Electrochemical Studies Of TiN-Coated Stainless Steel

By *Y.L.* Chen

Stainless steel (17-4 PH alloy) was coated with titanium nitride by physical vapor deposition. Corrosion studies were conducted as the preliminary evaluation. The studies included polarization test, galvanic current measurement, open potential measurement and salt spray teat, with emphasis on the polarization test. The test medium was a NaCl solution. The results indicate that a well-prepared TiN coating can significantly enhance the corrosion resistance of 17-4 PH alloy. When coating defects exist, the corrosion rate of the exposed spots may not be accelerated by the TiN coating. For come poorly prepared coatings, crevice corrosion of 17-4 PH alloy may occur at spots where defects and crevices are present.

Titanium nitride (TiN) has recently drawn great interest in coating applications. TiN coatings, because of their good chemical stability, hardness, and attractive golden luster, have been widely applied to improve the performance of cutting tools,' specialized steels,[2,3] and stainless steels.[4,5] Corrosion characteristics of TiN-coated metals, such as stainless steels 440C[4] and 304,[5] have been investigated. The results varied widely, partly as a result of variations in structure and composition associated with different coating techniques, and partly because of the variety of methods for preparing substrates prior to the coating process.

TiN coatings on the precipitation-hardening stainless steels, such as 17-4 PH alloy (AMS 5643)-which has been used to make compressor blades in gas turbine engines-have been investigated very little. The 17-4 PH alloy (normal composition 16-17% Cr, 4% Ni, 4% Cu, 0.3% Cb & Ta, maximum 1% Mn, maximum 1% Si) is known for its good corrosion resistance, excellent strength and toughness. It has been utilized in a variety of applications in the aircraft, rocket, chemical and nuclear industries for many years. Components made of this alloy have, however, experienced various levels of deterioration in hostile environments. It was thought that a TiN-coated 17-4 PH component might provide a better service life because of the presumed enhanced corrosion and erosion resistances attributed to TiN coating.

In the present work, the corrosion characteristics of TiN-coated specimens were studied by various corrosion test methods. The results were compared with those for uncoated specimens. The test medium used was sodium chloride solution.

Experimental Prorcedure

Specimen Preparation

The 17-4 PH alloy specimens studied were forged parts with dimensions ranging from approximately 50.8 x 12.7 x 0.159 cm to 101.6 x 25.4 x 0.318 cm. The parts were cleaned by vapor honing and vapor decreasing prior to the coating process. TiN coatings were applied by cathodic-arc physical vapor deposition (PVD) processes at a temperature lower than 900 oF, and were pure TiN with [1 11] preferred orientation. Coating thickness ranged from 5 to 13 pm. A considerable level of compressive stress was found in the coating by X-ray diffraction. The surfaces were generally smooth and uniform, although a few pinholes and tiny spits were sometimes found, as shown in Fig. 1.

Some coated specimens were intentionally indented with a spherical hardness indenter to generate open cracks in the coating, or scratched by a file to expose small areas of the base 17-4 PH alloy. These predamaged specimens were tested to see whether a defective TiN coating would accelerate corrosion of the alloy. It is acknowledged that although a zero-defect TiN coating can be achieved, various defects attributable to erosion or fatigue may occur during real-life service. Therefore, it is important to understand corrosion behavior at the damaged areas.

The uncoated specimens were polished with 400-mesh sandpaper, washed with water and then wiped with methyl ethyl ketone prior to the corrosion tests. All three types of specimens—TiN-coated, uncoated, and predamaged-were investigated in each test procedure.

Polarization Corrosion

The basic methodology is similar to that published by ASTM.[6] In this study, a specimen was setup as a working electrode; apiece of graphite rod was used as a counter electrode. The solution was 3.5-percent NaCl at room temperature and without agitation. Once the immersed specimen reached stable open potential (approximately 10 rein), polarization was started. The polarization cycle ranged from -0.5 V to +0.5 V then back to -0.5 V. The scan rate was 5 mV/sec. The reference was a saturated calomel electrode (SCE).

