CHAPTER 7 INFLUENCE OF ULTRASONIC SHOT PEENING ON CORROSION BEHAVIOR

7.1 Introduction

This chapter addresses the effect of surface nanostructure developed through ultrasonic shot peening (USSP) on corrosion behavior of the 7075 aluminum alloy in 3.5 wt.% aqueous solution of NaCl. USSP was performed with hard steel balls of 3 mm diameter for different durations of 15, 30, 60 and 300 seconds at a constant amplitude of 80 μ m. USSP develops surface nanostructure, induces severe plastic deformation, refines grain size up to certain depth and imparts compressive residual stress in the surface region. The sample USSP treated for 15 seconds (USSP 15) exhibited lower corrosion current density (0.564 μ A/cm²) and higher corrosion potential (-0.695 V) as compared with that of the un-USSP specimen with 1.269 μ A/cm² current density and -0.839 V potential respectively. The enhancement in corrosion resistance of the USSP treated sample is due to rapid development of uniform, homogeneous and effective passive layer on the nano-structured surface coupled with refinement of the coarse precipitates. Also, there is optimum combination of surface roughness, compressive residual stress, and dislocation density in the surface region to produce highest corrosion resistance in the USSP 15 condition.

7.2 Corrosion Characteristics

7.2.1 Potentiodynamic Polarization

Potentiodynamic polarization studies of the un-USSP and USSP treated samples were performed in 3.5 wt.% NaCl solution, following stabilization of their open circuit potential after exposure of 30 minutes in the test electrolyte. The potentiodynamic polarization curves for the different test samples are shown in Fig. 7.1.



FIGURE 7.1: Potentiodynamic polarization curves of the un-USSP and the different USSP treated samples in 3.5 wt% NaCl solution, following exposure of 30 minutes

The plots for the tested samples can be divided in to three zones. Region 'A' marked in the plots of Fig. 7.1 corresponds to polarization behavior of the test specimens near their corrosion potentials. This zone of polarization curves of the test specimens corresponds

Treatment condition	E _{corr} (V _{SCE})	i_{corr} μ A/cm ²	E _{pit} (V _{SCE})	eta_{a} (V/decade)	$eta_{\mathbf{c}}$ (V/decade)	Corrosion rate (µ m/year)
un-USSP	-0.839	1.269	-0.790	0.304	0.194	44.19
USSP 15	-0.695	0.564	-0.517	0.217	0.296	20.06
USSP 30	-0.778	1.07	-0.596	0.373	0.321	38.10
USSP 60	-0.674	1.02	-0.575	0.213	0.326	36.32
USSP 300	-0.819	1.55	-0.590	0.354	0.131	55.11

TABLE 7.1: Electrochemical paramaeters of the un-USSP and USSP treated samples in 3.5wt.% NaCl solution, extracted from potentiodynamic plots fitted in Tafel regions.

to the actual rate of corrosion of the test electrodes and may be quantitatively expressed by Stern-Geary equation.

$$i_{corr} = \frac{\beta_a \beta_c}{2.303 R_p (\beta_a + \beta_c)} \tag{7.1}$$

Where, i_{corr} is corrosion current density of the test specimens β_a and β_c respectively are anodic and cathodic tafel slopes and R_p is polarization resistance. The tafel slopes for the tested samples calculated in the range of 200 mv of cathodic and anodic polarization from the static corrosion potential are recorded in Table 7.1. The corresponding corrosion potentials (E_{corr}), corrosion current density (i_{corr}), pitting potential (E_{pit}) and corrosion rate are also presented in this table. These results will be discussed in the subsequent paragraphs.

The zone 'B' of the anodic part of the curves (Fig. 7.1) may be attributed to onset of pitting on the surface of the tested specimens. Due to higly aggressive nature of the test electrolyte (3.5% NaCl solution) and formation of thin layer of passive film on the surface of the tested samples which will be discussed later, the onset of pitting took place very close to their corrosion potentials. A closer look of the curves indicates that the samples

USSP treated for 30 to 300 second developed pits very close to each other at about - 0.590 V. However, the onset of pitting for the USSP 15 sample took place at considerably higher anodic potential of -0.517 V. These data indicate that shot peening of samples for 15 seconds led to development of a relatively less reactive surface with higher resistance against pitting than the samples shot peened for longer durations.

