Role of Surface Finishing on Pitting Corrosion of a Duplex Stainless Steel in Seawater

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Localized corrosion of duplex UNS S32550 stainless steel in seawater was investigated in the laboratory and in field trials for several surface finish conditions: polished, ground, and sandblasted. Electrochemical data obtained by polarization curves showed that the smoother, polished surface had better characteristics (higher pitting and protection potentials) than the ground or sandblasted surfaces. However, despite its high degree of roughness, the sandblasted surface was the most resistant in field conditions, exhibiting the lowest number of sites attacked. Internal compressive stresses created by sandblasting seem also to have an "unsensitizing" effect on sensitized zones that exist in cast steel (due to repairs of mold defects), reducing its susceptibility to microbiologically influenced corrosion (MIC). Such stresses are not generated in polished or ground surfaces, and localized MIC attack can occur.

Keywords

duplex stainless steel, electrochemical testing, field testing, grinding, microbiologically influenced corrosion (MIC), sandblasting, seawater

1. Introduction

DUPLEX stainless steels have been used for fabrication of a circulating seawater pump in a thermal power plant because other classes of stainless steels, such as austenitic, proved unsatisfactory (Ref 1). Duplex stainless steels combine excellent corrosion resistance with high mechanical properties, good weldability, and good castability (Ref 2, 3), making them adequate candidates for marine applications.

The addition of nitrogen to second-generation duplex stainless steels ensures an α/γ ratio of 50:50, which improves localized corrosion resistance by lowering α/α sensitive grain boundaries (Ref 4, 5). However, pitting corrosion in duplex UNS S32550 has occurred, especially in the impeller and discharge bowl parts of the pumps. Pit morphology is shown in Fig. 1.

Wrought and cast pump components of duplex UNS S32550 showed different corrosion resistance; a wrought shaft with a low roughness surface was not attacked, whereas other ground cast components suffered severe localized corrosion. Thus, the thermal history and surface condition of the steel appear to be important factors.

In this study, cast duplex UNS S32550 stainless steel with several surface finishes was tested under both laboratory and field trial conditions. The objective was to show the effect of surface preparation—polishing, grinding, and sandblasting—on localized corrosion of this steel. The role of a sensitized zone due to casting repairs was also seen in relation to surface conditions.

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2. Experimental Procedure

2.1 *Material Composition and Surface Preparation*

The cast duplex stainless steel studied was a second-generation commercial grade. Its composition was almost identical to that of ferralium 255 (UNS S32550) (Table 1).

The steel had been water quenched from 1100 °C after molding. Samples used for this study contained repairs of mold defects. Welded and heat-affected zones identified by optical microscopy are shown in Fig. 2. The approximate roughness factor was identified for each surface finish condition (Table 2).

2.2 *Laboratory Tests*

Electrochemical polarization tests were conducted in both synthetic ASTM D 1141-86 seawater and natural seawater. Samples of seawater were taken from the Mediterranean Sea near the northeastern Tunisian coast. Because of the proximity

Table 1 Duplex stainless steel composition (UNS S32550 type)

Element	Weight percent
Carbon	0.05
Silicon	0.65
Manganese	0.67
Chromium	24.94
Molybdenum	2.68
Nickel	6.68
Nitrogen	0.17
Copper	2.5

Table 2 Surface preparation and correspondent roughness of duplex stainless steel samples

Surface preparation	Roughness, μm
Polishing on 80-grit SiC	0.55
Ground mill finish	1.13
Sandblasting	3.36

(a) (b)

Fig. 1 Morphology (a) and actual dimensions (b) of localized corrosion attacks of duplex stainless steel as seen on the discharge bowl of the circulating pump

Table 3 Natural seawater analysis

Salinity, g/L	40.46
SO_4^{2-}, g/L	2.85
Cl^-, g/L	21.7
H_2S (deep sea), ppm	0.34
S^{2-} (deep sea), ppm	0.32
pH	8.3

of a port where merchant ships load and unload, natural seawater in this area can be classified as polluted (Ref 6).

An analysis of the natural seawater is given in Table 3. Samples of natural seawater were used within one week after their pickup.

