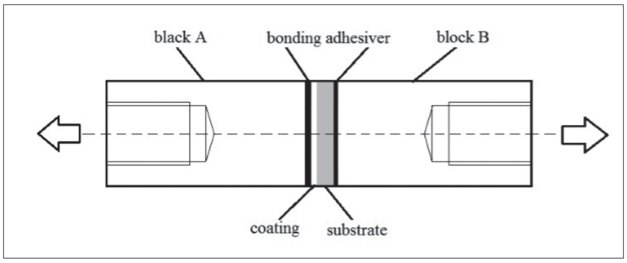


Fig. 1 - Schematic diagram of coating bond strength test sample

RESULTS

Cross-cut Test Results

The bond strength of copper plating under shear stress was tested by cross-cut test accord with standard ISO 2409 [17].

When 50N were loaded on scratch tester, the surface of specimens were cut in 6 lines in transversal and longitudinal directions respectively to form a square of 1 mm of the lattice, bond strength classification standard are shown in table 2.

Tab. 2 - Classification of test results

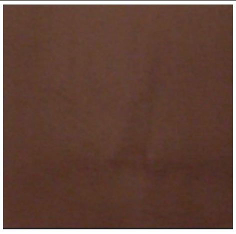
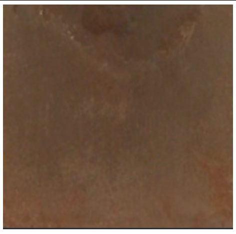
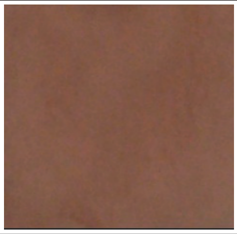
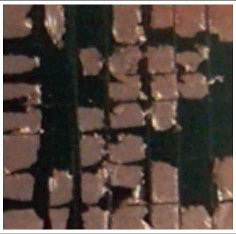
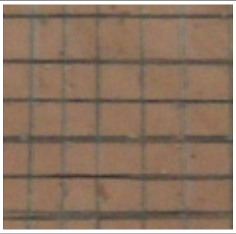
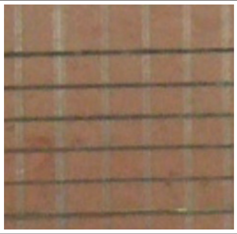
Classification	Description
0	The edges of the cuts are completely smooth; none of the squares of the lattices is detached.
1	Detachedment of small flakes of the coating at the intersections of the cuts. A cross-cut area not significantly greater than 5% is affected.
2	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area significantly greater than 5%, but not significantly greater than 15%, is affected.
3	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or has flaked partly or wholly on different parts of the squares. A cross-cut area significantly greater than 15%, but not significantly greater than 35%, is affected.
4	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area significantly greater than 35%, but not significantly greater than 65%, is affected.
5	Any degree of flaking that cannot even be classified by classification 4.

The breakage and flaked coating were characterized by adhesion score, which was calculated as follow:

$$s = \frac{N_u}{N} \quad (1)$$

Where S stands for adhesion score, Nu stands for number of blocks unshed, and N stands for number of all the squares.
Cross-cut test results are shown in Fig. 2, it can be concluded that the bond strength of copper plating was better when classification of cross-cut test was low and adhesion score was high. The contradistinction figures of samples before and after cross-cut test are shown in Tab. 3, it can be seen that the coating in A group had flaked along the edges of the cuts in large and most squares had detached after cross-cut test, the adhesion score of A group is only 24% and classification of cross-cut test result is 5. The coating in B group is better than A group, because lots of squares had detached, the adhesion score is 36% and classification of cross-cut test is 4. The coating in C and D group are much better, the edges of the cuts are completely smooth and none of the squares of the lattices is detached, the adhesion score of both C and D group are 100%, the classification of cross-cut test results are both 0. It can be concluded that active treatment had great affect on the bond strength of copper plating.

