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PLASMA SPRAYED Al_2O_3-13 wt. % TiO_2 COATING SEALED WITH ORGANIC-INORGANIC HYBRID AGENT AND ITS CORROSION RESISTANCE IN ACID ENVIRONMENT

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A novel organic-inorganic hybrid material of γ-methacryloxypropyltrime-thoxysilane (KH570)-SiO_2 was fabricated by Sol-Gel method. The hybrid material was used as the sealing agent for the plasma sprayed Al_2O_3-13 wt. % TiO_2 coating. Infrared spectrum and grafted mechanism of the hybrid agent (HA) were studied. Moreover, morphology and porosity, as well as characteristics of immersion plus electrochemical corrosion in acid environment of the coating with and without sealing treatment were evaluated, compared with those of the coating sealed with the conventional silicone resin agent (SRA). The results reveal that KH570 was successfully grafted onto the surface of SiO_2. The HA film sealed on the surface of the coating presents a little better quality than the SRA film. The porosities of the coatings after the sealing treatment decreased. Furthermore, the sealing treatment can improve efficiently the corrosion resistance of the coating in 5 vol. % HCl solution. The hybrid sealing agent can become a candidate for the plasma sprayed Al_2O_3-13 wt. % TiO_2 coating used in acid environment to overcome some disadvantages of organic agents such as severely environmental pollution.

INTRODUCTION

Plasma spray technology (PST) has been widely applied in aviation, metallurgical and mechanical industry due to its controllable process, high operating efficiency and excellent coating properties such as a good adhesion between coating-substrate [1-3]. Therefore, ceramic coatings are often fabricated using PST on metal substrate as protection coatings for the high demands of wear resistance and/or corrosion resistance [3-5]. However, a relatively high porosity (about 5 - 8 %) in ceramic coatings using conventional PST is inevitable, and it might deteriorate corrosion resistance of the ceramic coatings if the coatings work in a severely aggressive environment, because pores existing in the ceramic coatings could become as transmitting channels of corrosion medium and result in severe corrosion of the metal substrate [5-6].

Sealing treatment is deemed as an efficient and attractive method on overcoming the disadvantage of plasma spray coating (PSC) mentioned above [5-8]. In general, there are two sorts of sealing materials [7, 9-11]. One is organic agents such as epoxy resin and silicone resin, and coatings sealed with them are characterized by a good combination of corrosion resistance, strength, stiffness and density; however, poor thermal resistance and, especially, severe environmental pollution are also remarkable. The other is inorganic agents such as alkalis silicate and Aluminum metaphosphate, and coatings sealed with them present opposite characteristics comparing with the former.

Accordingly, organic-inorganic hybrid sealing materials are developed [12-14]. The researches reveal that, some hybrid films have been widely applied as protection films and they have a good characteristic combination of both organic and inorganic compounds, especially, they have good thermal impact resistance, corrosion resistance and environmental stabilization. In addition, different organic compounds including epoxy resin, PF resin, and silicone resin and so on are considered but usually inorganic compound of silicon oxide (SiO_2) is selected for preparing hybrid agents. However, no research on hybrid sealing agent applied in PSC is reported.

In this paper, a novel hybrid sealing agent of γ-methacryloxypropyltrime-thoxysilane (KH570)-SiO_2 was successfully fabricated by Sol-Gel method. Al_2O_3-13 wt. % TiO_2 PSC was prepared and sealed with the mentioned agent. The quality of the agent and the sealing result were studied. Moreover, corrosion resistance of the sealed coating was investigated in detail by means of electrochemical measurement and immersion test in an acid medium, and the results were compared to those sealed with conventional silicone resin at the same tested conditions.

EXPERIMENTAL

Preparation of PSC

Commercial high purity Al_2O_3-13 wt. % TiO_2 (AT13) powder with the average grain size of 30 μm and NiCrAl powder with the average grain size of 75 μm were considered to prepare the ceramic coating and the adhesive coating, respectively. Q235 steel plate with the dimensions of 24 × 20 × 6 mm was selected as the substrate.

Plasma spray process was carried out in air using PRAXAIR 3710 plasma spraying system. Before process the samples were degreased and grit-blasted in accordance with conventional method. The thicknesses of the adhesive coating and ceramic coating were approximately 90 μm and 320 μm, respectively. The spraying parameters are listed in Table 1. More details about the process please refer to [15].

