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Corrosion Resistance of Thermal Sprayed Titanium Coatings in Chloride Solution*

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The corrosion behavior of a resin-sealed flame-sprayed titanium coating in 3.5% NaCl solution was investigated by electrochemical polarization measurements. The composition and structure of the sprayed film was also analyzed by scanning electron microscopy (SEM) and electron probe x-ray microanalysis (EPMA). Although an as-sprayed titanium coating exhibited no resistance to corrosion because of its porosity, the sprayed titanium sealed with epoxy or silicon resin showed an excellent resistivity with respect to chloride corrosion. Although almost half of the titanium changed to oxides, nitrides, and carbides through the wire flame spraying, the conversion of the metal to those compounds had little effect on decreasing the corrosion resistivity. The sprayed and sealed titanium coating obtained by conventional on-site thermal spraying is expected to be an economical material for chloride containing environments.

Keywords chloride corrosion, flame spray titanium coating, electrochemical polarization test, immersion test, resin sealing

1. Introduction

Barrier type, corrosion-resistant sprayed coatings that can be produced by conventional on-site thermal spraying and applied as a large scale plant material have been studied.

Prior work (Ref 1) has shown that arc-sprayed coatings of stainless steel and alloy sealed with epoxy resin exhibited resistance to chloride corrosion. A sufficient corrosion resistance, however, was obtained only for a high-alloy sprayed coating such as 56Ni-16Cr-16Mo-5Fe-4W, because the selective oxidation of chromium through the spraying process caused a chromium-depleted zone in the matrix adjacent to the microcrevices among the deposited particles. On the other hand, a sufficient resistance of the thermal sprayed stainless steels is obtained in a high-alloy steel by plasma spraying without any post treatment (Ref 2).

The thermal sprayed composition of the material only changes for alloys and never for pure metals. Commercially pure titanium is well known as a most resistant metal against chloride corrosion that exceeds the performance of stainless steels and alloys.

Titanium is an extremely active metal, which would be expected to react with oxygen and nitrogen during the conventional thermal spray processes. Most investigations to reliably thermal spray titanium were conducted, therefore, under vacuum plasma spray (Ref 3, 4), laser consolidation (Ref 5), and a modified high-velocity oxygen fuel (HVOF) spray process (Ref 6).

The corrosion resistance of both the oxide and nitride of titanium is comparable to the titanium metal within a chloride environment. Thermal sprayed titanium is, therefore, expected to have a similar resistance to the solid titanium metal in spite of the fact that the deposit film by conventional spraying contains many nonmetallic inclusions.

In this investigation, a thermal sprayed titanium coating with a resin sealing is proposed as a corrosion-resistant system for chloride environments.

2. Experimental Procedure

Coatings for electrochemical experiments and the vessel immersion test were prepared by wire flame spraying with the commercial pure titanium, JIS H 4670, Gr. 2, followed by the posttreatment of sealing with resins. The spray conditions are shown in Table 1. Thickness of the coating films was controlled to 100 to ~200 μm. Epoxy resin (Epikote, Yuka Shell Epoxy K.K., Tokyo), epoxy-silicon resin (Suntomo DHX610, Daiho Paint Co. Ltd., Tokyo) and silicon resin (Ceraton, Suzuki Sangyo Co. Ltd., Tokyo) were applied as the sealing materials for posttreatment.

The anodic polarization characteristic was measured in deaerated 3.5% NaCl aqueous solution at 30 °C. The poten-

Table 1 Thermal spray process

Condition	Parameters
Substrate	Carbon steel, SS400
Blasting	White alumina, grit No. 24
Material	Titanium wire, grade No. 2, 3.1 mm diam
Method	Wire flame spraying, METCO 12E
Wire feed speed	1.1 m/min
Fuel gas	C_2H_2, 0.12 MPa, 1.0 m^3/h O_2, 0.20 MPa, 1.2 m^3/h
Atomizing	Air, 0.50 MPa, 1050 m^3/h
Stand off distance	150 mm

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tiodynamic method with a sweep rate of 20 mV/min was adopted. Test electrodes were cut rectangularly about 15 by 20 mm from the sprayed specimen and mounted in the epoxy resin, except for an exposed area of about 10 by 15 mm. To maintain electrical conductivity, the sealed electrode surface was polished with No. 320 emery paper until about 50% area of the sprayed titanium metal was exposed.