In order to determine E_{pit} (pitting potential) and E_{corr} (corrosion potential), polarization curves were recorded from −1500 to +1500 mV at a scanning rate of 1 mV/s. E_{prot} (protection potential) was obtained by the reverse scan at the same rate.

All potentials are referred to a saturated calomel electrode (SCE). Specimens for these tests were 60 to 80 mm^2 in area.

2.3 *Field Tests*

In order to obtain data on the role of surface finishing in the corrosion behavior of the duplex stainless steel under real conditions, 90 by 90 by 10 mm samples were immersed 5 m deep in the field near the circulating pump for 4 months. Sites where pitting attack could be observed were counted after 28, 58, and then 118 days of immersion. At the end of the fourth month, samples were removed and cleaned, and dimensions (depth and diameter) of pitting attack sites were measured.

Microstructural investigations via an optical microscope were conducted after polishing and chemical attack using a solution of 50 mL HNO_3, 100 mL HCl, and 450 mL ethanol. The two faces of each sample were identified as A and B (Fig. 3).

3. Results and Discussion

3.1 *Potentiodynamic Measurements in Synthetic and Natural Seawater*

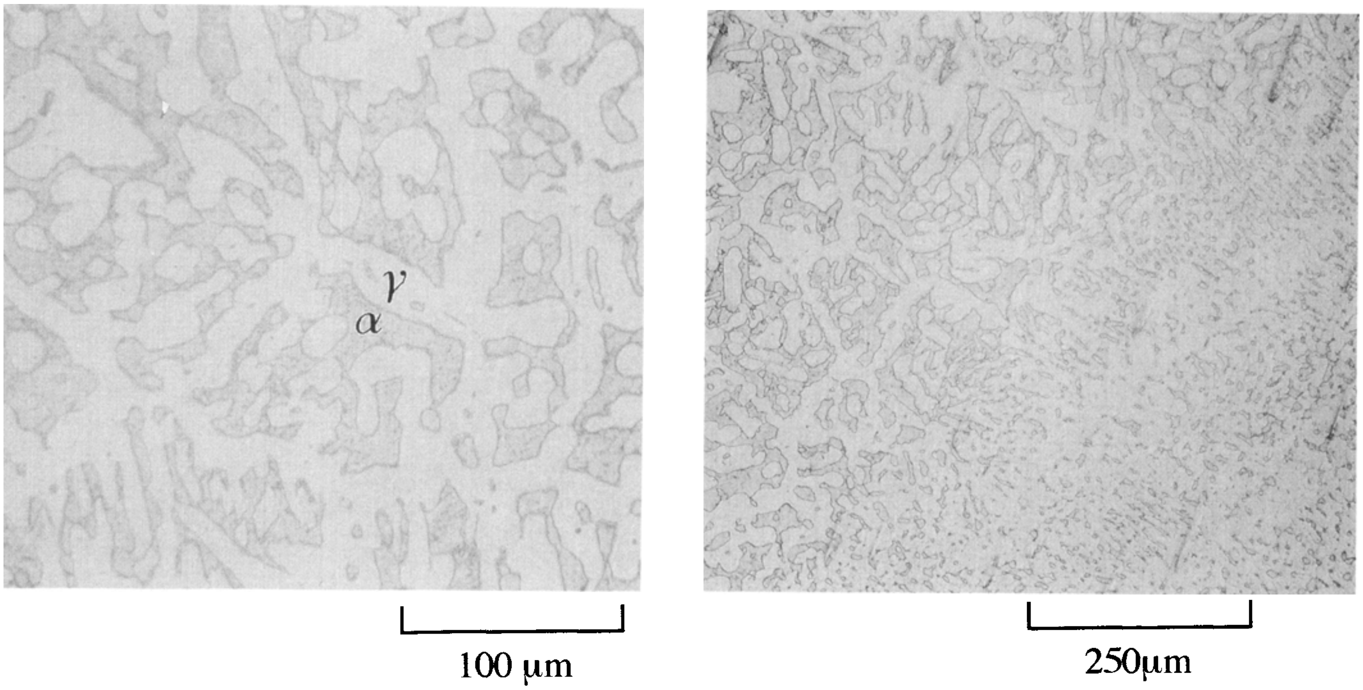
Cyclic polarization curves obtained for each surface finish in synthetic and natural seawater are shown in Fig. 4 to 6. Data obtained from these plots are summarized in Table 4.

