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Studies on Corrosion Behavior of Ceramic Sprayed Stainless Steels (Report II)†

— Utilization of Anodic Polarization Curves to Evaluate Corrosion Tendency —

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Abstract

The anodic polarization curves of ceramic plasma-sprayed samples, the blasted stainless steel itself and the coating films in 3.5%NaCl solution were separately determined. The parameters on the curves were sorted out and utilized to evaluate corrosion behavior in 3.5%NaCl solution.

The result obtained by the polarization curve method was similar to that obtained by the natural potential method. The high Al_2O_3-content coatings of Al_2O_3-TiO_2 system ceramics were affirmed to be much more beneficial than the high TiO_2-content coatings.

The parameter, termed the corrosion sensitivity taking the effect of both the mean passive current density and the passive potential range into account, was derived and regarded as an criterion for judging the corrosion behavior of sprayed samples.

KEY WORDS: (Anodic Polarization) (Corrosion) (Plasma Spray) (Al_2O_3) (TiO_2) (Stainless Steel) (Passivation)

1. Introduction

In previous report[1] the natural potential of the coating films and the base metals were separately measured and the difference between them was regarded as an important criterion for judging the corrosion behavior of sprayed base metals. As the actual corrosion process of the sprayed metals in electrolytic solution might be affected by many factors, the important one of which is the polarization phenomenon, or the anodic polarization as a more interesting one, the anodic polarization curves of the coating films, the base metal and the sprayed samples were respectively measured and the relation among them was discussed.

It is known that some characteristic points or parameters on anodic polarization curve such as polarization rate, primary passivation potential, passive current density and so on, may be used as the basis for judging the corrosion behavior of metals.[2],[3],[4] The research work in this paper attempted to utilize such a method to ceramic sprayed metal for selecting the proper composition of ceramic powders and to verify the identity of result with that carried out in previous report[1].

2. Experimental Procedure

The oxide ceramic powders and the base metal (SUS 304) surface treatment as well as spray conditions used for plasma-spray were the same as used in previous report[1].

All of the specimens, i.e., the working electrodes were painted by liquid RTV-gum with a fresh (no painted) working surface of 2×2 cm^2 left over. A copper wire used as the lead to the measure system was welded to the base metal of specimen by percussion-welder and was also isolated by such gum.

The usual three-electrode system was used in the measurement. The test cell was consisted of the working electrode of platinum sheet and was connected to a saturated calomel reference electrode by two-stage salt bridge.

The electrolyte was 3.5%NaCl solution prepared with sodium chloride of extra pure reagent grade and maintained at 25 ± 3°C by use of a thermostatic water bath.

The potentiostat/Galvanostat HA-303 (Hokuto Denko LTD.), the function generator HB-104 (ditto) and the XY-recorder Type 3066 (Yokogawa Hokushin Electric) were used to generate and simultaneously record the applied potential and current.

In order to achieve the cathodic polarization curve together with the anodic in one time, a single triangular wave of the stimulus of applied potential was used, i.e., started from −200 mV, the average natural potential of the tested specimens, to −1500 mV and then turned to the noble direction and stopped at +1500 mV.

Different potential scan rates were tried at 300, 100, 60, 30, and 6 mV/min and resulted in that the polarization current density on anodic curve increased with the increase of scan rate and, in the meanwhile, some variation details on potential-applied current density curve might be disappeared at higher scan rate.

The rate 60 mV/min was finally adopted with consideration of not only the reality of the recorded curves but also the shortening of the test process.
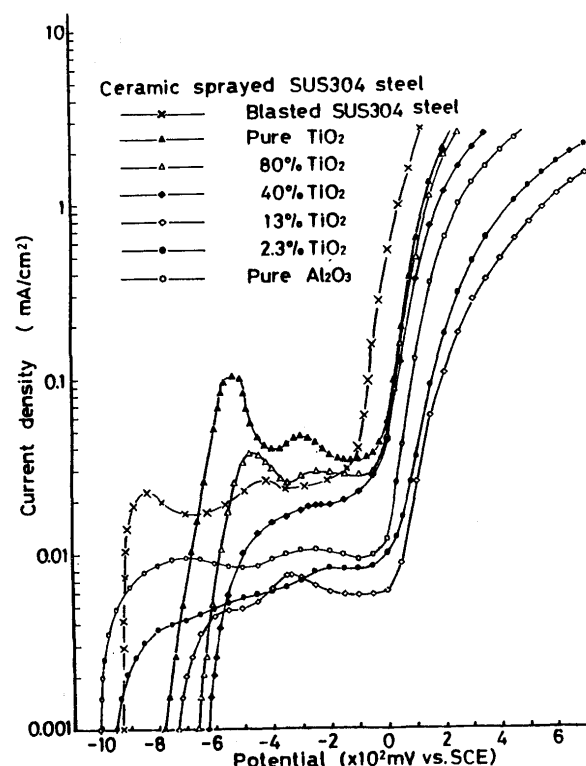

Fig. 1 Anodic polarization curves of ceramic sprayed samples on SUS 304 steel with different powders in 3.5%NaCl solution.

