

Corrosion Behavior in Boiling Dilute HCl Solution of Different Ceramic Coatings Fabricated by Plasma Spraying

Dianran Yan, Jining He, Xiangzhi Li, Yanchun Dong, Yangai Liu, and Jianxin Zhang

(Received November 4, 2003; in revised form May 21, 2004)

An Al_2O_3 ceramic coating (A), a 13 wt.% $\text{TiO}_2\text{-Al}_2\text{O}_3$ (13TA) composite ceramic coating, and a Ni-Al-13wt.% $\text{TiO}_2\text{-Al}_2\text{O}_3$ (NA-13TA) gradient composite ceramic coating were prepared on Q235 steel by plasma spraying. The corrosion behavior of samples sprayed with these coatings in a boiling 5% HCl solution was investigated. It was shown that an A ceramic coating and a 13TA composite ceramic coating were destroyed after immersion for 17 and 23 h, respectively. The NA-13TA gradient composite ceramic coating was still sound after 14 days of immersion. The corrosion resistance of samples with the NA-13TA gradient composite ceramic coating was sharply improved due to the decreased amount of connected pores in the coating. The corrosion of the sample sprayed with the gradient ceramic coating included the partial corrosion of the surface ceramic coating and the interlayer coatings. The corrosion weight loss depended on the degree of open porosity.

Keywords ceramic coating, corrosion mechanism, gradient coating, plasma spraying

1. Introduction

It is well known that engineering ceramics exhibit properties such as excellent chemical stability, corrosion resistance, and wear resistance (Ref 1, 2). Ceramic coatings sprayed onto the surface of a metal can change the corrosion behavior of the substrate and can provide outstanding protection, especially under conditions in which corrosion and wear coexist at an elevated temperature (Ref 3, 4). However, the metal substrate does experience corrosion to a certain extent due to the presence of porosity in the plasma-sprayed coating (Ref 5, 6). Therefore, the preparation of ceramic coatings with lower porosity and the study of their corrosion behavior are of great interest. In this article, the ideas of gradient and composite were applied to ceramic coatings. An Al_2O_3 (denoted as A) ceramic coating, a 13 wt.% $\text{TiO}_2\text{-Al}_2\text{O}_3$ (denoted as 13TA) composite ceramic coating, and a NiAl-13wt.% $\text{TiO}_2\text{-Al}_2\text{O}_3$ (denoted as NA-13TA) gradient composite ceramic coating were prepared on Q235 steel by plasma spraying. The corrosion behavior of the samples sprayed with these coatings in a boiling 5% HCl solution was investigated.

2. Experimental Procedure

The substrate material for all samples was Q235 steel (Fe-0.14–0.22wt.%C). The size of the corrosion samples was $\phi 10$ by

50 mm, and that of the other samples was 30 by 25 by 3 mm. All of the samples were grit blasted using 18 to 24 mesh alumina grit prior to spraying the coatings to get a rough surface. The starting materials were commercially available $\alpha\text{-Al}_2\text{O}_3$ powder, rutile TiO_2 powder, and nickel-aluminum alloy powder. The average grain size of Al_2O_3 and TiO_2 powders was 40 to ~ 60 μm , and that of the nickel-aluminum alloy powders was 80 to ~ 100 μm . The nickel-to-aluminum weight ratio of the nickel-aluminum alloy powder was 9. Composite spraying powders were made by mixing powders for 24 h using Al_2O_3 balls. The plasma spraying was carried out in a plasma-spraying system that was supplied by an electric power source (LP-50B, JiuJiang Spraying Device Company, Beijing, People's Republic of China) and a spray gun (BT-1 type, ShangKer Technology Ltd., Beijing, People's Republic of China). Prior to spraying the ceramic coating, a nickel-aluminum alloy bond layer of about 0.1 mm thickness was sprayed onto the surface of the samples to increase the adhesive strength of the ceramic coating to the steel substrate. The applied spraying parameters for the different materials are given in Table 1. The thicknesses of the A and 13TA ceramic coatings were 0.3 and 0.4 mm, respectively. The composition and thickness of the NA-13TA gradient composite ceramic coatings are given in Table 2, and the total thickness of the NA-13TA gradient composite ceramic coatings is 3.60 mm.