The pitting potential (E_{pit}) decreased when roughness increased in both synthetic and natural seawater. Even though the polished surface was more active than the ground or sandblasted surfaces, this state had a greater tendency to repassivate in either synthetic or natural seawater, as shown by the value of E_{prot}.

Sandblasted and ground surfaces had comparable E_{pit} and E_{prot} values in synthetic seawater. However, in natural seawater the sandblasted surface seemed to act worse despite its less active corrosion potential (E_{corr}). In addition, it exhibited an active zone in the polarization curve (I_{corr} ~ 70 $\mu A/cm^2$).

3.2 *Pitting Corrosion in Field Conditions*

Results of the field trial are summarized in Table 5 and Fig. 7. The histogram (Fig. 7) shows how many pits up to 0.5 mm deep each sample exhibited in faces A and B.



(a) (b)

Fig. 2 Microstructure of the duplex stainless steel (ferrite + austenite). (a) Base metal ($\alpha/\gamma = 0.5$). 250×. (b) Interface of the base metal and the repaired zone ($\alpha/\gamma > 0.5$). 100×

3.2.1 Role of Surface Finishing

The sandblasted surface exhibited the greatest resistance to pitting corrosion under field trial conditions. The number of sites attacked did not increase between the first observation (28 days after immersion) and the last one. In contrast, the number of sites attacked increased regularly for the ground mill finish surface. In the polished surface, pits appeared later in comparison with the ground one, but their maximum depth was greater by the end of the fourth month. It is clear that pits initiate more readily in the ground surface than in the polished one, but they propagate more slowly.

Note that the ground surface also became extremely rusted, whereas the polished and sandblasted surfaces maintained a good appearance. This means that the ground rough surface, which exhibited several microanodes and microcathodes, had difficulty passivating despite the intrinsic high passivation capability of the duplex stainless steel. This result corroborates potentiodynamic measurements which show that ground surfaces cannot repassivate in natural seawater ($E_{prot} = 70$ mV). This fact has been observed in other studies on type 316L stainless steel (Ref 7) where surface grinding had a detrimental effect on the initiation and growth of localized corrosion in seawater.

In contrast, the polished surface, which passivated easily, exhibited a high level of pit growth. The sandblasted surface, however, which had the highest roughness, showed neither uniform nor high localized corrosion.

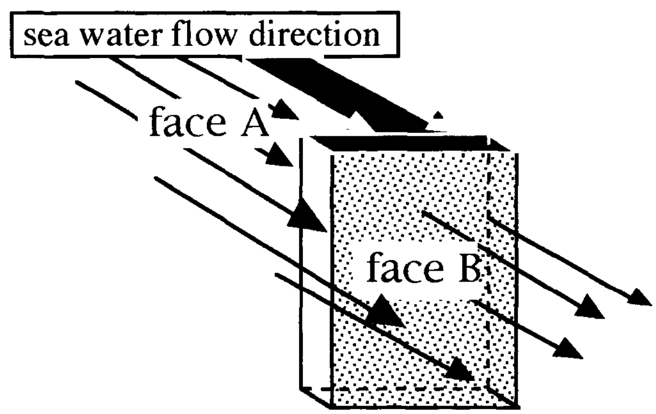


Fig. 3 Identification of faces A and B of field test samples

The strain hardening of superficial layers induced by the mechanical compression stresses generated by sandblasting impact seems to play a significant role in corrosion resistance. Other authors have noted that shot peening has a similar effect on the resistance of an austenitic stainless steel to intergranular corrosion (Ref 8).

In general, compressive stresses enhance resistance to stress corrosion cracking (SCC) because they reduce the applied tensile stress and thus reduce corrosion (Ref 9). However, they also seem to directly affect structure on the atomic scale.