3. Results and Discussion

3.1 Anodic polarization curves

The anodic polarization curves of the coating films, and the samples sprayed with different ceramic powders were determined respectively.

A representative one of the potential-applied current density diagrams of sprayed samples on SUS 304 steel with different ceramic powders and SUS 304 steel itself was shown in Fig. 1. We noticed that with the increase of TiO_2-content in the sprayed coatings, the current density became higher and the passive range more narrow. This distinction in appearance predicted the effect of coating ceramic content on corrosion behavior of the sprayed samples and will be discussed later.

We were interested in finding that the potential-applied current density curves of ceramic coating films themselves were quite different as shown in Fig. 2. With the increase of applied potential in noble direction, the current density of high Al_2O_3-content and pure Al_2O_3 coating films remained in the neighbourhood of zero-value. It increased gradually with the increase of TiO_2-content and for 80%TiO_2-20%Al_2O_3 and pure TiO_2 films, it rose steeply and presented a typical passivation feature. It might be herefrom expected, the chemical composition of coating films would play a important role in corrosion behavior.
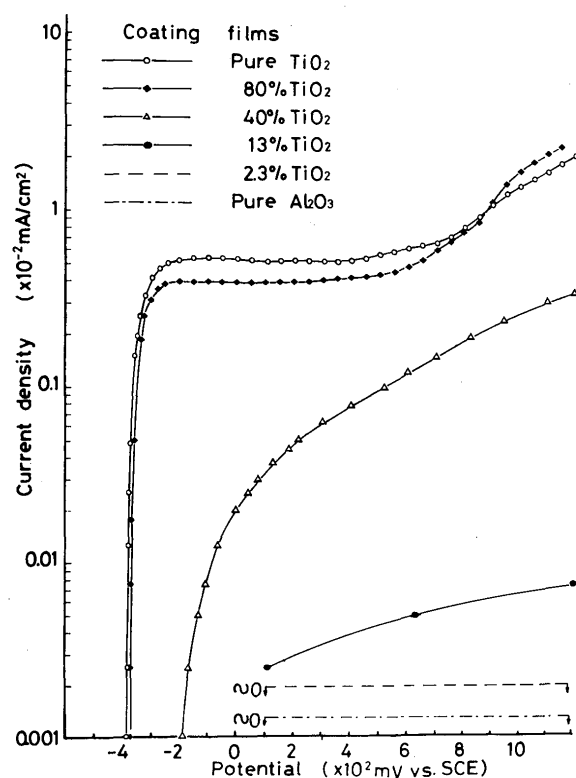

Fig. 2 Potential-applied current density diagrams of different ceramic coating films themselves in 3.5%NaCl solution

3.2 Characteristic parameters on polarization curves

By use of the prevailing way to obtain an understanding of the passivity of the specimens, some of the characteristic parameters were sorted out from the anodic polarization curves of the coating films, base metals and sprayed samples.

While the tested specimen is in the active stage, the recorded current increases rapidly with the increase of applied potential in noble direction. It indicates the tendency for the specimen to be corroded and the slope of the potential/applied current line represents the polarization rate which may be understood as the rate for the specimen entering the passive range.

For the sprayed samples of pure TiO_2 and 80%TiO_2-Al_2O_3 powders, the anodic polarization curves presented a typical passivation behavior. The measured current ceases to increase at a potential usually called the primary passivation potential and with applied potential it begins to decrease. The measured current density at this potential is called the critical passivation current density. Above this potential, the current density drops to the passive current density, and remains approximately at this value over a wide range of potential which is termed the passive potential range and defined the passivity for the given environment specimen combination.

On continuing to increase the applied potential in noble direction, the measured current will again begin to increase at the potential known as pitting potential, and the formation of corrosion pits on the tested specimen surface is accompanied in chloride containing solution. The slope of the potential-applied current curve represents the dissolution rate of the specimen in electrolyte.

