Electrochemical and Surface Analytical Approach to Passive Film on 200 Series Stainless Steels Formed in Sulfuric Acid

V. Shankar RAO and L. K. SINGHAL

1) Jindal Stainless Ltd., O. P. Jindal Marg, Hisar 125 005, India. E-mail: vshankarao@yahoo.co.in

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Electrochemical corrosion behaviour and chemical structure of the passive film of two newly developed austenitic stainless steels belonging to 200 series were studied in 1 M sulphuric acid (H₂SO₄). From polarization studies it was found that addition of Cu in the Cr–Mn–Ni stainless steel is beneficial in the passive range in terms of reduction in current density. X-ray photoelectron spectroscopy analysis of the passive film revealed enrichment of Cr ions on the surface irrespective of Ni and Mn content in the alloy. Mn in the passive film was relatively less considering its content in the alloy, but it increases with increase of Mn in the alloy. N compound was also observed in the passive film. Cu was present in the metallic as well as ionic form.

KEY WORDS: austenitic stainless steel; polarization; XPS; acid corrosion; passivity.

1. Introduction

On account of superior ductility, drawability, strength, toughness, wear resistance and inter-granular corrosion resistance etc., austenitic stainless steels account for three fourth of global stainless steel production. Elements, which promote austenitic structure when added to Fe–Cr alloys, are Ni, Mn, N, Cu and C. There are two broad categories of austenitic stainless steels: Cr–Ni stainless steels termed as 300 series and Cr–Mn/Cr–Mn–Ni stainless steels termed as 200 series. On account of developments in process technology such as argon oxygen decarburisation (AOD) refining and high price of nickel, 200 series constitute the fastest growing variety of stainless steels in recent years and currently account for more than 10% of the total stainless steel production. The future will place greater demands on 200 series alloys in replacement of 300 series for variety of applications. There is an excellent review on the Mn based austenitic stainless steels, which deals with physical metallurgy of Fe–Cr–Mn and Fe–Cr–Mn–Ni systems, effect of nitrogen, present status and future applications. However, the number of research works on the corrosion behaviour of 200 series is limited compared to that on 300 series stainless steels and there is some discrepancy on the role of Mn. Faurie and Bentley investigated the corrosion behaviour of austenitic stainless steels with replacement of 8% Ni by 15% Mn in 0.05 M H₂SO₄. They report addition of 15% Mn to Fe–17Cr alloy decreases the ability to passivate, but partial replacement of Ni with Mn does not change its passivity. This indicates a possibility of further development of Cr–Mn–Ni stainless steel with an appropriate combination of Ni to Mn ratio and incorporating other austenite formers such as N and Cu. Ahila et al. evaluated the repassivation kinetics of Cr–Mn and Cr–Ni steels, without and with N contents, using scratched electrode technique in a sulphate solution with different level of chloride contents. Repassivation behaviour of Cr–Mn alloys was found similar to that of Cr–Ni alloys, but effect of N was more pronounced in Cr–Mn steels leading to faster repassivation rate. Contrast to this fact, I.-ul-H. Toor et al. have reported deleterious effect of Mn on the repassivation behaviour and SCC behaviour of stainless steels in chloride containing solutions. The repassivation rate of the alloy decreases with an increase of Mn content. From slow strain rate tests it was shown that the resistance to SCC decreases with increase of the Mn content in the alloys. The slower repassivation rate of the alloy was linked to higher tendency of SCC. These failures were attributed to the presence of non-metallic inclusions such as sulphides and oxides in the alloy rather than chemistry of the base alloy. There was no detail on the production route of these alloys. However, it is speculated that if Cr–Mn–Ni alloys are produced by an advanced process route such as AOD the number of inclusions would be less and in turn corrosion resistance of the alloy will be enhanced. This review demonstrates that to have a clear picture of Mn on the corrosion behaviour of 200 series stainless steels further evaluation is needed, specifically understanding on the chemical structure of the passive film formed on the surface of Cr–Mn–Ni alloys.