Tab. 3 - Comparisons results of samples before and after cross-cut test

	A group	B group	C group	D group
Before				
After				

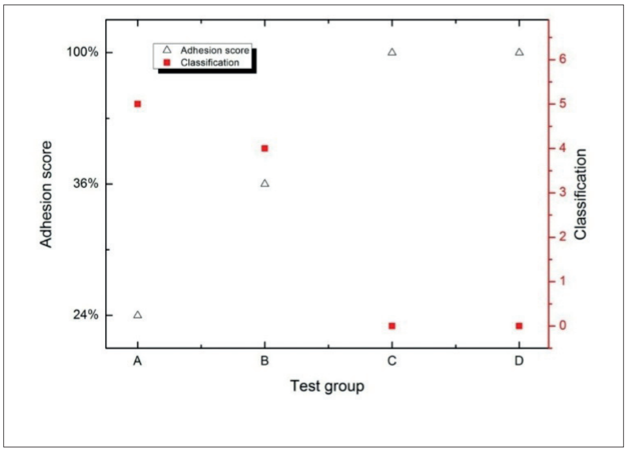
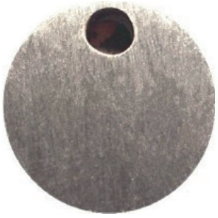


Fig. 2 - The classification and adhesion score of different pretreatment group

Coating adhesion strength test results

The coating adhesion strength and tensile test macro fracture figures are shown in Fig. 3 and Tab.4, respectively. By comparing the sample surface, the adhesion strength of coating increases by pre-coating nickel and active treatment.
The adhesion strength of coating in D group treated by Ni/Cu plating and activation is 12MPa, which is 5 times than that of coating without any pretreatment, the coating in A group peel off completely compare with the sample before tensile test, the coating in B group flake in large, the flakes are small and have layered structure, the coating treated by pre-active shows much smaller flakers and there are partly island-like distribution copper plating on the surface of sample. The coating in D group only peels off a little copper scrap.

Tab. 4 - Comparisons results of samples before and after tensile test

	A group	B group	C group	D group
Before				
After				

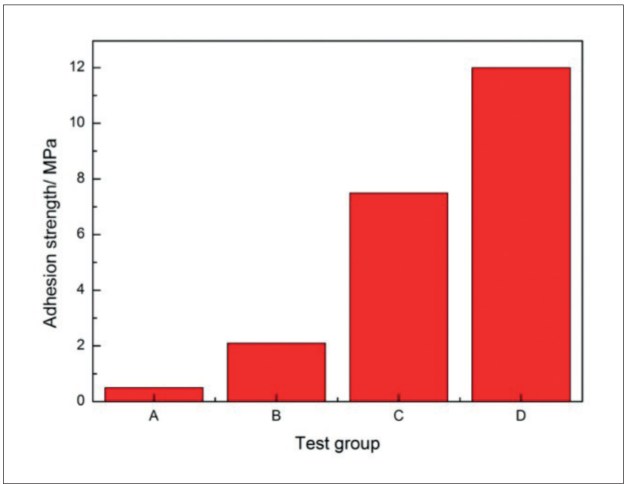


Fig. 3 - Coating adhesion strength of different pretreatment process

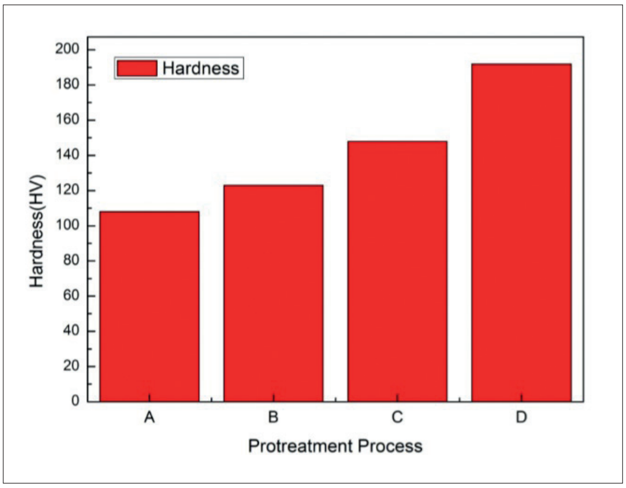


Fig. 4 - Copper plating micro-hardness of different pretreatments

COATING HARDNESS TEST RESULTS

Micro-hardness test result of coating in four different pretreatment groups is shown in Fig. 4.

