Surface Protection of Type 316LN in Neutral Chloride Solution

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The article presents the results of the effect of different surface finishes obtained by mechanical polishing and chemical treatments on the pitting corrosion resistance of Type 316LN stainless steel (SS) (UNS S37653) in 0.5 M sodium chloride (NaCl) solution. An increase in the pitting corrosion resistance with a decrease in surface roughness and a further enhancement owing to pickling and passivation was inferred. The passive effect of chromium in enhancing pitting corrosion resistance was confirmed by auger electron spectroscopy.

Type 316LN austenitic stainless steel (SS) (UNS S37653) has been chosen as the primary material of construction for the Prototype Fast Breeder Reactor (PFBR) to be built in Kalpakkam, India. The alloy has been indigenously developed and it is essential to document its corrosion properties. As Kalpakkam is a coastal area, the SS material is susceptible to localized pitting corrosion. The SS components of PFBR will be stored in a coastal atmosphere and the condensation of seawater would lead to pitting of such components. It is essential to avoid pitting in these components through corrosion protection methods, as the surface grinding required for removing such pits would introduce significant residual stress at the surface of the component.

Following the production of SS sheets, or after fabrication of the components, nitric acid (HNO_3)-based pickling or passivation treatments are often applied. A pickling treatment removes the surface inhomogeneities such as inclusions, high-temperature scale, surface contaminants, and any adjacent chromium layer of metal, and passivation favors the formation of a passive film. Generally, passivation is performed in 20 to 40% HNO_3 solutions at temperatures from 293 to 343 K.[1] This article presents the effect of mechanical and chemical treatments of the surface on the pitting corrosion resistance of Type 316LN SS in 0.5 M sodium chloride (NaCl) solution.

Experimental Work

Pitting Corrosion Study

Table 1 gives the chemical composition of Type 316LN SS used for the study. Solution annealed specimens (10 by 10 by 10 mm) were mounted in an araldite resin with sufficient care to avoid crevice attack during polarization. Mechanical treatment of the surface was done by

TABLE 1
Chemical composition of Type 316LN SS (wt%)

Grade Type	C	Mn	S	P	Si	Ni	N	Cr	Mo	Fe
316LN	0.020	1.76	0.01	0.03	0.5	12.09	0.076	17.93	2.43	Balance

TABLE 2
Pitting potentials after various surface treatments

Surface Finish Methods	Surface Roughness (μm)	Pitting Potential (mV)		
		Mechanical Treatment	Chemical Treatment	
			Pickling	Pickling Followed by Passivation
Diamond cloth finish	0.009	394	672	1,114
600 grit SiC abrasive polishing	0.05	326	651	1,040
320 grit SiC abrasive polishing	0.07	307	637	1,000
Lathe finish	0.5	152	631	865

1) wet grinding with 320 and 600-grit emery silicon carbide (SiC) abrasive paper, 2) polishing to a diamond finish, and 3) turning the sample surface on a lathe. Surface roughness measurements of the mechanically treated surfaces were carried out using a profilometer (Table 2).

These samples were then subjected to chemical treatment. Pickling was performed by immersing in 20% HNO_3/3% hydrofluoric acid (HF) mixture for 30 min and rinsed with distilled water. Following pickling, a passivation treatment was given in 20% HNO_3 for another 30 min at room temperature.[2] The samples were then subjected to anodic potentiodynamic polarization in 0.5 M NaCl under Argon purging, using a Model PGSTAT 30 Autolab Electrochemical System[†]. The experiments were repeated at least three times to check for reproducibility. The details of the experiments are given elsewhere.[3-4]

Auger Electron Spectroscopy Studies

The compositional analysis of the as-polished, pickled, and pickled/passivated surfaces was done by auger electron spectroscopy (AES). The measurements were carried in a vacuum of about 10^{-10} torr using an OMICRON CMA[†] (cylindrical mirror analyzer) having an energy resolution of 0.4%. The samples were sputtered for one minute, using an Ar + ion beam energy of 1 keV, and the AES surface analysis was made with beam energy fixed at 3 kV and beam current at 1 μA.