2. Experimental Procedure

Alloys used in the present study were produced by EAF-AOD route followed by slab casting and hot rolling in
Jindal Stainless Ltd. Hot rolled coil was cold rolled to a thickness of 1 mm. Specimens of required size were cut from this and subjected to a furnace annealing for 60 s at 1050°C, followed by water quenching and subsequent pickling in 15% nitric acid +1% hydrofluoric acid solution to remove scales. The nominal chemical composition of the alloys used in the present study is given in Table 1. Details of the mechanical properties are given in Table 2.

Specimens for electrochemical corrosion studies were polished on SiC paper down to 1200 grit and finally 1 μm diamond polishing. The samples were then cleaned ultrasonically in methanol followed by distilled water prior to testing. Electrochemical studies were performed as per ASTM G-5. A three-electrode cell consisting saturated calomel electrode (SCE) reference electrode, Pt counter electrode and specimen as working electrode was used. All the electrochemical experiments were conducted at ambient temperature of $25^\circ$C in aerated solution without stirring.

Passive film was formed on the alloys surface by holding them at passive potential of 100 mV SCE in 1 M H$_2$SO$_4$ for a period of 18 ks. X-ray photoelectron spectroscopy (XPS) was employed to examine chemistry of the passive film formed on these alloys. This analysis was performed with a model ESCA 3000 UK using monochromized Mg Kα X-ray with beam energy of 150 W at a takeoff angle of 45°. The binding energy (BE) scale of the instrument was calibrated on C1s 285 eV. For sputtering the passive film was bombarded with Ar$^+$ ions at 5 keV. The composite XPS peaks were deconvoluted into their components by means of software package based on Gauss–Lorenzian distribution (10 to 15%).

### 3. Results and Discussion

SEM microstructure of the alloy 1 and alloy 2 are shown in Figs. 1(a), 1(b) after electrolytic oxalic acid etch as per ASTM A 262 practice A, in which step structure are seen in both the cases. The structure is fully austenitic as ferrite checked by Ferritoscope model MP30 was found to be zero.

The polarization curves of alloy 1 and alloy 2 obtained for a scan rate of 0.5 mV/s in 1 M H$_2$SO$_4$ are shown in Fig. 2. The nature of anodic polarization curve of both the alloys is different. Alloy 1 is passivated starting from corrosion potential ($E_{\text{corr}}$) leading to a little difference in critical current density ($i_{\text{crit}}$) and passive current density ($i_{\text{pass}}$), while alloy 2 shows a typical active–passive transition behaviour. The low critical current density of alloy 1 compared to that of alloy 2 could be due to difference in Ni content. Notably, Ni helps in lowering of $i_{\text{crit}}$ in austenitic stainless steels, especially in 18Cr–8Ni stainless steel. The breakdown potential and nature of transpassivation curve are the same in both the alloys. Electrochemical parameters such as $E_{\text{corr}}$, $i_{\text{corr}}$, $i_{\text{crit}}$, $i_{\text{pass}}$ and passive potential ($E_{\text{pass}}$) calculated from polarization curves shown in Fig. 2 are tabulated in Table 3. Alloy 1 shows marginally positive $E_{\text{corr}}$, compared to alloy 2. The $i_{\text{corr}}$ value obtained by extrapolating cathodic Tafel line to the $E_{\text{corr}}$ line, $i_{\text{crit}}$ calculated from the peak of active dissolution current density and $i_{\text{pass}}$ value was taken as the minimum current density in the passive region. Evidently, the $i_{\text{corr}}$ and $i_{\text{crit}}$ values of alloy 1 are lower than that of the
alloy 2, while \( i_{\text{pass}} \) value is nearly the same in both the alloys.

A feature in alloy 2 that appears different from alloy 1 is the appearance of a secondary anodic peak. This can be attributed to the high Cu content in alloy 2 as other elements such as Cr, N, C and S are more or less similar in both the alloys. Other researchers have reported a similar feature and linked to oxidation of Cu on the electrode surface.8,9) The appearance of secondary anodic peak in ferritic stainless steels containing Cu in sulphuric acid has been reported by Seo et al.8) Anodic dissolution of metallic Cu (\( \text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^- \)) from stainless steel was attributed to the secondary anodic peak. In another study, Hermas et al.9) have observed the secondary anodic peak in AISI 304 SS containing 0.5 to 2% Cu. Their study however shows that the magnitude of anodic peak remains the same, irrespective of Cu content but depends on the amount of Cu accumulated on the surface during active dissolution. They related this to oxidation of adsorbed hydrogen by the Cu atoms on the surface.

