

Effect of vacuum conditions and plasma concentration on the chemical composition and adhesion of vacuum-plasma coatings

D P Borisov, V M Kuznetsov and V.A. Slabodchikov
Tomsk State University, Tomsk 634050, Russia

E-mail: borengin@mail.ru

Abstract. The paper reports on the chemical composition of titanium nitride (TiN) and silicon (Si) coatings deposited with a new technological vacuum plasma setup which comprises magnetron sputtering systems, arc evaporators, and an efficient plasma generator. It is shown that due to highly clean vacuum conditions and highly clean surface treatment in the gas discharge plasma, both the coating–substrate interface and the coatings as such are almost free from oxygen and carbon. It is found that the coating–substrate interface represents a layer of thickness ≥ 60 nm formed through vacuum plasma mixing of the coating and substrate materials. The TiN coatings obtained on the new equipment display a higher adhesion compared to brass coatings deposited by industrial technologies via intermediate titanium oxide layers. It is concluded that the designed vacuum plasma equipment allows efficient surface modification of materials and articles by vacuum plasma immersion processes.

1. Introduction

Vacuum plasma technologies can open up new possibilities of surface treatment that provides enhanced and even unique functional properties of materials, while providing high ecological safety. However, this type of technologies is rather rare in the market and the industry still gives preference to conventional methods like thermochemical treatment of steels and alloys, electrodeposition of coatings, etc. The cause is that the vacuum plasma technologies available to date fail to meet the desired efficiency and quality of surface modification. The major problem lies in the vacuum conditions which are to be clean and ensure high ultimate residual vacuum with no air leakage into the vacuum chamber, no impurity gas desorption from its walls and other elements, etc. So, for example, due to the presence of oxygen with a partial pressure of 10^{-6} Pa in the vacuum volume, the heated surface of steel is covered with an iron oxide film which impedes the nitrogen penetration into the steel surface and considerably lengthens the nitriding time or even stops the process [1]. The presence of oxygen, carbon, and other impurities in the vacuum chamber not only decreases the rate of nitriding but also results in coatings and their transition layers with poorly controlled chemical compositions and low properties, in particular adhesion.

In this context, it is required to develop new vacuum plasma equipment that would provide highly clean vacuum conditions, high-quality plasma processes in which impurity ion sputtering dominates over residual gas adsorption [2], and increased ion current densities (plasma densities) of inert and reactive gases to a substrate. The paper describes a new plasma vacuum setup designed at Tomsk State University (TSU, Tomsk, Russia) and reports on its efficient use that meets the foregoing requirements



and allows deposition of coatings with controlled chemical compositions and enhanced adhesive properties.

2. Experimental equipment, materials, and research technique

The materials under study were TiN and Si coatings obtained on the new vacuum plasma equipment and thin decorative brass (CuZn) coatings with a Zn content of 20 at. % obtained on the industrial equipment of ZCL Nonferrous Casting Plant (ZCL Advanced Technologies, Kurgan, Russia). The ZCL plant produces door furniture (locks, handles, etc.), car furniture, furniture fittings, and other consumer goods from zinc-aluminum alloys deposited with a lacquer undercoating and with decorative brass, aluminum, and nichrome coatings by vacuum plasma processes. For our comparative study we chose brass coatings because of their highest adhesion.