The zone 'C' of the curves exhibits high current density in the range of 10^{-2} A/cm². Such a high current density cannot be considered as passive current. This range of current density may be considered limiting current for dissolution of the metal surface. At higher anodic potentials, in the range of 0 V, (SCE) and above, the anodic curves of all the test specimens overlap indicating complete dissolution of the passive films formed on their surfaces.

7.2.2 Electrochemical Impedance Studies

The plots for the tested specimens in the Nyquist and Bode form are shown in Fig. 7.2. The best fitting results analyzed by constant phase element model (CPE) (schematically shown in Fig. 7.3) are recorded in Table 7.2. It is pertinent to mention here that the EIS data plotted in bode form provide more detail information than the Nyquist forms of plots. In view of this the Bode plots shown in Fig. 7.2(b-c and e-f) will be discussed in the forthcoming paragraphs. Frequency-log modulus plots presented in Fig. 7.2(b) and (e) for 24 h and 360 h of exposure vary distinctly show a linear relationship forming about 45° angle in intermediate frequency ranges. This behavior is strong indication that the reaction of the studied samples are controlled by the diffusion process.



FIGURE 7.2: EIS plots of un-USSP and different USSP treated samples in 3.5 wt.% NaCl solution recorded at their respective open circuit potentials for immersion durations of 24 h (a-c) and 360 h (d-f).

Treatment Condition	Immersion time (h)			Electrochemica	ul param	eters	
		$\mathbf{R}_u(\Omega \mathbf{cm}^2)$	$\mathbf{R}_p(\Omega \mathbf{cm}^2)$	$Y_0 (\Omega^{-1} cm^{-2} Sn)(x10^{-6})$	α	$W_d(Ss^{1/2}x 10^{-3})$	Chi-sqaure(x 10 ⁻³)
	24	1.67	401	375.6	0.77	20.4	35.6
Jecu-lin	360	2.89	822	527.9	0.689	8.53	5.8
21 (1991)	24	4.02	12214	126.1	0.84	1.88	8.446
	360	1.02	10523	339.9	0.747	2.04	9.17
	24	1.42	2287	135.1	0.785	2.95	1.44
UC JOON	360	2.02	1187	344.1	0.745	3.81	2.47
09 (1351)	24	0.83	286	873	0.771	15.62	50.86
	360	0.88	762	662	0.715	5.41	5.97
1166D 300	24	0.83	286	873	0.771	41.67	19.8
UNC JOON	360	0.88	762	799	0.715	6.73	20.07

The log modulus of impedance in the lower studied frequency range (<1 Hz) remains practically unchanged with decrease in frequency. This is more true for untreated and lower duration of USSP treated specimens. USSP 15 and USSP 30 samples, on the other hand, exhibits an increasing trend in log modulus values with decrease in frequency. These facts suggest that the passive film on USSP 15 and USSP 30 specimens have diffusion effects which is supported by Warburg diffusion coefficient in the equivalent electrochemical circuit. In log frequency phase shift plots, the phase shift moves towards zero angles for un-USSP and higher duration of USSP treated samples which may be due to time constant. The USSP 15 and USSP 30 specimens on the other hand exhibit higher angles phase shift indicating the presence of capacitive film in the passive layer of these samples. These observations are applicable for both 24 h and 360 h exposed specimen. The following inferences may be derived from the results recorded in this table.

- 1. The constant phase element symmetry factor (α) for all the test specimens are very close to each other (0.69 to 0.84).
- 2. The polarization resistance (R_p) is appreciably higher for the USSP 15 samples than the others, both for 24 h and 360 h of exposures. A substantial decrease in the R_p values is recorded with increase in the duration of shot peening.
- 3. The constant phase element impedance (Y_0) , which indicates the ease of facilitation of reaction is also lower for the USSP 15 sample than the other treated and untreated samples.

4. The value of Warburg diffusion coefficient (W_d) for the USSP 15 samples are again lower than those of the other treated and un-treated samples.

The above results suggest that the USSP 15 sample develops a passive film on its surface which creates hindrance for diffusion of ions and oxygen through it. On the other hand the passive films formed on the other samples (USSP 30 to USSP 300) are less protective and deteriorate with time.