The general as well as localized corrosion behaviour of a stainless steel profoundly depends upon the stability of the passive film formed on the surface; XPS has been an excellent tool for analysis of the passive film. The high-resolution XPS spectra of Cr 2p, Mn 2p, Ni 2p and Fe 2p taken from surface of alloy 1 are shown in Figs. 3(a)–3(e). The spectra of each element in these figures correspond to the passive film before sputtering and after sputtering for 10 min (1st sputtering) and 15 min (2nd sputtering). Figure 3(a) corresponding to Cr 2p spectra shows two peaks. High intensity peak at 576.9 eV corresponds to Cr 2p\(^{3/2}\) and other peak at 586.6 eV to Cr 2p\(^{1/2}\).10–12) The difference in BE between these two peak is 9.7 eV which is close to the reported value.10 With increase of sputtering time, intensity of the Cr peak increases and the peak position remains unchanged. Figure 3(b) shows deconvolution of the Cr 2p\(^{3/2}\) peak obtained on 1st sputtered spectra. It reveals presence of Cr in multiple states. The peaks at BE 576.6 eV and 577.5 eV were assigned to chromium oxide (\( \text{Cr}_2\text{O}_3 \)) and chromium hydroxide (\( \text{Cr(OH)}_3 \)), respectively. While the peak at BE of 575.6 eV corresponding to Cr–N bonding and chromium hydroxide (\( \text{Cr(OH)}_3 \)), respectively. While the peak at BE of 575.6 eV corresponding to Cr–N bonding.

Mn spectra are shown in Fig. 3(c), in which Mn is absent in the outermost surface of the passive film. After sputtering, a peak with low intensity appears at 642±0.2 eV corre-
spond to $2p_{3/2}$ of Mn–O. This wide spectrum raises the possibility of Mn-oxide in the form of MnO, MnO$_2$, and Mn$_3$O$_4$. Presence of Mn in the passive film in multiple forms (Mn$_2$O$_3$, MnO and Mn$_3$O$_4$) has also been reported by Zhang and Zue in a study related to the passive film analysis of high manganese austenitic stainless steels. Enrichment of Ni and Fe on the surface of the passive film is little as seen from curves in Figs. 3(d)–3(e). With increase of sputtering time sharp peaks start appearing. Hence, here we report BE for the sputtered surface. With respect to Ni, the $2p_{3/2}$ peak at BE 852.6 ± 0.2 eV is assigned to Ni$^{0.10,20}$ The iron $2p_{3/2}$ peak at 707 ± 0.1 eV (Fig. 3(e)) indicates it is present in the metallic form.$^{21}$ In contrast to the present finding, the work of Marcus and Olefjord shows that the passive film formed on the surface of FeCr and Fe–Cr–Mo alloys in 0.5 M H$_2$SO$_4$ contains Fe in ionic states of Fe$^{2+}$ and Fe$^{3+}$. Studies carried out by Raja et al. on Mn based austenitic steel in 1 M hydrochloric solution showed the presence of Ni ions along with Cr and Mn ions, but this film was formed during exposure at open circuit potential ($-0.15$ V SCE). This shows that the nature of the film formed on Cr–Mn stainless steel depends upon the solution exposed and the potential maintained in addition to alloy composition.