Results and Discussion

Figure 1 shows the polarization curves for Type 316LN SS in 0.5 M NaCl after various mechanical treatments. It was observed that the diamond-finished surface (0.009 μm roughness) exhibited the highest pitting potential (394 mV), while the lathe-finished surface (0.5 μm) exhibited the least pitting potential (152 mV). The pitting potentials of the SiC emery-finished surface fell between those for diamond and lathe-finished surfaces. A finer surface reduces the number of sites available for pit initiation, which reduces the probability of pitting and increases the pitting potentials. It was found that the combination of an electrochemically active site (inclusion) and a depression in the metal surface is required at a site for a metastable pit to be initiated. The depression acted as a barrier to diffusion of dissolved corrosion products, protons, and Cl^- ions from the pit site. When the surface roughness was greater, it was more likely that an electrochemically active inclusion was associated with a concavity in the surface that was deep enough to support pit initiation by generation of the diffusion barrier. A greater surface roughness increased the number of available pit sites, even for a given distribution of inclusions. When the surface roughness was lower, the inclusions could not act as pit sites because their depression into the surface was not great enough to provide an adequate diffusion barrier.[5] Figure 2 shows the polarization curve for the specimens initially mechanically treated and further subjected to pickling treatment. The lathe-finished surface showed a substantial increase to a value of 631 mV after pickling. A further increase to a value of 865 mV was observed after pickling-passivation treatment for the pickled/passivated surface as shown in Figure 3. A similar enhancement in the pitting corrosion resistance was observed for the samples with other surface finishes. The enhancement in the pitting potentials was more profound in the 320-grit, 600-grit emery-finished, and diamond-polished surfaces. Surface roughness had no significant effect on the pitting potentials after chemical treatments, however. Table 2 summarizes

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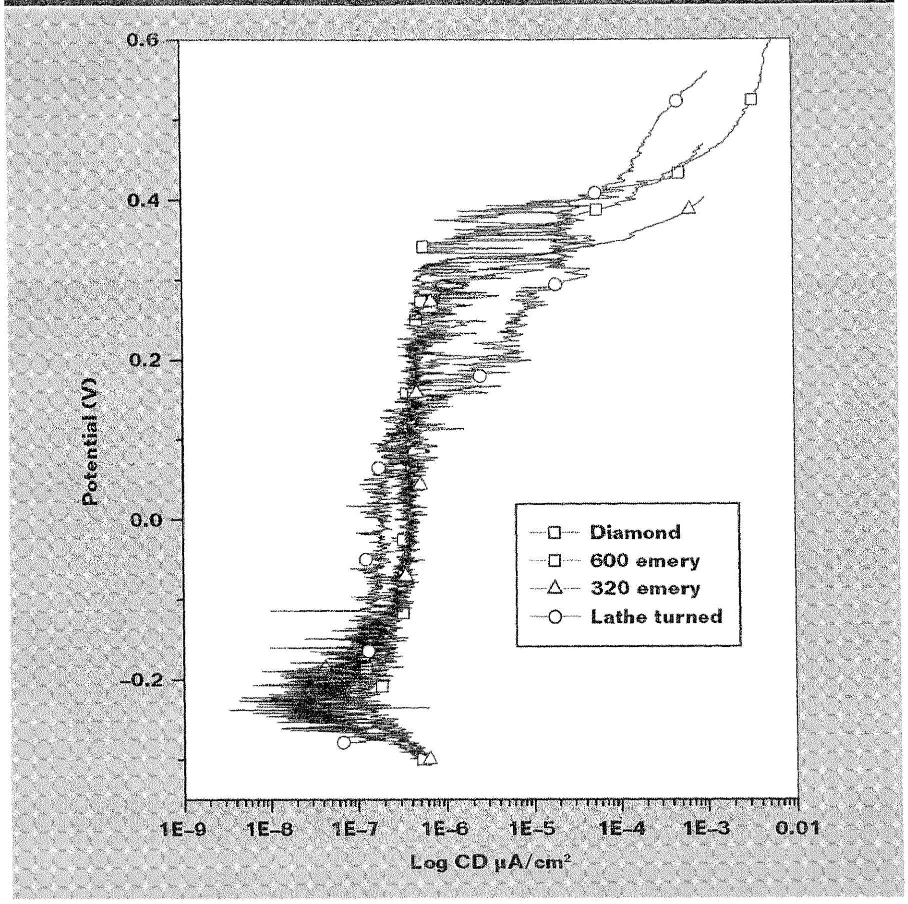
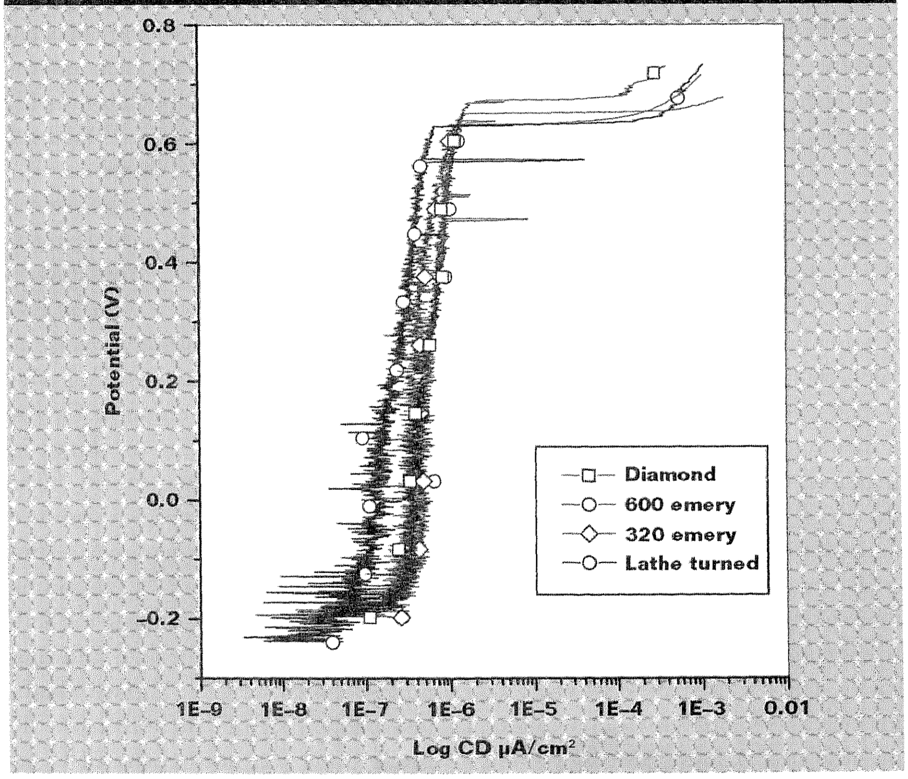
[†] Trade name.

