Corrosion resistance of austenitic stainless steels in non-aqueous neutral chloride solution

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The corrosion resistance of two standard austenitic stainless steels (AISI 304 and 321 SS) has been investigated in non-aqueous methanolic solution containing lithium chloride. The effect of chloride concentration on the general corrosion behaviour of the steels has been investigated using open circuit potential (OCP), potentiostatic polarization and scanning electron microscopic (SEM) techniques. Both the steels have undergone active corrosion. The rate of corrosion is found to depend directly on the concentration of chloride ion in methanol similar to the aqueous solutions. The polarization measurements reveal that the corrosion resistance of the Ti-alloyed 321 SS is superior as compared to the 304 SS due to the presence of titanium in it. AISI 321 SS suffer from pitting corrosion whereas grain boundary attack is apparent in 304 SS.

Keywords: Stainless steel, Corrosion, Pitting, Methanol, Scanning electron microscopy

Austenitic stainless steels are regarded as one of the most widely used structural materials in chemical, nuclear, petrochemical industries, food processing plants, transportation, cryogenic containers etc. because they are low cost materials and possess high mechanical strength and corrosion resistance in many aggressive environments¹⁻³. It is well-known that the high resistance to corrosion in aqueous medium is due to the presence of a protective passive film on the surface of the steel which is an oxide/oxyhydroxide film containing water molecule^{4,5}. However, in nonaqueous organic solvents, the structure and type of organic functional group is believed to influence the reactivity of metals differently as compared to aqueous medium due to difference in their solvation non-aqueous properties. Among the solvents, in particular methanol has alcohols, gained considerable interest due to its widespread use in organic syntheses. Another emerging potential application of methanol is in direct methanol fuel cells (DMFC) for portable application. It has been also recognized as a fuel alternative as a whole or as an additive to gasoline to combat the environmental problems and increasing fuel prices over the years⁶. Some contaminants such as acids and inorganic salts, usually the chlorides are present in methanol in appreciable amounts⁷. Thus, the steel materials

exposed to methanol environment can face serious corrosion problems leading to premature failure of metallic components.

Although substantial information is available on the corrosion behavior of stainless steels in numerous aqueous solutions, the study in non-aqueous organic solvents like methanol is relatively less investigated⁸⁻¹⁵. These studies mainly concerned to the effect of water and/or acid concentration on passivation and pitting properties. On the other hand, the dissolution behavior of these steels in organic solvents may vary from that in aqueous solutions due to differences in physicochemical properties like dielectric constant, viscosity and solubility of reactants/products.

The purpose of the present work is to investigate the corrosion behavior of standard austenitic stainless steels (AISI 304 SS and 321 SS) in methanol solution containing chloride ions, in relation to the influence of titanium (in 321 SS) on the rate of corrosion. Titanium alloys have been finding application in many chemical and aerospace industries including reactors for organic reactions because of their high strength and corrosion resistance. In this respect, the corrosion behaviour of titanium alloyed 321 SS was studied in comparison to the standard 304 SS in neutral methanol-chloride solutions using different electrochemical techniques such as open circuit potential (OCP) and potentiostatic polarization. Scanning electron microscopy (SEM) was employed to document the surface morphology.

Experimental Section

The working electrode materials used in this work were AISI 304 and 321 austenitic stainless steels (Good Fellow, UK). The chemical compositions of the steels are given in Table 1. The working electrode surface was polished using emery papers of increasing fineness followed by fresh polishing with alumina powder until mirror bright. Then the specimens were washed thoroughly with double distilled water, cleaned ultrasonically in acetone, dried quickly in air and were kept in a vacuum desiccator prior to use. The measurements were carried out in methanol containing different concentrations of LiCl (0.001, 0.01, 0.1 and 0.25 M). Prior to the preparation of the solution, lithium chloride was dried at 110°C so as to keep the water content of methanol-LiCl solutions below 0.001 wt.%. All electrolytic solutions were made from analytical grade chemicals (Merck) and distilled purified reagent-grade methanol.

