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Author(s)	Arata, Yoshiaki; Ohmori, Akira; Zhou, Guang-Qi et al.
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Studies on Corrosion Behavior of Ceramic Sprayed Stainless Steels (Report I)[†]

—Electrochemical Approach on Ceramic Sprayed Coatings—

Yoshiaki ARATA*, Akira OHMORI**, Guang-Qi ZHOU*** and Jin XUE****

Abstract

The natural potential and natural current of the plasma sprayed ceramic coating films and stainless steels with various surface treatments themselves in 3.5% NaCl solution were separately measured. The potential difference between them was regarded as an important criterion for judging the corrosion behavior of ceramic sprayed base metals. And so a simple method for selecting the proper composition of sprayed coatings was suggested.

The high Al_2O_3 -content coatings of Al_2O_3 - TiO_2 system were affirmed to be more beneficial to corrosion resistance and striving for reducing porosity would be the key to use such coatings successfully. Oppositely, the coatings sprayed with high TiO_2 -content powders were referred to be incommendable, though the porosity might be lowered to an extent. However, the natural potential as well as the natural current of the samples sprayed with high Al_2O_3 ceramic powders depended on those of the base metals themselves, and those of the samples sprayed with high TiO_2 ceramic powders depended on those of the coating films themselves.

KEY WORDS: (Electrochemical) (Corrosion) (Spray coating) (Al_2O_3) (TiO_2) (Stainless steel)

1. Introduction

Ceramic sprayed coating^{1),2)} is increasingly sure to be an alternative means of effectively protecting metal structures and equipments exposed to severe environment such as corrosion and/or abrasive action. However, there are a number of practical and theoretical problems, e.g., the mechanism of adhesion and the adhesive strength, the corrosion behavior and the effective measures of prevention etc. to be solved in using such kind of technique.

On basis of the previous works^{3),4)} as reported before, in this study a series of research items were arranged which would be more significant in terms of theory or practice. For examples, some of them are listed as follows:

- (1) the feasibility using electrochemical method for selecting and evaluating ceramic sprayed coatings;
- (2) the relation between corrosion behavior of the ceramic sprayed samples and the anodic polarization curves measured on them;
- (3) Effect of base metals and their surface condition on corrosion behavior;
- (4) Effect of the spray technology and the perfectness of sprayed coatings on corrosion behavior;
- (5) the nature of corrosion occurred on the ceramic sprayed stainless steel at high humidity;
- (6) possible measures preventing corrosion.

In this report the electrochemical feature of the coat-

ing films and the base metals themselves as well as the ceramic sprayed samples was individually researched and the effect of them on the corrosion behavior of the latter was made clear. Meanwhile, a simple method for selecting suitable composition of the ceramic powder to be sprayed on the base metal was suggested. Using such method the high Al_2O_3 -content ceramic of Al_2O_3 - TiO_2 system was confirmed to be more corrosion-resistant and the high TiO_2 -content ceramic coatings were incommendable.

2. Materials and Experimentals

The oxide ceramic powders used for spraying in this experiment were all marketed and melted, with the exception of that for 20% Al_2O_3 + 80% TiO_2 which was mechanically mixed with pure Al_2O_3 and TiO_2 , and their chemical compositions are listed in Table 1.

The base metals used for plasma-sprayed coating were stainless steels such as SUS 304, SUS 304L, SUS 321, SUS 316 and SUS 316L and their chemical compositions are listed in Table 2.

The specimens of base metals used were different in surface treatment in accordance with the different test purposes and were marked with a letter as follows:

- A — blasted conventionally with corundum sand;
- B — polished first with 1500 grade emery paper and then on a polishing wheel;

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* Professor

** Associate Professor

*** Visiting Professor (Associate Professor, Xi'an Jiaotong University, China)

**** Foreign Research Fellow (Lecturer, Xi'an Jiaotong University, China)

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Table 1 Chemical compositions of ceramic powders used