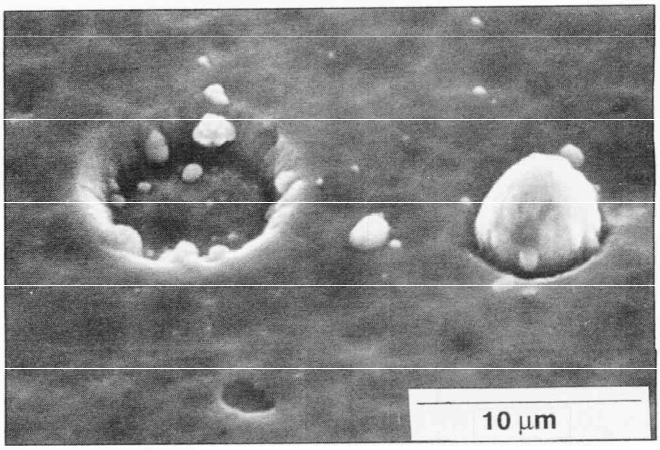

Fig. 1—TiN coating morphology, showing a pinhole and tiny spits.

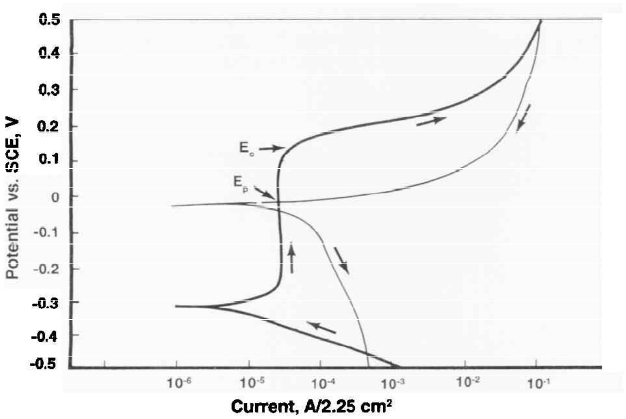

Fig. 2—Polarization curve of a polished 17-4 PH specimen after *one cycle in 3.5% NaCl solution. E_o Is the critical pitting potential; E_p is the protection potentiaL*

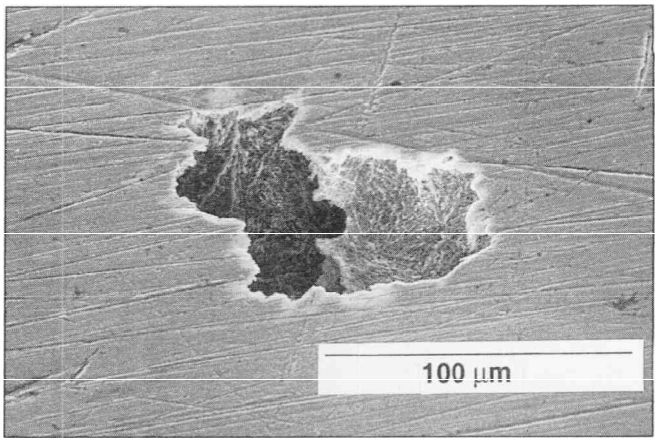

Fig. 3-Pitting pattern of a polished 17-4 PH specimen after one cycle of polarization in 3.5% NaCl solution.

Open Potential

The experiment set-up consisted of several workplaces surrounding a reference electrode (SCE) in a plastic container. Each specimen was held by a small alligator clip at the dovetail. The specimens were then inserted approximately two-thirds of their length into the NaCl solution, keeping the clips above the solution level. The container was covered to prevent dust infall and to reduce water loss. The potential of each specimen was measured vs. the SCE and recorded in a strip chart. The specimens were immersed for approximately two months,

In a similar but separate test, two predamaged coated specimens (damaged by indentation and scratching) were immersed in the 3.5-percent NaCl solution for about two months. No open potential was measured. The purpose was to see whether the damaged coating would affect the corrosion rate of the 17-4 PH base metal.

Galvanic Corrosion Current

In this set-up, an uncoated specimen was connected to the working electrode lead, and a TiN-coated specimen was connected to the counter electrode lead, which was shorted with the reference electrode lead. The galvanic current was measured with a potentiostat* set and maintained at zero applied potential between the uncoated and the TiN-coated specimens. At zero potential difference, corrosion current (which is the true short circuit current and is proportional to the corrosion rate) as a result of galvanic reaction can be directly measured and recorded. The total current charge is theoretically proportional to the total amount of metal corroded. This technique has been used very successfully to determine the galvanic corrosion rate of two dissimilar metals.[7-10]

The measurement was made in 3.5-percent NaCl solution, at room temperature, and without agitation. The open potential of the uncoated vs. the TiN-coated specimens was measured after the couple was immersed for about 10 min. The cell was then activated at zero applied potential. The galvanic current and the accumulated coulombs were recorded for a period of 24 hours. Various area ratios of uncoated specimens to the TiN-coated specimens were obtained by taping the specimens.

