

CHAPTER 4

HOT CORROSION BEHAVIOR OF SUPERALLOY IN718 AT 700°C

4.1 INTRODUCTION

This chapter presents hot corrosion behavior of the superalloy IN718 at 700°C for 100 h, in 100 wt% NaCl (salt 1S) and in salt mixtures of 60 wt% Na₂SO₄ + 40 wt% V₂O₅ (2SM) and 75 wt% Na₂SO₄ + 15 wt% NaCl + 10 wt% V₂O₅ (3SM), deposited separately by spray gun technique. The weight gain per unit area at 700°C was increased by 49% for salt 1S, 153% for the dual salt mixture 2SM and only 8% for the triple salt mixture 3SM, in comparison with that observed earlier at 600°C. The marked increase in the severity of corrosion at 700°C is attributed to formation of the highly damaging compound NaVO₃ that significantly enhances the oxygen activity, in the 2SM coated samples. The effect of surface roughness and dislocation density on corrosion behavior at 700°C, however, is found to be similar to that at 600°C discussed in Chapter 3. Ultrasonic shot peening, a novel technique of surface modification is found to enhance the hot corrosion resistance in the salt mixture 2SM at 700°C appreciably due to extensive grain refinement to nanoscale and enhanced formation of highly protective Cr₂O₃ layer in the surface region.

4.2 RESULTS

4.2.1 VISUAL OBSERVATION

Samples with different surface roughness were visually examined after every heating cycle to check the surface condition of the corroded samples. The features of the corrosion scale were recorded using a digital camera and are shown in Fig. 4.1. Table 4.1 presents details of visual observation of the samples oxidized/corroded at 700°C for 100 h. The colour and scale characteristics of the different salt coated samples remained unaffected by surface roughness.