Powders	Chemical compositions (wt%)						
	TiO ₂	Al ₂ O ₃	Ti ₂ O ₃	SiO ₂	Na ₂ O	MgO	CaO
Al ₂ O ₃	-	99.65	0.03	0.04	0.13	-	-
2.3% TiO ₂	3.3	95.23	0.07	0.64	-	0.38	0.09
13% TiO ₂	12.83	87.12	0.01	0.01	-	-	-
40% TiO ₂	36.85	63.73	0.05	0.08	0.08	-	0.07
TiO ₂	99.41	0.14	0.03	0.07	-	-	-

Table 2 Chemical compositions of stainless steels used

Steel type	Chemical Compositions (wt%)								
	C	Si	Mn	P	S	Cr	Ni	Mo	Ti
SUS 304	0.07	0.61	1.47	0.033	0.005	18.32	8.35	-	-
SUS 304L	0.011	0.56	1.15	0.029	0.005	18.38	10.45	-	-
SUS 321	0.05	0.60	1.24	0.036	0.006	17.19	9.54	-	0.43
SUS 316	0.06	0.53	1.06	0.031	0.005	16.77	10.38	2.07	-
SUS 316L	0.018	0.55	1.12	0.034	0.002	17.42	12.51	2.07	-

C — heat-treated after blasting by a plasma-arc with the same technological condition as used in the plasma spray of samples;

D — chemically passivated in 50% HNO₃ solution for 2 hrs after being blasted.

To match with the measurement of the potential of coatings, i.e., the coating films separated from the sprayed samples, the base metal was at first slightly blasted and then sprayed, and soon afterwards the sprayed samples were rapidly cooled by compressed air so that to have the bonding severed into independent coating films.

The natural potential and natural current were measured with a high impedance electrometer, Model HE-101A (Hokuto Denko Ltd.) and a zero shunt ammeter, Model HM-101 (id.) respectively. The test was conducted in 3.5% NaCl solution which was prepared from the sodium chloride of extra pure reagent grade and the temperature of which was kept at $25 \pm 3^\circ\text{C}$ by use of a thermostatic water bath.

The measurement of the potential of coating film or base metal itself was conducted with a calomel reference

electrode and the measurement of the current with a platinum electrode used as a counter electrode of the system. The potential difference between the coating and the base metal was determined indirectly in two ways for comparison. The first was by using a coating film and a base metal specimen as a pair of electrodes (direct measurement) and the second was subtracting the potential of the coating film from that of the base metal which were measured individually as mentioned above (indirect measurement).

The potential and current of the ceramic sprayed stainless steel were measured similarly as above-mentioned.

All the natural potential data were adopted at the end of 30 min test, at which moment the data recorded usually became stable. The measurement of natural current was conducted after 30 min potential measurement and lasted 5 min for each specimen to have a steady datum.

The conventional plasma spray condition used for ceramic sprayed coating films and ceramic sprayed samples were the following: current 800 A, voltage 38 V, spray distance 100 mm, argon pressure 60 Psi, helium pressure 60 Psi and with such a combination of spray speed and powder feed rate as to have the coating thickness around 0.20 ~ 0.22 mm.

3. Results and Discussion

3.1 The electrochemical feature of coating films

The natural potential of the coating films sprayed with

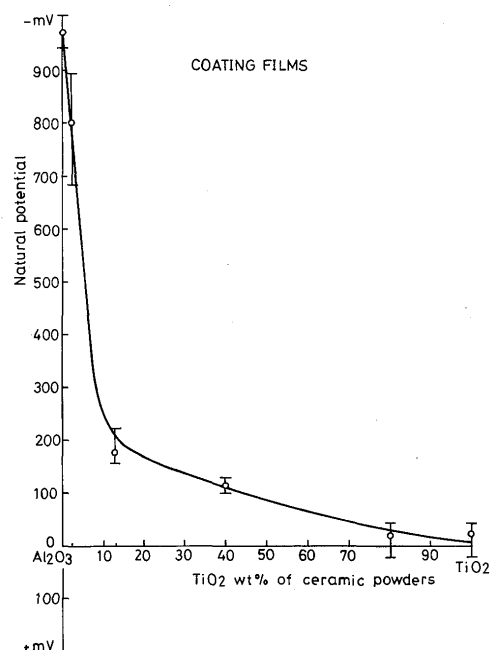


Fig. 1 Natural potential of coating films themselves sprayed with different ceramic powders of Al₂O₃-TiO₂ system

the ceramic powder of pure Al_2O_3 or those with small content of TiO_2 as shown in Fig. 1, appeared extremely negative to an extent as -1000 mV approximately. They tended to be more positive as the TiO_2 content increased and reached to an average value about -30 mV as in the case of 80% and pure TiO_2 .