The test CuZn coatings were deposited on polycrystalline Si plates at the ZCL plant. The deposition technology was as follows. The Si substrates were degreased by ultrasonic cleaning in trichloroethylene, rinsed in deionized water, dried, and placed into a vacuum chamber pumped to an ultimate residual vacuum of $6 \cdot 10^{-3}$ Pa for final surface cleaning in a glow discharge. The glow discharge was ignited between the vacuum chamber and magnetron target (titanium) for which a mixture with 60 % of industrial argon and 40 % of carbon dioxide was supplied to the vacuum chamber to a pressure of 1 Pa. The plasma density in the glow discharge was $\sim 10^9$ cm⁻³; the treatment time of the Si substrates in the glow discharge plasma was 8 min. The inventors of the technology consider that the ion cleaning in the mixture containing carbon dioxide provides not only removal of impurities (water, organic films, etc.) from the Si substrate surface but also its activation by oxygen and carbon, and this is bound to ensure high adhesion of the intermediate Ti coating formed at the next stage and of the final coating as whole. The Ti undercoating was deposited on the Si substrates cleaned in the glow discharge plasma. The deposition was through magnetron sputtering of VT 1-0 titanium at an argon pressure of 0.3 Pa in the vacuum chamber. The same argon pressure was used to deposit final CuZn coatings through magnetron sputtering. Both the intermediate and final coatings were deposited with no bias potential to the Si substrates.

The other types of coatings, as mentioned above, were TiN and Si coatings deposited using the new vacuum plasma equipment – a SPRUT technological setup designed at TSU [3]. A photo and schematic of the setup are shown in figure 1.

The main plasma device of the setup is its plasma generator based on thermionic or so-called hot cathodes. The cathode units are located on the diametrically opposite flanges of the vacuum chamber measuring 0.7 m³ in volume. The voltage applied between the hot cathodes and grounded vacuum chamber with gas supply to the cathode cavities at the same flow rate causes the ignition of a non-self-sustained arc discharge the operation of which is ensured by thermionic emission from the hot cathodes. The working volume of the vacuum chamber is thus uniformly filled with “shadow-free” bulk plasma (argon, nitrogen, etc.) which provides efficient treatment such as cleaning, etching, heating, and nitriding of all sides of articles immersed in the plasma. By varying the discharge current from 10 to 250 A, the density of the gas discharge plasma can be varied from 10^8 to 10^{11} cm⁻³ over a wide pressure range of 0.13–0.67 Pa. The setup also comprises four magnetron sputtering systems and two arc evaporators equally spaced over the lateral surface of the vacuum chamber. The vacuum chamber is pumped by a cryogenic pump rated at 5000 l/s.

Once specimens are placed in the vacuum chamber of the SPRUT setup for coating deposition, the chamber is pumped to an ultimate residual vacuum of $6 \cdot 10^{-4}$ Pa and is checked for possible air leak-in and gas desorption from its walls and other elements. For this check, the control system of the setup closes the high-vacuum valve, records the pressure in the vacuum chamber, and starts its timer. Within 30 s after start of the timer, the control system again records the pressure and calculates the leak-in from two pressure values in [Pa·m³/s] or [sccm]. The leak-in acceptable for further vacuum plasma treatment is defined by specifications of the setup and is no more than $3.4 \cdot 10^{-5}$ Pa·m³/s (0.02 sccm). If the leak-in exceeds this value, the vacuum conditions are considered to be emergency conditions requiring routine and preventive repair to eliminate the excess leak-in and bring it to the level

acceptable for realization of technological processes. Under trouble-free conditions, the technological processes are continued and the specimens are subjected to final surface cleaning for 30 min in the dense gas discharge plasma of high-purity argon (99.998 %) in which the specimens can be heated to the desired temperature by varying both their negative bias and plasma density. Due to the high ion cleaning efficiency in the gas discharge plasma of the setup, the only preliminary treatment of the specimens outside the vacuum is their rinsing in benzine.