The microstructure and composition of the sprayed titanium layer were also analyzed chemically and observed by scanning electron microscopy (SEM) and electron probe x-ray microanalysis (EPMA) elemental mapping.

Penetration of the sealing resins among the sprayed titanium particles was also checked by energy dispersion x-ray analysis (EDAX) for the major elemental components of the resins, i.e., carbon and/or silicon.

A bench pilot corrosion test apparatus (Fig. 1) was used for the immersion tests. The inner surface of the test vessel, made of carbon steel and 254 mm in diameter and 300 mm in height, was sprayed with titanium and sealed with an epoxy resin. The test procedure was as follows: the test vessel was exposed to a cycle of steam heating at 120 °C for 1 h, followed by immersion in 3.5% NaCl at 30 °C for 95 h in a 4 day cycle. This cycle was continued for about 200 days.

3. Results and Discussion

The cross-sectional SEM observation Fig. 2(a) and the elemental mapping for iron, titanium, oxygen, nitrogen, and carbon are shown in Fig. 2(b-f). To clarify the influence of alumina grit used as the blasting media prior to spraying and also as an abrasive during specimen preparation, the relation between oxygen and aluminum in the EPMA maps is shown (Fig. 3). The results of chemical analysis for oxygen, nitrogen, carbon, hydrogen, and titanium and the calculated composition of the compounds in the coating layer are shown in Table 2.

Fig. 1 Bench pilot corrosion test apparatus

The map of oxygen, nitrogen, and carbon in Fig. 2 show that the titanium changed mostly to oxide, nitride, and carbide, which were distributed homogeneously in the coating layer. The amount of pure titanium is very small. As shown in Fig. 3, the extremely rich area of oxygen does not correspond to titanium oxide but to voids, which have been filled with alumina from the abrasive media. The dense region of aluminum suggests the existence of many voids and defects in the coating film. Alumina from blasting media that have become lodged in the substrate can also be observed near the surface of the steel substrate.

The data of chemical analysis (Table 2) indicate that almost half of the titanium changes to oxide, nitride, and carbide and agree with the mapping results.

Anodic polarization curves of the as-sprayed titanium coating on the steel substrate and the detached titanium coating after spraying are shown in Fig. 4 with the curves for solid (bulk) titanium and the carbon steel substrate. Anodic dissolution behavior of the as-sprayed titanium coating is nearly the same as that of the carbon steel substrate in the active region, with diffusion controlled dissolution with a high current density larger than $10^4 \mu A/cm^2$. On the other hand, the titanium coating film detached from the substrate has nearly the same resistance as the bulk titanium, especially in the passive region. The results suggest that the poor resistance of the as-sprayed titanium is attributed to the dissolution of steel through the pores among the deposited particles in the sprayed layer and that the sprayed titanium itself is expected to have a superior resistance similar to that of the bulk titanium.

The effect of the resin sealing on the anodic polarization characteristics of the sprayed titanium is shown in Fig. 5, in contrast with the as-sprayed and the solid titanium. The corrosion resistance of the sprayed titanium is improved markedly by the resin sealing, and is comparable to the corrosion resistance of the bulk titanium. From the standpoint of stability in a passive current, performance of the resins as the sealing material is superior in the epoxy form, followed by performance in the epoxy-silicon and the silicon resins.