Table 1. Technique parameters of plasma spraying process.

Spraying parameters	NiCrAl	AT13
Current/A	700	900
Voltage/V	39.5	40
Primary gas flow for Ar ($l\cdot min^{-1}$)	60	45
Secondary gas flow for He ($l\cdot min^{-1}$)	125	150
Carrier gas flow for Ar ($l\cdot min^{-1}$)	40	40
Spray distance (mm)	100	100
Gun moving speed ($mm\cdot s^{-1}$)	150	80

Preparation of hybrid sealing agent

γ-methacryloxypropyltrime-thoxysilane, a sort of silane coupling agent, was used as the organic compound of the hybrid system. Tetraethyl orthosilicate (TEOS) was selected as the precursor to prepare SiO_2 inorganic compound. N, N-dimethyl formamide (DMF) was used to decrease dehiscence of the gelatin in the drying process. In addition, nitric acid (HNO_3) and ammonium hydroxide (NH_4OH) were used to adjust PH value in the different process period, and ethyl alcohol (EtOH) as well as distilled water (H_2O) was employed as the solvent and the hydrolysis reactant of TEOS, respectively. The Sol-Gel procedure for preparing the KH570-SiO_2 hybrid agent is shown in Figure 1.

Effects of different additive amounts of TEOS, EtOH, H_2O, KH570 and PH value on the hybrid agent were systematically investigated through a comprehensive evaluation of the film properties (solid content, gel point time, chemical binding property) and the sealing coating qualities (porosity, film quality). And the optimization of the additive amount was decided: TEOS: EtOH: H_2O: KH570 was 4: 3: 1: 5 (volume ratio), pH value of the solution was adjusted to 3 by adding HNO_3 in the step 2 (Figure 1), and DMF amount was 30 % of the total volume of the reagent. The detail of the effects of the additives on the hybrid agent is not studied further as this paper focuses on sealing result and the corrosion resistance of the sealing coating.

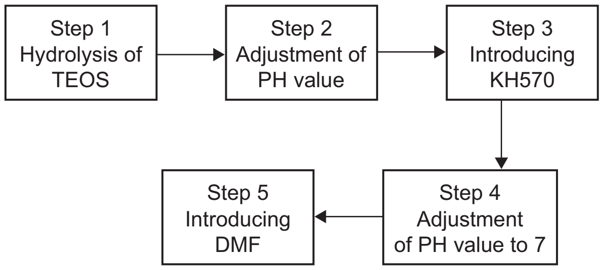


Figure 1. Sol-Gel procedure for preparing KH570-SiO_2 hybrid agent.

Sealing treatment

Commercial silicone resin (45 % of solid content) was selected as the comparing sealing agent. So both the hybrid agent (HA) and the silicone resin agent (SRA) were used in sealing treatment. The coating specimens were first immersed into HA and SRA solutions for 30 minutes, respectively; and the specimens were slowly pulled out and painted with the same solutions to remove air in the pores and in the micro-cracks of the coatings; the specimens were immersed into the mentioned solutions again for another 30 minutes, respectively; and then the solidification of the sealing gelatins was performed in air and in the furnace at 115°C in sequence. To ensure a good sealing result, the mentioned sealing processes were repeated.

Apparatuses and methods of analysis

NICOLET IS10 Fourier-transform infrared spectrometer was used to evaluate the chemical binding property of HA.

Corrosion resistance of the coatings before and after sealing treatment was evaluated by both immersion test and electrochemical measurement. The immersion test was performed according to Chinese Standard GB 10124-88 and the corrosion resistance was evaluated by the conventional weight loss method. Prior to the test, only the tested surface of the specimens were exposed to air and the other surfaces were wrapped with epoxy resin to protect them from corrosion. 5 vol. % HCl solution was used as the immersing medium and the tested times were 50, 100, 200, 300, 500, 900 and 1700 hours, respectively. The electrochemical characteristics (corrosion current density i_{corr} and corrosion potential E_{corr}) of the coatings were determined by the Tafel slope method via PARSTAT 2273 Advanced Electrochemical Potentiostat with a three-electrode system. The system contains a saturated calomel reference electrode and a Pt counter electrode. The experiment was conducted in 5 vol. % HCl solution with a scanning speed of 5 $mV\cdot s^{-1}$.