Contrary to the appearance of natural potential the natural current (Fig. 2) started from zero of the films composed of pure Al_2O_3 and $\text{Al}_2\text{O}_3 + 2.3\%$ TiO_2 content and reached the highest value, more than $2\mu\text{A}$ averagely in the case of pure TiO_2 .

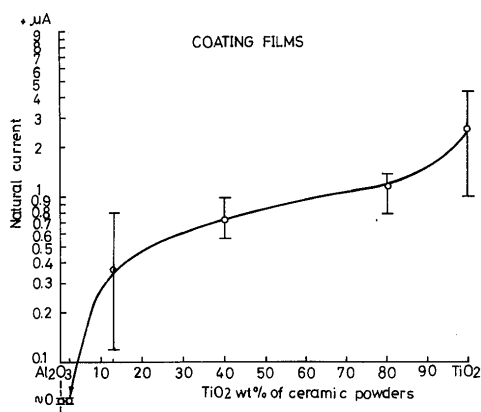


Fig. 2 Natural current of coating films themselves sprayed with different ceramic powders of Al_2O_3 - TiO_2 system

This showed a distinct difference in electrochemical feature of the coating films composed of ceramic powders with different composition and therefrom, a certain effect on corrosion behavior of the ceramic sprayed base metals as shown after might be predicted.

3.2 The natural potential and natural current of base metals with different surface treatment

The natural potential and natural current of different base metals with different surface treatment as above-mentioned were measured and summarized in Fig. 3 and Fig. 4 respectively. All the blasted base metal (surface treatment A) had the most negative potential and the

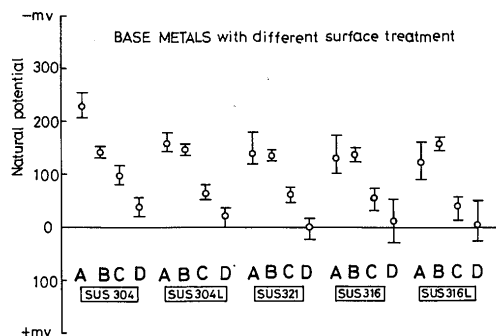


Fig. 3 Natural potential of stainless steels with different surface treatment

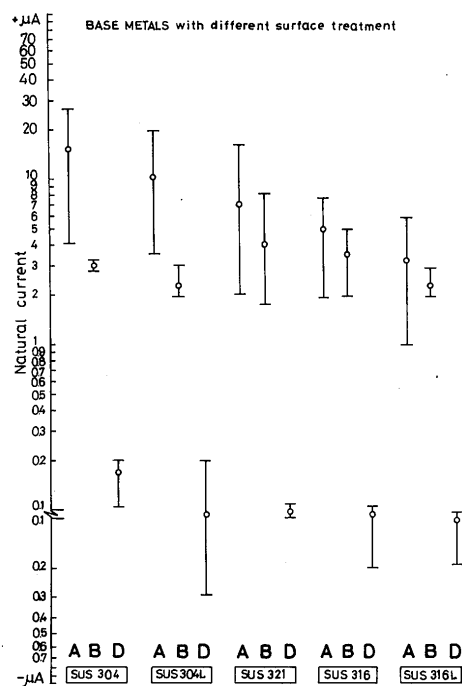


Fig. 4 Natural current of stainless steels with different surface treatment

highest current. Oppositely, the nitric acid solution treated base metal (surface treatment D) had the best results, the most positive potential and the lowest current, probably due to the presence of thick passivated film on its surface. All the polished base metals (surface treatment B) with fresh smooth surface presented roughly the same potential and current which predicated that the unpassivated surfaces of the researched five stainless steels made no any distinct difference to their electrochemical feature in 3.5% NaCl solution. The plasma-arc heat-treated specimens (surface treatment C) which simulated the practical spray technology of the sprayed samples, improved the potential to more positive nearing that of treatment D.