Table 2 Results of chemical analysis for sprayed titanium coating

Element	Mass%
As analyzed	
O	10.9
N	3.7
C	0.9
H	0.003
Ti	balance
As calculated	
TiO_2	27.3
TiN	16.4
TiC	4.5
TiH_2	0.075
Ti	51.7

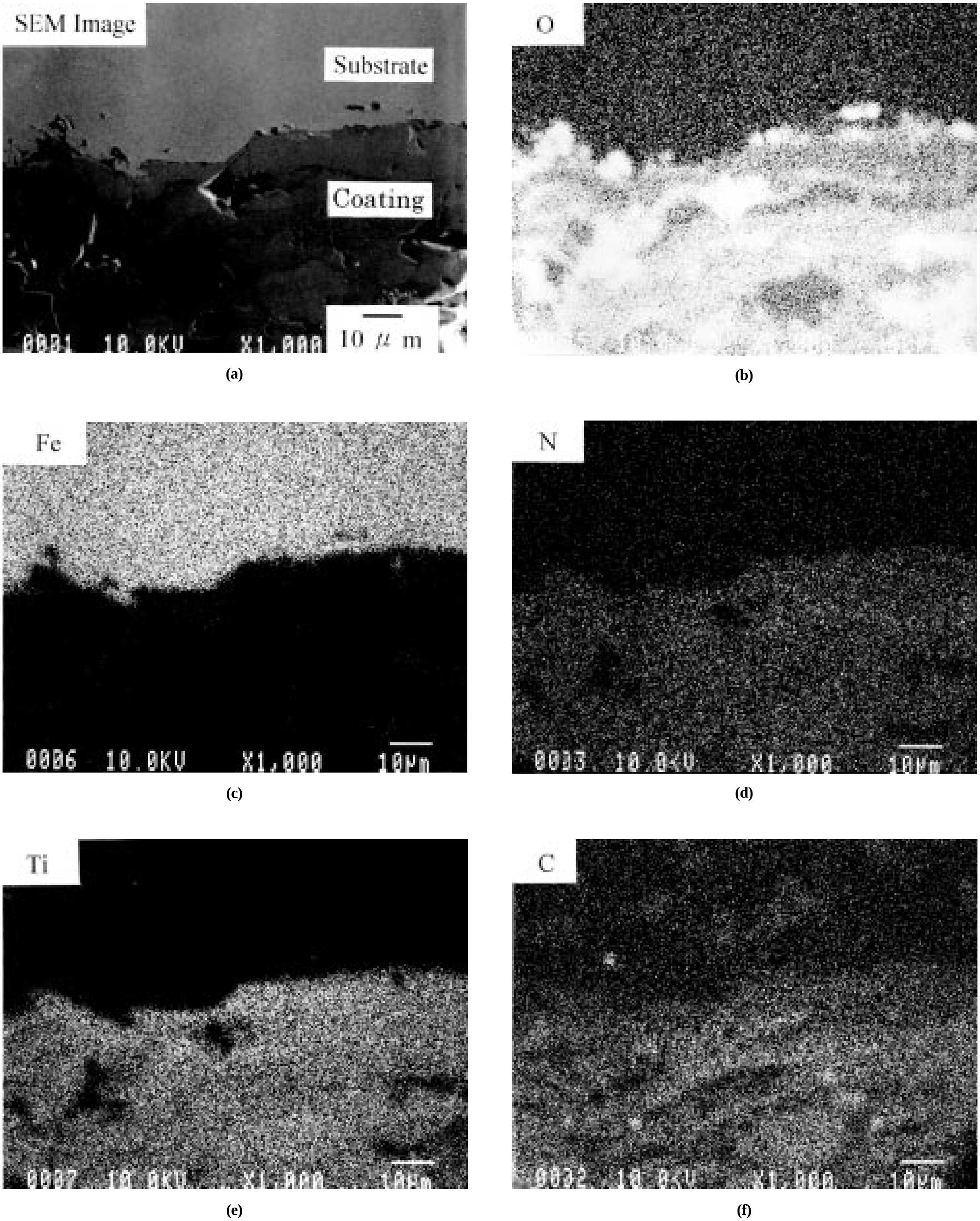
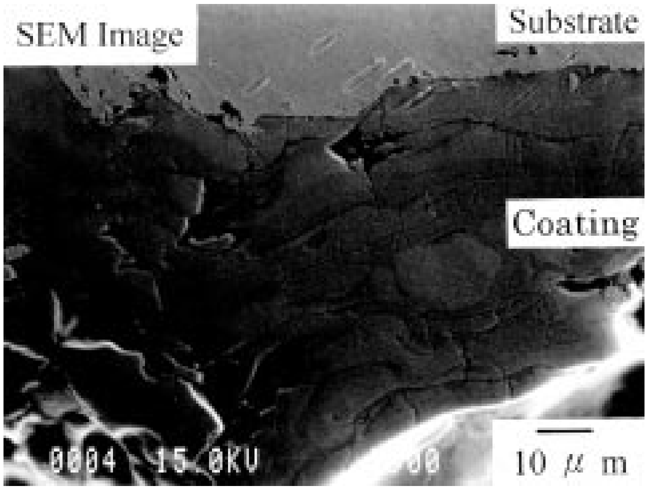