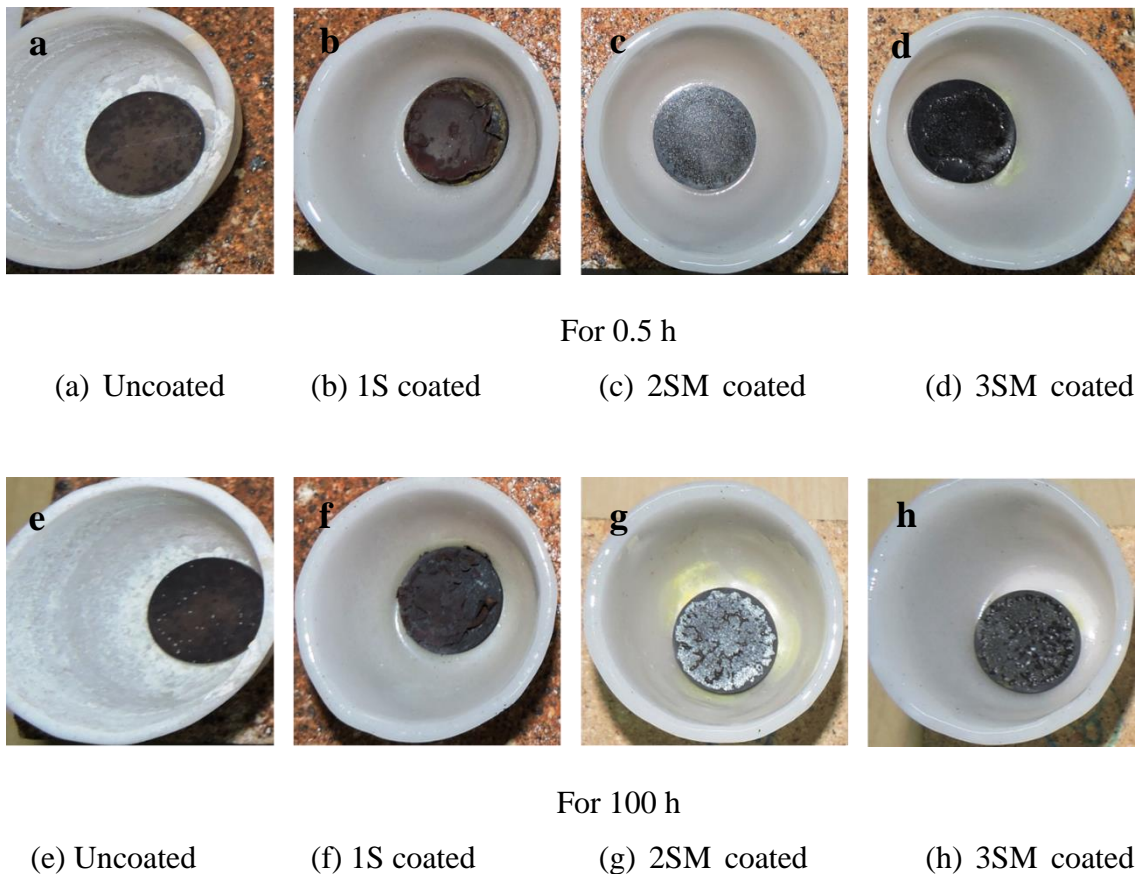


Fig. 4. 1: Digital photographs of the #400 grit ground samples oxidized/hot corroded at 600°C for 0.5 h (a-d) and 100 h (e-h).

Table 4.1: Visual observation of the samples oxidized hot corroded at 700°C up to 100 h.

Salt coating	Colour	Scale characteristics
Uncoated	Dark brown	No scale formation, thin adherent oxide layer formed.
1SM	Dark redish brown	Heavy scaling, formation of fragile scale and spalling of scale.
2SM	Gray	Adherent coating and less spalling
3SM	Dark gray with yellow spots on the surface	Scaling and porosity of the oxide layer.

4.2.2 HOT CORROSION KINETICS

The influence of salt/salt mixtures on the hot corrosion behavior was established from the plots of weight gain per unit area with the time of exposure (Fig. 4.2 a, 4.3 a and 4.4 a). Negligible weight gain was found in the uncoated samples from exposure at 700°C. However, significantly large weight gain was there in the samples coated with the salt 1S and the salt mixture 2SM as compared with that coated with the salt mixture 3SM. The plots of the square of weight gain per unit area of the samples exposed at 700°C for a period of 100 h are shown in Fig. 4.2 (b), 4.3 (b) and 4.4 (b). The samples coated with salt/salt mixture show parabolic behavior for the entire period of exposure of 100 h. The plot of the square of weight gain/area (mg^2/cm^4) versus time (h) is used to establish rate law for the process of hot corrosion. The parabolic rate constant k_p is calculated using equation $(\Delta W/A)^2 = k_p * t + C$, where $\Delta W/A$ is weight gain per unit surface area (mg/cm^2), t is the time of exposure and C is a constant [Pilling et al. 1923].

The calculated values of the parabolic rate constants are shown in Table 4.2. A higher value of k_p implies faster rate of oxidation/corrosion at a given temperature. The value of k_p is found to be maximum for 700°C in the sample coated with salt 1S. The weight gain plots are best fitted using linear least-square method. It is obvious from Fig. 4.4 that the value of k_p is higher for the sample exposed to salt 1S for all the different grades of roughness, than for those coated with the salt mixtures 2SM and 3SM. Further, k_p increases with roughness of the surface in all the samples coated with 1S, 2SM, and 3SM. It is important to mention that at 600°C the samples coated with 2SM showed lowest corrosion among the samples coated with salt 1S and the salt mixtures [Chapter 3]. On the other hand, the present study at higher temperature of 700°C shows opposite behavior and the salt mixture 2SM is much more corrosive than the three salt mixture (3SM).