Pores connected with atmosphere were defined as open pores, and pores connected with the substrate and atmospheres were defined as connected pores. The open porosity of the ceramic coating was measured by the Archimedes method, referring to the industry standard DIN51056 of Germany. By submerging the sprayed samples in a CuSO_4 solution, a copper deposit was seen to appear in the connected pores in the coating. The average number of copper spots in a visual field of magnification 400 \times was defined as the connected porosity of the ceramic coating. The corrosion test was performed by submerging the sprayed samples in a boiling 5% HCl solution (pH = 1). The weight-loss method (in milligrams per cubic centimeter) was

Dianran Yan, Jining He, Xiangzhi Li, Yanchun Dong, and Jianxin Zhang, School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300130, Peoples Republic of China; and Yangai Liu, School of Materials Science and Engineering, Tsinghua University, People's Republic of China. Contact e-mail: dryan@hebut.edu.cn.

Table 1 Plasma-spraying parameters for the different spraying materials

Processing parameters	Ni-Al alloy powder	NA-13TA powder	Al ₂ O ₃ or 13TA powder
Plasma gases, m ³ /h			
Ar	2.2	2.0	1.8
N ₂	1.0	1.0	1.0
H ₂	...	0-0.4	0.4
Powder feed rate, kg/h	0.5	0.5	0.5
Arc current, A	350	370	400
Arc voltage, V	70	75	80
Arc power, kW	24.5	28	32
Torch-to-substrate distance, mm	120	100	90
Torch traversing speed, cm/s	30	30	30
Spraying times	1	3	3

Table 2 Composition of NA-13TA gradient composite ceramic coating

Ceramic coating	Sublayer No.	Composition, wt. %		Sublayer thickness, mm
		Ni-Al	13TA	
Bond layer		100	0	-0.1
Gradient composite layer of NA-13TA	1	90	10	0.35
	2	80	20	0.35
	3	70	30	0.35
	4	60	40	0.35
	5	50	50	0.35
	6	40	60	0.35
	7	30	70	0.35
	8	20	80	0.35
	9	10	90	0.35
Working layer		0	100	0.35

used to measure the corrosion degree of the sprayed samples and the ceramic coatings, which were dried by heating to 150 °C before weighing with a balance (with 0.1 mg accuracy). The test results were obtained from the average of three samples. The microstructures of the cross sections of the samples before and after corrosion were observed using a scanning electron microscope (SEM) (model XL30/TMP).

3. Experimental Results and Discussion

3.1 Corrosion of Samples Sprayed with Ceramic Coatings

Figures 1 and 2 show the curves of weight loss versus immersion time of samples sprayed with three ceramic coatings. It can be seen from Fig. 1 that the samples with the A ceramic coating showed an increase in weight at the beginning of corrosion and a decrease thereafter. The weight loss of the samples with the 13TA composite ceramic coating was evidently smaller than that of those with the A ceramic coating after 10 h of immersion. The weight losses of the samples with the A and 13TA coatings increased sharply after 17 and 23 h of immersion, respectively, due to the corrosion of both of the ceramic coatings. The weight loss of the samples sprayed with the NA-13TA gradient com-

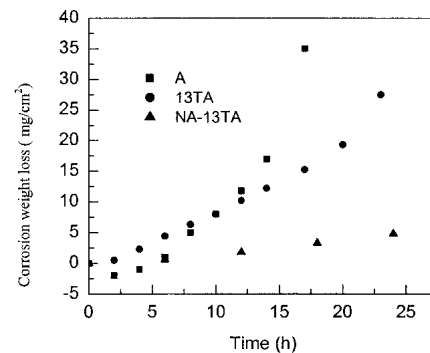


Fig. 1 Corrosion weight loss of samples with three ceramic coatings in a boiling 5% HCl solution for 24 h