FIGURE 7.3: Equivalent electrochemical circuit of CPE model.

7.2.3 Anodic Polarization

Corrosion rate of aluminum based alloys is controlled by the stability of the passive film formed on their surface. The stability of the films strongly depend on the aggressiveness of the electrolyte, temperature and the time of exposure. In view of the above facts, the un-USSP and USSP treated samples were exposed in 3.5 wt.% NaCl solution for 360 hours at room temperature (27 °C) and subsequently their potentiodynamic anodic polarization curves were recorded as shown in Fig. 7.4.

The plots of the treated and untreated samples exhibit very different behavior. The un-USSP sample exhibits considerably higher negative open circuit potential than the USSP treated samples indicating relatively more thermodynamic unstable than that of the



FIGURE 7.4: Anodic polarization curves of the un-USSP and USSP treated samples after 360 h of exposure in 3.5 wt.% NaCl solution.

latter ones. The un-USSP sample shows passivity near its corrosion potential of -1.095 V (point 'A' in the curve) during its anodic polarization. This passivity breaks down at about -0.794 V (point 'B') where a steep increase occurs in the current density with increase in potential and is followed by a limiting state of dissolution of the surface film (point C). The above polarization diagrams further show that all the USSP treated samples attain considerably nobler steady state potentials than that of the un-USSP treated sample.

7.2.4 Weight gain during exposure

Studies were carried out on gain and loss of weight of the samples, intermittently exposed in 3.5 wt.% NaCl solution for 60 days and the results are summarized in Figs. 7.5 and 7.6. Following inferences may be drawn from the trend of the plots of this figure.

- There is continuous increase in the weight of the un-USSP sample and the samples USSP treated for 60 and 300 seconds are recorded.
- 2. There is highest gain in weight with time in the 300 USSP treated sample.
- 3. There is lowest gain in weight of the sample USSP treated for 15 seconds.
- 4. There is decrease in the weight of the samples USSP treated for 15 and 30 seconds after 45 days of their exposure.



FIGURE 7.5: Variation of weight gain of the 7075 Al alloy with duration of immersion in 3.5 wt.% NaCl solution for the un-USSP and different USSP treated samples.

The above observations indicate that the un-USSP treated sample and those USSP treated for longer durations of 60 and 300 seconds experienced higher corrosion due to rapid formation of corrosion products on their surfaces. The 15 & 30 sec USSP treated



FIGURE 7.6: Corrosion rate of aluminium alloy 7075 in different USSP conditions after 60 days of immersion in 3.5 wt.% NaCl solution.

samples, however, showed slower rates of corrosion and there was relatively less weight gain. The corrosion product formed during 15 days of exposure was characterized as aluminium hydroxide by XRD (Fig. 7.7).

After 60 days of immersion, corrosion products on the exposed samples were removed from the surface as detailed in experimental section. The corrosion rates of the different samples are shown in Fig. 7.6. It is seen that USSP 300 sample exhibits highest rate of corrosion among the other treated as well as untreated samples. The corrosion rate is the highest in the sample USSP treated for 300 seconds followed in decreasing order by those of un-USSP, USSP 60 & USSP 30 and being lowest for the USSP 15. These results unambiguously confirm that USSP for 15 and 30 seconds on surface of the 7075 Al alloy led to improvement in corrosion resistance of the alloy in comparision with that of the un-USSP.





FIGURE 7.7: X-ray diffractograms of the 7075 Al alloy after exposure in 3.5 wt.% NaCl solution for 15 days in the un-USSP and different USSP treated conditions.

7.3 Discussion

Potentiodynamic polarization and electrochemical impedance studies (Fig. 7.1 & 7.2) revealed that samples USSP treated up to 60 seconds of duration are more resistant to corrosive attack than the un-USSP. The values of E_{corr} , i_{corr} and E_{pit} compiled in Table 7.1 show that i_{corr} , is the lowest for the USSP 15 amongst all the samples, including the un-USSP. The value of R_p is the highest even after 360 h of exposure for the USSP 15 sample as shown in Table 7.2. Proneness to corrosion is found to increase with increase in the duration of USSP beyond 15 seconds and is the highest for the USSP 300. These results show that corrosion resistance is the highest for the USSP 15 and is followed in decreasing order by those of USSP 30, USSP 60, un-USSP and USSP 300.