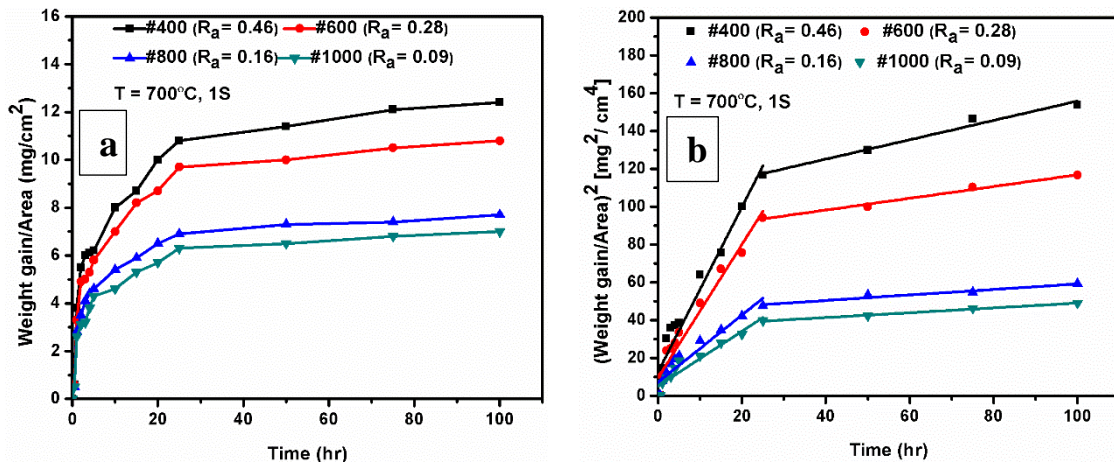


Fig. 4. 2: Effect of surface roughness on corrosion behavior of the specimens coated with 1S salt and exposed at 700°C up to 100 h: (a) weight gain per unit area vs time; (b) square of weight gain per unit area vs time.

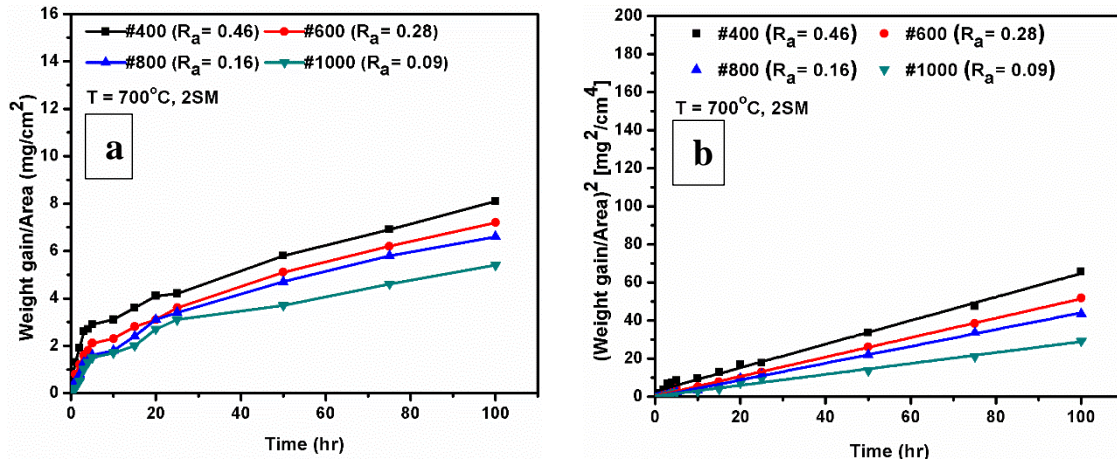


Fig. 4. 3: Effect of surface roughness on corrosion behavior of the specimens coated with 2SM salt mixture and exposed at 700°C up to 100 h: (a) weight gain per unit area vs time; (b) square of weight gain per unit area vs time.