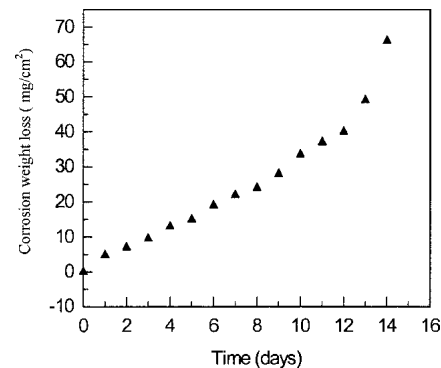


Fig. 2 Corrosion weight loss of samples with the NA-13TA gradient composite ceramic coatings in a boiling 5% HCl solution for 14 days

posite ceramic coating showed a much slower increase (Fig. 2), and no traces of damage were seen in the coating even after 14 days of immersion. From the above experimental results, it was seen that the samples with the 13TA composite ceramic coating proved to be more resistant to corrosion in a boiling 5% HCl solution than those with the A ceramic coating and that the samples with the NA-13TA gradient composite ceramic coating were the most resistant to corrosion.

3.2 Corrosion of Substrate-Free A and 13TA Ceramic Coatings

A comparison of the corrosion behavior was made using the substrate-free A ceramic coating and the 13TA composite ceramic coating under the same immersion conditions, as shown in Fig. 3. It can be seen from Fig. 3 that the weight loss of the 13TA coating was a little higher than that of A coatings, but the tendency of the change in the weight loss versus the immersion time of the coatings was the same. The weight losses of both of the coatings occurred quickly at an early stage of corrosion and tended to be stable after 16 h of immersion. From the x-ray diffraction patterns of both coatings before and after corrosion, the large weight losses at the beginning of immersion were mainly caused by the dissolution of γ -Al₂O₃ in the coatings (Ref 5). The weight loss of the 13TA coating was larger than that of the A coating all the time, which was attributed to the anatase TiO₂ that

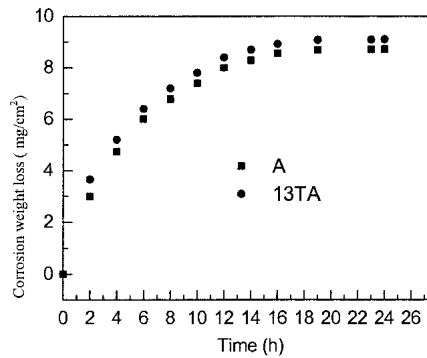


Fig. 3 Corrosion weight loss of the substrate-free A and 13TA coatings in a boiling 5% HCl solution

was produced with less corrosion resistance. Compared with the sprayed samples (Fig. 1), the corrosion weight losses of both the substrate-free A and 13TA coatings were smaller for a long duration of immersion. Therefore, most of the corrosion weight loss occurring in the samples sprayed with ceramic coatings was not caused by the corrosion of the ceramic coating itself.

3.3 Porosity and Pores Corrosion of Ceramic Coatings

In a corrosion solution, pores in ceramic coatings, especially connected pores, played a very important role in the corrosion behavior nickel-aluminum of samples sprayed with a ceramic coating (Ref 5). Figures 4 and 5 show the open and connected porosity of the three ceramic coatings, respectively. Of the three ceramic coatings, both the open and connected porosity in the A coating were the highest. For samples sprayed with this coating, the nickel-aluminum alloy bond layer and the substrate were readily corroded by the 5% HCl solution through connected pores at the beginning of corrosion. Because the exchange rate of corrosion products from inside to outside is lower than the depositing rate of the corrosion products, most of the corrosion products were deposited in the connected pores (Ref 5). As a result, the weight of the samples sprayed with this coating increased at first, which agreed with Fig. 1. With the corrosion continuing, the exchange rate of corrosion products with the outside increased, which also promoted the corrosion rate of the nickel-aluminum bond layer and the substrate, and enhanced subsequent weight loss. This coating was rapidly destroyed in a boiling 5% HCl solution due to its high-connected porosity. The 13TA composite ceramic coating had both lower open and connected porosity than the A ceramic coating, which resulted from the fact that the high-melting-point Al_2O_3 coating structure with much porosity was filled in by low-melting-point TiO_2 during spraying. Therefore, although the substrate-free 13TA composite ceramic coating had less corrosion resistance than the substrate-free A ceramic coating, the corrosion resistance of the samples sprayed with the 13TA coating was enhanced due to its lower porosity. The lowest amount of open porosity and no connected porosity were detected in the NA-13TA gradient composite ceramic coating. The connected porosity in a ceramic coating decreases with increases in the coating thickness (Ref 7). Theoretically, the thicker the coating, the lower the number of