The above-mentioned experimental result predicated, the electrochemical feature of the real sprayed samples might be more or less improved in comparison with that tested on the blasted base metal. Moreover, it inspired us to greater efforts for improving the corrosion resistance of sprayed metal by certain surface treatment of the base metal.

3.3 The potential difference between the coating films and the base metals with different surface treatment

The potential difference between the coating film and the base metal is the motive force for the sprayed metal to generate corrosion current and then to be corroded in electrolytic solution. So the measurement of potential difference will be helpful to the estimation of corrosion

behavior of the ceramic sprayed samples.

The indirectly measured potential difference between the coating films and the base metals with different surface treatment or the different base metals with the same surface treatment showed the same regularity as shown in Fig. 5 and Fig. 6 for SUS304 with different treatment and different base metals with the same treatment A,

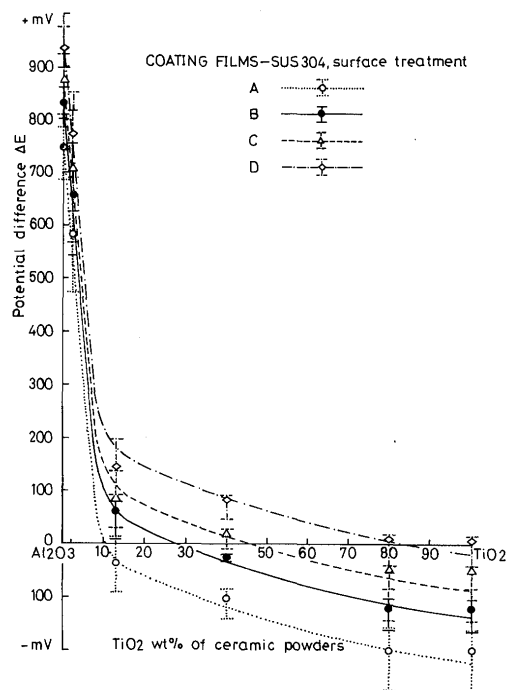


Fig. 5 Potential difference between the coating films and SUS304 steel with different surface treatment (indirectly measured)

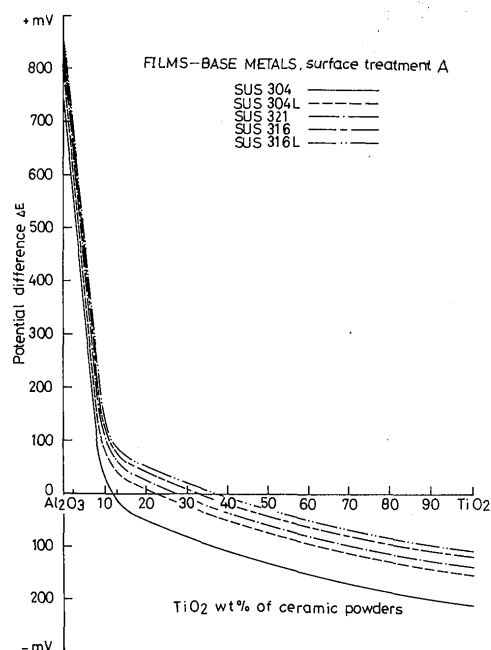


Fig. 6 Potential difference between the coating films and different base metals with same surface treatment A (indirectly measured)

respectively. The curves in the figures all extended around the average values and within the range of the data obtained.

The potential difference between all the coating films with high Al_2O_3 -content and the base metals with different surface treatment was highly positive which meant the films would play a role of the negative electrode and the base metal the positive in electrolytic system. It decreased with the increase of TiO_2 -content to zero or to negative which meant the possibility for the base metal playing a role of negative electrode. The more the downward shifting of the potential difference curve, the more the base metal might be sensitive to corrosion. By use of such yardstick, the sensitivity of the five studied base metals with different surface treatment to corrosion might all be estimated in this order: A, B, C and D. Similarly, the sensitivity of the base metals with the same surface treatment might be roughly evaluated in the following order as SUS304, SUS304L, SUS321, SUS316 and SUS316L.