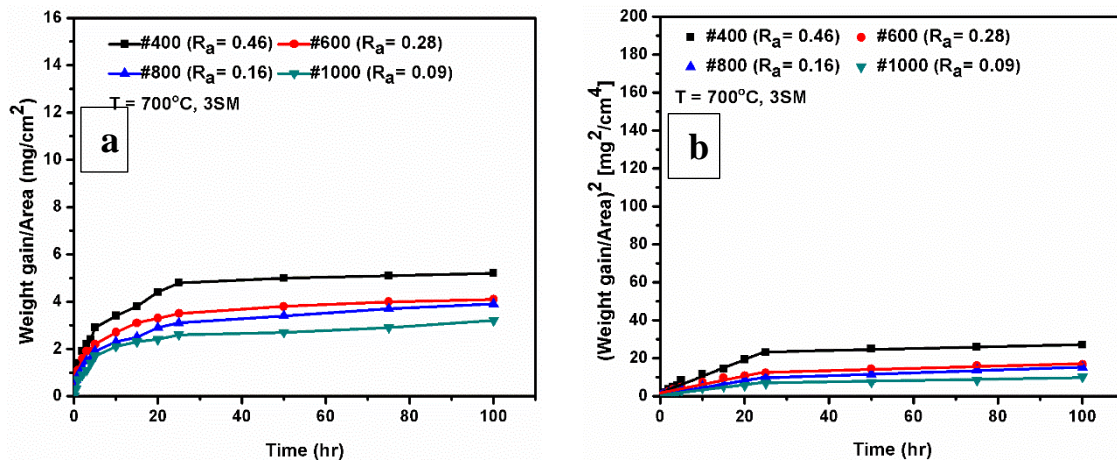


Fig. 4. 4: Effect of surface roughness on corrosion behavior of the specimens coated with 3SM salt mixture and exposed at 700°C up to 100 h: (a) weight gain per unit area vs time; (b) square of weight gain per unit area vs time.

Table 4.2: Parabolic rate constant (k_p) of the samples with different roughness, corroded at 700°C up to 100 h.

Salt/salt mixture corrosion	#400 ($R_a = 0.46 \mu\text{m}$)		#600 ($R_a = 0.28 \mu\text{m}$)		#800 ($R_a = 0.16 \mu\text{m}$)		#1000 ($R_a = 0.09 \mu\text{m}$)	
	k_p	R^2	k_p	R^2	k_p	R^2	k_p	R^2
1S								
Up to 25 h	4.35	0.95	3.52	0.98	1.44	0.93	1.23	0.96
Up to 100 h	0.51	0.98	0.31	0.97	0.12	0.99	0.16	0.95
2SM								
Up to 100 h	0.61	0.99	0.51	0.99	0.44	0.98	0.28	0.99
3SM								
Up to 25 h	0.87	0.97	0.48	0.94	0.37	0.96	0.29	0.97
Up to 100 h	0.08	0.94	0.06	0.94	0.06	0.99	0.05	0.96

Further, it is important to mention that at 700°C the highest hot corrosion is from the coating of salt 1S, but the relative increase in the weight gain/area at 700°C compared with that at 600°C for the sample coated with salt 1S is only 49%, whereas it is 153% for the sample coated with the salt mixture 2SM, and only 8% for that coated with the 3SM (Fig. 4.5).