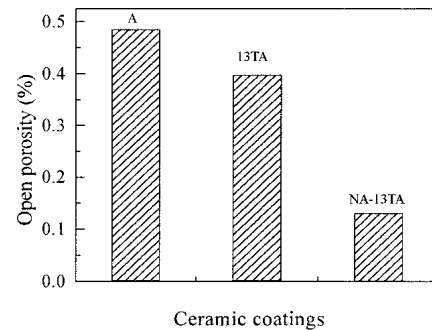


Fig. 4 Open porosity of the three ceramic coatings

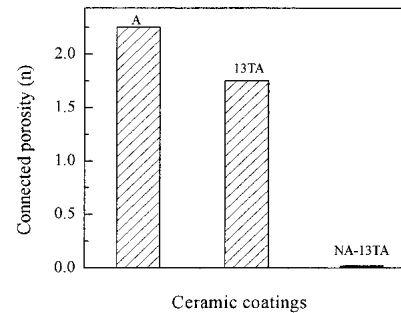


Fig. 5 Connected porosity of three ceramic coatings (the average number of copper spots in visual field of magnification 400 \times)

connected pores. There would be no connected pores in a ceramic coating of a certain magnitude of thickness. However, for a single layer of ceramic coating, as it got thicker, the residual stress produced during spraying was likely to cause the coating to crack or peel off. Therefore, the thickness of a single ceramic coating was limited greatly by the residual stress introduced during spraying. The residual stress in the ceramic coating was caused mainly by the difference in thermal expansion parameters between the spraying materials and the substrate. The gradient interlayer coatings can sharply reduce the residual stress in a ceramic coating. The cracking tendency of a gradient ceramic coating decreases. At the same time, the thickness of the gradient coating can be significantly increased due to the relaxation of residual stress in the coating (Ref 8). Therefore, the NA-13TA gradient composite ceramic coating combined the characteristics of the high density of the 13TA composite ceramic coating and the high thickness of the gradient ceramic coating, leading to the lowest connected porosity. Samples sprayed with this coating had the best corrosion resistance, and this coating was not damaged even after 14 days of corrosion in a boiling 5% HCl solution. However, it was seen from Fig. 2 that, as the corrosion time reached 13 days, the corrosion weight loss sharply increased due to the higher exchange rate of corrosion products from inside to outside than the depositing rate (Ref 5).

3.4 Microstructure of Ceramic Coatings Before and After Corrosion

It was shown by SEM observation that more micropores and microcracks existed in the A ceramic coating than in the 13TA