Role of nitrogen on the corrosion behaviour of the present alloys could not be differentiated in the electrochemical corrosion behaviour because N content is nearly the same in both the alloys. However, XPS analysis demonstrates the involvement of N in the passive film formation. The N spectra obtained from the surface of alloy 1 are shown in Fig. 4(a). Importantly, N is enriched on the surface despite having low concentration compared to major alloying elements Ni and Mn. A broad peak at low BE 400.3 ± 0.5 eV corresponds to N 1s, while another peak adjacent to this at 407.7 eV could not be assigned due to lack of reference data. After curve fitting N 1s spectra reveals its presence in two forms (Fig. 4(b)), the major peak at BE of 400.2 eV suggests for NO or NH$_2$ and another peak at BE of 399.3 eV for CrN/Cr$_2$N. Considering potential-pH equilibrium diagram for N–H$_2$O system it is noticed that NH$_4^+$ ions are stable at lower potential and NO$_3^-$ ions are at higher potential. Hence, in the present study for the given potential (100 mV SCE) and pH (0.5), NO is more likely to form. Moreover, this N–O bond could be either in the form of nitrite (NO$_2^-$) or nitrate (NO$_3^-$). This is because for the given potential and pH there is a borderline between NO$_3^-$ and NO$_2^-$ ions. However, both the ions are known for their inhibiting affect. For example Baba and Katada reported that the nitrogen in solid solution of austenitic stainless steel gets dissolved during exposure in a corrosive electrolyte and forms NO$_3^-$ which improves corrosion resistance of the alloy. Beneficial effect of N on the resistance to localized corrosion is well established and explained by various models. Enrichment of N at the film matrix interface is generally considered responsible for enhancing the corrosion resistance of stainless steel.

For a detailed investigation, high resolution XPS analysis was performed also on the passive film formed on alloy 2. Chemical nature of this passive film was found similar to that reported for alloy 1 i.e. enrichment of Cr and N ions along with O. To avoid repetition, these data are not shown here. Mn being element of the interest its spectra are shown in Fig. 5. Peak position of the Mn $2p_{3/2}$ is the same as it was in the case of alloy 1. Intensity of the peak is more compared to the previous one and it increases with sputtering. These findings imply that Mn content in the passive film formed in acid solution increases with increase of Mn content in the alloy.

Since Cu is also an alloying element in these alloys, it would be interesting to know its role in the passive film. Alloy 2 has more Cu content than alloy 1, hence Cu spectra taken from passive film of alloy 2 before and after sputtering is shown in Fig. 6. There are two peaks in these spectra.
The peak at high BE from 951 to 953 eV is assigned to Cu 2p1/2 and another peak at low BE from 931 to 933 eV is assigned to Cu 2p3/2. Appearance of Cu 2p3/2 for a wide range of BE indicates its presence in the passive film both in metallic as well as ionic form. BE value below 932.4 eV suggests Cu0 while above 932.7 eV is assigned to cupric oxide (CuO)/cuprous oxide (Cu2O).28,29 It is worthwhile to mention that in case of alloy 2 despite having high dissolution rate and corrosion rate it has improved passivation behaviour. This could be attributed to the presence of Cu in the passive film. In a recent work, Freire et al.30 reported that the improved resistance of the low Ni alloy AISI 204Cu SS in chlorinated alkaline media is due to Cu cementation at active corrosion sites. While number of studies on the role of Cu on passive film behaviour of 200 series SS is limited, it is worth to discuss with respect to 300 series SS. Kim and Park31 made investigation on the role of Cu on corrosion behaviour of high-performance austenitic stainless steel in highly concentrated H2SO4 solution. According to them, the addition of 3.2% Cu in the alloy enhances its corrosion resistance by decreasing icorr, ian, and current density of hydrogen evolution. They found that the passive film was enriched with metallic Cu as well as CuO. Present results corroborate this perception. The enrichment of the Cu was attributed to the selective dissolution of active metallic Fe, Ni and Cr from the surface.

4. Conclusions

Electrochemical corrosion behaviour and chemistry of the passive film formed on 200 series alloys were investigated in 1 M H2SO4. Following conclusions are drawn from these studies.

(1) The alloy with high Cr and Ni contents has lower icorr and ian values.

(2) Beneficial effect of Cu was found in the passive range, it helps in lowering passive current density of the alloy. A secondary anodic peak appears during anodic polarization just above the passive potential in Cu containing alloy.

(3) XPS analysis shows passive film is mostly enriched with Cr3+ ions. Presence of Mn ions in the passive film found to be small but it increases with increase of Mn in the alloy.

(4) N is enriched in the passive film in the form of Cr–N and N–O bonds. With respect to Cu, it was found in the passive film in metallic as well as in ionic form.

REFERENCES