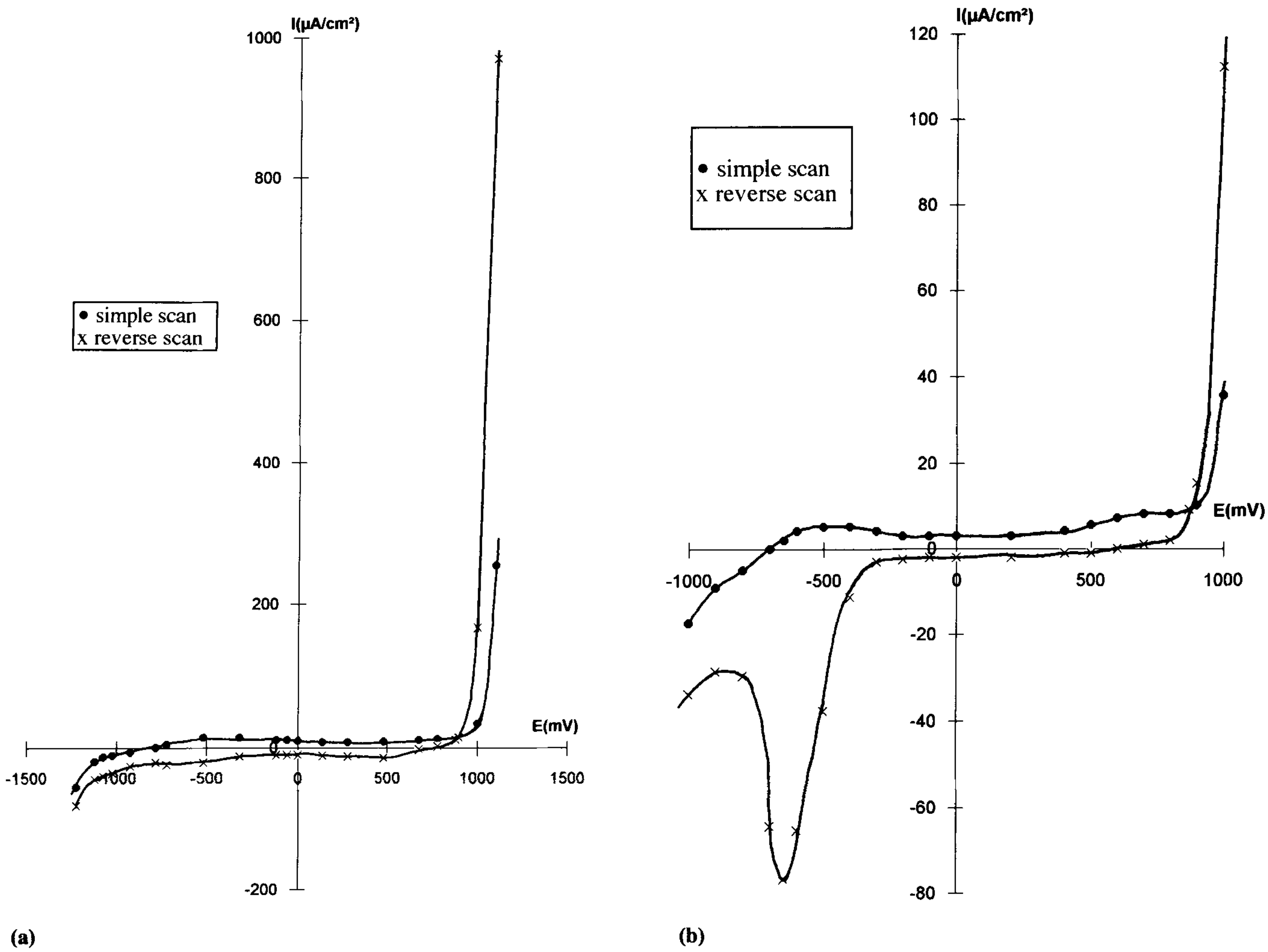


Fig. 4 Cyclic polarization curves for the polished surface of duplex stainless steel in synthetic (a) and natural (b) seawater

Table 4 Results of cyclic polarization tests in synthetic and natural seawater

Surface condition	Roughness, µm	Potential, mV(SCE) Synthetic seawater E_{pit}	E_{prot}	E_{corr}	Natural seawater E_{pit}	E_{prot}	E_{corr}
Polished	0.55	1000	900	−780	1000	870	−700
Ground	1.13	900	−180	−450	900	−70	−610
Sandblasted	3.36	900	−130	−660	880	...	−540