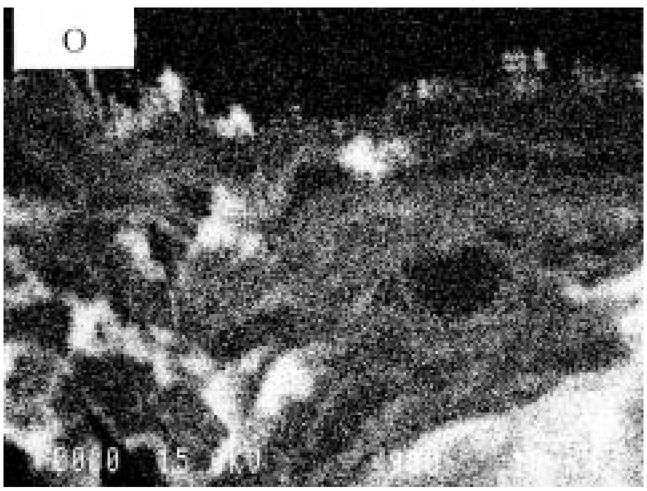
Fig. 2 Scanning electron microscopy (SEM) image (a) and (b-f) electron probe x-ray microanalysis (EPMA) elemental mapping for Ti, Fe, O, N, and C on sprayed titanium

The cross-sectional distribution of the resins on the sprayed and sealed titanium layer was determined by EDAX elemental mapping for carbon and silicon, which were selected as the major elements of the resins (Fig. 6). In epoxy resin sealing, the existence of carbon is detected at voids adjacent to the interface between titanium and the resin (for example, 1 in the figure, but not in regions remote from the substrate, that is, region 2). This result indicates that the epoxy resin can penetrate into the voids near the surface (although epoxy resin cannot penetrate the entire coating thickness). In the case of the epoxy-silicon and the silicon resin, penetration of the resins among the deposit particles is not observed. The existence of silicon in a large void (for example, 4 in the figure) is believed to be a result of contamination through the sample preparation, because there were no signs of silicon near the surface (that is, region 3). These results substantiate the electrochemical behaviors of the resin sealed specimens.

All the experimental results indicate that the sprayed titanium, containing many inclusions of oxides, nitrides and carbides, has an excellent resistance to chloride corrosion if the pores, voids, and defects in the coated layer are sealed with epoxy resin.



(a)



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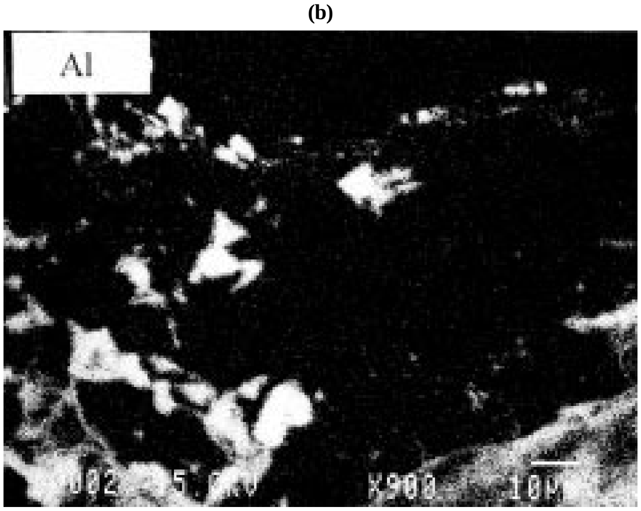