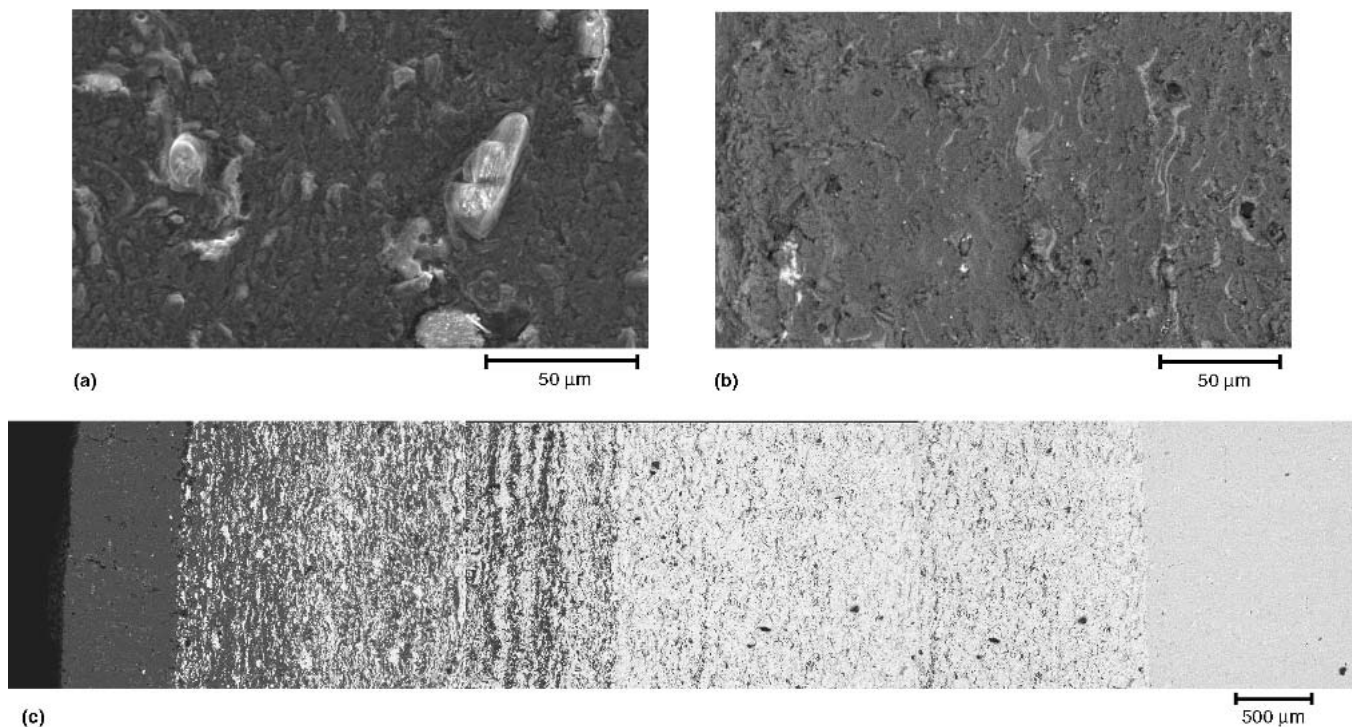


Fig. 6 SEM photographs of cross sections of samples with (a) a ceramic coating, (b) the 13TA composite ceramic coating, and (c) the NA-13TA gradient composite ceramic coating before corrosion

composite ceramic coating, as shown in Fig. 6(a) and (b). More micropores and microcracks easily linked up with each other to form connected pathways. The composition and microstructure of the NA-13TA gradient composite ceramic coating changed continuously from the substrate to the surface ceramic coating, and evident interfaces between the ceramic layer and the nickel-aluminum alloy layer were eliminated (Fig. 6c), which resulted in the lowest residual stress in the coatings. Microstructures of samples with the 13TA and NA-13TA coatings after corrosion are shown in Fig. 7. It was seen that the corrosion behavior of the sample with the 13TA ceramic coating was different from that with NA-13TA gradient ceramic coating. After 23 h of immersion, evident corrosion traces were seen in the 13TA ceramic coating. In addition, the corrosion medium had reached the nickel-aluminum alloy bond layer and the substrate through connected pores in the coating, causing the nickel-aluminum alloy bond layer and the substrate to be corroded severely. For the sample with the NA-13TA gradient ceramic coating, besides the corrosion of the surface ceramic coating and interlayer coating, other corrosion traces were not observed at the nickel-aluminum alloy bond layer and the substrate after 14 days of immersion, which indicated that the corrosion medium had not penetrated to those materials.