Only connecting pores and/or micro-cracks from coating surface to substrate serve as transmitting channels of corrosion medium, so iron reagent test was considered to evaluate the porosity of ‘connecting pores and or micro-cracks’ of the coatings [7, 15]. And the procedure is in accordance with the Chinese standard of the porosity test method for thermal spray coating (JB/T 7509-94),

HITACHI-S3400N Scanning Electronic Microscopy (SEM) and Hirox KH-7700 Stereomicroscope (SM) were used to observe microstructure and eroded surface morphology of the coating.

RESULTS

Infrared spectrum and grafted mechanism of HA

Fourier-transform infrared spectrum (FTIR) of the hybrid agent is shown in Figure 2. The broad peak of 3400 cm^{-1} and the absorption peak of about 1640 cm^{-1} are due to the stretching vibrations of the –OH group and the H–O–H group, respectively, which might derived from rudimental hydrone absorbed in the network structure of the hybrid agent. The absorption peak of 2980 cm^{-1} is corresponding to the $–CH_2$ and $–CH_3$ group of KH570, and the peak of 1725 cm^{-1} should belong to C=O of KH570. Meanwhile, the peaks of both 1120 and 800 cm^{-1} are characterized by the main absorption peaks of SiO_2, which are assigned to the stretching vibrations of the Si-O-Si symmetric and asymmetric groups, respectively. However, the characteristic absorption peaks of $Si–O–CH_3$, which should locate at 2817 and 1190 cm^{-1}, become inconspicuous; and the absorption peak of Si–OH (950 cm^{-1}) presents a same tendency. The reason is possibly attributed to $Si–O–CH_3$ transferred to Si–OH after the hydrolyzation of KH570, and then the hydrolysate interacted with the hydroxyl on the surface

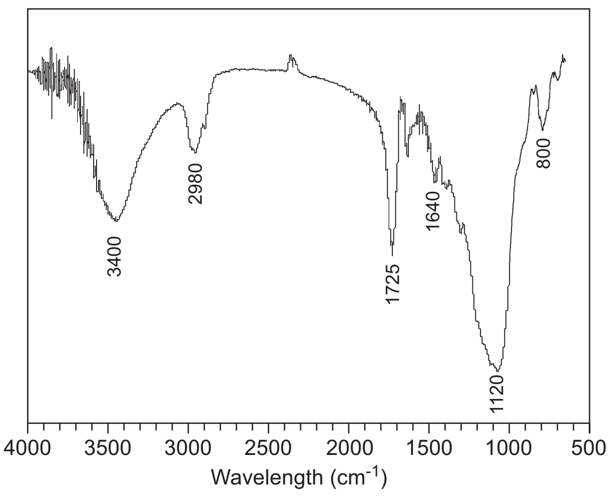
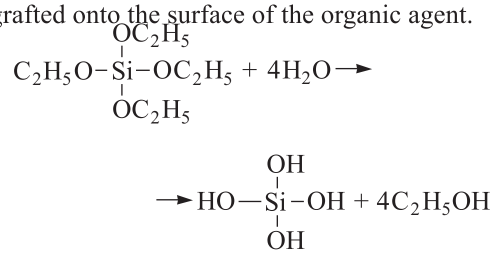


Figure 2. Fourier-transform infrared spectrum (FTIR) of hybrid agent.

of SiO_2 soliquid [16]. Therefore, the mentioned facts indicate that KH570 was successfully grafted onto the surface of SiO_2, and the organic-inorganic hybrid material was successfully fabricated using Sol-Gel method.

Actually, the grafted mechanism of HA includes the following procedures [17-18]: Hydrolysis of TEOS and correspondingly polycondensation of the hydrolysis products (Equation 1 and 2), and lots of Si–O–Si groups in the solution mean that SiO_2 molecules form; Hydrolysis of KH570 and polycondensation of the hydrolysis products (Equation 3 and 4); the polycondensation pro-duct from KH570 reacts with the hydroxyl group bonding SiO_2 molecules (Equation 5). Thus, SiO_2 is grafted onto the surface of the organic agent.