(c)

Fig. 3 SEM image and EPMA elemental mapping for O and Al on sprayed titanium

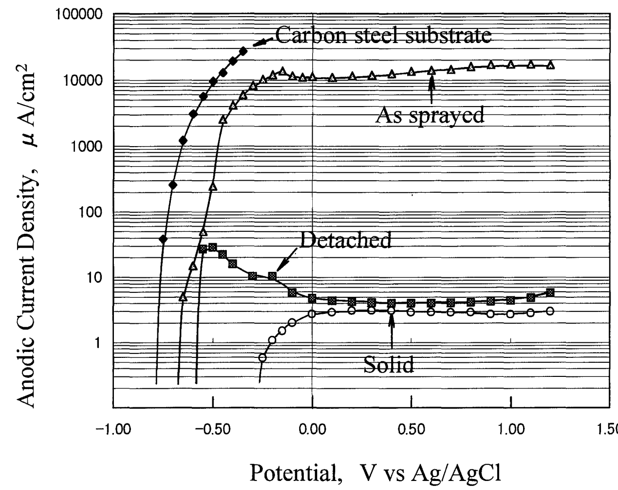

Fig. 4 Anodic polarization curves of as-sprayed titanium on carbon steel, detached titanium coating after spraying, solid titanium, and carbon steel substrate in deaerated 3.5% NaCl at 30 °C

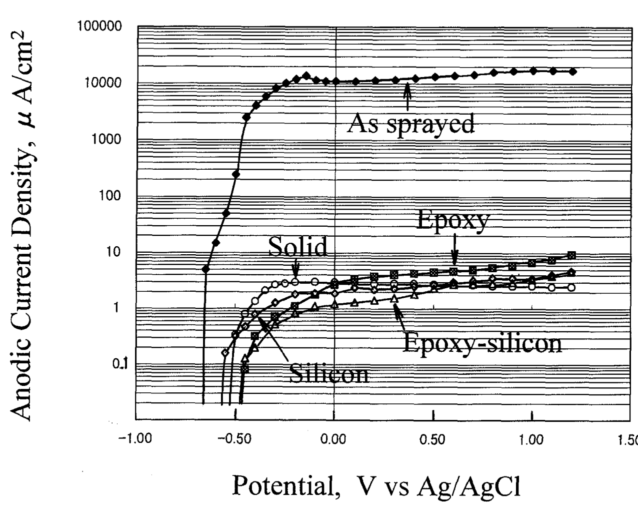

Fig. 5 Effect of resin sealing on anodic polarization characteristics of sprayed titanium coating in deaerated 3.5% NaCl, 30 °C

The surface appearance of the test vessel after 200 days immersion is shown in Fig. 7. A few rust spots were observed through the coated layer; however the performance was expected to be generally good for practical use.

4. Conclusions

The corrosion resistance of thermal sprayed titanium was studied by electrochemical polarization measurements and by surface analysis by SEM and EPMA. Performance findings were also confirmed with a bench pilot immersion test. The results are summarized as follows:

- As-sprayed titanium coating formed by conventional wire flame spraying has no resistance to chloride corrosion because of its porosity. Despite the fact that almost 50% of titanium changed to compounds such as oxides, nitrides, and carbides, there was negligible deterioration observed in the resistance of the sprayed layer itself.

- Sealing with resins such as epoxy and silicon in posttreatment improved the resistance of the sprayed titanium to that on a level comparable to the resistance of the bulk material. The procedure of titanium coating combined with resin sealing is expected to be an effective material system for chloride environments.