To reveal the morphology of the surfaces following 15 days of exposure, the un-USSP, USSP 15 and USSP 300 surfaces were examined by scanning electron microscope and the micrographs are shown in Figs. 7.8(a-c). In all the cases deposition of corrosion products is seen on their surfaces. The deposited layer is more pronounced on the surface of the USSP 15 sample (Fig. 7.8b). On the USSP 300 sample cracks are visible in the deposited layer. These observations suggest that corrosion products on the USSP 15 surface were more tenacious and uniform in comparison with those of the un-USSP and USSP 300 surfaces. The EDX analyses of these surfaces are shown in Figs. 7.9(a-c). The quantitative results show that the weight% of Al and oxygen are very close for all the exposed samples and are approximately in the range of 32-35% and 58-63% respectively.





FIGURE 7.8: SEM micrographs of the 7075 Al alloy after exposure in 3.5 wt.% NaCl solution for 15 days: (a) un-USSP, (b) USSP 15, and (c) USSP 300 conditions.

Stoichiometric calculation of these values indicates that the primary corrosion products formed on the exposed samples are identical in nature and may be $Al(OH)_3$. In order to examine it, the exposed samples were subjected to XRD studies and X-ray diffraction peaks are presented in Fig. 7.7. Interestingly in all the cases there are identical peaks and the peaks of $Al(OH)_3$ are recorded in all the cases. These facts suggest that the major corrosion product on all the exposed samples was $Al(OH)_3$. This corroborates with the results shown by EDX analysis (Fig. 7.9) where stoichiometric weight ratio of Al and oxygen was approximately 1:2, indicating formation of $Al(OH)_3$ as the main corrosion product.

It is important to discuss the reasons as what resulted in formation of very stable, tenacious and uniform corrosion products on the surface of USSP 15 vis-à-vis un-USSP and higher duration USSP treated samples. It is evident from the Fig. 3.2c and Fig. 3.2d that the degree of inhomogeneity increased from USSP 30 to USSP 300 samples, consequently the inhomogeneity of the passivated oxide layer also increased and likewise the tendency for pitting and localised corrosion (Fig. 7.8c). The sharp edges in the USSP 60 (Fig. 3.3b) and USSP 300 (Fig. 3.3c) samples clearly show chipping (shown by arrow) and multilayer chipping respectively. Normally, the surface of Al and its alloys in solution treated condition are covered with thin, uniform and homogeneous layer of oxide film. However, the oxide film becomes non-uniform and inhomogeneous at the sites of coarse precipitates on the surface and causes localised corrosion on surface of the un-USSP [73]. On the other hand, there was fragmentation/refinement of the precipitates from USSP in surface region of the USSP 15 specimen, hence there was little tendency



FIGURE 7.9: EDX results of the 7075 Al alloy following immersion in 3.5 wt.% NaCl solution for 15 days: (a) un-USSP, (b) USSP 15 and (c) USSP 300.

of localized corrosion in this sample. It is also likely that precipitates are extensively fragmented and get dissolved in the matrix. Thus, the size as well as the volume fraction of the precipitates is drastically reduced in surface region of the specimen. However, with continuous increase in plastic deformation of the USSP treated surface roughness of the surface increases and formation of uniform and effective passive layer is hindered and localized corrosion is enhanced. In general, compressive residual stress in the surface

region enhances the corrosion resistance but in this investigation corrosion resistance of the USSP 300 sample was drastically reduced in spite of its residual compressive stress being highest among all the USSP treated specimens (Fig. 3.17). This behavior may be attributed to highly detrimental effects of the high level of roughness and consequent large inhomogeneity of USSP treated surface. Such a state of the USSP treated surface leads to high rate of corrosion due to enhancement of localized corrosion resulting from large disparity in the compressive residual stresses, concentration of constituent elements, dislocation density and the thickness of the resulted passive film, from one to other region of the surface subjected to long durations of USSP.