The potential difference between the coating films and all the five base metals researched with different surface treatment was also directly measured. For an example, that for SUS304 steel with surface treatment A was shown in Fig. 7, from which the same regularity or the tendency of the graph was observed, though the absolute value varied to an extent.

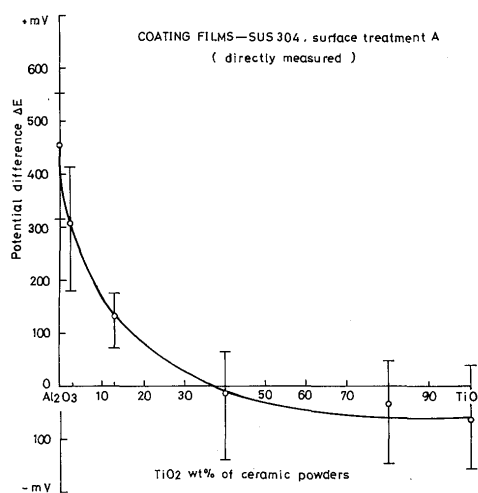


Fig. 7 Potential difference between the coating films and SUS304 steel with surface treatment A (directly measured)

3.4 A simple method for selecting the proper composition of sprayed coatings

As emphasized above, the potential difference between coating films and base metals is an important criterion in judging the corrosion behavior of ceramic sprayed base

metal. Moreover, its magnitude is firstly determined by the potential of coating film. Where the potential of coating film is more negative as compared with that of base metal, the former will be the anode and the latter the cathode of the corrosion couple. Keeping a viewpoint to the macro-system, it would be expected that the base metal might be protected from corrosion or only be corroded slightly.

On basis of above-mentioned anticipation and after having compared the natural potential of the base metal with different surface treatment with those of coating films, as an example shown in Fig. 8, we noticed that, from the viewpoint of electrochemistry, the SUS304 steel with surface treatment from A to D might be sprayed,

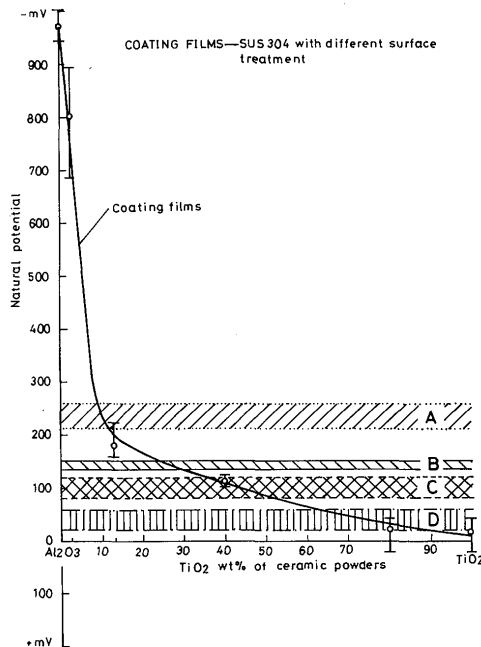


Fig. 8 Comparison between the potential of coating films and SUS304 steel with different surface treatment

roughly to say, with the powder of max. TiO_2 -content from 5 to 50% successively without being seriously corroded.

Similarly, the studied five base metals with surface treatment A might also have their own limitation of TiO_2 -content of coatings, below which they would not be suffered to corrosion remarkably as shown in Fig. 9.

So a simple method may be put forward for selecting the optimum composition of corrosion-resistant sprayed coatings. Although a number of practical problems would happen once the method was put into use, for example, whether the combination of the surface treatment and the base metal would be optimum or not and obtainable or not, it might be accepted at least as a qualitative means for solving such kind of complex problem.

