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Densification of Plasma-Sprayed Titanium and Tantalum Coatings

T. Kinos, S.L. Chen, P. Siitonen, and P. Kettunen

Thermal spraying of corrosion-resistant coatings of titanium and tantalum is difficult; dense coatings are not produced, and oxidation of these metals increases coating porosity. In this study, oxidation during plasma spraying was reduced with a shrouding system. Porosity and oxide content also were minimized by optimizing the spraying parameters. After optimization, the coatings still had open porosity and thus were incapable of protecting the substrate material against corrosion in water solutions containing 3% NaCl. Therefore, posttreatments for improvement of corrosion resistance were studied. Electron beam fusion produced corrosion resistance equal to or better than that of bulk commercial samples of titanium and tantalum.

Keywords corrosion-resistant coatings, electrochemistry, shrouded spraying, titanium and tantalum feedstocks

1. Introduction

TITANIUM and tantalum both have excellent corrosion resistance, but both are also very reactive and cannot be used or fabricated at temperatures above 500 °C without a hazardous reaction with gases such as O_2, H_2, N_2, and CO_2. Oxidation causes loss of ductility and cracking of the surface of the material. When heated and molten, titanium and tantalum must be protected against reactive gases. Therefore, thermal spraying or welding of titanium and tantalum must be performed in an oxygen-free atmosphere to produce high-quality, ductile, and dense coatings.

Small components can be thermally sprayed in a vacuum chamber by plasma or arc spraying techniques. Large components, however, must be sprayed in an inert gas tent or by using external gas shielding, as is done in the shrouding technique. Such methods are also applicable when spraying under field conditions. Shrouded plasma spraying (SPS) of titanium and tantalum requires special considerations, including a shroud designed with sufficient shielding capability to protect against oxidation and ascertainment of the optimum spraying parameters. The suitability of the SPS method also depends on the surface to be sprayed; it is best for smoothly changing surfaces where the gas flow on the substrate remains sufficiently homogeneous.

The objectives of this study were to check the shielding characteristics of developed systems and to investigate the effects of several posttreatments with respect to the corrosion properties of titanium and tantalum coatings.

2. Experimental Procedure

The coatings were prepared using a Plasma-Technik (Sulzer Metco AG, Wohlen, Switzerland) A3000 S plasma spraying unit equipped with an F4-MB plasma torch. The shroud itself (Fig. 1) was a short tube with a coaxial feed of shielding argon gas. Argon and hydrogen were used as the plasma spraying gases, and the coatings were sprayed on steel or stainless steel substrates. The titanium and tantalum powders had purities greater than 99.6 and 99.95%, respectively. The powder fraction for both powders was 20 to 45 μm.

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Coating hardness and oxygen content were measured and coating structure studied by optical and scanning electron microscopy. The corrosion behavior of the coatings was studied by anodic polarization tests in salt water. Their porosity was assessed by water impregnation tests. Hydrogen content in the coatings was determined with Leco RH-2 equipment, and the Leco TC-136 (Leco Corp., St. Joseph, MI) to determine oxygen and nitrogen content.

3. Results and Discussion

Titanium coatings produced by plasma spraying under air atmospheric (APS) conditions have a high oxygen content of 6-9 wt%. The coatings are hard (700 HV) and brittle. Oxides also tend to increase the amount of porosity, because they do not deform as easily as metal feedstocks which impinge onto the substrate. Thus, the APS method is not beneficial if dense coatings are required. Titanium coatings formed by SPS exhibit a more homogeneous structure, and the oxygen content of SPS titanium coatings is much lower than corresponding APS titanium coatings. Table 1 indicates the positive effect of shrouding in the prevention of titanium oxidation during plasma spraying.