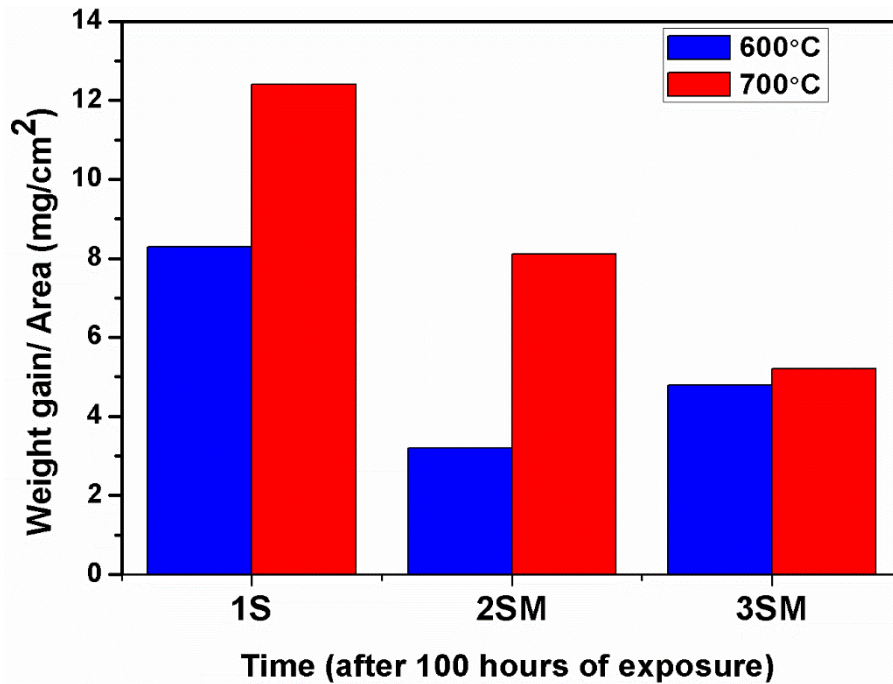


Fig. 4. 5: Comparison of weight gain/area vs time of exposure at 600 and 700°C for different salt/salt mixture coatings.

4.2.3 X-RAY DIFFRACTION ANALYSIS

The nature of the phases formed from high temperature corrosion affects the process of corrosion of the material. The XRD patterns of the un-shot peened and 5 min USP treated samples coated with 2SM salt mixture after the exposure of 100 h at 700°C, are shown in Fig. 4.6. Several oxides, sulphides, vandates such as Cr_2O_3 , Fe_2O_3 , Fe_3O_4 , NiVO_3 , FeVO_4 , NaVO_3 , NiV_2O_7 , $\text{Ni}(\text{VO}_4)_7$, FeS , CrS , NiS , $\text{Na}_2\text{Cr}_2\text{O}_7$, NaCrO_4 , NiFe_2O_4 may be seen to form.

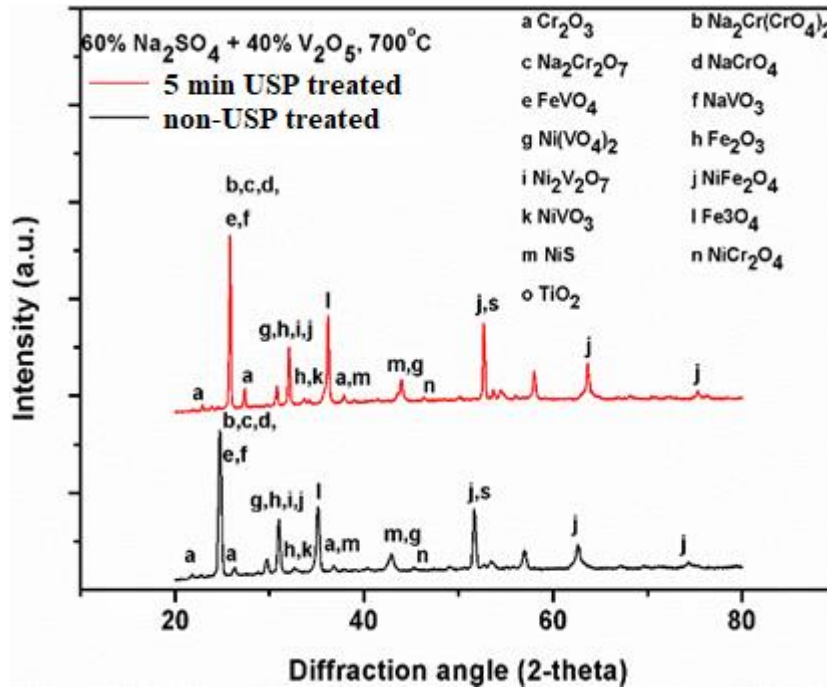


Fig. 4. 6: X-ray diffraction patterns of the un-shotpeened and 5 min ultra sonic shot peened samples coated with 2SM salt mixture and exposed at 700°C up to 100 h.