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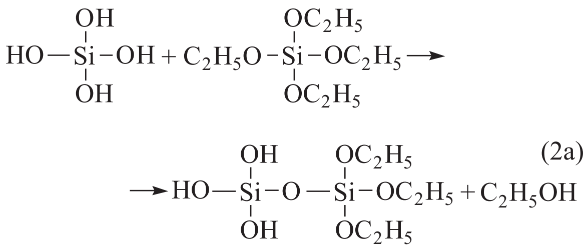
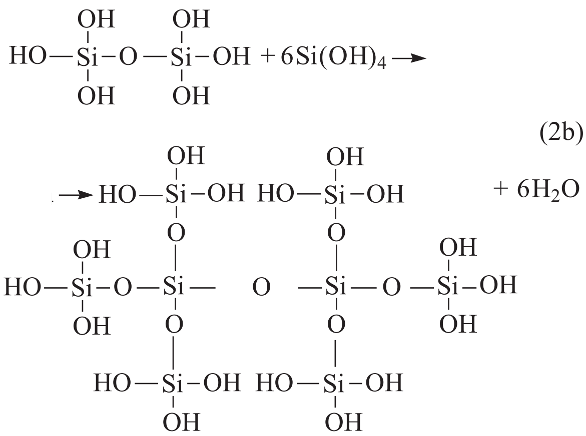


(2a)



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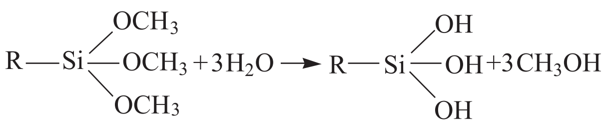

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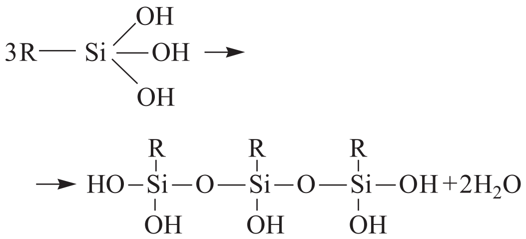
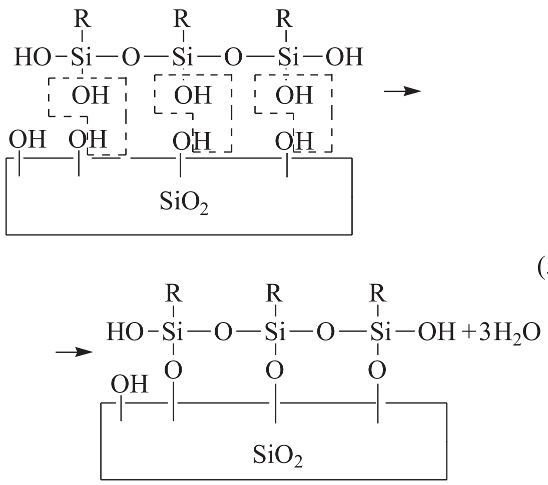


(4)



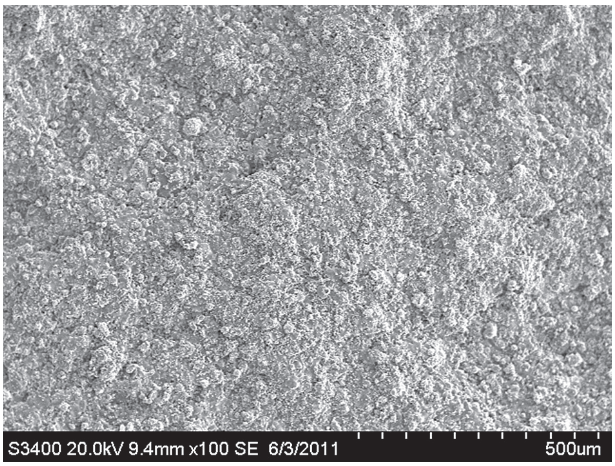
(5)

In the Equations 3, 4 and 5, R means $CH_2=C(CH_3)COOC_3H_6$.