All of the above-mentioned characteristic parameters of the sprayed samples on SUS 304 steel with different TiO_2-content for TiO_2-Al_2O_3 system powders were shown in **Fig. 3-5**.

The primary passivation potential and the critical passivation current density of sprayed samples were shown in Fig. 3. The higher was the TiO_2-content in their coatings of the sprayed samples, the nobler the primary passivation potential became and the higher the critical passivation current density, except the sprayed sample of pure Al_2O_3. This meant that, it was easier for the high Al_2O_3-content samples to be passivated as compared with the high TiO_2-content ones. The former might initiate to be passivated at a lower current density and a more negative potential.

Figure 4 shows the change of mean passive current density and passive potential range of ceramic sprayed samples with TiO_2-content of powders. The variation of mean passive current density with TiO_2 content of sprayed coatings was similar to that of critical passivation current density as shown in Fig. 3. The passive potential range which is defined as potential difference between the
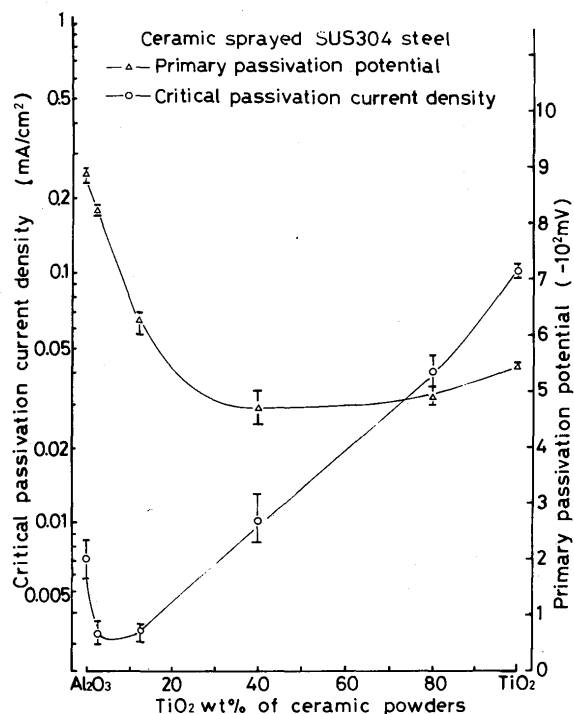

Fig. 3 Critical passivation current density and primary passivation potential of ceramic sprayed samples on SUS 304 steel with different powders in 3.5%NaCl solution
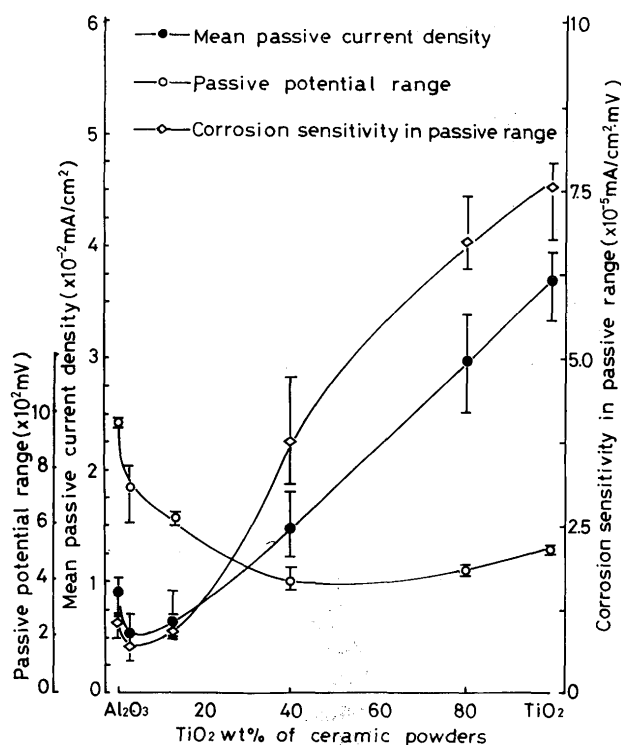

Fig. 4 Effect of TiO_2-content of ceramic powders on the mean passive current, passive potential range and corrosion sensitivity in passive range of ceramic sprayed samples on SUS 304 steel in 3.5%NaCl solution

pitting potential and primary passivation potential tended roughly to decrease with the increase of TiO_2-content. The lower critical passivation current density for the high Al_2O_3-content samples signified that they were easier to be passivated, while the wider passive potential range meant the higher persistency for them to be maintained in passive state. Considering that the variation of mean passive current density did not always coincide with that of passive potential range, i.e., a lower passive current density might match with a more narrow passive potential range or reversely, we adopted a new criterion given by dividing the mean passive current density by the passive potential range and termed "the corrosion sensitivity" of the tested specimen. The change of the corrosion sensitivity with TiO_2 content is shown in Fig. 4, too. From this figure it varied with a similar regularity as the mean passive current density.