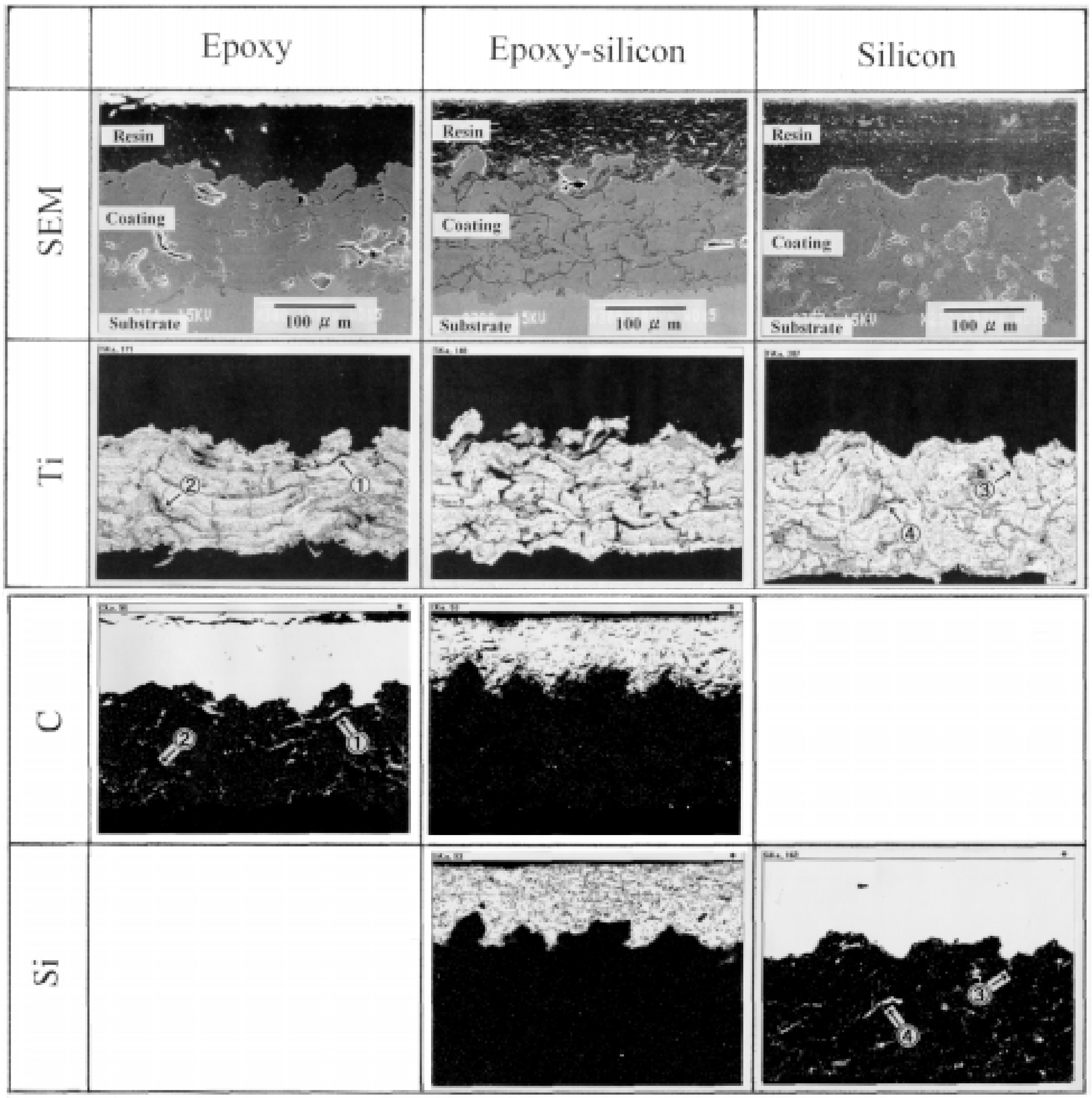

Fig. 6 SEM and EDAX elemental mapping for Ti, C, and Si on sprayed titanium followed by resin sealing

Fig. 7 Surface appearance of test vessel after immersion of 200 days

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