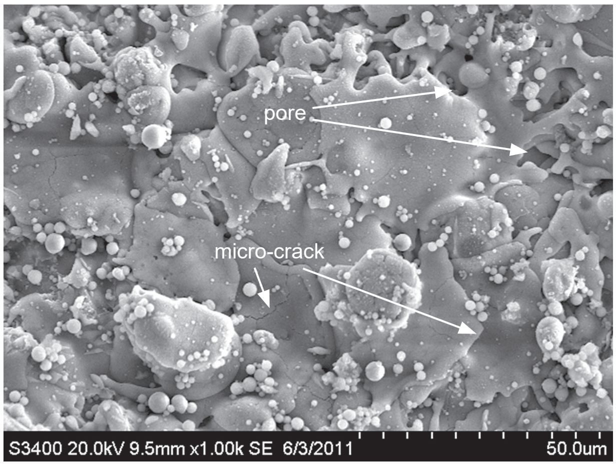
Morphologies of coatings before and after sealing treatment

Figure 3 shows the surface and polished cross-section morphologies of the as sprayed coating. The surface of the coating is flat on the whole but a few open-pores, partially melted particles and even some micro-cracks are observed on the surface (Figure 3a and b). The coating presents a typical lamellar structure and both the ceramic coating-adhesive coating and the adhesive coating-substrate exhibit good bonding effects (Figure 3c). In addition, some closed pores exist in the coating (Figure 3d).

Figure 4 shows the surface morphologies of the sealed coatings with different sealing agents. Clearly,



a)



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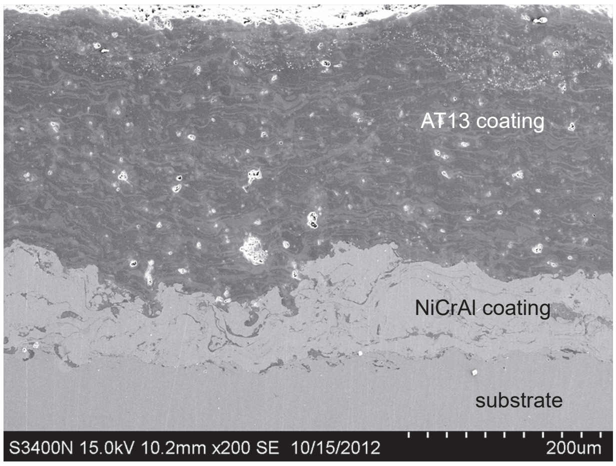
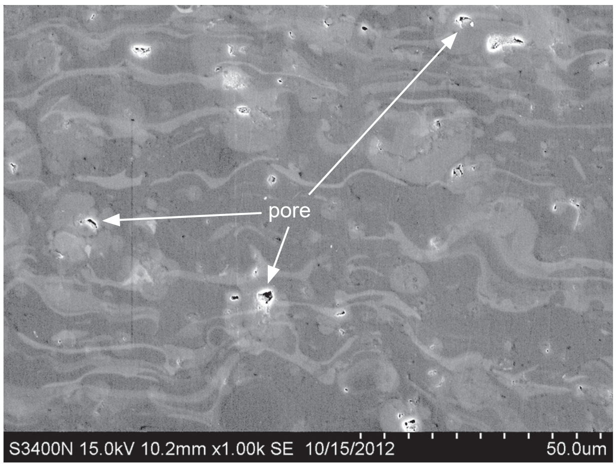


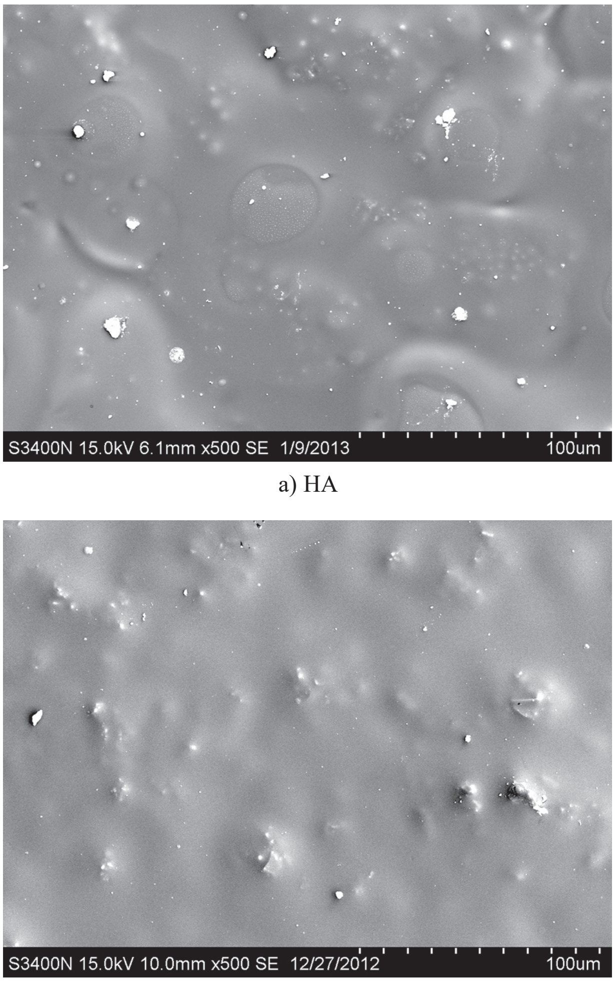
c)