Salt Spray

The salt spray test was conducted per ASTM B117 procedure by using five-percent NaCl solution. A group of randomly selected specimens, coated and uncoated, was tested for as many as 15 days. The cut-off time was chosen when most of the coated specimens showed surface staining.

Another salt spray teat was conducted for predamaged specimens. Two pre-indented coated specimens and one uncoated specimen were tested for two months. The purpose was again to see whether the damaged areas might experience corrosion.

Results

The experimental result of each teat is described as follows, with emphasis on the polarization corrosion study.

Polarization Corrosion Study

There are two types of results generated by a polarization test; a current vs. potential curve plotted by an X-Y recorder, and the corroded specimen. The curve can be used to predict what kind of corrosion might occur in actual service, while the corroded specimen can generally simulate a corrosion pattern similar to that of a specimen in actual field service for several years.

Figure 2 illustrates the representative polarization curve of a polished 17-4 PH specimen after one cycle in 3.5-percent NaCl solution. The heavy line represents polarization from active to noble potentials. The light line represents reverse polarization back to more active potentials. The critical pitting potential, EC, as shown in the curve, is the most important feature for the corrosion behavior of 17-4 PH alloy in a seawater environment, and is typical for many stainless steels. Polarization above E_o results in a sharp increase in current from initiation of pitting. The reverse polarization generates a hysteresis loop, indicating that propagation of existing pits or localized corrosion occurs. At the protection potential, E_p, the current was reduced to the passive region. Below E_p, propagation of existing pits and localized corrosion does not occur; the metal is in a passive condition. A metal with a lower E_c and a larger difference between E_o and E_p is more susceptible to pitting corrosion and propagation of localized corrosion. Figure 2 clearly indicates that 17-4 Pi-f alloy is susceptible to pitting and localized corrosion in a seawater environment.

Photomicrographs of a polished, uncoated specimen after one cycle of polarization are shown in Fig. 3. The cross

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Model 273, EG&G, Princeton, NJ.

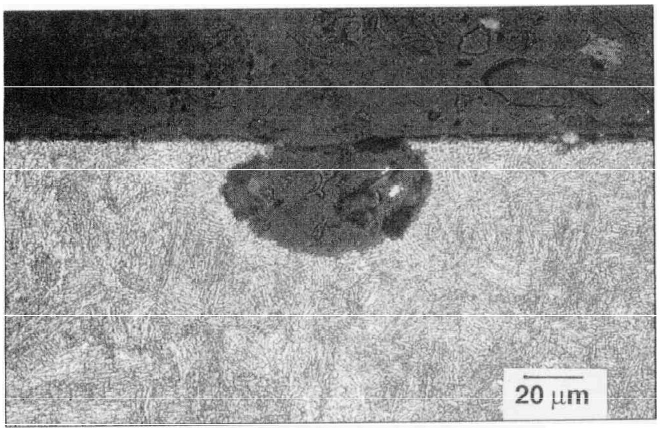


Fig. 4—Cross section of a corrosion pit on a polished 17-4 PH specimen after one cycle of polarization In 3.5% NaCl solution. The surface was chemically etched.

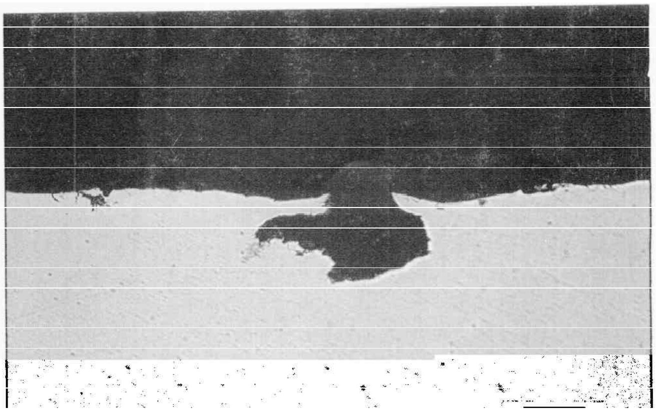


Fig. 5—Cross section of a corrosion pit on a field service specimen of 17-4 PH alloy.

section of a pit, shown in Fig. 4, is similar to a corrosion pit formed on a field service component, as shown in Fig. 5.

The TIN-coated specimens, interestingly, showed three different types of polarization curves among the many specimens tested. Each type of polarization curve corresponded to the physical appearance of the tested specimen. In other words, the TiN-coated specimens showed three levels of merit regarding corrosion resistance.