It can be seen that hardness of coating increase from none to Ni/Cu plating and activation pretreatment, which means hardness of coating are greatly affected by pretreatment chosen.

It is because that the hardness of middle nickel plating is much bigger than that of copper plating, the copper layer deposited on nickel layer is much denser than copper directly deposited on the surface of titanium alloy, the grains of copper deposited on nickel layer are more smaller and uniform.

COATING MICROSTRUCTURE

The surface morphology of coating in four different pretreatment groups were analyzed by scanning electron microscope, the results are shown in Fig. 5. There are plenty of pores on the surface of copper coating in A group, and the surface is dark, as shown in Fig. 5(a). Surface of copper coating treated by pre-coating nickel is more flat and have little pores, the copper coating looks like spherical agglomerates and discontinuous distribution at high magnification, as shown in Fig. 5(b). Surface of copper coating in C group have lots of big pore and the film is rough, as shown in Fig. 5(c). Surface of coating in D group treated by Ni/Cu plating and activation is much smooth and distributes continuously, pores is much less, as shown in Fig. 5(d). It can be concluded from the surface morphology that the coating treated by pre-coating nickel was uniform and complete, porosity is low, after activation and nickel plating, copper film is more stable and flat. Therefore, nickel plating pretreatment on titanium alloy surface can improve the cleanliness and smoothness of the titanium alloy copper plating film.

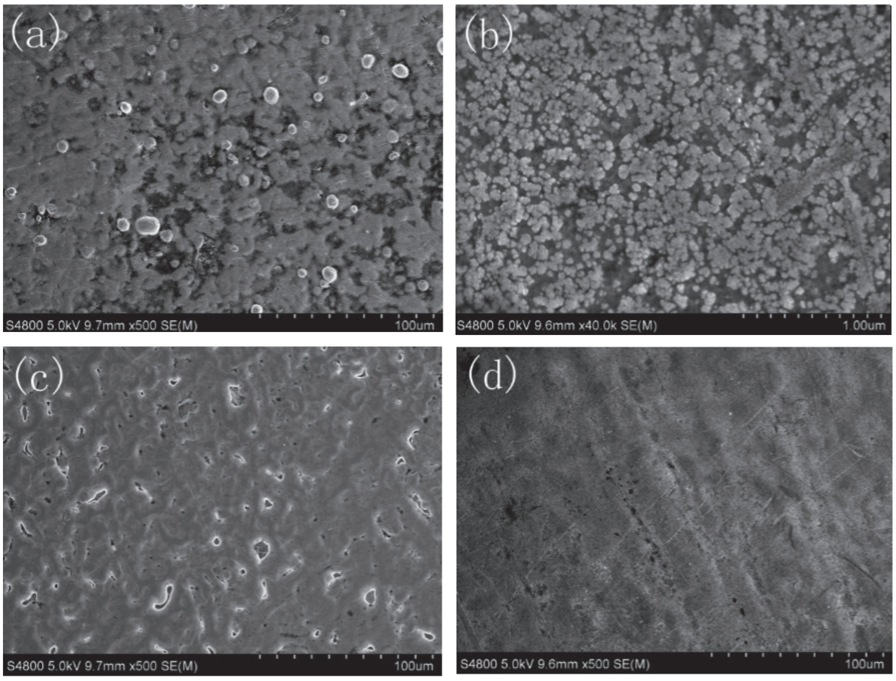


Fig. 5 - SEM microstructure of different pretreatment group
(a) group A, (b) group B, (c) group C, (d) group D