FIGURE 1



Polarization curves in 0.5 M NaCl for Type 316LN SS after mechanical treatments.

FIGURE 2



Polarization curves in 0.5 M NaCl for Type 316LN SS after pickling.

these results. Several authors have reported that pickling yields a higher corrosion resistance compared to mechanical polishing.[6-9] The ennoblement in the pitting corrosion resistance of chemically treated surfaces can be attributed to several factors.

Removal of surface irregularities, mainly inclusions, from the metal surface is important. In Type 316 SS (UNS S31600), ~70 to 80% of the inclusions are sulfides or mixed sulfide/oxide particles.[10] The majority of the results on pit initiation on SS indicate that sulfide inclusions, especially manganese sulfide (MnS) particles, act as preferential sites for attack. The major beneficial effect of pickling has been associated with the removal of these inclusions.[10] Since MnS is thermodynamically unstable below pH 5, it is rapidly attacked by HNO_3 according to this reaction:

$$MnS + 2\,H^+ = Mn^{2+} + H_2S \qquad (1)$$

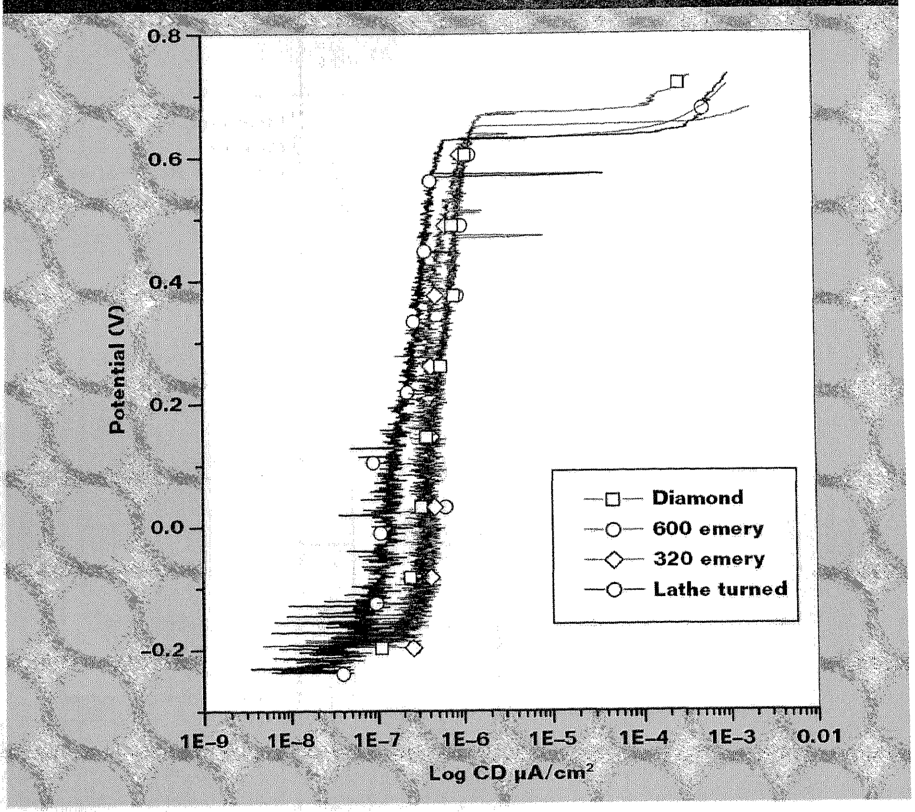
Another major benefit of chemical treatment is the enrichment of chromium in the passive film, which is higher in chemically treated surfaces than mechanically treated surfaces.[11] Figure 4 shows the compositional analysis for the diamond-finished surface (as mechanically polished and after chemical treatment) by AES. The intensity of the chromium peak was found to increase from mechanical polishing to pickling to pickling/passivation. Pickling followed by passivation yielded the highest enrichment of chromium when compared to the pickling and as-polished surface; this led to superior pitting corrosion resistance.