d)

Figure 3. Surface and polished cross-section morphologies of as-sprayed (a: surface; b: magnified surface; c: cross-section; d: magnified cross-section).

both the sealed films are smooth and continuous, which means the mentioned flaws on the surface are sealed efficiently. Furthermore, the film quality prepared with HA seems to be better than that with SRA.



a) HA

b) SRA

Figure 4. Surface morphologies of sealed coatings with different sealing agents; a) HA, b) SRA.

Porosities of coatings before and after sealing treatment

The tested result indicates that the porosity of the 'connecting pores and/or micro-cracks' of the as-sprayed coating is 1.847 %, but the porosities of the coating sealed with SRA and HA are 0.047 % and 0.049 %, respectively. It means HA is close to SRA in sealing effect and the treatment is remarkably useful to decrease the porosity of the coating.

Characteristics of immersion corrosion

The weight loss rates of the coatings with/without sealing treatments at different immersion times in 5 vol.% HCl solution were calculated and are shown in Figure 5 (For the convenience of comparison, the immersion time shown in X-axis was divided based on tested point). The results indicate that all three sorts of the coatings had not an obvious weight loss before the tested time of 450 hours (In the early time of immersion, a bit of weight increase was observed for all the coatings, it might result from that a few corrosion products existing in the deep pores are difficult to be removed). However, with increasing immersion times, the weight loss rate decreased rapidly for the un-sealed coating, but the rates decreased rather slowly for the both coatings sealed with HA and SRA. In addition, the coatings after different sealing treatments are similar in weight loss, and the rule is in accordance to that of porosity of the coatings.

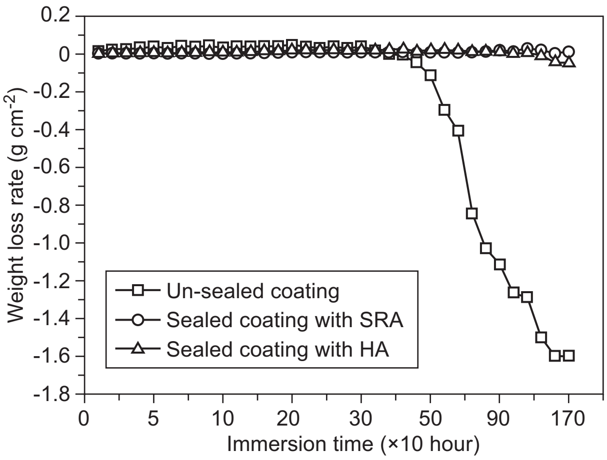
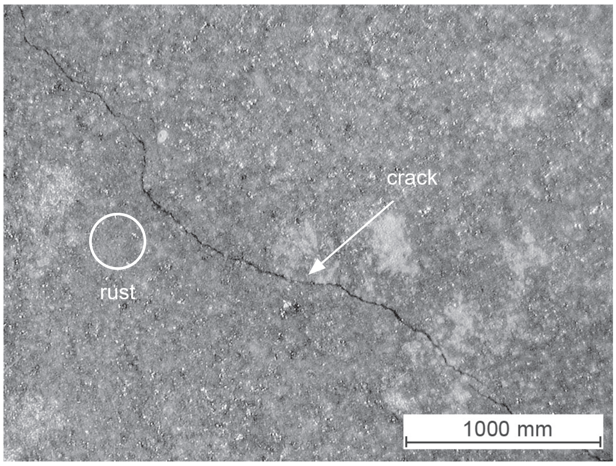