3.1 *Effect of Shrouding Parameters*

The ability of the shroud to prevent oxidation of powder particles during spraying was found to depend on two major parameters: the flow rate of the shielding gas and the standoff distance between the end of the shroud and the substrate. The results of experiments in which the flow rate of the argon shielding gas and the standoff distance were varied suggested that the flow rate should be greater than 350 L/min to adequately protect against oxidation and that the standoff distance must not exceed 10 mm. If the distance is 5 mm, the required flow rate is about 300 L/min. Thus, by decreasing the standoff distance, the flow rate of the shielding gas can be decreased. For the shroud used in this study, the maximum standoff distance is about 10 mm; greater standoff distances result in poor coating structures

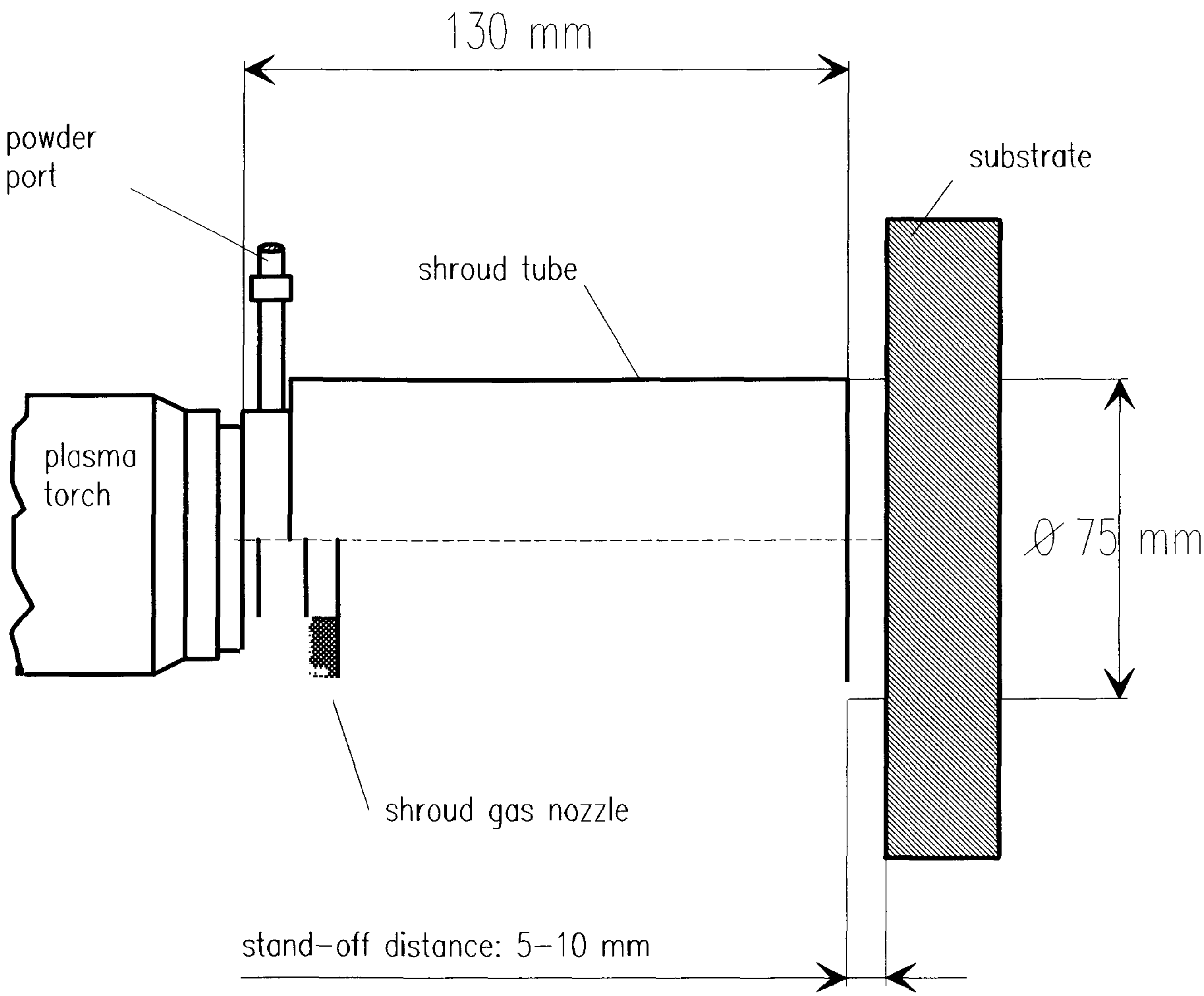

Fig. 1 Schematic of SPS apparatus

Table 1 Oxygen, nitrogen, and hydrogen content of APS and SPS titanium coatings

Coating	Content, ppm Oxygen (±10%)	Nitrogen (±4%)	Hydrogen (±10%)
APS Ti	57,000	24,000	...
SPS Ti	4,400-19,000	460-3,100	1,500-3,100
Titanium powder	6,100	480	160
Low-pressure plasma spray (LPPS)(a)	5,350	1,150	120

(a) See Ref 1.