Table 5 Pitting corrosion data for duplex stainless steel under field conditions

Surface condition	Face	After 28 days Number of sites attacked(a)	After 58 days Number of sites attacked(a)	After 4 months Number of sites attacked(a)	After 4 months Maximum depth, mm	Surface aspect
Polished	A	0	3	8	4	Good
	B(b)	0	1	3	2	Good
Ground	A	6	11	22	2	Corrosion products
	B(b)	5	19	19	1.5	Corrosion products
Sandblasted	A	0	0	0	...	Good
	B(b)	1	1	1	2	Good

(a) Includes pits with depth of less than 0.5 mm. (b) Fouling deposits developing

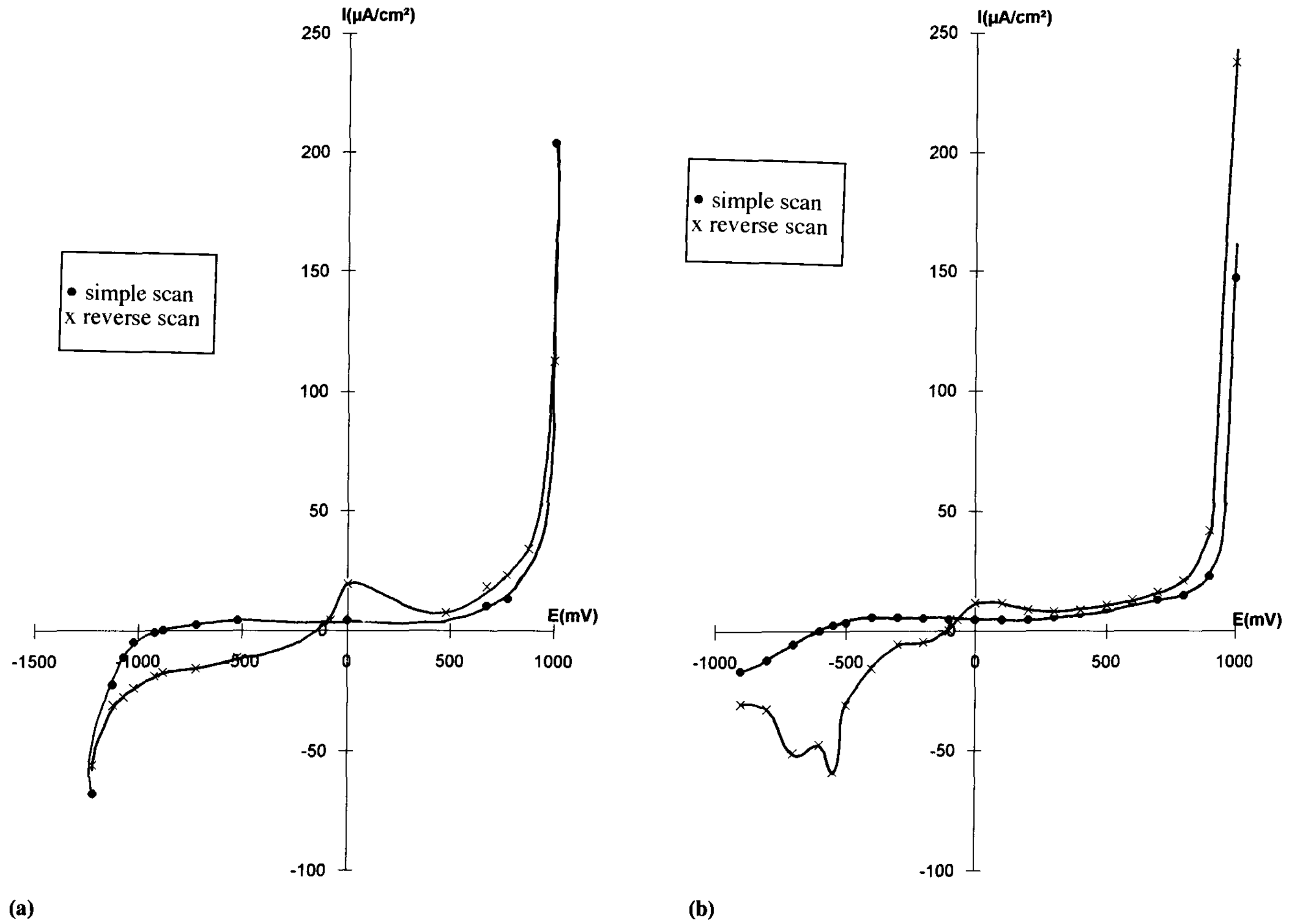


Fig. 5 Cyclic polarization curves for the ground surface of duplex stainless steel in synthetic (a) and natural (b) seawater

We believe that there is a synergistic effect between the substructure of the duplex stainless steel and the surface compressive stresses. As a matter of fact, according to results developed by us elsewhere (Ref 10), a nonstandard austenitic stainless steel (UNS S31726) tested under conditions similar to those of this study, showed no resistance to localized corrosion in the sandblasted condition.