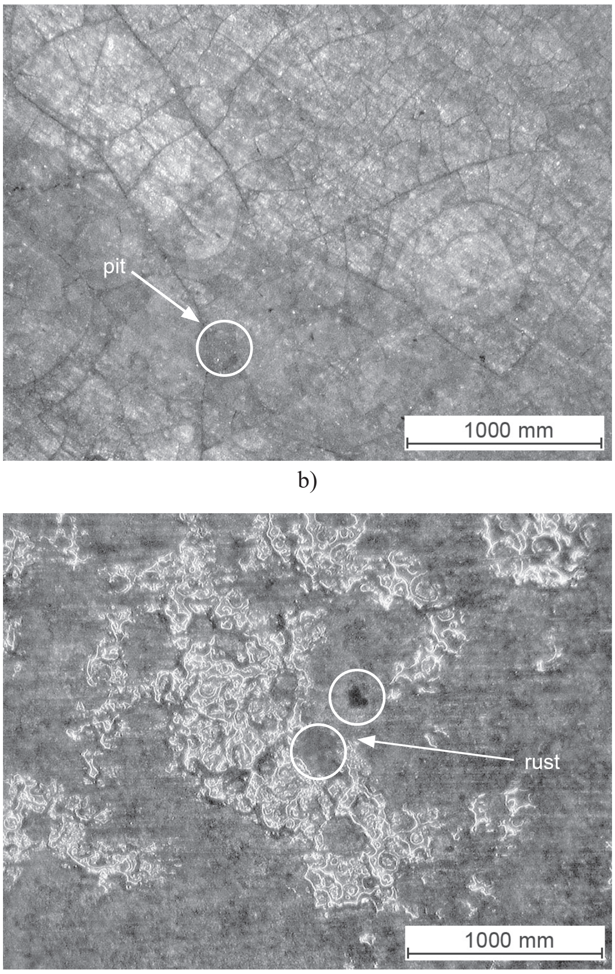
Figure 5. Weight loss rates of coatings with/without sealing treatments at different immersion times in 5 vol.% HCl solution.

Moreover, the surface morphologies of the coatings after 1700 hours immersion test shown in Figure 6



a)

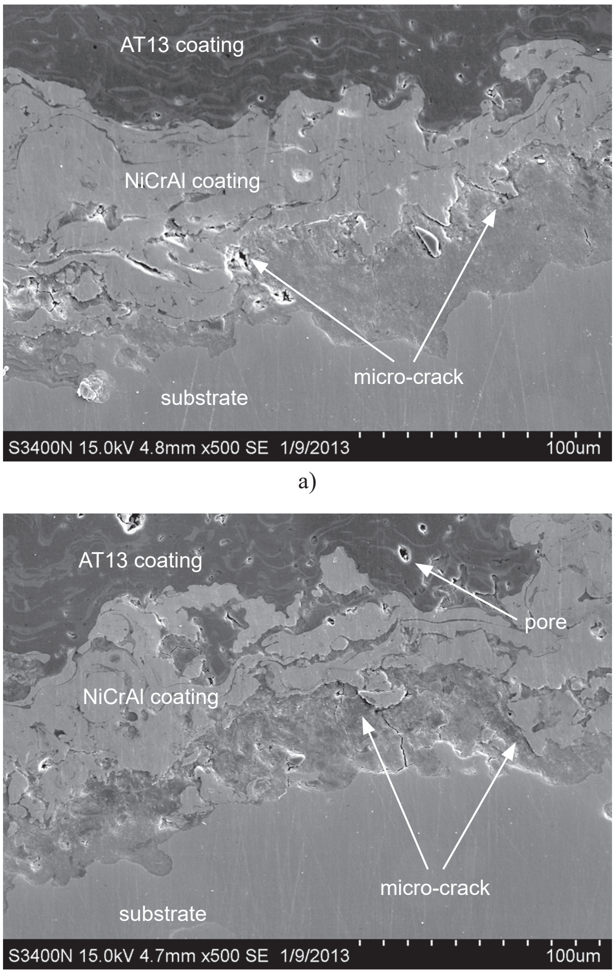
Figure 6. Surface morphologies of different coatings after 1700 hours immersion test; a) as-sprayed coating. *Continue on next page*.



b)

c)

Figure 6. Surface morphologies of different coatings after 1700 hours immersion test; b) sealed coating with HA, c) sealed coating with SRA).



a)

b) graphite and ZrO_2 mixture

Figure 7. Cross-section morphologies of sealed coatings after 1700 hours immersion test; a) sealed coating with HA, b) sealed coating with SRA.

support strongly the results of weight loss that, there are a long crack and rusts on the surface of the un-sealed coating but a few corrosion evidences on the surface of the sealed coatings.