(Fig. 2). The hardness and oxygen content of the structure shown in Fig. 2(a) were 340 HV and 1.5 wt%, respectively, and in Fig. 2(b) were 530 HV and 3.3 wt%, respectively.

3.2 *Optimization of SPS Titanium and Tantalum Coatings*

The properties of plasma-sprayed coatings depend on the spray parameters. The critical spray variables are the flow rates of plasma and carrier gases, applied current (I), and standoff distance. In this study, spray parameters were optimized by applying the ORO method (orthogonal block design of spraying experiments, regression analysis, and optimization of created equations (Ref 2). Application of the method proceeds in three steps. First, the orthogonal block design is used to arrange the experiments with the selected important spraying parameters in order to reduce the number of experiments. The flow rate of plasma argon was found to have a strong effect on the shielding characteristics of the shroud and thus on the structure of the SPS coatings. The property of the coating is a function of the selected

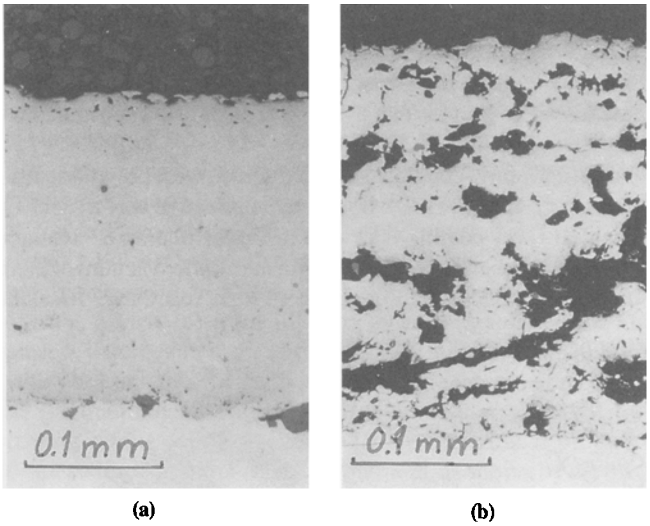

Fig. 2 Structures of SPS titanium coatings sprayed with different standoff distances. (a) 10 mm. (b) 25 mm. Spraying parameters: argon, 25 slpm; H_2, 3 slpm; I, 612 A; flow rate of argon shroud gas, 400 L/min

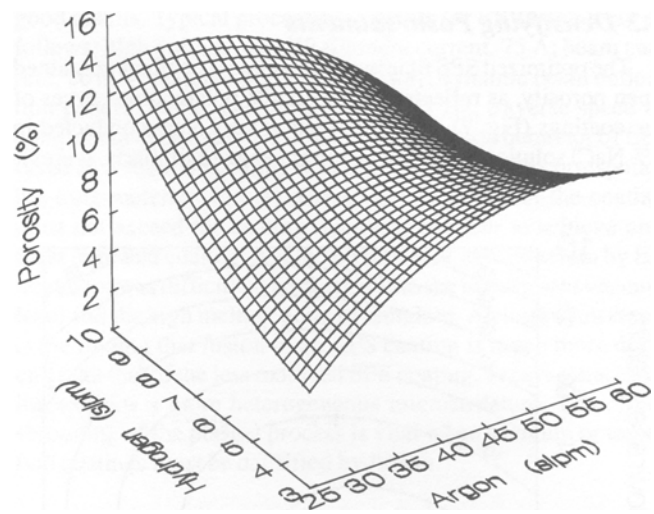

Fig. 3 Porosity in SPS titanium coatings as a function of flow rates of argon and hydrogen plasma gases. Current, 612 A; standoff distance, 7 mm.; flow rate of argon shroud gas, 375 L/min

variables and also of the interactions among them. Application of regression analysis allows direct relations between spraying variables and coating properties to be obtained as a second-order equation. Finally, based on this analysis, the selected coating property can be optimized by a suitable mathematical algorithm.