The decrease in current density of the USSP 15 sample may be due to formation of the very tenacious and uniform corrosion products on its surface, development of nano grains in the surface region with less microstrain and low dislocation density. Balusamy et al. [77] studied the effect of ball diameter with varying treatment time on corrosion behavior of AISI 409 stainless steel and found that the sample SMATed with 2 mm balls showed passivation and better corrosion resistance as compared to those SMATed by 5 mm and 8 mm diameter balls due to its lower roughness, less volume fraction of martensite and low dislocation density. Wang et al. [145] also observed that surface nanocrystallization improved potentiodynamic polarization of the 1Cr18Ni9Ti stainless steel by maintaining passivation and decreasing the anodic current density.

There are several factors responsible for the enhancement of corrosion resistance of metallic materials such as grain size, surface defects, associated stresses, surface roughness, hardness, temperature etc. Ultrasonic shot peening is a novel method of surface

modification which refines the surface grains up to nano level without altering chemical composition of the system. These results show that the nanostructured surface grains enhance formation of adherent and more effective passive layer on the USSP treated samples which improves the corrosion resistance. The higher number of grain boundaries in surface region of the USSP treated samples as compared to that in the un-USSP state facilitates faster rate of formation of effective passive layer, enhancing the reaction of Al and oxygen ions at the interface and restricting the passage of metal ions from the surface towards the solution [146]. In the case of stainless steel, it was observed that nanocrystallization promoted formation of passive layer enhancing the diffusion of Cr to the surface and formation of homogeneous oxide layer [147]. Many researchers have also reported strain induced martensitic transformation in steels which caused reduction in corrosion resistance through galvanic coupling between the austenite and martensite phase [148, 149]. The improvement in corrosion resistance of the USSP 7075 alloy may be attributed to refinement of the second phase precipitates which reduced the galvanic coupling with the α -matrix. Using scanning kelvin probe force microscopy Rouleau et al. [150] showed that precipitate matrix potential gradient either gets preserved or reduced from laser shock peening of 2050-T8 aluminium alloy. Chen et al. [151] used shot peening for surface nanocrystallization of 6061 aluminium alloy to an average grain size below 100 nm and found significant improvement in corrosion resistance. Corrosion resistance of ultra fine grained AA1100 and AA5052 alloy produced by equi-channel angular pressing (ECAP) was studied in 0.6 mol/L of NaCl by Joon Son et al. [152]. They attributed the improvement in pitting corrosion from ECAP to decrease in the size of precipitates and increase in the rate of formation of oxide layer. In the present investigation, it is found that the surface grains of the test samples after USSP treatment are refined to 16-20 nm size. This refinement of surface grains in to nanostructured surface region enhanced the formation of passive layer. The USSP15 sample shows best corrosion resistance due to much higher efficiency for passivation because of the nano crystallised surface with minimum defects. The USSP 30, USSP 60 and USSP 300 show further refinement in the surface grain size but the effect of passivation on the corrosion resistance continuously decreases due to increase in inhomogeneity of the surface, increase in density of defects and the tendency for surface cracking. Hence, it is obvious that the refinement of grains in the surface region is not the sole means of governing corrosion resistance of metallic materials. The combination of the other factors like type of phases, surface inhomogeneity and roughness, residual stresses, dislocation density and surface defects like cracks play important role in controlling the process of corrosion.

It is well known that increase in surface roughness decreases polarization resistance of metals [153, 154]. Increase in surface roughness increases the overall surface area which deteriorates the corrosion resistance [155–159]. Lee et al. [78] used shot peening and ultrasonic shot peening to study corrosion behavior of AISI 304 stainless steel and found that shot peened samples showed lower corrosion resistance than that of the bare sample whereas the ultrasonically shot peened sample showed superior corrosion resistance. They attributed the increase in roughness as the main cause for poor resistance of the shot peened specimen. Walter et al. [160] reported that increase in the surface roughness increased susceptibility for pitting in the AZ91 magnesium alloy and also affected its passivation. Similar type of behavior is observed also in the present investigation, in which there is best passivation in the USSP 15 sample with comparatively less surface roughness. On the other hand, in the USSP treated 30, 60 and 300 samples higher roughness, increased inhomogeneity, surface cracking deteriorated the nature of the passive film and causing poor corrosion resistance.

