Chromium Oxide Anticorrosion Deposition on the Inner Surface of Fine Tube by Multiple Porous Plasma Jet

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Metal pipe fittings are widely utilized across various industries, including oil transportation, marine engineering, aerospace, and defense, owing to their exceptional mechanical properties and durability. However, a prevalent issue during their operation is the occurrence of failures caused by severe corrosion on the internal surfaces of the fittings. Therefore, the development of effective anticorrosion coatings for the inner surface of pipelines holds paramount significance. Nonetheless, developing such coatings for small-diameter pipes remains a significant challenge due to spatial constraints. To address this challenge, this study proposes an innovative surface modification strategy employing rigid plasma brush technology. By employing a pulsed power-driven multiple porous plasma jet apparatus, controlled deposition of chromium oxide is achieved on the internal surface of the fittings. The spiral motion of the fittings ensures uniform coating deposition along the entire length of the pipeline. A comprehensive characterization approach is employed to analyze the deposited coating, encompassing surface morphology, cross-sectional morphology, film thickness, elemental composition, and chemical structure. Advanced techniques, including scanning electron microscopy, spectroscopy, and X-ray diffraction, are utilized for accurate and detailed characterization of the coating. Furthermore, extensive corrosion resistance testing is conducted to evaluate the coating's efficacy in enhancing corrosion resistance. Electrochemical testing and simulated seawater contact angle testing are employed to assess the coating's corrosion resistance performance. The research findings demonstrate a significant increase in contact angle and a corrosion resistance improvement of over 90% following the application of the chromium oxide coating. By overcoming the limitations associated with traditional high-temperature deposition processes, such as thermal damage to the pipeline and poor film uniformity, this study presents a practical and versatile method for modifying the inner surface of small-diameter pipes under mild conditions. This innovative approach not only enhances the corrosion resistance performance of metal pipe fittings but also extends their service life, thereby rendering them more reliable and economically efficient for diverse industrial applications.

NOMENCLATURE

slm = standard liter per minute

1. Introduction (Times New Roman 10pt)

Metal pipe fittings are widely used in petrochemical, equipment manufacturing, marine engineering, aerospace and military defense and other industry fields. As the main component of the transmission system, the inner wall of the pipe usually undergoes corrosion and wear due to the corrosive and abrasive materials contained in the transmission medium [1]. Metal fragments and ionic releases not only contaminate the transport medium, but also exacerbate the corrosion and wear process, ultimately leading to a shortened service life. In addition, in the military field of national defense, firearms and artillery bore is constantly subjected to high temperature, high pressure and high-speed gunpowder or cartridge extrusion and scrubbing and other comprehensive mechanical effects. Eventually, the surface of the bore is constantly abraded and worn out, affecting the ballistic performance of the fired munitions. The use of coating technology can effectively reduce the damage of the inner wall surface under extreme working conditions without changing the performance of the base material, and improve the service life and service safety of metal pipe fittings [2,3]. Therefore, the development of anti-wear and corrosion-resistant surface treatment technology for the inner wall of tubes is of great significance to the development of national economy and the enhancement of national defense force.

2. Methods and Results

2.1 Methods

In this study, a set of plasma etching and coating as an integrated atmospheric pressure multiple porous plasma jet for treating the inner surface of slender tubing was built, as shown in Fig. 1. The multiple porous plasma jet adopts a typical single-electrode structure, and the hollow stainless steel tube is wrapped by a dielectric quartz tube. The dielectric quartz tube is closed at the end and has small holes on its side to allow the plasma multi-hole jet to be ejected. The plasma jet is excited by a high-voltage AC power supply with an adjustable output voltage in the range of 0 to 50 kV and an adjustable output frequency in the range of 1 kHz to 100 kHz. When the inner surface of the tubing is subjected to plasma etching treatment, research-grade high-purity argon (Ar, 99.999% purity) is used as the working gas of the plasma, which enters into the plasma jet device at a gas flow rate of 3 slm to discharge. The plasma is stimulated to generate a large amount of active substances to clean, etch, and introduce polar groups on the inner surface of the tubing. After plasma etching treatment, the precursor was heated and carried by argon gas to plasma jet discharge area. The precursor molecules dissociation, oxidation and nucleation processes occur. The discharge voltage and current during the plasma discharge were measured by a high voltage probe and a current coil, respectively. The high voltage probe and current coil were connected to an oscilloscope for real-time monitoring of electrical signals. The metal tubing was helically moved on a movable platform driven by a stepper motor to achieve uniform deposition.