The first type of polarization curve for a TiN-coated specimen is illustrated in Fig. 6. The curve is similar to that of an uncoated specimen and suggests that pitting and localized corrosion occurred. Visual examination of the tested specimen confirmed that pitting exists, as shown in Fig. 7. Repeated tests for other coated specimens, which had as-received coating defects or indented or scratched defects, all showed a polarization curve similar to that of the uncoated specimen of Fig. 6, The post examination also showed that all pitting was initiated at the damaged areas where base metal was exposed.

The second type of polarization curve for a TiN-coated specimen is illustrated in Fig. 8. The critical pitting potential, EC, is much lower, and the passive region is smaller than those shown in Fig. 6, indicating that this specimen suffered severe localized corrosion. Visual examination of the tested specimen revealed that pitting and localized corrosion occurred. Figure 9 shows the pitting pattern after one cycle of polarization. Note that a fairly large crack also developed.

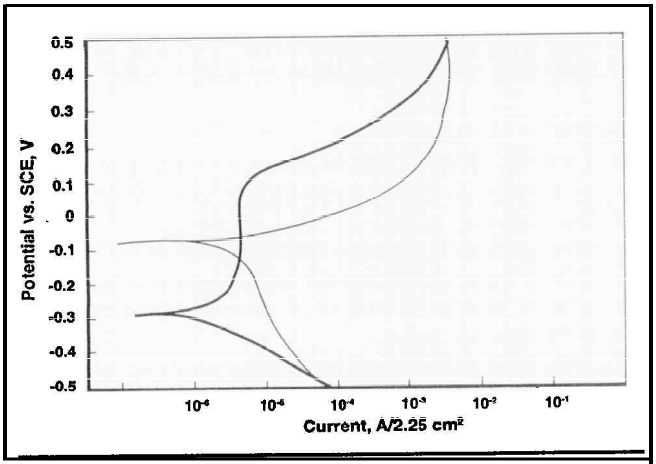


Fig. 6—Polarization curve for a T/N-coated f 74 PH specimen showing pitting at damaged areas.

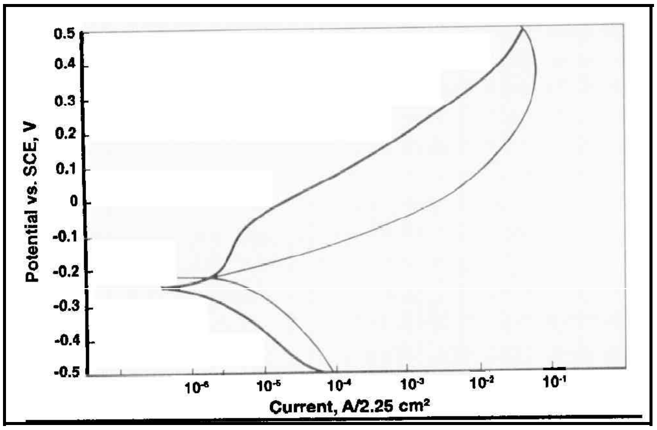
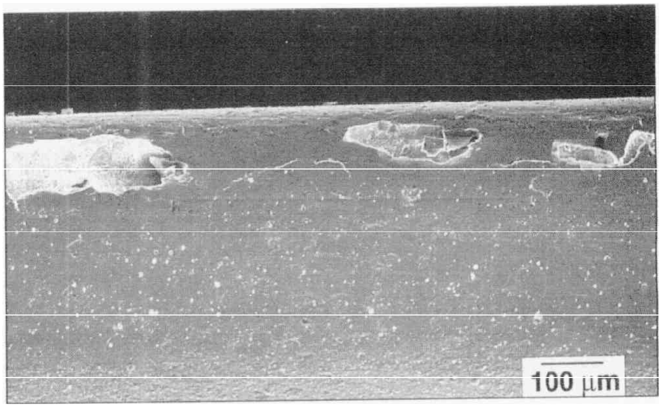


Fig. 8—Polarization curve for a TIN-coated 17-4 PH specimen showing severe pitting and localized corrosion as a result of poor coating.



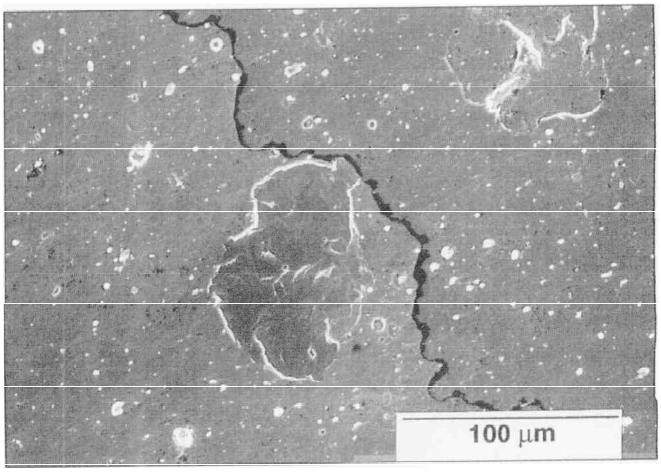


Fig. 9—Pitting and cracks on the face of a TiN-coated 17-4 PH specimen after one cycle of polarization, as shown in Fig. 8.