The cross section morphology of copper plating in four groups were also analyzed by SEM. From Fig. 6 (a), it can be seen that coating film is separated obviously from titanium substrate and the thickness of the coating is approximately 15μm. The coating treated by pre-coating nickel in B group has a good bonding with titanium substrate, but the nickel film is hard to recognize and the thickness of the coating is approximately 6~10μm, as shown in Fig. 6 (b). Coating in C group is the same as in B group, the thickness of the coating is 6~10μm. The coating in D group has the best bonding with titanium substrate and the nickel film can also be recognized, as shown in Fig. 6 (d) ,the thickness of Ni/Cu coating is about 10μm. It can be concluded that activation can effectively remove passive film on the surface of the titanium substrate, pre-coating nickel can get good adhesion strength bonding with substrate after activation, nickel is easy electroplating metal and also easy to combine with other metal, so the copper coating will get good adhesion strength with titanium after activation and pre-coating nickel,

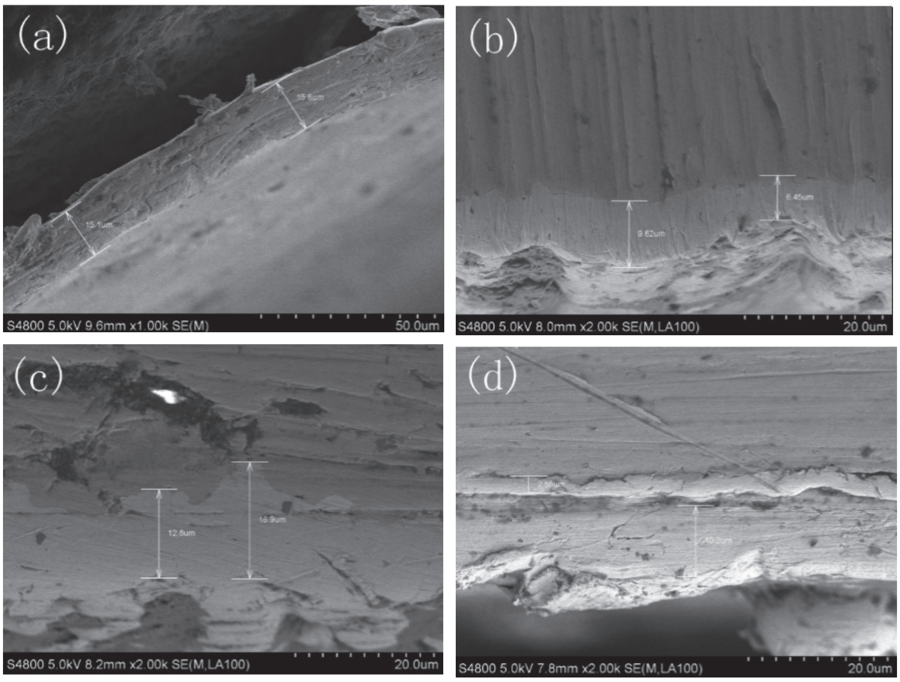
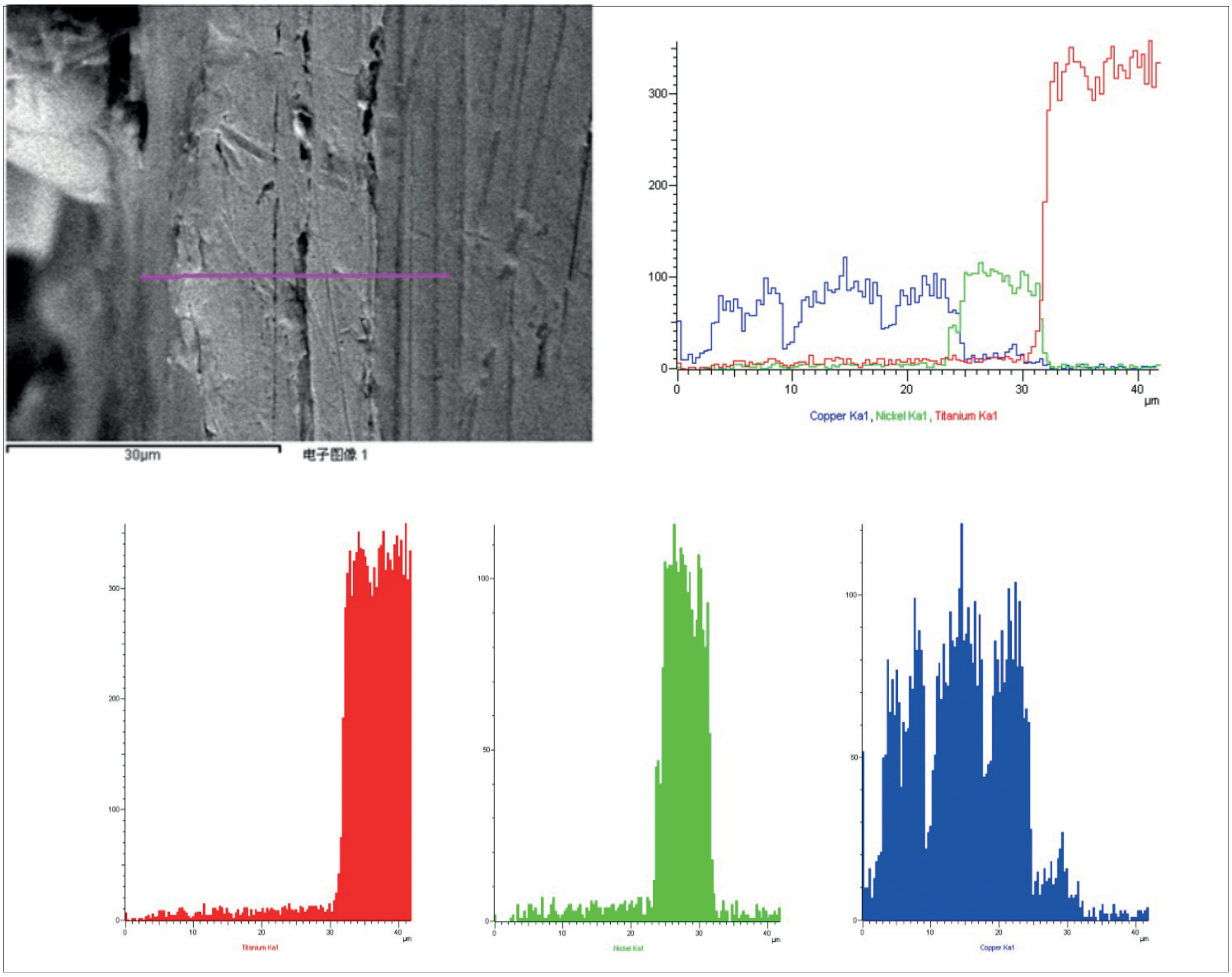