However, results of field testing seem to be contradictory to electrochemical results, which have shown that sandblasting is not the best method of surface finishing with regard to localized corrosion in both synthetic and natural seawater. But we believe that despite the extreme care with which sampling was carried out for electrochemical tests, internal metastable compressive stresses introduced by sandblasting were relaxed. In addition, seawater samples picked up for electrochemical tests were used within one week, probably a time delay sufficient to change the makeup of their biological life (bacteria, microorganisms).

3.2.2 Role of Flow Rate

Faces A and B of all samples were subjected to different flow conditions. Face A faced the flow, while face B was in a quasi-stagnant condition. Nevertheless, in general face B exhibited greater corrosion resistance. Observations of the surfaces revealed thin fouling deposits, which seem to have been a barrier to further attacks. These deposits consisted of long and thin shellfish that adhere tightly to the steel surface. All pits observed had developed where this fouling had not been deposited. This phenomenon has been observed on the circulating pump under actual service conditions (Ref 11). On the ground surface, the mechanism of corrosion seems to have occurred more rapidly than the development of fouling deposits that are unable to arrest corrosion.

3.2.3 Morphology and Localization of Pits

Pit morphology was characterized by a small surface opening and a large subsurface cavity associated with localized deposits of corrosion products (Fig. 8), similar to those observed on the discharge bowl of the circulating pump (see Fig. 1). This type of pit has been reported by other authors on austenitic stainless steels when microbiologically influenced corrosion (MIC) occurred (Ref 12, 13). It is certain that our tests involved MIC since they were conducted in seawater. These same authors have observed that MIC occurred in combination with SCC and/or sensitized structures. This can explain two fundamentals of our work:

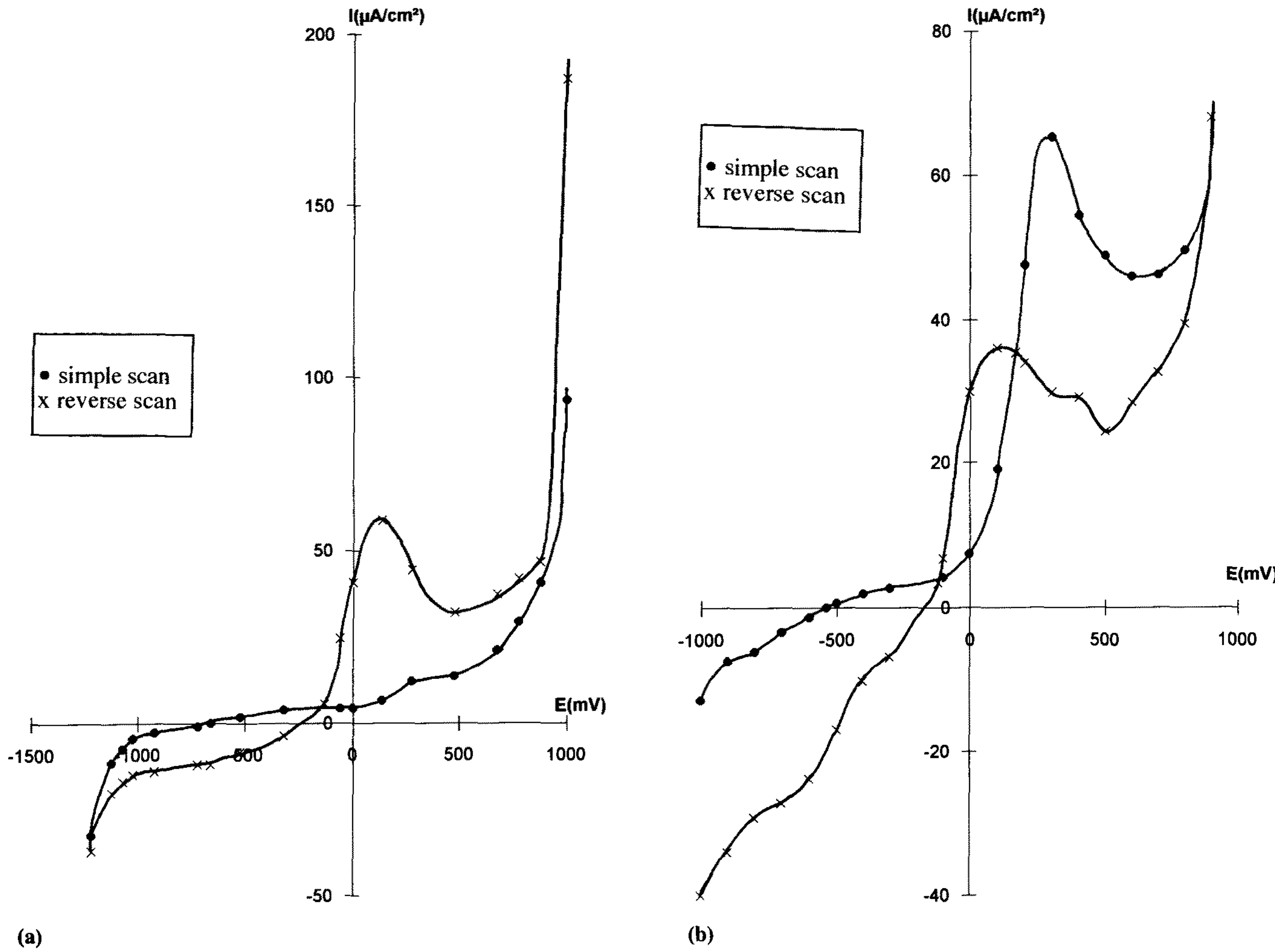


Fig. 6 Cyclic polarization curves for the sandblasted surface of duplex stainless steel in synthetic (a) and natural (b) seawater

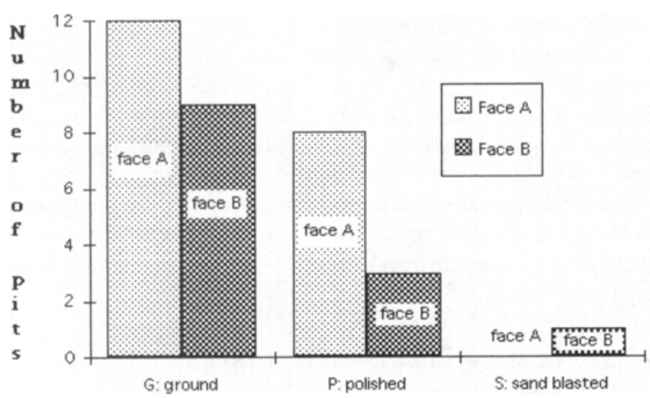


Fig. 7 Number of pits (depth ≥ 0.5 mm) versus surface and flow rate (A and B) conditions

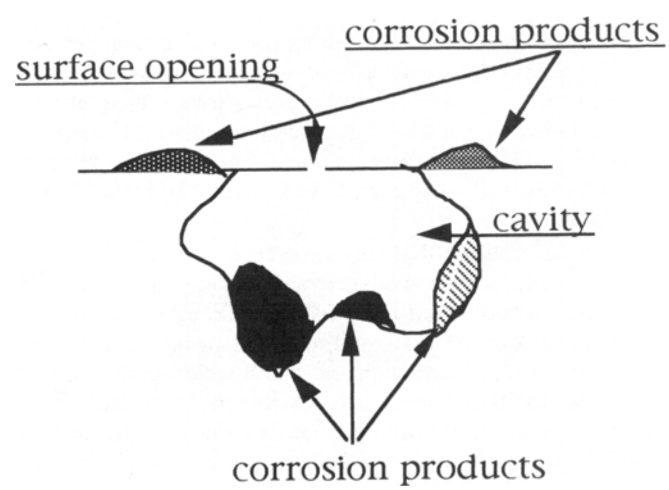


Fig. 8 Pit morphology

- Sandblasted surfaces with compressive stresses that enhance resistance to SCC become resistant to MIC.
- Sensitized zones in the other samples that can resist conventional chloride corrosion cannot resist MIC.