4. Corrosion Mechanisms of Samples Sprayed with Different Ceramic Coatings

In a boiling 5% HCl solution, for the sample sprayed with a single layer of the A and 13TA ceramic coatings, the ceramic

coating corroded first. With the corrosion medium reaching the nickel-aluminum alloy bond layer through connected pores, the nickel-aluminum alloy bond layer corrodes. Because the nickel-aluminum alloy bond layer was much thinner and more connected pores existed in the ceramic coating, as soon as the corrosion solution contacted with the substrate, the substrate was severely corroded, which resulted in a sharp increase in the corrosion weight loss of the sprayed sample as well as damage of the ceramic coating. Besides the corrosion of the ceramic coating itself, the corrosion of the sample sprayed with a single layer of ceramic coating was mainly the corrosion of the nickel-aluminum alloy bond layer and the substrate caused by penetration of the corrosion medium through the connected pores in the coating. The corrosion weight loss mainly depended on the degree of connected porosity of the coating, which was shown by Fig. 1 and 3. For the sample with the NA-13TA gradient ceramic coating, while the corrosion medium corroded the surface ceramic coating, penetrated to the interlayer coatings, and contacted the nickel-aluminum alloy particle through open pores, the nickel-aluminum alloy particles were corroded (Fig. 8). Owing to the nickel-aluminum alloy particles in interlayer coatings that were distributed homogeneously and surrounded by ceramic of better corrosion resistance, the corrosion penetration ended at the nickel-aluminum alloy particles after the nickel-aluminum alloy particles were corroded. Because there are no connected pores in the gradient coating, the corrosion medium did not corrode the nickel-aluminum alloy layer and the substrate. The corrosion of the sample sprayed with gradient ceramic coating included the partial corrosion of the surface ceramic coating and the interlayer coatings. The corrosion weight loss relied on the open porosity. The corrosion mechanisms of samples with a single layer

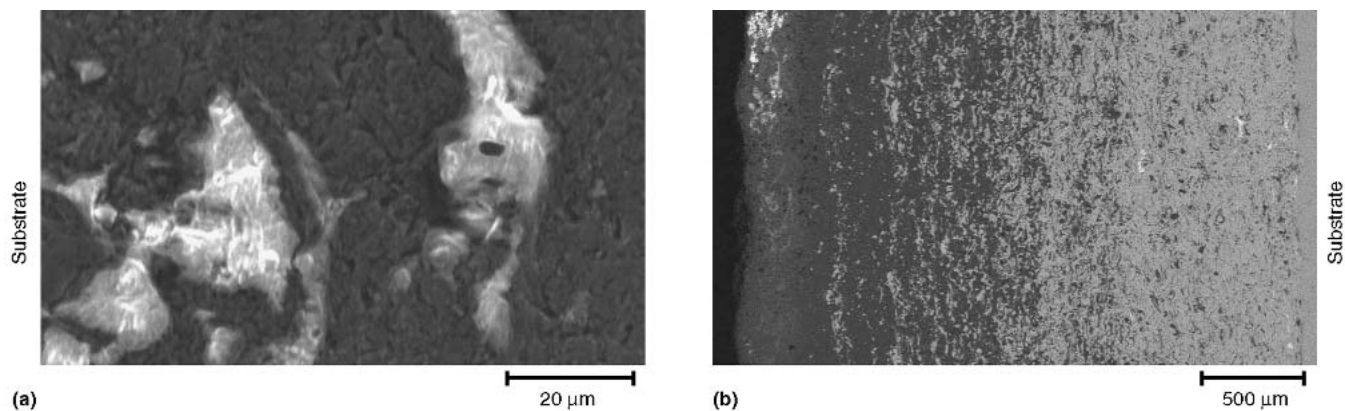


Fig. 7 SEM photographs of cross sections of samples with (a) the 13TA ceramic coating after 17 h of corrosion and (b) the NA-13TA gradient ceramic coating after 14 days of corrosion