The concentration of iron appeared less in the pickled/passivated surface when compared to the as-polished surface. The enrichment of chromium in the surface film has occurred at the expense of dissolution of iron and oxidation of chromium, as also reported in literature.[10-13] The surface composition of iron was lowest in the pickled surface. Due to the oxidation of iron in the formation of the surface film, the passivated surface showed a higher intensity iron peak when compared to the pickled surface.

Shibata, et al.[13] attributed the enhancement of pitting resistance to the degree of chromium enrichment in the passive film. They showed that the maximum benefit of HNO_3 treatment was associated with the attainment of an optimum corrosion potential during pre-treatment. An increase in corrosion potential causes an increase in Cr/Fe ratio.

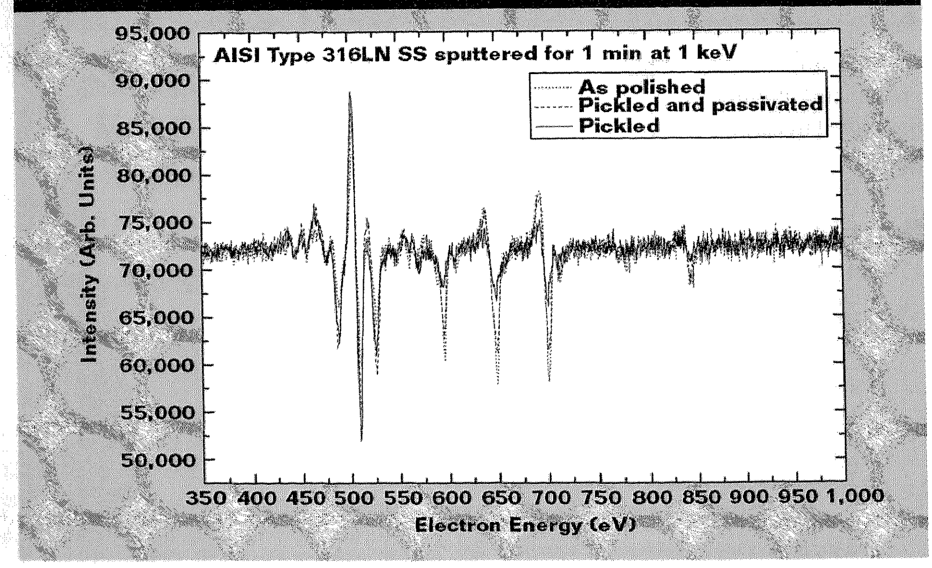
For 1 h immersion in HNO_3, the highest pitting potentials and the peak Cr/Fe ratio within the passive film were observed for 20 to 25% HNO_3 pretreatments. Haltquist and Leygraf[10] and Barbosa, et al.[14] attributed the improvement of the pitting resistance to the removal of surface inhomogeneities primarily and only secondarily to the enrichment of chromium in the passive film. Figure 5 summarizes the results of the present study. The pitting resistance was obtained by normalizing the pitting potentials with respect to the highest potential of 1,114 mV obtained for a diamond-finished surface with a pickling and passivation treatment. The contribution of each treatment process in enhancing the pitting resistance of the material is clearly depicted.