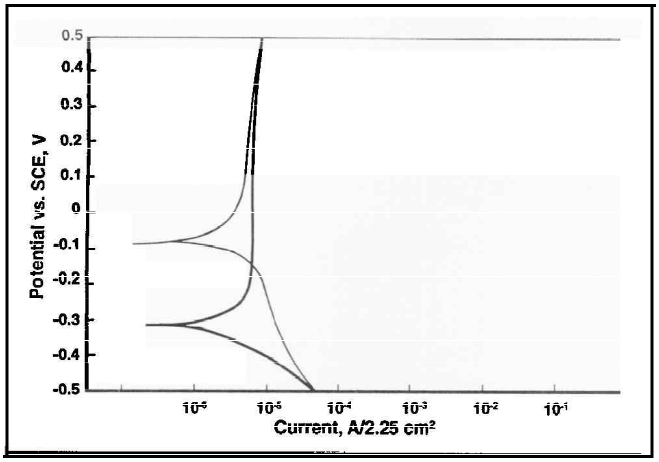


Fig. 10-Polarization curve for a TiN-coated 17-4 PH specimen showing complete passivation with no corrosion.

The third type of polarization curve for a TiN-coated specimen is illustrated in Fig. 10. No critical pitting potential, E_c, or protection potential, E_p, appears, indicating that the specimen was completely passivated and no corrosion occurred. Visual examination confirmed that this tested specimen had no staining or bare spots after one cycle. The specimen was polarized for another four cycles and still displayed the same polarization curve and surface appearance with no sign of corrosion. Repeated tests for a prechecked specimen that had no visible defects confirmed that a 17-4 PH alloy well-coated with TiN could have superior corrosion resistance in seawater.

It appears that the polarization technique can be a very useful method to evaluate the quality of TiN-coated parts. The advantages of the polarization technique are many: It is fast (takes only a few minutes); it is a full check for an entire piece; and it is a nondestructive test for a good coating. As described previously, if a coated part yields a polarization curve similar to that of Fig. 10, the part must be well-coated and may have corrosion resistance superior to that of an uncoated part.

Open Potential

Results of open circuit potential measurements made in NaCl solution are shown in Table 1. Data were based on the potentials at the end of 24-hr immersion. Potentials of either coated or uncoated specimens were unstable at the beginning of immersion, and began to show unrealistic potential after more than one day because of passive film formation or other surface damage. According to Table 1, TiN coating had an average electrochemical potential of -0.14 V vs. SCE, while 17-4 PH alloy had an average electrochemical potential of -0.07 V vs. SCE in salt water. The theory of corrosion potential says that if two dissimilar metals forma couple, the one with a more negative open potential becomes the anode and corrodes. Therefore, the base 17-4 PH alloy has no tendency to experience galvanic corrosion in salt water if it is coupled with a TiN coating. The small difference of open potentials (0.07V) between the TiN coating and the 17-4 PH alloy, as referred to the potential series of various metals in seawater,[10] suggests that little cathodic protection may be provided by the TiN coating.

The specimens set up for the open potential measurement remained in the 3.5-percent NaCl solution for as much as two months. After the two-month immersion, one TiN-coated specimen showed severe coating spalling and slight corrosion at the spalled areas; the other three TiN-coated specimens and the uncoated specimens all showed little staining or corrosion. The results indicated that the quality of TiN-coated specimens was widely scattered. Figure 11 shows the filament type of spalling developed on this specimen, together with another specimen showing no spalling. A close-up photo of the spalled area is shown in Fig. 12.