The electrochemical polarization experiments were carried out in a three-electrode assembly cell using a potentiostat (Wenking POS 73). The reference electrode was a saturated calomel electrode (SCE) equipped with a Luggin capillary filled with saturated potassium chloride and the counter electrode was platinum of large surface area. Details of experimental set up and working procedures were described elsewhere¹⁶. The working electrode specimen of 2 cm² exposed area was immersed in the experimental solution for two hours in order to stabilize the surface at open circuit potential (OCP). The polarization curves were recorded potentiostatically, starting at a negative potential (-1000 mV/SCE) and then the potential was increased in the positive direction in steps of 20 mV/ min. All measurements were conducted at 35±1°C under unstirred conditions in deaerated solutions. The morphological studies of the surface of the samples after potentiostatic polarization tests were performed on scanning electron microscope (Jeol JSM 5600).

Results and Discussion

Open-circuit potential measurements

Figure 1 shows the variation of the open-circuit potential (OCP) with time for 304 SS and 321 SS immersed in methanol-LiCl (0.001-0.25 M). It can be seen that the OCP vs. time curves of both the steels follow similar trend. The open-circuit potential shifts to more positive values with time and tend to stabilize within ~60 min from electrode immersion in the electrolyte corresponding to the free corrosion of the bare metal¹⁷. This positive shift of the OCP with time indicates the thickening of the naturally formed pre-immersion surface film on the electrode surface, although such film may not be passive^{18,19}. The



Fig. 1 — OCP vs. time curves of AISI 321 SS in different concentrations of LiCl in methanol at 35° C. (a) 304 SS; (b) 321 SS.

Table 1 — Chemical composition of the austenitic stainless steels (wt.%).											
Alloys	Cr	Ni	Mn	Ti	Mo	Ν	Si	Cu	С	S	Fe
304 SS	18	10	2	-	-	-	1.0	-	0.08	0.03	Bal.
321 SS	18	8	1.98	1.96	-	-	1.0	-	0.08	0.03	Bal.

potential stabilisation to a steady state value reflects the dynamic balance between the advance of the corrosion and the deposit of the corrosion products. The OCP shifts to more negative values as the concentration of chloride ion increases from 0.001 to 0.25 M. This indicates that surface film formed on the electrode surface has deteriorated with the increase of chloride ion concentration owing to increase in aggressiveness of the electrolytic solution with chloride concentration. The results are consistent with earlier investigations performed in aqueous chloride solution, which report that usually a more negative OCP is associated with a higher rate of hydrogen evolution and consequently higher corrosion rates²⁰.

It can be seen from Fig. 1a that the OCP values at all studied concentrations of lithium chloride are slightly higher (more noble) for titanium alloyed 321 SS than those for 304 SS, suggesting that 321 SS has higher stability (corrosion resistance) than 304 SS which could be attributed to the presence of titanium. Similar results have been reported showing positive shift of OCP due to titanium alloying in nanocrystalline Al-Cu alloys²¹.

Potentiostatic polarization measurements

Potentiostatic cathodic and anodic polarization curves of the steels in methanol– LiCl (0.001-0.25 M) are shown in Figs. 2 and 3. The corresponding corrosion parameters as derived from the polarization measurements are summarized in Table 2. It is evident from the figures that the nature of the cathodic polarization curves in both the steels is almost similar indicating similar type of reaction mechanism associated with the cathodic process. The cathodic polarization curves exhibit linearity over a large range



Fig. 2 — Polarization curves of AISI 304 SS in different concentrations of LiCl in methanol at 35°C

of potential indicating activation control of the cathodic process. The cathodic Tafel slopes (b_c) were found to be between 130 and 185 mV/dec for both the steels. The average values of cathodic Tafel slopes are 157 and 149 mV/ dec for 304 and 321 SS, respectively, which are close to the values previously reported for the hydrogen evolution reaction. Therefore, the cathodic reaction seems to be the evolution of hydrogen²². The near neautral and deaerated conditions of the methanol-lithium chloride solutions imply that the concentration of proton/dissolved oxygen is very small to facilitate the reduction of proton/oxygen.