The cross-section morphologies of the sealed coatings after 1700 hours immersion are shown in Figure 7 (because of severe corrosion of the un-sealed coating, it could not be observed for more information). There are lots of corrosion-cracks existing in the coatings sealed with SRA but few in the coating sealed with HA. And no obvious corrosion product in the latter is observed, which means the coating sealed with HA exhibits a good corrosion resistance in the acid environment.

Characteristics of electrochemical corrosion

The Tafel polarization curves of the coatings with/without sealing treatment tested in 5 vol. % HCl solution are shown in Figure 8, and the corresponding electrochemical characteristics (corrosion current

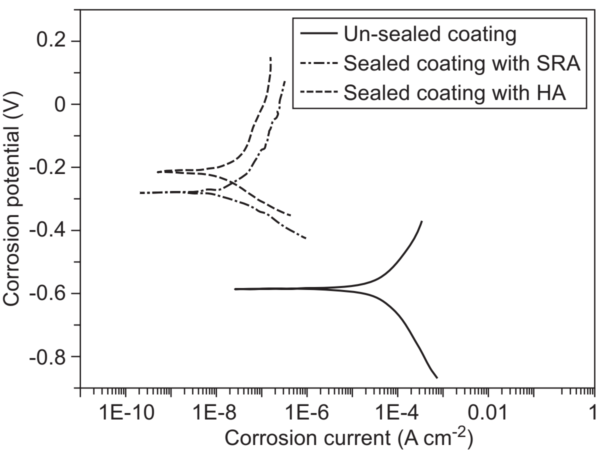


Figure 8. Tafel polarization curves of coatings with/without sealing treatment tested in 5 vol. % HCl solution.

density i_{corr} and corrosion potential E_{corr}) are listed in Table 2. Clearly, the sealing treatments resulted in a remarkable change in electrochemical characteristics of the coating: both E_{corr} and i_{corr} of the sealed coatings are substantially less than those of the un-sealed one; especially, i_{corr} of the coatings sealed with HA and SRA are 5.7 ‰ and 6.7 ‰ of the latter, respectively. Moreover, the electrochemical characteristic of the coating sealing with HA are a little better than those of the coating sealing with SRA. The tested evidence matches enormously the fact of the immersion corrosion.

Table 2. Corrosion current density i_{corr} and corrosion potential E_{corr} of three sorts of coatings tested in 5 vol. % HCl solution.

	Corrosion potential E_{corr} (V)	Corrosion current density i_{corr} (μA·cm^{-2})
Un-sealed coating	-0.587	51.6
Sealed coating with SRA	-0.284	0.0346
Sealed coating with HA	-0.225	0.0292

CONCLUSION

A novel KH570-SiO_2 organic-inorganic hybrid sealing agent used for plasma sprayed Al_2O_3-13 wt. % TiO_2 coating was fabricated by Sol-Gel method. The infrared spectrum indicates that KH570 was successfully grafted onto the surface of SiO_2. The hybrid agent (HA) film sealed on the surface of the coating presents a little better quality than the silicone resin agent (SRA) film. The porosities of the coatings after the sealing treatment decreased, and the porosity of the coating sealing with HA (0.047 %) is a little less than that sealing with SRA (0.049 %). Both the immersion evidences and the electrochemical results support the fact that the sealing treatments can improve efficiently the corrosion resistance of the coating in 5 vol. % HCl solution, and the effect of the coating sealed with HA is a little better than that sealed with SRA. Thus, the hybrid sealing agent can become a candidate for the plasma sprayed Al_2O_3-13 wt. % TiO_2 coating used in acid environment to overcome some disadvantages of organic agents such as severely environmental pollution.

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