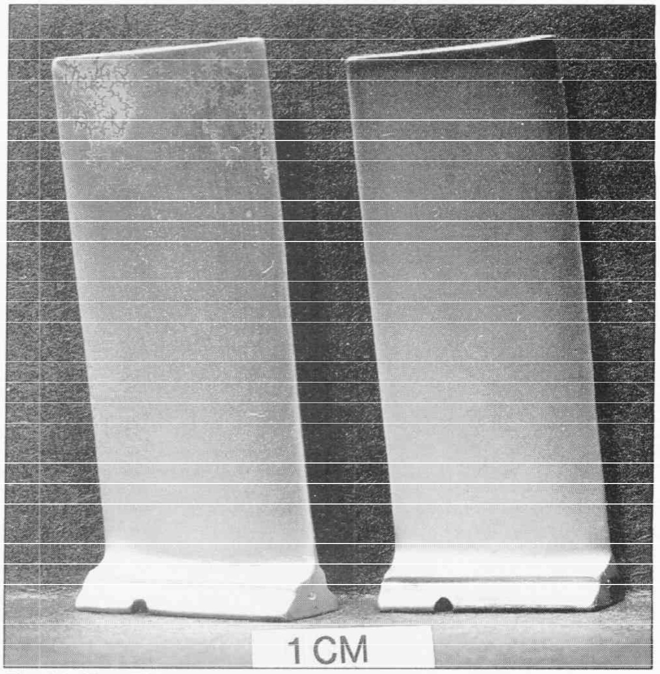


Fig. 11—Two TiN-coated specimens after a two-month immersion test in 3.5% NaCl solution, showing spalling at left and illustrating dramatically different coating qualities of TIN.

Table 1
Potentials vs. SCE of TiN Coated and Uncoated 17-4 PH Specimens After 24 hr Immersion in NaCl Solution

Specimen		Potential (V)	Average (V)
TiN Coating	1	-0.12	
	2	-0.05	
	3	-0.13	-0.14
	4	-0.25	
	5	-0.11	
	6	-0.16	
17-4 PH	1	-0.07	
	2	-0.07	-0.07
	3	-0.07	

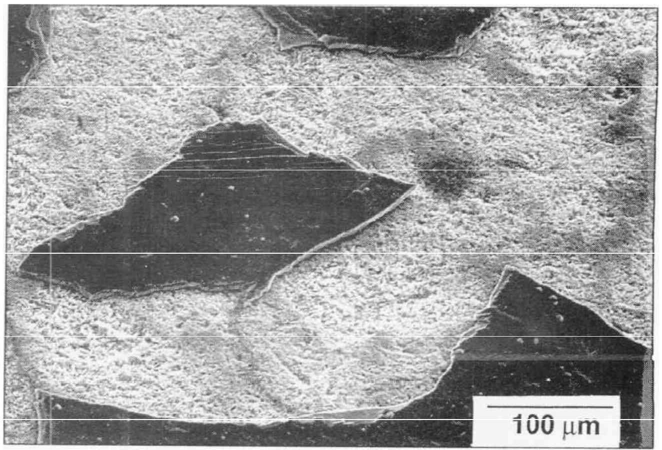


Fig. 12-Close-up of the spalled area of Fig. 11.

Table 2
Result of Galvanic Current Measurements

Test no.	Area of 17-4 PH, cm^2	Area of TiN, cm^2	Galvanic current, µA Start	End	Coulombs in 24 hr, 10^{-3}Q
1	1	30	-1.2	-0.2	-22.0
2	2	36	-0.6	+0.02	-8.5
3	1	8	+0.5	-0.3	-10.4
4	6	6	0	-0.2	-13.0
5	8	8	+0.3	0	+0.7

In a separate immersion test of predamaged specimens, no sign of staining or corrosion occurred in the damaged areas in as much as two months of immersion. The TiN coatings around the damaged spots were still intact. A similar result was observed in the salt spray test to be discussed later.

Galvanic Corrosion Current

Table 2 summarizes the data obtained from the galvanic corrosion current measurement. The area ratio of 17-4 PH metal to the TiN coating varied from 1:30 to 1:1. In the present set-up, a positive current means that the 17-4 PH metal had a tendency to corrode when coupled with the TiN coating.

Tests No. 3 and 5 began with positive current, which was reduced to zero or negative current after approximately one hr. Tests No. 1 and 4 had negative current continuously. Test No. 2 maintained a negative current in most of the 24 hr, but switched to a very low positive current toward the end. Overall, Table 2 suggests that the TiN coating was undergoing a slow rate of corrosion/oxidation when it was coupled with the 17-4 PH alloy.

The area ratio seems to have no significant effect on the corrosion rate, as Table 2 shows. This is because the TiN coating was the surface undergoing corrosion; its area was either larger or equal to that of the 17-4 PH metal. It must also be pointed out that the corrosion reaction of the TiN coating might be a type of oxidation rather than a physical dissolution of the TiN.

