Chemistry Letters 1997 909

Corrosion Resistance and Antibacterial Activity Performances of Ni-TiO₂ Composite Coatings

Zhao Zhi-hong,* Yoshikazu Sakagami,† and Tetsuya Osaka†† Satosen Co., Ltd., 2-20-65, Tamadenishi, Nishinari-ku, Osaka 557

†Division of Pharmaceutical Affairs, Osaka Prefectural Institute of Public Health, 1-3-69, Nakamichi, Higashinari-ku, Osaka 537 ††Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1, Okubo, Shinjuku-ku, Tokyo 169

(Received May 22, 1997; CL-970385)

The novel properties for the corrosion resistance in a 5% NaCl salt-spray-test and the inhibitory capability of Ni-TiO $_2$ composite coating for the growth of pathogenic bacteria (*E. faecalis*, *E. coli*, and *P. aeruginosa*), under fluorescent irradiation and using a "drop-method" antibacterial experiment was set forth in this paper. The antibacterial activity of Ni-TiO $_2$ composite coating became more significant by increasing the TiO $_2$ contents in the composite coatings.

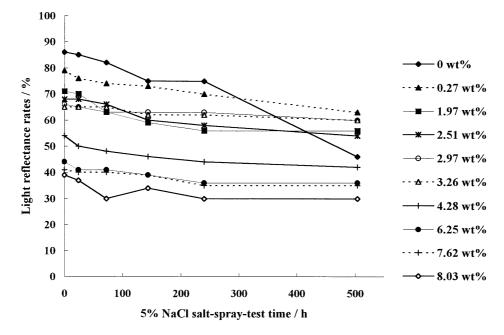
Our previous investigations have shown that corrosion resistance coatings always resulted in weak antibacterial activity. Whereas, although the coatings possessed a significant inhibition capability for the growth of bacteria, but they usually corroded very quickly. ^{1,2} In order to solve the difficult problem that is present in the application of industry, we suggest and attempt to demonstrate that the contained TiO_2 nickel composite coatings play an important role.

There is a range of composites, such as alumna, silicon nitride, etc., which, when dispersed in nickel, ^{3,4} show a definite improvement in corrosion resistance, compared to the matrix metal alone. The Ni-TiO₂ composite coatings whether possess a better corrosion resistance or not have been studied in our tests. In addition, the TiO₂ photocatalytic destruction of microbial cells has also been described, ⁵ even though these studies have primarily used the TiO₂ particle to operate on the microorganisms or organisms. ^{6,7} Therefore, we hypothesized that as the TiO₂ photo-catalytic property was applied in the electrolytic composition field, under the condition of light irradiation, the Ni-TiO₂

composite coatings may be able to induce antibacterial activity, and that the inhibition could be enhanced by increasing the TiO₂ contents in nickel matrix coating. Our experimental results ascertained this.

Corrosion studies were performed in a 5% NaCl salt-spray-test that is based on JIS Z 2371 at 35°C from 0 to 500 h, respectively. After tested, the light reflectance rates from the surface of Ni coating and Ni-TiO₂ composite coatings were measured by a Gloss Checker. In our antibacterial experiments, the gram-positive bacteria used were *Enterococcus faecalis* IFO 12965, and the gram-negative bacteria were *Escherichia coli* IFO 3806, *Pseudomonas aeruginosa* IFO 13275.

Figure 1 shows the variations in light reflection rates from the surface of different TiO₂ contents in Ni-TiO₂ composite coatings with exposure time in the salt-spray-tests. It was found that before corrosion tests, with increasing TiO₂ contents in the nickel matrix, the light reflection rates gradually decreased. However, a significant depression only occurred in the nickel coating after a long lapse of time in the salt-spray-test. The test results indicate that the light reflection rates of nickel coating decreased more rapidly than that of other Ni-TiO₂ composite coatings when the exposure time was over 240 h, in other words, the violent corrosion reaction was curried out on the surface of nickel coating. After 240 h, the light reflection rates of nickel coating continually fell with rapid velocity, but Ni-TiO₂ composite coatings showed very little variation by prolonged exposure time. It was also evident that Ni-TiO₂ composite coatings provided a better corrosion-resistance than only nickel matrix at longer time exposure to salt spray



Figour 1 Variation in light reflectance rates of different TiO₂ contents in composite coatings with the exposure time in a 5% NaCl salt-spray-test at 35°C.