The dissolution rate in transpassive stage increased with the increase of TiO_2-content in the coatings, yet it reached a very high value as shown in **Fig. 5**. The high TiO_2-
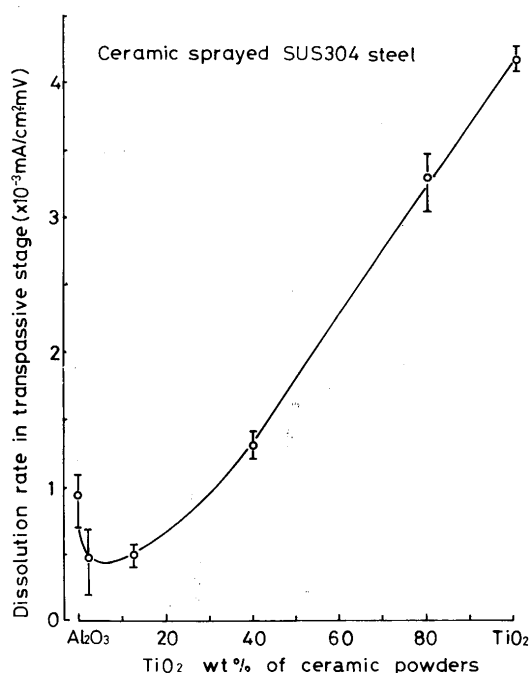

Fig. 5 Dissolution rate of ceramic sprayed samples on SUS 304 steel with different powders in transpassive stage in 3.5% NaCl solution

content samples would be dissoluted with a rate much higher than the high Al_2O_3-content ones and even to an extent of nearing the case of uncoated blasted base metal.

To sum up the above-mentioned results, it was observed that all the parameters relevant directly to current density varied in a same regularity, i.e., they increased with the increase of TiO_2-content in the coatings, only with an exception of the pure Al_2O_3 coated sample. It signified that the high Al_2O_3-content coatings were much more benefitial to corrosion resistance for the samples sprayed with Al_2O_3-TiO_2 system ceramic powders in

3.5%NaCl solution. This might be due to that for high Al_2O_3-content coatings the porosity was much higher than that for high TiO_2-content coatings and the electric conductivity of films themselves for the latter in NaCl solution was incomparably higher than that of the former. While the sample sprayed of high Al_2O_3-content powders was tested in solution under an applied potential, the current could be generated only at the partial surface of the base metal exposured to solution through the pores because the films of high Al_2O_3 content coating showed no electric conductivity in solution as shown in Fig. 2 and so the mean passive current density was always lower than that of the base metal itself. The more the porosity in the coatings, the higher the current might be measured for high Al_2O_3 content powder coated samples. The electric conductivity of films themselves in 3.5%NaCl solution increased gradually with the inerease of TiO_2-content in the sprayed coating films which might play a role of electric conductor to the base metal. On high TiO_2-content powder sprayed samples the current measured might be the sum of those generated from both the coating film and the partial surface of the base metal exposured to solution through the pores in the coating.

The increase rate of current density measured on all samples sprayed with different powders in transpassive stage was lower than that of the base metal, increase with the increase of TiO_2-content. It indicated the positive effect of the coatings composed of different ceramic powders on corrosion behavior of the samples. The samples sprayed of high Al_2O_3-content powders would be corroded in a very low rate even at the transpassive stage, while those sprayed of high TiO_2-content powders would behave nearly like an uncoated base metal.

4. Conclusion

The result obtained by utilizing the anodic polarization curves to evaluate the corrosion tendency of ceramic sprayed samples was similar to that by using the natural potential method.

The corrosion tendency increased with the increase of TiO_2-content in the coatings, might be judged by the primary passivation potential, the critical passivation current density, the mean passive current density as well as the passive potential range and the dissolution rate in transpassive stage, except pure Al_2O_3 sprayed sample. Dividing the mean passive current density by the passive potential range, a simple and clear parameter, the corrosion sensitivity termed, was derived and might be regarded as a criterion for evaluating the corrosion behavior.

The studied high Al_2O_3-content coatings sprayed of 2.3% and 13%TiO_2 affirmed to be most beneficial to corrosion resistance in conditions tested from the anodic polarization curves.

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