4.2.4 DEPTH OF PENETRATION OF CORRODANT

The samples hot corroded in the 2SM salt mixture, from the exposure of 100 h at 700°C, were sectioned transversely, perpendicular to the corroded surface, to assess the depth of penetration of the corrodants below the surface, at different surface roughness and dislocation densities. Fig. 4.7 shows that the depth of penetration of the corrosion products in the sample with different surface roughness is in the order: $R_{a4} > R_{a3} > R_{a2} > R_{a1}$, for the 2SM salt coated samples. Oxidation and sulfidation are found to be the main cause of damage for the 2SM coated samples.

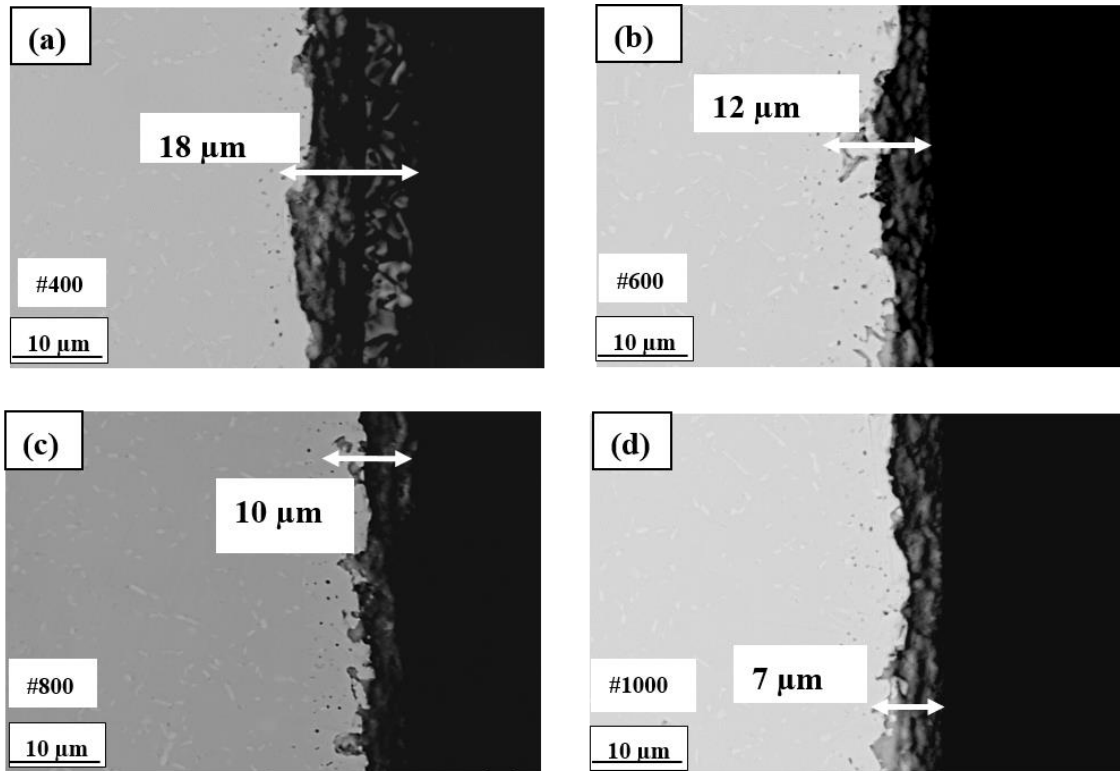


Fig. 4. 7: SEM micrographs showing the effect of surface roughness on the depth of penetration of corrosion products in the samples coated with salt mixture 2SM and exposed at 700°C for 100 h: : (a) #400, (b) #600, (c) #800 and (d) #1000.