In such a case, the most probable cathodic reaction is the evolution of hydrogen from reduction of water as shown in scheme 1:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \dots (1)$$

The origin of water molecules is most likely the methanol which usually contains ~ 200 ppm water, even after distillation and purification, which is

Table 2 — Corrosion parameters of 304 and 321 SS in												
methanoi-LiCi at 35°C.												
Alloys	Conc. Of	$E_{\rm corr}$	i _{corr.}	b_a	$b_{\rm c}$							
	LiCl (M)	(mV)	$(\mu A/ cm^2)$	(mV/ dec)	(mV/ dec)							
304 SS	0.001	-170	0.35	75	185							
	0.01	-170	2.6	60	170							
	0.1	-220	15	40	145							
	0.25	-260	36	40	130							
321 SS	0.001	-160	0.22	65	170							
	0.01	-180	0.30	45	140							
	0.1	-200	1.0	40	145							
	0.25	-240	2.3	35	140							



Fig. 3 — Polarization curves of AISI 321 SS in different concentrations of LiCl in methanol at $35^{\circ}C$

sufficient to initiate the cathodic reaction. Chen et al.²³ have also suggested that the cathodic partial reaction in deaerated methanol-lithium chloride solution for zinc is the evolution of hydrogen. Active anodic dissolution was observed for both the steels in the initial region of the anodic polarization curve as indicated by continuous increase in current density with small applied potential. As can be seen from Figs. 2-3 and Table 2, the corrosion current density (i_{corr}) increases and corrosion potential (E_{corr}) exhibits negative shift with increase in chloride concentration. Thus, the higher the i_{corr} value, the higher is the rate of corrosion. It can be observed that irrespective of the difference in alloying composition of both 304 and 321 SS, the corrosion resistance decreases upon increasing the concentration of chloride in methanol. This negative effect of chloride ion on the corrosion resistance of alloys in methanol is found to be similar to aqueous environments^{24,25}. In addition, the results reveal that the value of i_{corr} depends also on the composition of the alloys at a given chloride concentration. The i_{corr} values are always higher for the 304 SS than those for 321 SS. At low chloride concentration (0.001 M), icorr of 304 SS was marginally higher than 321 SS; however, the difference was much larger as the chloride concentration increased to 0.25 M. Similarly, $E_{\rm corr}$ of 304 SS was observed to be more active to the extent of 10 to 20 mV compared to 321 SS. The present results indicate clearly that these parameters are dependent on the molar concentration of chloride of the medium. The increase of the chloride concentration has a pronounced effect on the corrosion current and consequently on the dissolution rate.

Figure 4 illustrates the relationship between i_{corr} and chloride concentration for both the steels. As can be observed, the log i_{corr} vs. log C relations are linear for the two tested steels over the concentration range studied, as shown in Eq. 2^{26} :

$$\log i_{\rm corr} = a + n \log C \qquad \dots (2)$$

where i_{corr} represents the rate of corrosion, *C* is the molar concentration of chloride ion. *a* and *n* are the two empirical constants where *a* is the value of log i_{corr} at C = 1. *n* is the slope of the linear plot which represents the electrochemical reaction order. From Fig. 4, the slope of the straight line (*n*) for 321 SS is observed to be ~0.41 and that for 304 SS is ~0.55, indicating that the order of the reaction for the 304 SS is higher than that for 321 SS. Thus, the rate of dissolution of 304 SS is higher



Fig. 4 — Variation of log i_{corr} with log *C* of 304 and 321 SS in methanol LiCl in at 35°C

than the 321 SS which is in good agreement with the OCP measurements. Moreover, the positive value of the slopes for the two steels suggests that the corrosion rate is directly proportional to the chloride concentration, where i_{corr} value increases with increasing the aggressiveness of the medium. The results indicate that the corrosion susceptibility of 321 SS in methanolic chloride solution is significantly lower than 304 SS. The relatively higher corrosion resistance of 321 SS can be attributed to the presence of 2.0 wt.% titanium in the steel. Vigen Karimi et al.²⁷ have also reported that titanium deposited 316 SS shows higher corrosion resistance than 316 SS in $0.5 \text{ N H}_2\text{SO}_4$ and 0.5 N HNO_3 aqueous solutions. Similar beneficial results due to Ti addition have also been observed by Wang et al.²⁸ for corrosion behavior of titanium coated SS316L in Hanks' solution. Thus, the presence of titanium improves the corrosion resistance of stainless steel in different aggressive media.