Salt Spray

In the 15-day test, the results of the as-received coated specimens were widely scattered, based on visual examination. Some coated specimens showed various degrees of staining or pitting/localized corrosion, while some remained intact. In comparison, only a few uncoated specimens displayed minor staining; most were unattached. Apparently the coated specimens behaved irregularly in the salt spray test, even among those prepared by the same source. Those results revealed one notable fact–some poorly prepared TiN-coated 17-4 PH alloy may corrode faster than uncoated alloy.

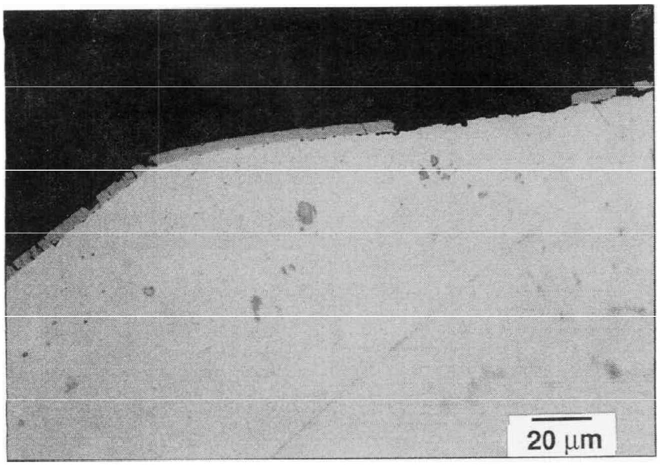
In the two-month test of the predamaged coated specimens, no sign of staining or pitting appeared at the damaged areas, similar to results obtained in the two-month immersion test. Figure 13 shows a cross section of an indented spot area, indicating that no corrosion occurred at the open spots where the TiN coating was broken.

The results of the three tests for evaluating the predamaged coated specimens, including polarization, immersion and salt spray, are consistent. It may be concluded that the damaged TiN coating will not degrade the corrosion resistance of the base metal, and the remaining coating is still capable of protecting the covered substrate.

Discussion

Based on the results obtained in this study, it is fair to say that all the as-received TiN-coated specimens had widely varying quality. Good coatings can significantly enhance the corrosion resistance of 17-4 PH alloy, even if minor defects are present; the exposed bare spots show little sign of accelerated corrosion, compared to an uncoated specimen. Bad coatings, however, can cause substantial pitting or localized corrosion of the 17-4 PH alloy. The significant question becomes What makes a TiN-coated specimen corrode faster than an uncoated specimen? To answer this question, a thorough investigation of the tested and corroded specimens is essential.

Figure 14 shows a typical corroded pit on a TiN-coated specimen after a 15-day salt spray test. The pit was opened up, under low magnification, by crushing the remaining TIN



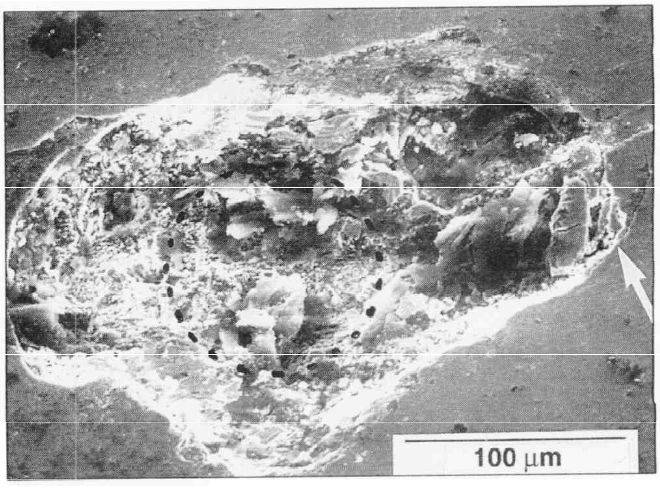


Fig. 14—Typical corrosion pit, pressed and opened up, on TiN-coated 17-4 PH specimen after 15-days salt spray test. Dotted circle indicates original pit.

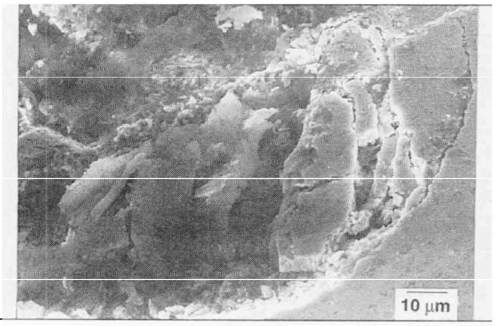


Fig. 15-Close-up of the location in Fig. 14 indicated by arrow.