4.2.5 EFFECT OF ULTRASONIC SHOT PEENING (USP) TREATMENT

The plots of weight-gain per unit area and square of weight-gain per unit area of the non-USP and USP treated samples coated with 1S salt and salt mixtures 2SM and 3SM exposed at 700 °C for a period of 100 h are shown in Figs. 4.8, 4.9 and 4.10 respectively, and show the effect of ultrasonic shot peening on the hot corrosion resistance against the exposure of salt/salt mixtures. The samples exposed to salt 1S showed highest weight-gain, followed by those exposed to 2SM and 3SM salts mixtures respectively, in both, non-USP as well as USP treated condition. The USP treated samples exposed to salt 1S and the salt mixtures of 2SM and 3SM showed linear variation in weight for the entire period of exposure. The plots of square of weight-gain/unit area (mg/cm^2) versus time

(h) were used to establish the rate law for the process of hot corrosion. The rate constant (k_p) shown in Table 4.3 was calculated using the parabolic rate law equation [Pilling et al. (1923)]: $(W/A)^2 = k_p t + C$, where W/A is the weight-gain per unit surface area (mg/cm^2), t is the time of exposure, and C is a constant.

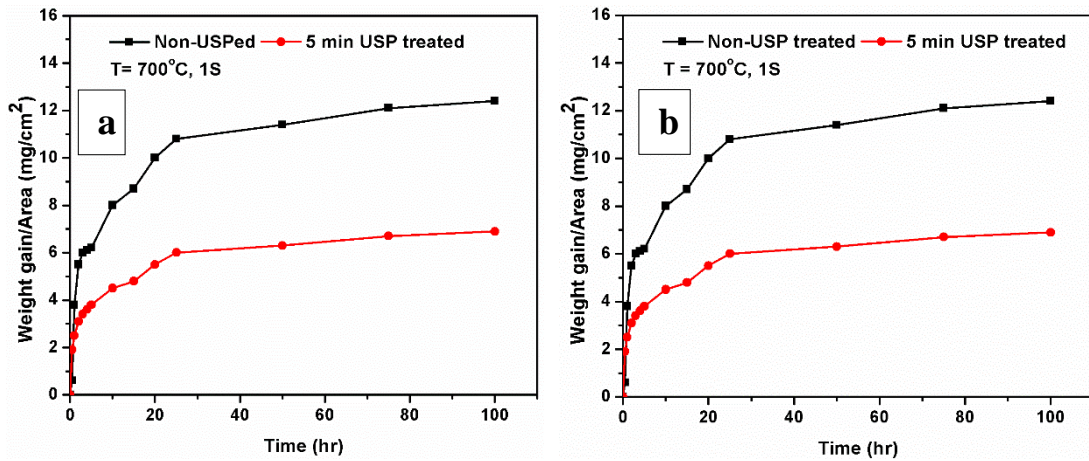


Fig. 4. 8: Effect of ultrasonic shot peening for 5 min on hot corrosion resistance of the specimens coated with 1S and exposed at 700°C up to 100 h: (a) weight gain per unit area vs time; (b) square of weight gain per unit area vs time.