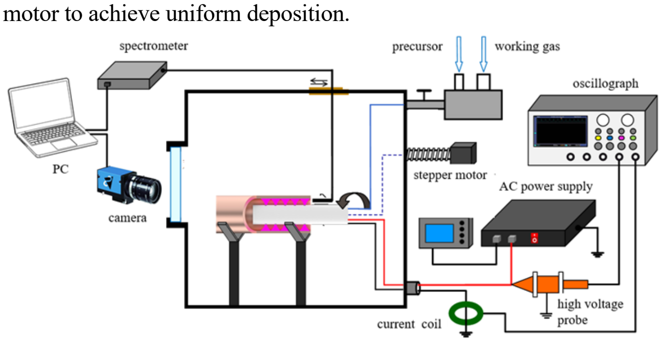


Fig. 1 The schematic diagram of atmospheric pressure plasma multi-hole jet platform for treating the inner surface of slender tubing

2.2 Results

Four observation points in the axial direction of the tubing were selected at equal intervals to observe the morphology of the plating layer. SEM tests showed that the plating layer was relatively uniform and smooth, and the surface morphology of the tubing was roughly the same at four different locations in the axial direction of the tubing, as shown in Fig. 2. Under high magnification, it is found that the coating is a dense layer composed of many small spherical particles on the surface. The elemental composition of the plated surface includes four elements, namely, chromium, carbon, oxygen, and silicon, as shown in Fig. 3, where the silicon is caused by the large EDS penetration depth and the measured substrate signal. The four elements are more uniformly distributed on the surface of the plating layer, which proves that the uniformity of the elemental composition of the plating layer is good.

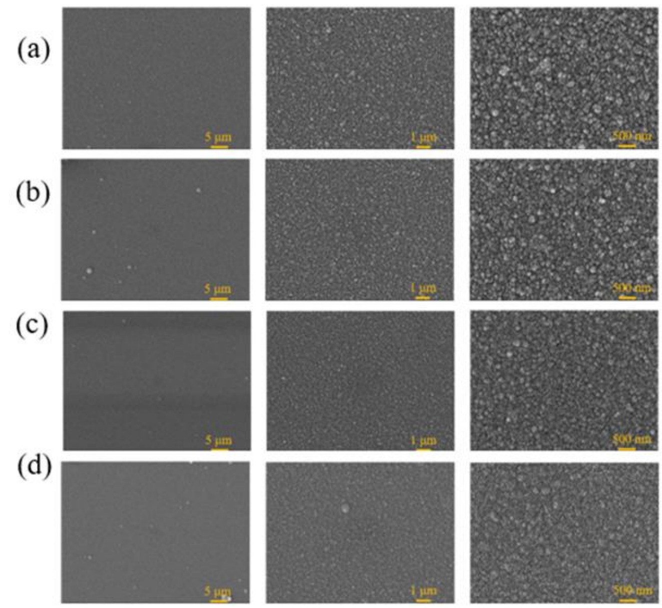


Fig. 2 Surface morphology of the plating at four different locations in the axial direction of the tubes

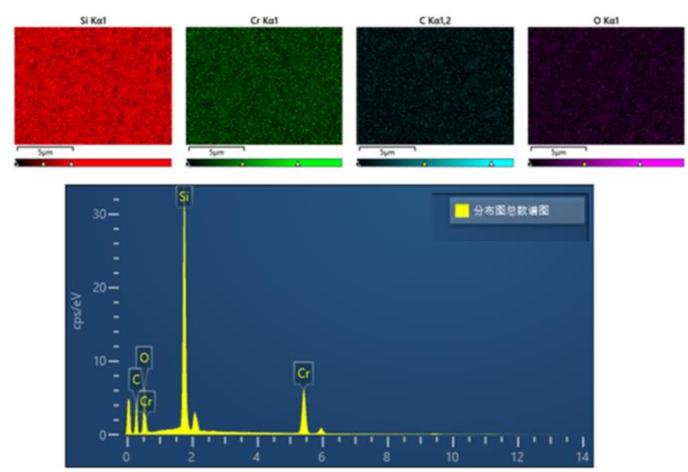


Fig. 3 Plated surface element distribution

SEM was used to observe the cross-sectional morphology of the plating at four different locations in the axial direction of the tubing, as shown in Fig. 4. It was found that the thickness of the plating layer was presented consistently and uniformly dense. The average thickness of the plated layer was 4.5 μm, and the thickness uniformity was 4.2%. The average deposition rate was calculated to be 1.1 μm/h.