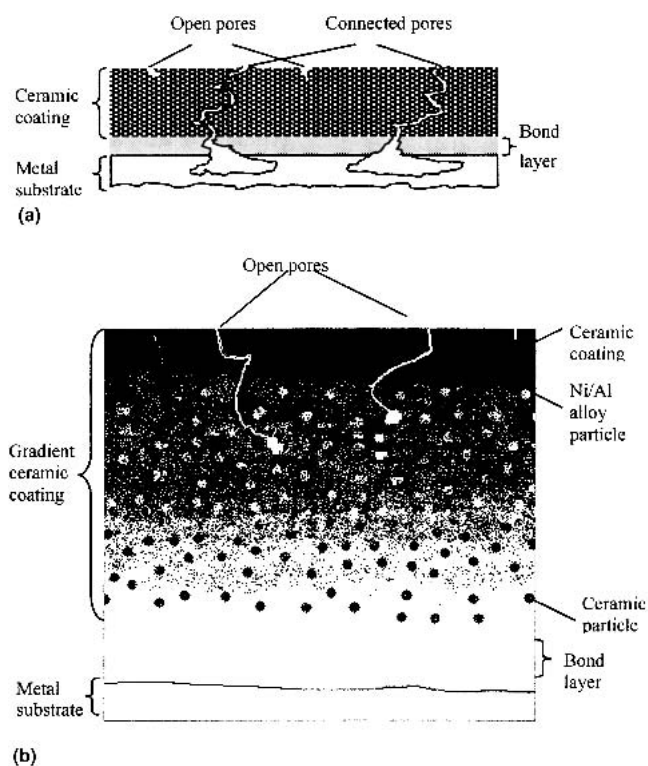


Fig. 8 Corrosion mechanisms of samples with (a) a single layer of ceramic coating and (b) a gradient ceramic coating

of ceramic coating and the gradient ceramic coating are shown in Fig. 8(a) and (b), respectively.

5. Conclusions

In a boiling 5% HCl solution, samples sprayed with the 13TA composite ceramic coating proved to be more resistant to corrosion than those with the A ceramic coating, due to the lower connected pores in the 13TA coating. No connected pores were

detected in the NA-13TA gradient composite coating. Samples sprayed with this ceramic coating were the most resistant to corrosion in the test solution. Besides the corrosion of the ceramic coating itself, the corrosion of the sample sprayed with a single layer of ceramic coating included the corrosion of the nickel-aluminum bond layer and the substrate that was caused by the penetration of the connected pores in the coating. The corrosion weight loss depended on the degree of connected porosity of the coating. The corrosion of the sample sprayed with gradient ceramic coating included the partial corrosion of the surface ceramic coating and the interlayer coatings. The corrosion weight loss relied on the open porosity to the interlayer coating.

Acknowledgment

This work was supported by the Natural Science Foundation of Hebei Province (grant No. 597053).

References

1. M.L Thorpe, How Recent Advances in Arc Spraying Technology Have Broadened the Ranges of Applications, *Proceedings of ITSC '88*, 1988, p 376-383
2. S. Hisao, *High Technology Ceramic*, Trans., Tung-Chi University Press, Shanghai, China, 1990, p 17 (in Chinese)
3. J.X. Zheng, X.Ai, and Z.L.Ding, Oxidation of $Al_2O_3/TiB_2/SiC_w$ Ceramic Composite, *J. Chinese. Soc. Corros. Protect.*, Vol 17 (No. 2), 1997, p 152-156 (in Chinese)
4. J.P.Cai and B.Li, Thermal Spraying Ceramic Coatings, *Mater. Mech. Eng.*, Vol 24 (No. 1), 2000, p 5-7 (in Chinese)
5. Y. Dianran, H. Jining, W. Jianjun, Q. Wanqi, and M. Jing, The Corrosion Behaviour of a Plasma Spraying Al_2O_3 Ceramic Coating in Dilute HCl Solution, *Surf. Coat. Technol.*, Vol 89 (No. 1-3), 1997, p 191-195
6. M.A. Uusitala, P.M.J. Vuristo, and T.A. Mantyla, High Temperature Corrosion of Coatings and Boiler Steels in Reducing Chlorine-Containing Atmosphere, *Surf. Coat. Technol.*, Vol 161 (No. 2-3), 2002, p 275-285
7. M. Fukumoto, Y. Wada, M. Umamoto, and O. Kane, Effect of Connected Pores on the Corrosion Behaviour of Plasma Spraying Alumina Coatings, *Surf. Coat. Technol.*, Vol 39/40, 1989, p 711-720
8. Lai, Z.A. Munir, B. Mccoy, and S.H. Risbud, Formation of Functionally Graded Materials Through Centrifugally-Assisted Combustion Synthesis, *Proceeding of the Fourth International Symposium on Functionally Graded Materials*, 1996, p 275-281