The ORO optimization of titanium coatings sprayed with the SPS method was started with some preliminary experiments. On the basis of the results, the flow rates of the argon and hydrogen plasma gases and the magnitude of plasma current were selected as variables for experimentation. These parameters were varied at five levels, and a total of 15 experiments were conducted. The standoff distance was 7 mm, and the flow rate of the argon shroud gas into the shroud tube was about 375 L/min. The properties to be optimized were porosity and hardness of the SPS titanium coatings. Titanium coatings are very attractive for corrosion protection applications, where they must be very dense with no open porosity. Therefore, the pore diameter must be below a critical value. The hardness of the coating is partly related to its oxide content, thus revealing the extent of oxidation that occurs during spraying.

After spraying experiments and microstructural studies of the SPS titanium coatings, the porosity variation, as based on water impregnation measurements, was modeled according to the ORO procedure as a function of flow rates of argon and hydrogen in the plasma. These results are presented in the form of a three-dimensional surface in Fig. 3. In this model, the plasma current value was selected to be the maximum (612 A), since this was found to be beneficial for achieving minimum porosity. According to this model, the minimum porosity can be obtained by low flow rates of argon and hydrogen together with a high current value. This result confirms earlier observations that low argon flow rate (low plasma jet velocity) provides good protection against oxidation due to reduced turbulence of the plasma jet. Figure 4 illustrates the structures of unoptimized and optimized coatings of SPS titanium.

Tantalum is a refractory metal with a 3000 °C melting temperature and a high affinity to gases such as oxygen, nitrogen,

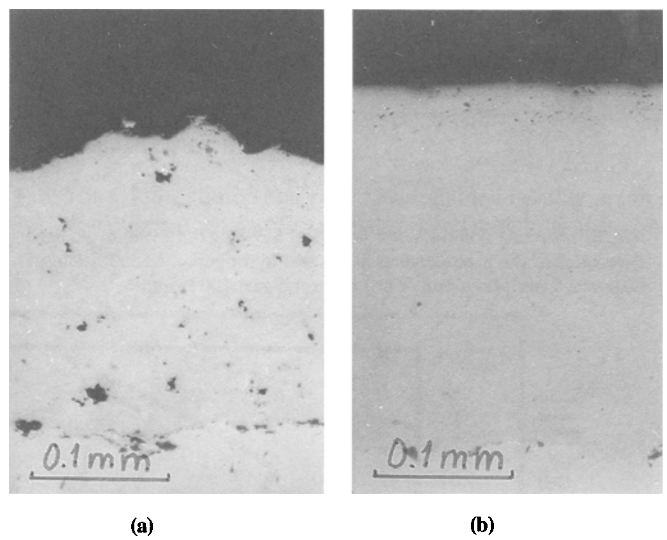

Fig. 4 Optical micrographs of SPS titanium coatings. (a) Unoptimized (argon, 50 slpm; H_2, 3 slpm; I, 500 A). (b) Optimized (argon, 25 slpm; H_2, 3 slpm; I, 612 A). Standoff distance was 7 mm in both cases

and hydrogen. The literature (Ref 3, 4) has reported tantalum coatings sprayed by the LPPS method. In the present study, the SPS method was also applied to tantalum. The ORO optimization procedure had two variables: the flow rates of the argon and hydrogen plasma gases.

The current was selected to be constant at 612 A to ensure a high power level to melt the tantalum. After spraying experiments and analysis of SPS tantalum coatings, the dependence of coating porosity and hardness on the two variables can be presented as shown in Fig. 5 and 6. The minimum values of porosity and hardness cannot be obtained at exactly the same values of the spraying variables, but they are reasonably close. For high-quality SPS tantalum coatings, the hydrogen flow rate should be high (about 10 slpm) and the argon flow rate low to moderate (25 to 35 slpm).

3.3 *Densifying Posttreatments*

The optimized SPS titanium and tantalum coatings contained open porosity, as reflected in the anodic polarization curves of the coatings (Fig. 7). The polarization tests were conducted in 3% NaCl solution, and both coatings behaved similarly. It is evident that this thermal spraying technique is not capable of producing fully dense coatings. Thus, some type of densifying posttreatment is vital if thermal spray coatings of titanium and tantalum are to provide corrosion protection to the substrate material.