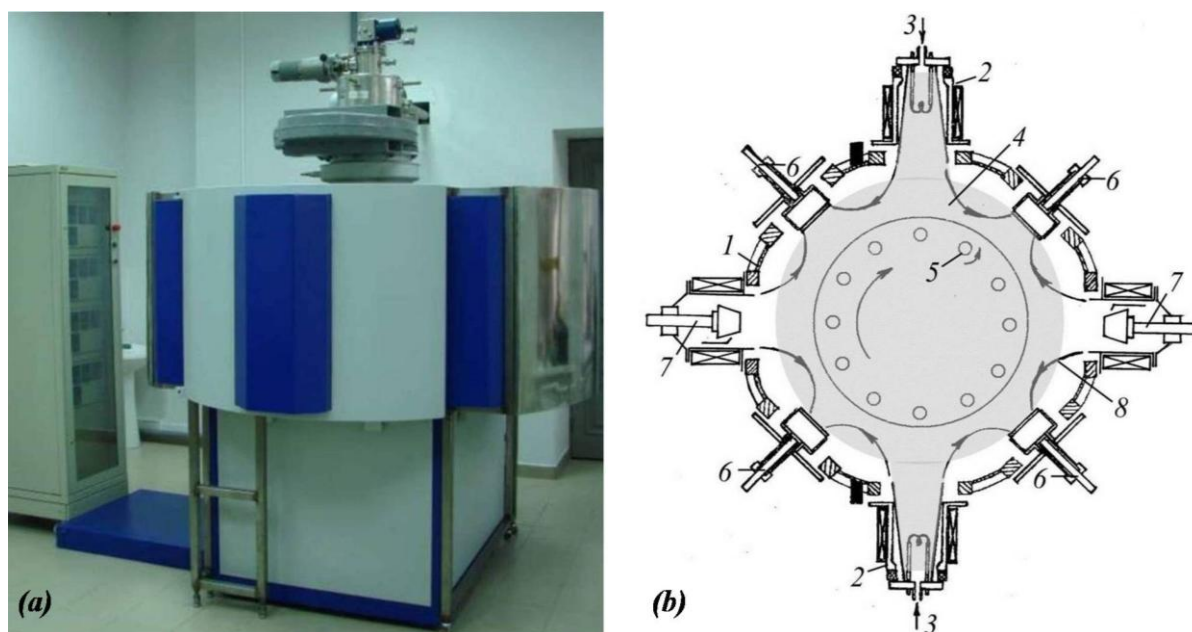


Figure 1. Photo (a) and schematic (b) of the SPRUT vacuum plasma setup: 1 – vacuum chamber; 2 – cathode units of the plasma generator; 3 – gas supply; 4 – bulk gas discharge plasma; 5 – treated objects; 6 – magnetron sputtering systems; 7 – arc evaporators; 8 – closed magnetic field lines (magnetic wall).

The TiN coatings deposited using the SPRUT setup were of nonstoichiometric composition and were similar in thickness to the polycrystalline Si substrates and in light yellow (brass) color to the decorative CuZn coatings described above. The Si substrates were preliminarily cleaned in the argon plasma of density 10^{11} cm^{-3} with no bias potential applied to them. The coatings were also deposited with no bias potential to the substrates; their floating potential with respect to the vacuum chamber was -20 V . The deposition was realized using arc evaporators of VT 1-0 titanium at a pressure of high-purity nitrogen (99.9997 %) of 0.2 Pa ; the density of the nitrogen plasma assisting the deposition was 10^{11} cm^{-3} . The temperature of the Si substrates throughout the deposition was no greater than 150°C .

As an additional example to demonstrate the efficiency of the SPRUT setup as technological equipment ensuring enhanced control of vacuum conditions and chemical composition of coatings, Si coatings were also deposited on nickel-titanium (NiTi) substrates with a Ni content of 50.9 %. Both ion cleaning and deposition of the coatings were realized in the plasma of high-purity argon with a plasma density of $5 \cdot 10^{10} \text{ cm}^{-3}$. The coatings were deposited through sputtering of pure silicon with all four magnetron sputtering systems at a pressure of 0.4 Pa . The bias potential of the NiTi substrates with respect to the vacuum chamber throughout the treatment had a repetitive pulsed form with a pulse frequency of 30 kHz and pulse duration of $17 \mu\text{s}$. The pulse amplitude was $\leq 160 \text{ V}$ and was controlled to hold the substrate temperature at 300°C .