Fig. 6 - Cross section SEM microstructure of different pretreatments
(a) group A, (b) group B, (c) group C, (d) group D

The cross section of copper coating in D group were analyzed by EDS, the results shows that a layer of nickel existed obviously Between titanium substrate and copper coating, the thickness of nickel layer is about 10μm, as shown in Fig. 7.



Ti Ni Cu

Fig. 7 - EDS results of Cu coating in group D

DISCUSSION

Due to high activity of titanium element and a dense layer of oxide layer on the surface of titanium alloy, it is difficult to obtain copper plating with good binding strength on the surface of titanium alloy, so activation treatment is very important process for titanium plating. Activation treatment can not only inhibit the oxide layer formation but also generate a thin layer of conversion coating or metal layer on titanium alloy surface, which make the titanium alloy substrate not be oxidized before electroplating copper. Mr. Wallac found that hydrogenated layer generated by activator not only reduced the activity of titanium surface, avoid the passivation, but also formed metallic bonding between the substrate and layer[18]. In this study, four group copper plating samples with different pretreatment were tested by cross-cut and tensile method. The results above show that active treatment has great affect on bond strength of copper plating, it is because active treatment can generate hydrogenated layer TiH_2 on the surface of Ti-6Al-4V titanium alloy, which can avoid the passivation effect caused by the oxygen diffusion and improve the combination effect of coating. When nickel plating processing was introduced on the hydrogenated layer, the metallic bonding transition structure will be formed between Ni-Ti layers, which can lead to produce Ni_3Ti, NiTi and $NiTi_2$ intermetallic compounds in the subsequent heat treatment, at the same time, due to the fact that copper atom and nickel atom are similar, the copper and nickel atoms in Ni-Cu layers can diffuse in each other easily and an infinite solid solution can be formed[19], so the samples treated by activation and pre-coating nickel have best coating adhesion strength, the Ni-Cu layer combined closely with the substrate and the copper surface is much smooth.