Thermal spray coatings are often sealed with polymeric materials (e.g., epoxy resins); however, an effective way to densify a thermal spray coating is to fuse it. Consolidation of titanium and tantalum coatings must be performed under vacuum or inert atmosphere conditions due to their high reactivity. Possible

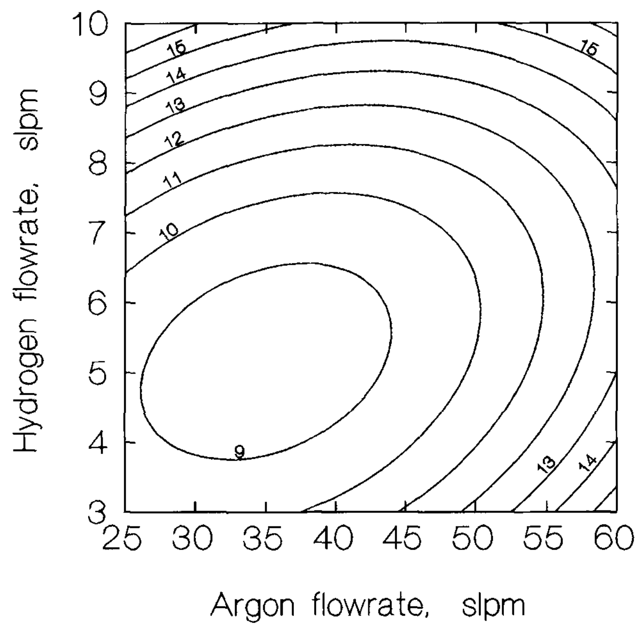

Fig. 5 Porosity contours of coatings of SPS tantalum versus the used flow rates of the plasma gases argon and hydrogen. *I*, 612 A; standoff distance, 7 mm; flow rate of argon shroud gas, 400 L/min

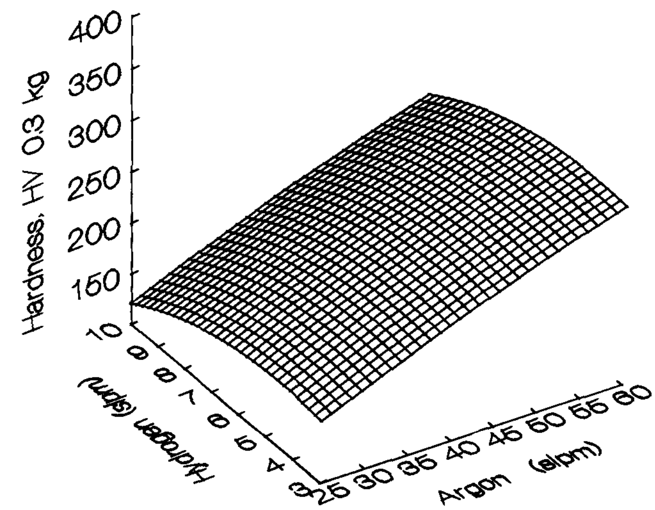

Fig. 6 Coating hardness of SPS tantalum versus flow rates of argon and hydrogen plasma gases. *I*, 612 A; standoff distance, 7 mm; flow rate of argon shroud gas, 400 L/min