Metallographic examinations of zones adjacent to pits revealed that α/γ boundaries are preferentially attacked (Fig. 9), propagation occurring first in the ferritic phase. Selective electrolytic attack with 40% NaOH solution revealed the precipitation of a secondary phase within α/γ boundaries (Fig. 10), which means that corrosion has occurred in sensitized zones. In this kind of stainless steel, the only intergranular phase that can precipitate is either $M_{23}C_6$ or σ phase (Ref 5, 14). In sand-

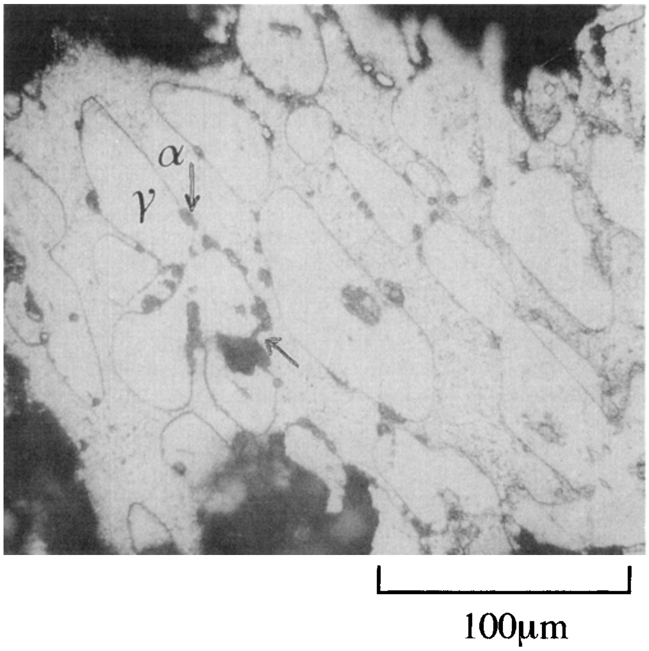


Fig. 9 Localization of pits in α/γ boundaries

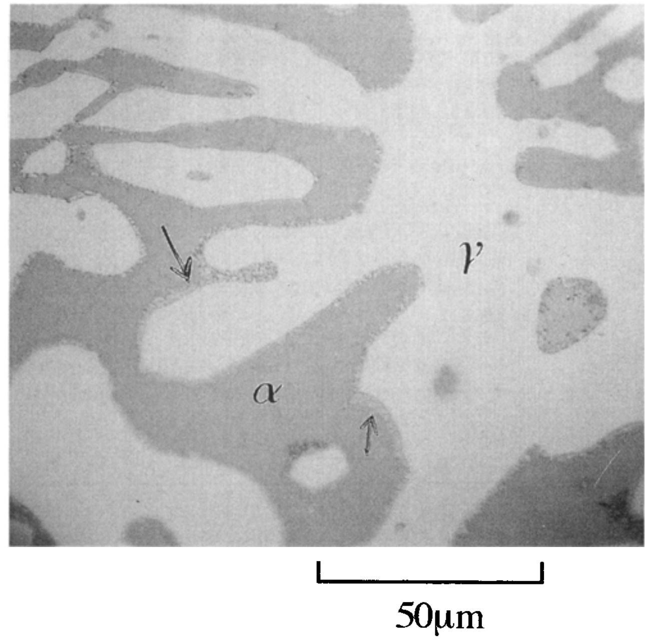


Fig. 10 Precipitation of secondary phase in α/γ boundaries (40% NaOH electrolytic attack)

blasted samples, the existence of sensitized zones does not seem to be detrimental to the localized corrosion resistance.

4. Conclusions

Mechanical surface finishing of cast and repaired UNS S32550 duplex stainless steel was found to decrease its localized corrosion resistance in natural seawater when surface roughness increased. However, when the mechanical treatment introduced compressive stresses, as was the case for sandblasting, the duplex stainless steel became unsensitive to localized MIC attacks. Unlike field tests, polarization curves conducted in the laboratory were unable to duplicate the beneficial role of sandblasting.

Acknowledgments

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