3.5 The natural potential and natural current of ceramic sprayed base metals

The natural potential and natural current of the ceramic sprayed base metals were examined by direct

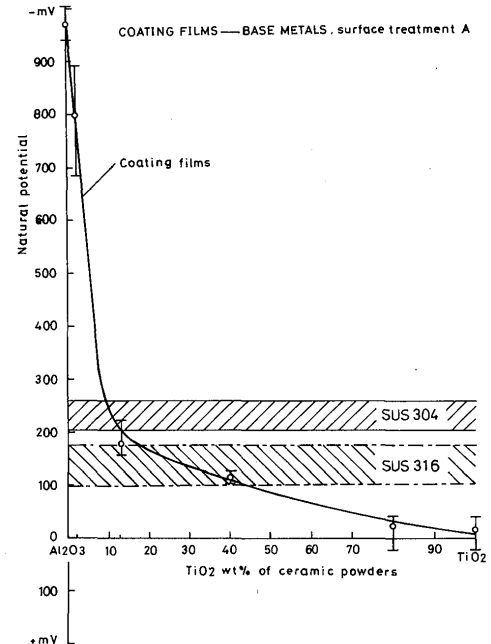


Fig. 9 Comparison between the potential of coating films and SUS304 and SUS316 steels with surface treatment A

measurement. Fig. 10 and Fig. 11 were the natural potential and natural current of the ceramic sprayed SUS304 steel respectively.

An interested phenomenon was discovered once compared the natural potential (Fig. 10) and natural current (Fig. 11) of the ceramic sprayed base metals with those of the films (Fig. 1 and Fig. 2) and the base metals (Fig. 3 and Fig. 4) themselves. For the convenience of comparison, all the values used were the approximate ones. The compared results were summarized in Table 3.

We were herefrom distinctly impressed that the measured natural potential and the natural current as well of

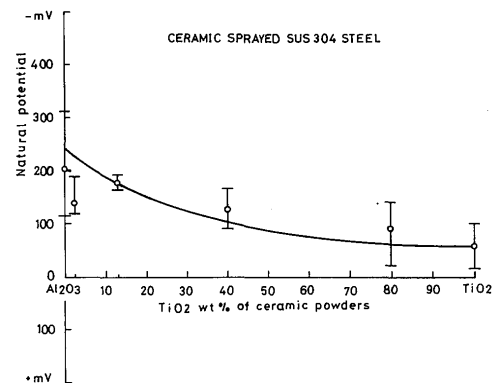


Fig. 10 Natural potential of ceramic sprayed SUS304 steel

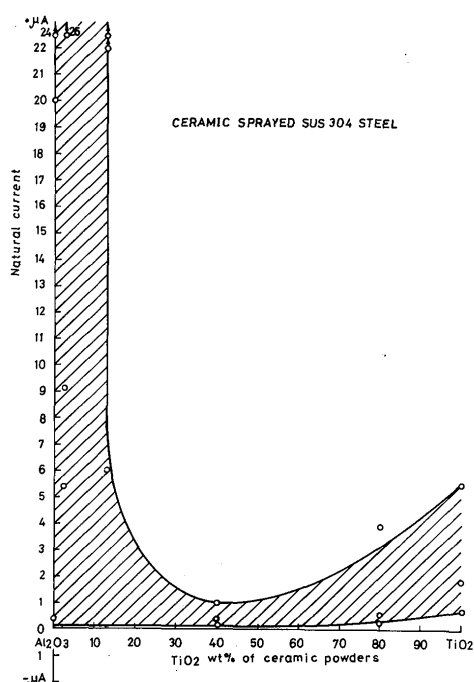


Fig. 11 Natural current of ceramic sprayed SUS304 steel

Table 3 The comparison of the natural potential and current of the ceramic sprayed base metals with those of the films and the base metals themselves

Ceramic powders	Potential (mV)			Current (A)		
	E_F	E_M	E_{SM}	I_F	I_M	I_{SM}
High Al_2O_3	-1000	-200	-200	0	20	20
High TiO_2	-50	-200	-50	2-3	20	2-3

Note: F - Film; M - Base metal; SM - Sprayed base metal

the sprayed base metal with high Al_2O_3 -content were just the same as measured from the base metal itself, however, that with high TiO_2 -content showed the same value as measured from the coating film.