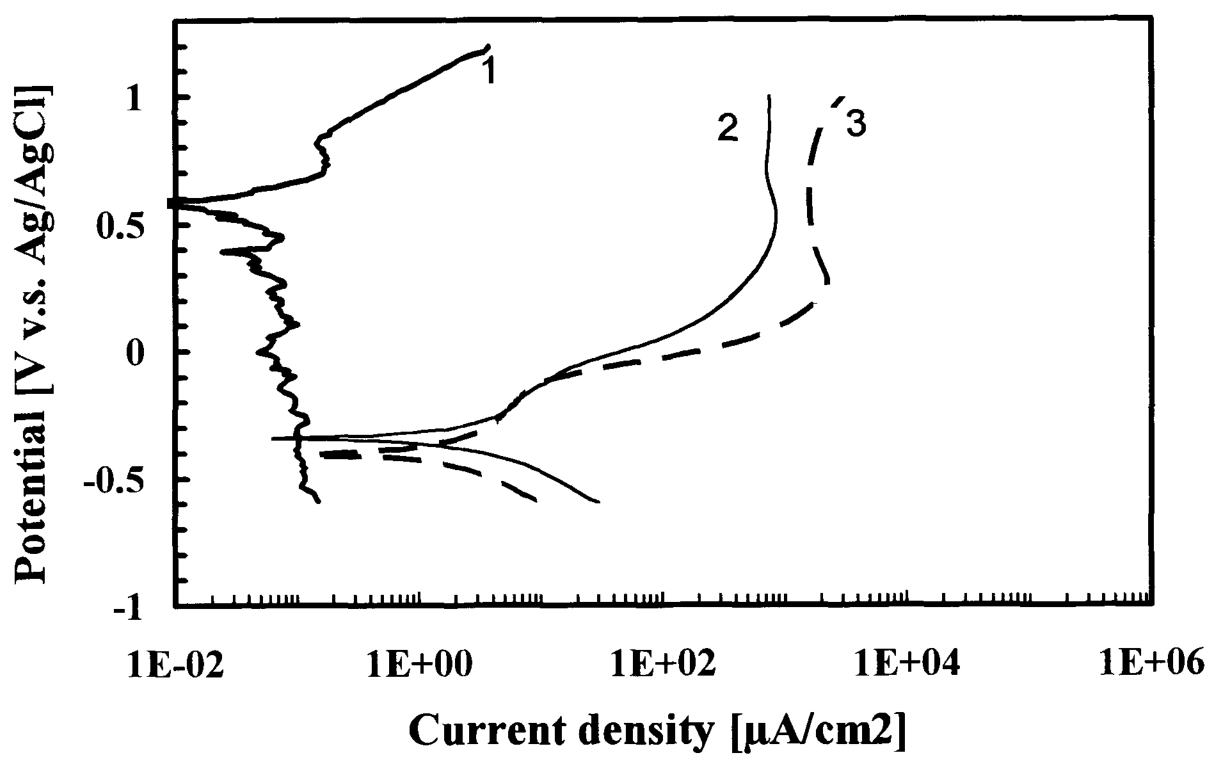

Fig. 7 Anodic polarization curves of SPS titanium and tantalum coatings in 3% NaCl solution at room temperature. 1, tantalum sheet; 2, SPS titanium (substrate, AISI 304); 3, SPS tantalum (substrate, AISI 304)

methods include vacuum annealing, fusion by laser or electron beam (EB), and hot isostatic pressing (HIP). On the basis of the results of this study, some of these densifying methods work well for both materials—especially for titanium, because of its lower melting temperature compared to tantalum. Figure 8 shows anodic polarization curves of densified SPS titanium and tantalum coatings.

For HIP processing, the coatings with a stainless steel substrate (AISI 304) were first covered with hexagonal boron nitride paint and then packed with alumina powder into a steel capsule, which subsequently was evacuated and sealed. The process parameters were as follows: $T = 900$ °C, $p = 130$ MPa, with a holding time of 3 h. The SPS tantalum was sprayed onto an SPS titanium bond layer to prevent spallation of the tantalum coating during HIP processing. This posttreatment produced dense coatings in the case of SPS titanium, as shown by the electrochemical corrosion tests (Fig. 8). However, this HIP process could not densify the SPS tantalum coating since the HIP temperature was too low with respect to the high melting temperature of tantalum. Therefore, the HIP temperature could be increased by several hundred degrees, but this causes high-temperature stability problems for the substrate material. Thus, a densifying posttreatment of a tantalum coating on a steel substrate by HIP processing remains a demanding technological challenge.

The fusion of SPS titanium and tantalum coatings by EB welding apparatus (Wentgate CVE 68B28, Wentgate Dynaweld, Agawam, MA) was satisfactory for SPS titanium coatings if the components were planar or cylindrical, because the electron beam must be precision focused on the coating surface to obtain good results. Typical process parameters for EB fusion were as follows: high voltage, 40 kW; filament current, 75 A; beam current, 20 mA; chamber pressure, 10^{-3} torr; dynamic beam deflection pattern, circle; beam oscillation, 55 Hz; traverse speed of component to be treated, 3 mm/s. The corrosion behavior of EB-fused SPS titanium coating is better than that of the corresponding bulk material (Fig. 8). However, the fusion of the coating must not exceed the coating thickness in order to achieve uniform remelted coating. Again, the fusion of SPS tantalum by EB treatment was difficult to perform due to the insufficient vacuum level and the high melting point of tantalum. An important result is the finding that fusion of an APS coating is much more difficult than that of the less oxidized SPS coating, because this coating exhibits a more heterogeneous microstructure. Therefore, shrouding of the plasma process is vital when titanium or tantalum coatings must be densified by fusion.