The copper plating thread samples of full-size titanium alloy tubing with optimized pretreatment process was tested by make-up and break-out experiment. The diameter of Ti-6Al-4V titanium alloy tubing is Φ88.9mm×7.01mm, the couple was treated by D group treatment and test samples are shown in Fig. 8, the anti-galling tests were carried out by 10-times make-up and break-out experiment accord with ISO 13679 standard, the thread lubricant was 4010NM produced by BESTOLIFE company, the make-up speed was 2-5rpm and the make-up torque is around 4500N•m. After 10-times make-up and break-out experiment, morphology of titanium tubing thread is shown in Fig. 9, there are no galling phenomenon happened on the surface of both pin and box thread, the seal part of thread is smooth, it can be seen that copper plating with activation and nickel plated pretreatment can improve the anti-damage properties of titanium ally surface and effectively solve thread galling problem of titanium alloy tubing.

Fig. 8 - TC4 titanium alloy tubing connection samples with Cu coating in make-up/break-out tests

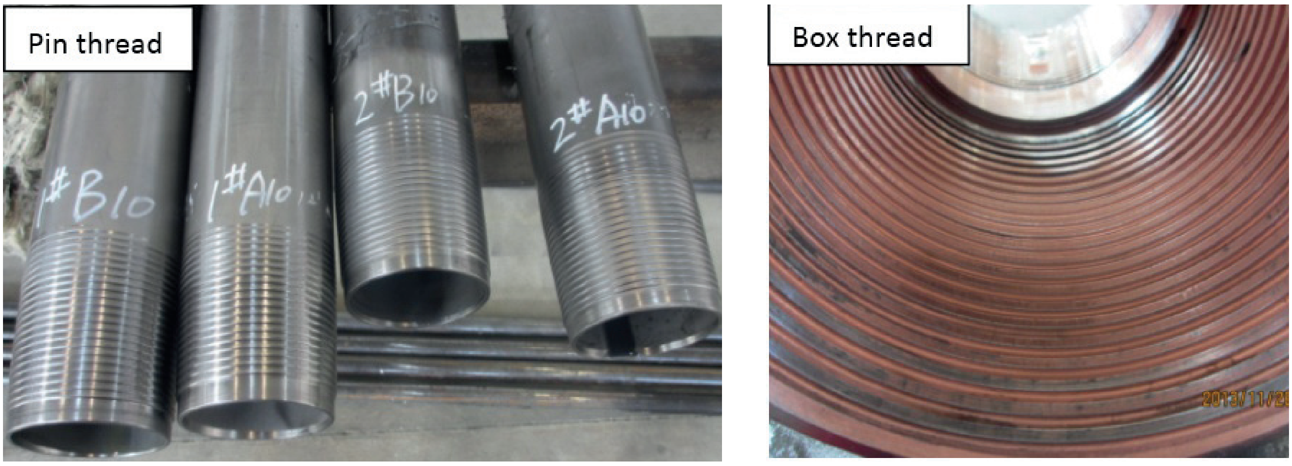


Fig. 9 - Morphology of titanium thread after 10-times make-up and break-out tests with group D treatment

CONCLUSION

1) The copper plating on titanium alloy surface with activation and nickel plated pretreatment have best coating adhesion strength, the coating layer is compact and uniform, porosity is low, which much better than any other treatment.
2) Active treatment before Ni/Cu plating can generate hydrogenated layer TiH2 on the surface of Ti-6Al-4V titanium alloy, which can avoid the passivation effect caused by the oxygen diffusion and improve the combination effect of coating, after nickel plating process, the Ni-Cu layer combined closely with the substrate.
3) Copper plating with activation and nickel plated pretreatment can improve the wear properties of titanium ally surface and effectively solve thread galling problem of titanium alloy tubing.

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