The chemical composition of all coatings was analyzed by Auger spectrometry. The adhesive properties of the CuZn and TiN coatings on the Si substrates were studied using a CSEM micro scratch tester. In the tester, the surface of a coating is scratched by a special indenter with a tip of

radius 20 μm the load on which is increased throughout its motion (track) to record a signal of acoustic emission and its abrupt rise being indicative of separation and fracture of the coating. The critical load for separation (in Newton) or the adhesion strength of each of the test coatings was determined from no less than six scratch tracks by two methods: from acoustic emission signals and from visual observation of fracture in an optical microscope.

3. Results and discussion

Figures 2, 3, and 4 show Auger profiles of the chemical elements in the CuZn coatings (ZCL technology) and in the TiN and Si coatings (SPRUT setup). It is seen in Fig. 2 that the intermediate Ti layer used in brass deposition contains $\sim 40\%$ of oxygen the presence of which, like the presence of carbon, can be due to ion cleaning in the gas mixture containing carbon dioxide. The large amount of oxygen and carbon in the intermediate Ti layer can also be due to the properties of titanium as a good getter which, when sputtered and transported to the substrate, traps oxygen and carbon molecules present in the vacuum chamber because of inadequate vacuum conditions (high residual gas concentration, gas release, and leak-in). The latter explanation is confirmed by the rather high oxygen content $\geq 10\%$ in the brass coating as such (figure 2). According to the ZCL technology, it is likely the formation of titanium oxides and carbides in the intermediate layer between the silicon substrate and brass coating that ensures their high adhesion. The adhesion, in this case, is essentially defined by the adhesion strength of the oxide film to the silicon substrate and outer coating.

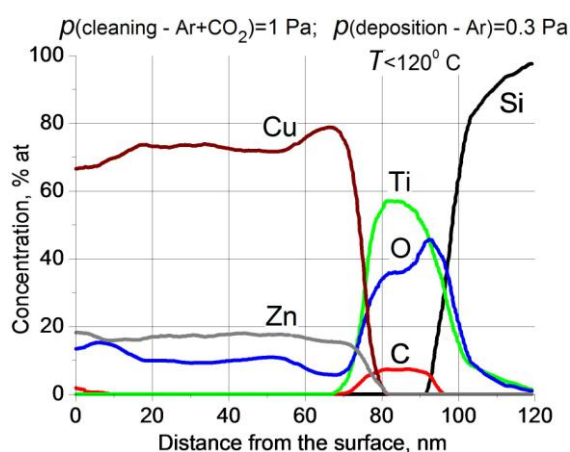


Figure 2. Auger profiles for the CuZn coating on the Si substrate.

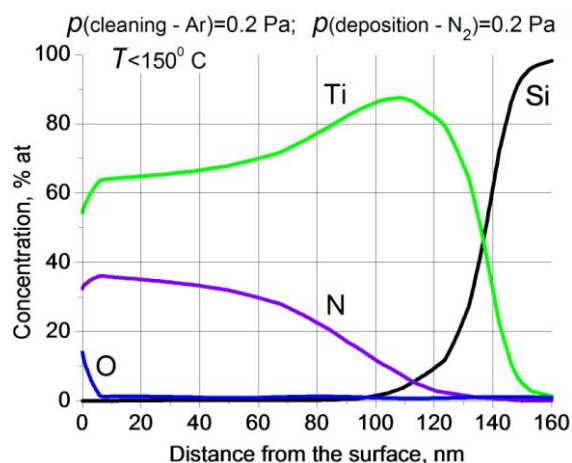


Figure 3. Auger profiles for the TiN coating in imitation of brass on the Si substrate.

Conversely, as can be seen from figure 3, the TiN coating deposited using the SPRUT setup is free from oxygen-containing impurities both at the coating–substrate interface and in the coating itself. The same is true for the Si coating deposited on the NiTi substrate as an additional example. It is seen in figure 4 that the content of oxygen and carbon in the Si coating is clearly negligible compared to their content in the alloy, and this is due to the stringent requirements on vacuum and gas conditions and associated purity of technological vacuum plasma processes realized in the SPRUT setup.