910 Chemistry Letters 1997

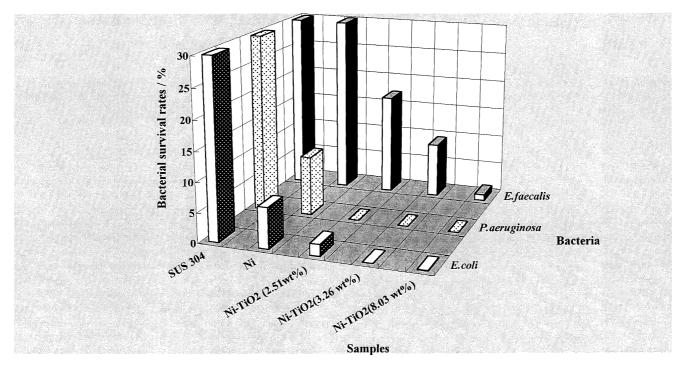


Figure 2 Relationship between antibacterial activity and the TiO₂ contents in composite coatings. Under irradiation incubation at 25°C for 24 h.

environment.

On the other hand, we have evaluated the effect of the TiO₂ contents in composite coatings on the antibacterial liability under 7500 Lux light irradiation (Figure 2). On the basis of the experimental data, we found not only did Ni-TiO₂ composite coatings show more significant antibacterial activity than stainless steel (SUS 304), which was used as a control in our antibacterial experiments. But also antibacterial activity was enhanced with increasing the TiO₂ contents in nickel matrix coating.

The Ni-TiO₂ composite coatings showed survival rates of grampositive bacteria E. faecalis to decrease with increasing TiO₂ weight content in coatings. When TiO₂ in coating was 8.03 wt%, the survival rate of E. faecalis was approximately 1%.

As pointed out in Figure 2, the survival rates of gram-negative bacteria $E.\ coli$ on the surface of the composite coating contained 2.51 wt% TiO_2 was obviously less than that of the nickel matrix. Furthermore, as the TiO_2 contents in composite coating were continually increased, the survival rates of $E.\ coli$ were drastically decreased and were close to zero.

Regarding P. aeruginosa, proof significant antibacterial activity of the Ni-TiO $_2$ composite coatings was achieved. The number of survived P. aeruginosa bacteria on the surface of pure nickel coating was approximately 10%. The level of survival rates of P. aeruginosa was decreased to approximately zero even when the TiO_2 was only 2.51 wt% in coatings.

The Ni-TiO₂ composite coatings possessed greater inhibitory capability than nickel coating alone. It is considered feasible that TiO₂

homogeneous dispersed in composite coatings, as a photocatalyst, causes photochemical reactions to generate antibacterial chemical materials, resulting in being primarily responsible for bacterial degradation and bacterial death.⁷

Based on the comparison of our experimental results, we found out that when the TiO_2 particles were added in nickel matrix, not only the corrosion resistance property of coatings was strengthened, but also the inhibitory capability for the normal proliferation of bacteria was promoted at the same time.

The authors express their gratitude to Mr. Y. Sato, Dr. M. Yokoi, Dr. T. Morikawa, and Mr. T. Nakade of the Technology Research Institute of Osaka Prefecture for their valuable discussion. We also would like to thank Dr. H. Yokoyama, Mr. K. Kazimura, and Mr. H. Katsuki, Division of Pharmaceutical Affairs of Osaka Prefectural Institute of Public Health, for their cooperation.

References and Notes

- 1 Zhao Z. H., S. Eguchi, Y. Okada, and T. Osaka, Chem. Lett., 1996, 55.
- Zhao Z. H., K. Hasebe, Y. Sakagami, and T. Osaka, Bull. Chem. Soc. Jpn., 70, 1(1997).
- 3 E. P. Rajiv and S. K. Seshadri, *Plating and Surface Finishing*. **June**, 85(1992).
- 4 B.A. Movchan, Surface and Coating Technology, 46(1), 1(1991).
- 5 Ireland, J., P.Klosterman, E. Rice, and R. Clark, Appl. Environ. Microbiol., 59, 1668(1993).
- 6 Halliwell, B., and J.M.C. Gutteridge, "Free radicals in biology and medicine, 2nd ed", Clarendon Press, Oxford (1989).
- 7 Cai R, K.Hashimoto, A.Fujishima. Chem. Soc. Jpn., 64, 1268(1991).