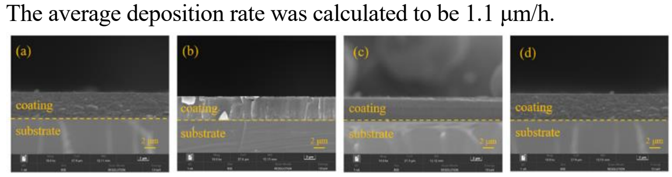


Fig. 4 Cross-sectional morphology of the plating at four different positions in the axial direction of the tubing (a) Position 1; (b) Position 2; (c) Position 3; and (d) Position 4

Four positions in the axial direction of the tubing were selected for IR spectroscopic tests and were found to present good agreement. The peaks observed at 545 cm^{-1} and 613 cm^{-1} are Cr-O bonds, which are the vibrational modes of Cr_2O_3, while the peak at 409 cm^{-1} is attributed to the Eu vibrational mode. It indicates the dominance of Cr_2O_3 phase in the prepared coatings. Similarly, four different positions of the plating were selected for Raman spectroscopy, and all of them showed the characteristic peaks of chromium oxide, and the peaks at the four different positions were of the same intensity, which indicates the homogeneity of the physical phase composition of the plating layer.

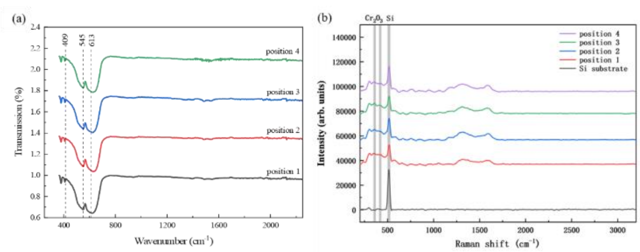


Fig. 5 (a) Infrared spectroscopy; (b) Raman spectroscopy

The contact angle of different positions of the substrate to the seawater simulating solution was observed using an optical method contact angle/interfacial tensiometer. A 3.5 wt.% NaCl solution simulating seawater was used to evaluate the wettability of the coatings. It should be noted that the droplet volume was kept consistent at less than 10 µl for each measurement to avoid possible interference of the droplet weight on the contact angle measurement. As shown in Fig. 6, the contact angle of the seawater simulation solution after the deposition of the plating layer was observed, and it was found that the contact angle increased significantly from 80° to 140° after the deposition of the plating layer, indicating that the plating layer produced a good impedance to the seawater simulation solution, which, together with the barrier formed by the dense plating layer, formed the corrosion-resistant effect of the plating layer.

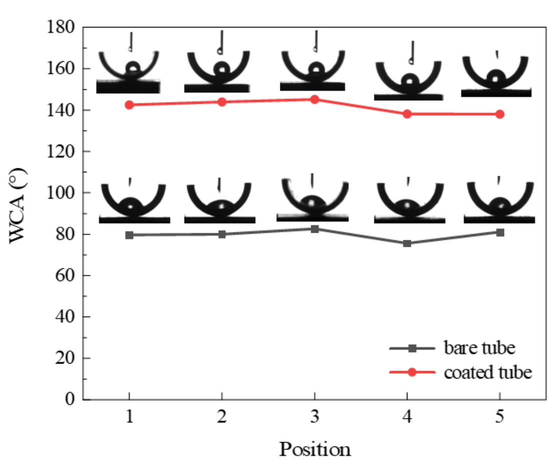
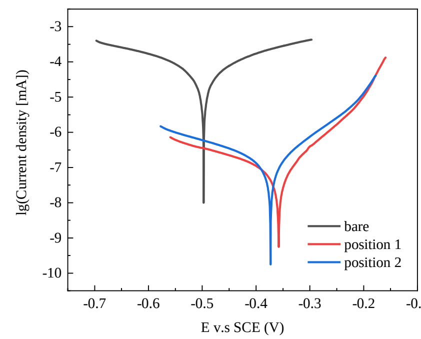


Fig. 6 Contact angle of substrate to seawater simulant before and after deposition

Referring to the electrochemical test standards, the Tafel curve test was performed on the deposited plating with 3.5% NaCl solution as the corrosion medium to evaluate the corrosion resistance before and after the coating was deposited. After the deposition of the coating, the corrosion potential was significantly positively shifted and the corrosion current significantly decreased by more than two orders of magnitude, as shown in Fig. 7, indicating that the corrosion resistance efficiency was higher than 99% and the coating presented excellent corrosion resistance.

Fig. 7 Tafel curves before and after deposition of the coating

3. Conclusions



In this work, a multiple porous plasma jet device was developed to deposit coating on the inner surface of a tube in combination with its helical motion. The surface morphology and cross-section morphology of the coating at different locations were observed and found to be in good agreement. The deposition rate was calculated to be up to 1.1 µm/h. Microscopic examination of the coatings at different locations by infrared spectroscopy and Raman spectroscopy revealed that the phase compositions were also in good agreement. The corrosion resistance of the coatings was tested by seawater simulated liquid contact angle test and electrochemical test, and it was found that the contact angle increased significantly and the corrosion resistance efficiency was improved by more than 90% after coating. Our work overcomes the drawbacks of conventional deposition processes, providing a generalized method for surface modification of the inner surfaces of elongated tubes under mild conditions.

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