Figures 3 and 4 suggest that the SPRUT setup provides deposition of TiN and Si coatings without any clearly defined coating–substrate interfaces. The interfaces represent transition layers formed through mixing of the substrate and coating materials. The transition layer thickness is 60 nm for the TiN coating deposited on the Si substrate at a temperature of no more 150 $^{\circ}\text{C}$ and is clearly larger than 100 nm for the Si coating deposited on the NiTi substrate at 300 $^{\circ}\text{C}$. Likely the mixing of the coating and substrate materials, along with the absence of oxygen-containing impurities at their interface, ensures an obvious and extremely positive effect on the adhesion of the TiN coating compared to that of the CuZn coating. The results of scratch testing by the procedure described above show that the

adhesion strength of the CuZn and TiN coatings is ≈ 7 N and ≥ 15 N, respectively. Some adhesion ambiguity for the TiN coating is due to surface fracture of the Si substrate along the indenter track at ≥ 15 N with no separation of the coating (figure 5). Hence, the load ≈ 15 N represents the critical load for fracture of the substrate rather than characterizes the TiN coating and its adhesion the value of which can actually be higher.

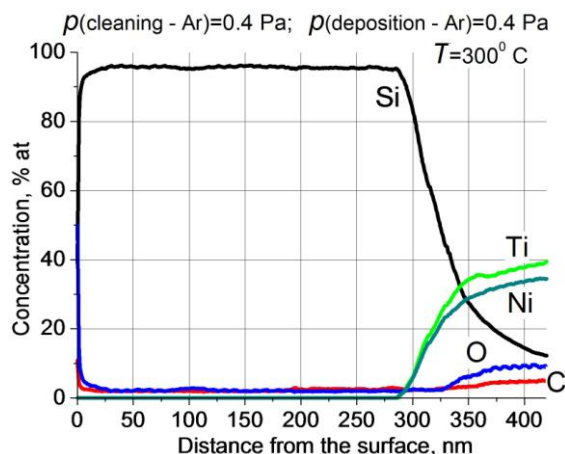


Figure 4. Auger profiles for the Si coating on the NiTi substrate.

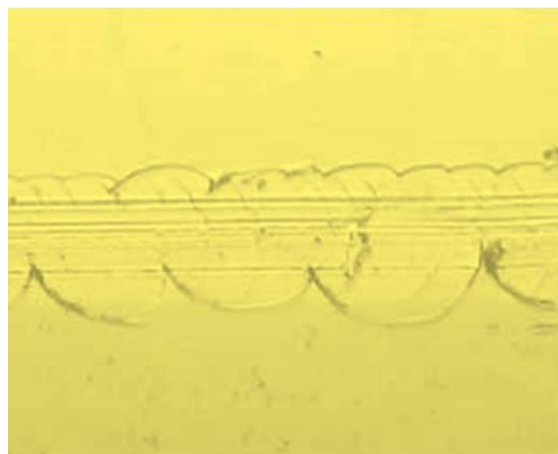


Figure 5. Image of the indenter track for the TiN coating in scratch testing.

4. Conclusion

The SPRUT setup, while providing the generation of dense gas discharge plasma, meets the stringent requirements on vacuum conditions and allows one to enhance the quality of plasma processes, realize the processes with no surface contamination during intense cleaning and activation, and increase the coating adhesion compared to the industrial technology of coating deposition with intermediate oxide layers. The deposition of coatings with the SPRUT setup involves the formation of an extended layer of thickness 60 nm and more through vacuum plasma mixing of the coating and substrate materials. The phenomenon is observed even at low bias potentials of no more than 160 V to the substrate and temperatures of ≤ 300 °C and is likely to be due to the absence of impurities on the treated surface. The observed effects give grounds for developing plasma immersion methods based on the new vacuum plasma equipment for surface doping with a wide range of chemical elements in a single vacuum cycle.

Acknowledgments

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