No significant differences are detected in the shape of the anodic polarization curves for the two different alloys, suggesting identical reaction kinetics. The current density increases rapidly from corrosion potential and thereafter attains limiting values beyond a certain anodic potential. The limiting current values and hence the consequent appearance of the limiting current region (LCR) indicates the mass transfer control of the reaction possibly due to the precipitation of reaction products on the alloy surface in the form of a salt film. Literature suggests the presence of a thin salt film on the anode surface at the limiting currents²⁹. Supersaturation of the solution in the vicinity of anode leads to precipitation of salt film resulting in rate limiting diffusion of cations of the dissolving metal from the anode into the bulk. In the present investigation, the salt film associated with the LCR region is considered to be mixed FeCl₂ and Fe(OH)₂ or a hydroxychloride complex (Fe(OH)Cl) due to preferential dissolution of iron in the active potential region³⁰.

SEM studies

Figures 5a-c shows the morphological features of 304 and 321 SS surface after potentiostatic polarization in 0.1 M LiCl in methanol. The 304 SS evidenced intergranular corrosion (IGC) as shown in Fig. 5a. A significant number of granular precipitates were located both at grain boundaries and in grain interiors. The grain boundary attack in 304 SS (containing 0.08% carbon) can be related to the precipitation of $Cr_{23}C_6$ at the grain boundaries with consequent chromium depletion adjacent to the precipitates³¹. The $Cr_{23}C_6$ precipitates are likely due to sensitization originating from exposure of the steel to elevated temperature during production, fabrication, welding or improper heat treatment.

The potential difference between grain-boundary and the Cr₂₃C₆ precipitates causes the preferential dissolution in chromium depleted areas resulting in IGC. In spite of the same amount of carbon content (0.08%), IGC did not develop in the 321 SS because, titanium present in 321 SS acts a strong carbideforming element and the carbides of titanium are much more stable than $Cr_{23}C_6$. Thus, they preferentially combine with the available carbon and lessen the opportunity for $Cr_{23}C_6$ to nucleate thereby preventing sensitization³². Unlike the grain boundary attack in 304 SS, type 321 steel suffered from severe pitting in chloride solutions of methanol with a high density of pits on the surface (Fig. 5b). Large open pits of several micron sizes and of irregular shape can be observed. Fig. 5c shows a hexagonal pit with a considerable deep cavity. The characteristic hexagonal geometry of the pits is probably due to the propagation of pitting along a hexagonal crystallographic plane. Similar hexagonal pits have been reported previously for zinc³³. Although no passivation is observed in lithium chloride solutions as evidenced by the polarization curves, the event of pitting may seem unlikely yet it can not be ruled out. Pitting can occur on the bare metal surface during active dissolution for a material not exhibiting passivity. This is because certain regions of the



Fig. 5 — SEM photomicrographs of stainless steels after polarization in methanol -0.1M LiCl. (a) 304 SS; (b) 321 SS; (c) Hexagonal pit on 321 SS.

surface are more susceptible to pitting and tend to dissolve faster than the rest of the surface possibly due to difference in their local chemical composition or energy³⁴.

Conclusion

The corrosion resistance of 304 and 321 austenitic stainless steels in non-aqueous methanol solution containing different concentrations of chloride has been investigated. The results can be summarized as follows:

- 1. Both 304 and 321 SS undergo active anodic dissolution in neutral methanolic solution containing chloride. The corrosion behaviour is observed to be similar to aqueous solutions. The cathodic reaction is assumed to be the reduction of water inherent in methanol.
- 2. Alloying element like titanium is found to have pronounced effect on both the general corrosion and surface morphology of the steels. The corrosion resistance of 321 SS is higher than 304 SS most likely due to the presence of 2.0 wt.% titanium in 321 SS.
- 3. Intergranular corrosion (IGC) occurs only on 304 SS and not on 321 SS. The absence of IGC is most likely due to the formation of stable titanium carbides in 321 SS. However, 321 SS developed pitting corrosion with the formation of typical hexangular pits even in the absence of a passive film.

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