4. Conclusions

- Shrouded plasma spraying can clearly reduce the oxide content of titanium and tantalum coatings.
- Coatings produced by SPS are of good quality if the standoff distance is short enough and the flow rate of the shielding gas is suitable in terms of the optimized spraying parameters.
- The ORO optimization procedure enabled reliable predictions for properties of coatings sprayed with optimized parameters.

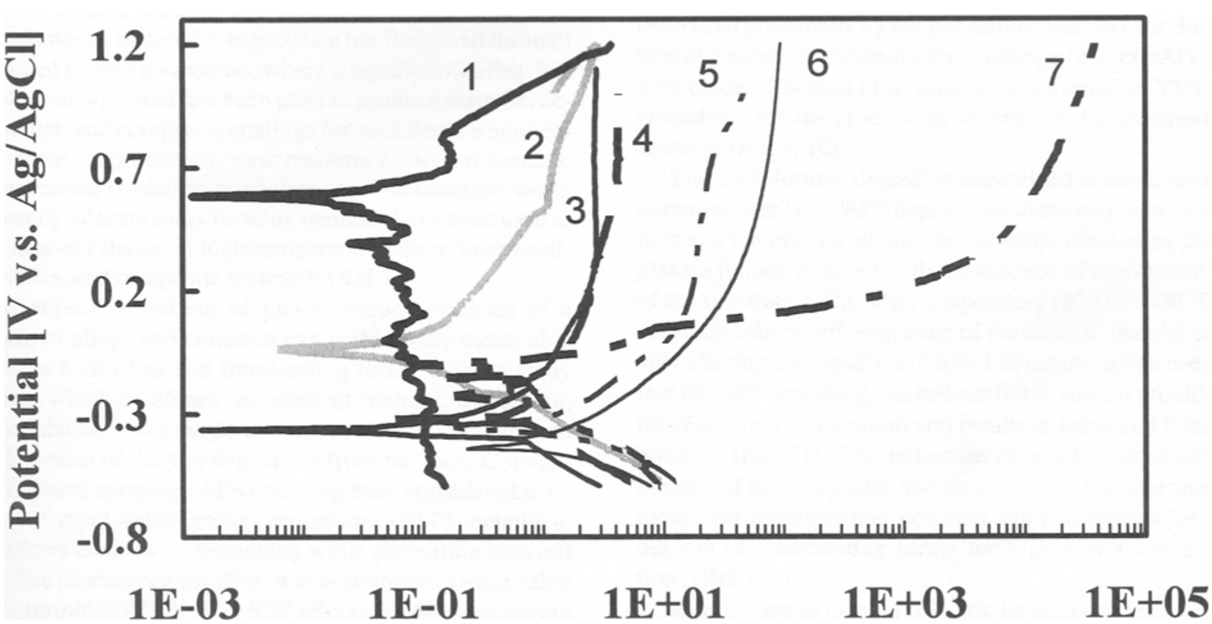

Fig. 8 Anodic polarization curves of densified SPS titanium and tantalum coatings in 3% NaCl solution at room temperature. 1, tantalum sheet; 2, SPS titanium + EB fusion (substrate, AISI 304); 3, SPS titanium + HIP (substrate, AISI 304); 4, titanium sheet; 5, APS titanium + HIP (substrate, AISI 304); 6, SPS titanium/tantalum + HIP (substrate, AISI 304); 7, substrate of AISI 304

- As-sprayed SPS titanium and tantalum coatings are not fully dense and thus are incapable of providing corrosion protection to the substrate material. Densifying posttreatments, such as HIP and EB fusion, were found suitable for SPS titanium coatings, but were less suitable for APS titanium and SPS tantalum coatings because of their more heterogeneous microstructure and/or higher melting point.

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