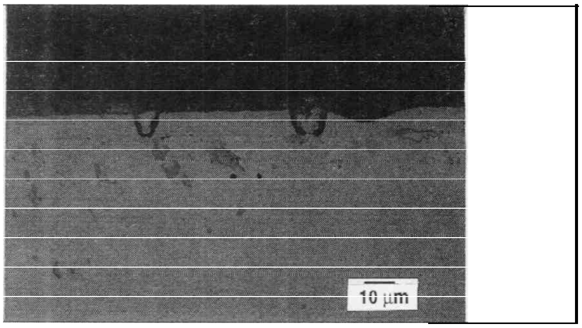


Fig. 16—Profile of pinholes on specimen after 15-day salt spray test, showing little corrosion and no crevices at bottoms of pinholes.

layer around the original pit. Some broken TiN pieces still remain. A much higher magnification, at the location indicated by the arrow, is shown in Fig. 15, which clearly indicates that, *under* the original TiN coating, there was a loose or hollow area generated by corrosion. Figures 14 and 15 imply that crevice corrosion occurred on 17-4 PH alloy under the TiN coating.

According to published literature,[11] 17-4 PH alloy is susceptible to crevice corrosion in a seawater environment. A preliminary crevice corrosion test was conducted by partially taping an uncoated specimen, then immersing it in a 3.5-percent NaCl solution. The areas under the loose tape corroded after a few days, which confirmed that 17-4 PH alloy is susceptible to crevice corrosion in a seawater environment. Therefore, if a crevice is formed between the TiN coating and the metal surface, and this crevice is connected to an open spot (formed either by crack or coating pinhole), allowing NaCl solution to penetrate it, crevice corrosion will propagate.

If crevice corrosion is the dominant form of corrosion of TiN-coated 17-4 PH alloy, then the reason that an intentionally pre-damaged coating had no effect on the corrosion of the base metal is easy to explain. It must be that no crevices were generated when the TiN coating was damaged by indentation or scratching. Consequently, strong adhesion between the TiN coating and the metal surface is critical for good corrosion protection.

The reasons why a crevice forms are not clear, but impurities between the coating and the metal surface, and the high residual stress of the coating could be the two major factors. The opened spots that allow NaCl solution to enter the crevices are attributed to the spitted titanium particles, as well as to crack formation.

Tiny pinholes alone, even if they are open down to the base metal, may not cause severe corrosion if there are no crevices connecting the pinholes. Figure 16, a profile of pinholes from a specimen tested 15 days in salt spray and showing pitting and localized corrosion in some areas, indicates that little corrosion developed, and that no crevices were present around the pinholes.

Conclusions

The test results were sufficient to confirm the following conclusions:

- The polarization technique is a useful method to evaluate the quality of TiN coating on 17-4 PH stainless steel with respect to corrosion resistance.
- A good TiN coating can provide superior corrosion protection for 17-4 PH alloy.
- Predamaged TiN coating of a well-coated part had no effect on the corrosion of 17-4 PH alloy; the exposed bare spots simply behaved like the 17-4 PH alloy itself.
- No tendency for galvanic corrosion was evident when the 17-4 PH alloy was coupled with a TiN coating and exposed to NaCl solution.
- The 17-4 PH alloy is susceptible to pitting and crevice corrosion in NaCl solution.
- Open pinholes/cracks that connect with crevices (poor adhesion) between the TiN coating and the base metal surface are the major factors causing a poor coating and severe corrosion.

References

1. R.L. Hatschek, *Amer. Machinist,* 129, (Mar., 1983).
2. A. Raman, G. Nnaike, A. Choudhury and C. Das, *Corrosion Science,* 25(2), 107 (1985),
3. A. Erdemir, W.B. Carter and R.F. Hochman, Mat. *Sci. and Eng.,* 69, 89, (1985).
4. El. Meletis, W.B. Carter and R.F. Hochman, *Microstructure Science,* 13, 417 (1986).
5. S. Motojima and M. Kohno, *Thin Solid Films,* 137, 59 (1986).
6. ASTM Standards, Vol. *03.02,* G3, G5 and G61, 1988.
7. ASTM, ibid., G71.
8. S.R. Brown and J.J. Deluccia, *Proc. Conf. on Environmental Degradation of Engineering Materials,* Virginia Polytech. Inst., Blacksburg, 277(1978).
9. M.S. Walker, *Mat. Performance, 18(4),9(1979).*
10. *Metals Handbook* 9th Ed., 13, ASM International, Metals Park OH, 1987 p. 235.
11. F.L. Laque. *Marine Corrosion Causes And Prevention.* John Wiley & Sons, New York, NY, 1975; p. 173. “’

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