Ultrasonic shot peening induces compressive residual stress up to a certain depth in the material. Krawiec et al. [75] used electrochemical impedance spectroscopy (EIS) to study electrochemical behavior of laser shock peened AA2050-T8 in 0.1M NaCl solution. Oxide film and charge transfer resistance were found to increase sharply from laser shock peening (LSP) and were attributed to increased compressive residual stress. Similarly, corrosion behavior of LSP treated AA6082-T651 was studied in 0.6M NaCl solution by Trdan et al. [161]. Anodic shift in pitting potential with substantial decrease in corrosion current density was observed and was attributed to higher compressive residual stresses. After 24h of exposure also the LSP treated sample showed almost seven times higher R_p value than that of the bare sample. Thangaraj et al. [79] reported that the compressive residual stresses increased for the 304 stainless steel SMATed with 5 and 8 mm balls, however, a decrease in corrosion resistance was observed as compared to that treated with 2 mm balls.

Increase in dislocation density can also be one of the factors for deterioration of corrosion resistance of longer USSP treated specimens in the present investigation like that reported earlier [162, 163]. According to Laleh et al. [164] corrosion resistance of the AZ91D magnesium alloy samples SMATed using 5 mm balls decreased due to increase

in defect density whereas substantial increment was observed in corrosion resistance of the samples SMATed using balls of 2 mm diameter. Pitting corrosion susceptibility of the 5052 aluminium alloy deformed by accumulative roll bonding was studied by Naeini et. al. [165], it was found that pitting corrosion resistance was deteriorated due to increased dislocation density and defects. With increase in the treatment time it was found that the dislocation density increased and also the surface roughness of the USSP treated alloy 7075 increased. Ultrasonic shot peening increased the dislocation density in the surface region which acted as an active site due to its higher energy state for the corrosion phenomenon to take place. It is combined effect of increased dislocation density and surface roughness which caused deterioration of corrosion resistance of the presently studied USSP treated samples in spite of the surface nanocrystallization. Intrui et al. [166] showed that large number of uniformly distributed defects were present in the fine-grained layer prepared from sputtered deposition, reducing the concentration of chloride ions at each defect and thus improving the pitting corrosion resistance. Wen et al. [74] compared corrosion behavior of the 2024 Al alloy SMATed using steel and ceramic balls. Nanocrystallization near the surface region was achieved in both the conditions, but in the case of steel balls Fe containing layer was induced after SMAT. The dense passive film formed using ceramic balls enhanced the corrosion resistance whereas the defective passive film of Fe induced from SMAT using steel balls diminished the corrosion resistance of the 2024 Al alloy.

In the present investigation, USSP 15 sample shows superior corrosion resistance as

compared to the other USSP treated as well as the un-USSP sample. Potentiodynamic polarization, electrochemical impedance studies (EIS), anodic polarization and weight loss studies corroborate with each other, showing best corrosion resistance of the USSP 15 sample. The deterioration in corrosion resistance of the USSP 30, USSP 60 and USSP 300 samples is essentially due to increase in their surface roughness which acted as active sites for pitting. The combination of lower degree of deformation, low density of dislocations and nanostructured surface layer resulted in formation of compact passive layer and improved corrosion resistance in the USSP 15 sample. Also, the refinement of second phase particles due to USSP reduces the galvanic coupling between the α -matrix and the precipitates and improved the pitting resistance. The above observations confirm that there is no single parameter which governs the corrosion behavior of USSP treated metallic materials. It is optimum combination of the several factors, referred to above, which ultimately improves the corrosion resistance.

7.4 Conclusions

The following conclusions are drawn from this chapter:

1. The USSP 15 sample exhibits best corrosion resistance among all the samples, including the samples USSP treated for longer durations as well as un-USSP one. It is due to higher passivation resulting from the nanostructured surface layer, lower plastic deformation, less microstrain, lower dislocation density and compressive stress in the USSP 15 sample which promote formation of dense, stable and tenacious passive film of aluminium hydroxide.

- 2. USSP treatment for long duration of 300 seconds develops largest surface roughness, which acts as active site for pitting and reduces the corrosion resistance.
- 3. Thus, it is not only the nanostructured surface layer which governs the process of corrosion of the USSP treated peak aged 7075 aluminium alloy in 3.5 wt.% NaCl solution but also the other factors like surface roughness, compressive residual stress, microstrain and dislocation density and formation of effective protective passive film which play very vital role.