The explanation may be given as follows. The natural potential as well as the natural current of the sprayed base

metals was affected mainly by two factors, the porosity and the electric conductivity of the sprayed coatings. In the coatings sprayed with high Al_2O_3 -content ceramic powder the porosity was much higher than in those with high TiO_2 -content as verified by metallographic photographs of their cross-section, Fig. 12. Higher porosity signifies the higher possibility for the base metal to be exposed to the electrolytic solution. This must be the main reason why the natural potential of the samples increased from the very negative value (-1000 mV) to the level of base metal (-200 mV) and the natural current of the samples leapt from zero to that near the base metal (20 μA) too, once coated with high Al_2O_3 -content powders.

Meanwhile, we noticed that the natural potential and especially the natural current values measured (Fig. 10 and Fig. 11) were highly dispersive, which came just as a result of high and inconstant porosity of the coatings.

Anyhow, the high current of the samples located on the left side of the Al_2O_3 - TiO_2 system does not mean that such a kind of coatings will be inapplicable but indicates only the seriousness of the porosity. In fact, it is the current generated by the partial base metal exposed to liquid through the pores and factually the value of it was in the neighborhood of that measured directly on the uncoated base metal.

On the other hand, the natural potential and current of the samples sprayed with high TiO_2 -content powders was essentially controlled by the high electric conductivity of the coatings inspite of lower but really in some degree existing porosity. This may be referred to that the electrochemical process always conducts at first on the surface of the coating where it is more electrically conductive. And so, the natural potential as well as the natural current in electrolytic solution approached that of film after the base metal was sprayed. However, it might be expected that the effect of porosity on electrochemical feature would be more or less increased if the sprayed samples were tested in the atmosphere of high humidity but not in solution.

The lowest point was noticed on the current graph

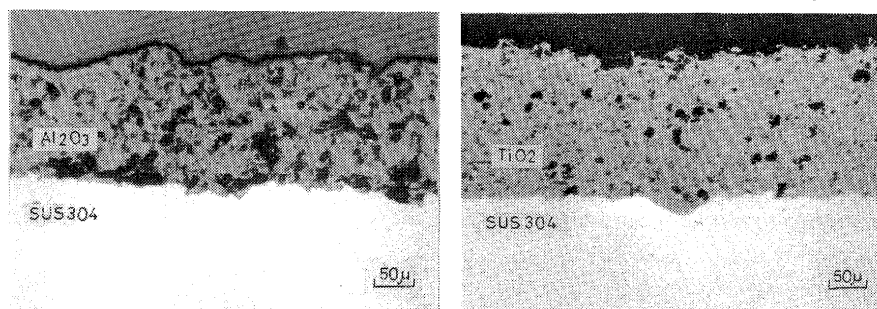


Fig. 12 Photographs of the cross-section of samples sprayed with pure Al_2O_3 (left) and pure TiO_2 (right) showing the porosity in their coatings

(Fig. 11) at about 40% TiO_2 -content coating showing the maximum effect on reducing the porosity of coatings by adding more TiO_2 , over which the electric conductivity of the coating would play a greater role causing the current increasing.

4. Conclusion

A simple method for selecting the proper composition of sprayed coatings by comparing the natural potential of coating films with that of base metals was suggested.

The potential difference between the coating films and the base metals was regarded as an important criterion for judging the corrosion behavior of the sprayed base metals, i.e., if the potential of the base metals was more positive than that of the coating films, the base metals would be protected and in the reversed case, they would be corroded.

The high Al_2O_3 -content coatings might be more beneficial to corrosion-resistance due to the result of more negative natural potential in comparison with that of the base metals. Nevertheless, the porosity of high Al_2O_3 -content coatings is much higher than that of those composed of high TiO_2 -content powders, so striving for reducing porosity would be the key to use such coatings successfully.

Oppositely, the coatings sprayed with high TiO_2 -

content powders had their potential more positive than that of base metals and were referred to be incommensurable, though the porosity might be lowered to an extent.

The natural potential as well as the natural current of the high Al_2O_3 -content ceramic powder sprayed samples were confirmed depending on those of the base metals and those of the samples sprayed with high TiO_2 -content powders, adversely, depending on the coating films.

Acknowledgement

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