FIGURE 3



Polarization curves in 0.5 M NaCl for Type 316LN SS after pickling and passivation.

FIGURE 4



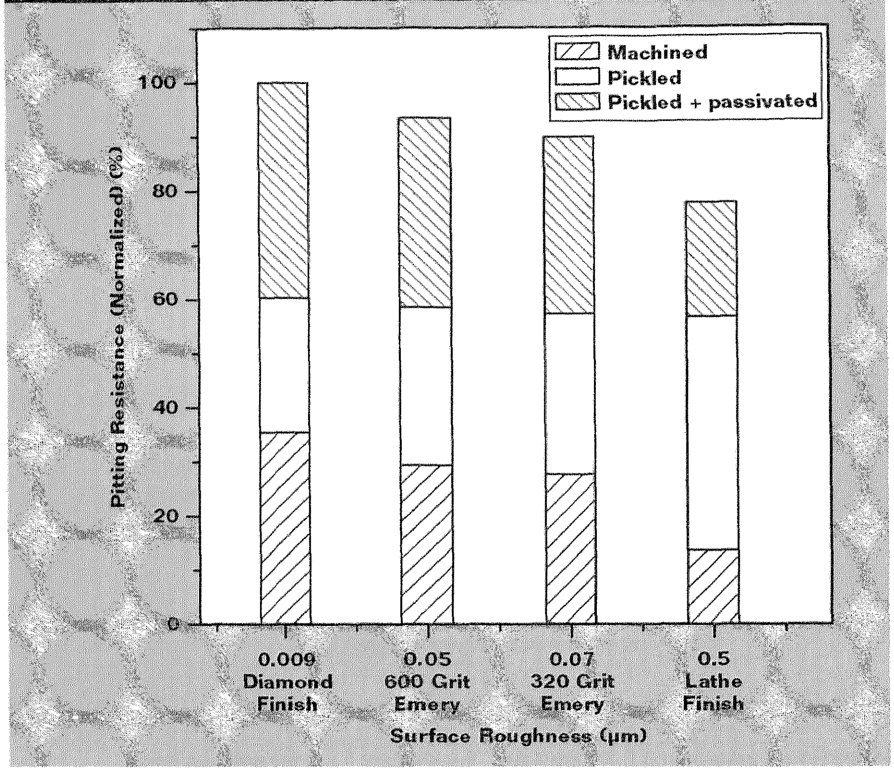
Auger electron spectra of the diamond-polished, pickled, and pickled/passivated surface.

Conclusions

The present study revealed that mechanical treatments of the surface decreased the surface roughness from machined surface to wet grinding with SiC abrasive paper to a diamond-polished surface. A corresponding improvement in the pitting corrosion resistance was observed in this same order. Pickling, and pickling followed by passivation, enhanced the pitting corrosion resistance, and the surface roughness had no significant effect on pitting corrosion resistance after chemical treatments. Compositional analysis of the surface by AES showed chromium enrichment in the order of pickled/passivated > pickled > as-polished surface.

It is recommended that any engineering component after fabrication, even nitrogen-bearing SS, be pickled and passivated prior to commissioning in a plant, especially for coastal environments.

FIGURE 5



Pitting resistance (normalized) as a function of surface roughness.

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