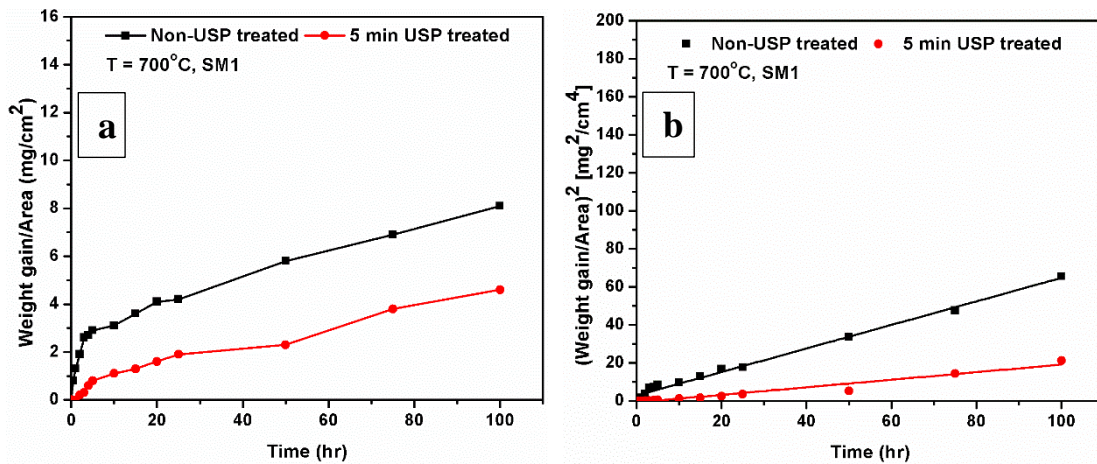


Fig. 4. 9: Effect of ultrasonic shot peening for 5 min on hot corrosion resistance of the specimens coated with 2SM and exposed at 700°C up to 100 h: (a) weight gain per unit area vs time; (b) square of weight gain per unit area vs time.

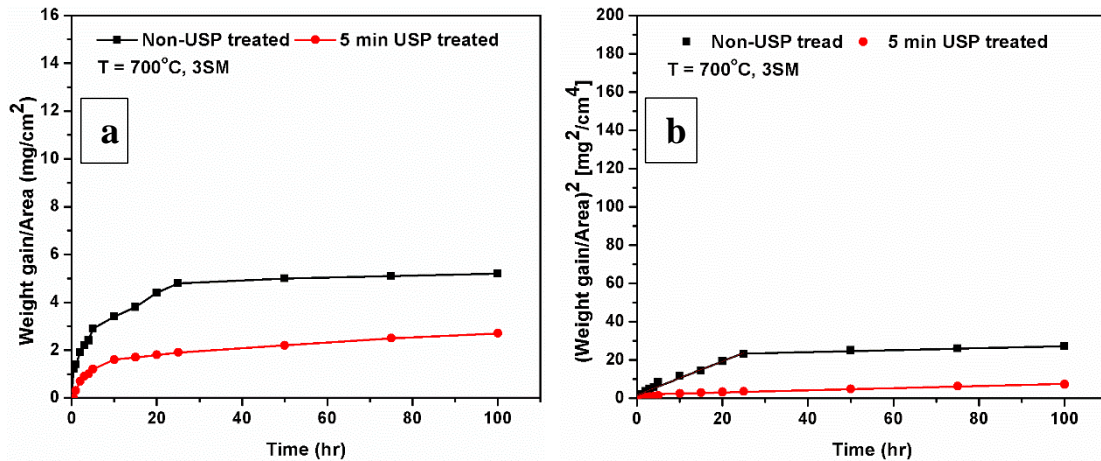


Fig. 4. 10: Effect of ultrasonic shot peening for 5 min on hot corrosion resistance of the specimens coated with 3SM and exposed at 700⁰C up to 100 h: (a) weight gain per unit area vs time; (b) square of weight gain per unit area vs time.

Table 4.3: Parabolic rate constant (k_p) of the non USP and USP treated samples, corroded at 700°C up to 100 h.

Salt/salt mixture corrosion	#400 polished ($R_a = 0.46 \mu m$)		5 min USP treated ($R_a = 1.43 \mu m$)	
	k_p	R^2	k_p	R^2
1S				
Up to 25 h	4.35	0.95	1.26	0.97
25 to 100 h	0.51	0.98	0.16	0.95
2SM				
Up to 25 h	0.61	0.99	0.19	0.95
25 to 100 h	0.61	0.99	0.19	0.95
3SM				
Up to 25 h	0.87	0.97	0.27	0.92
25 to 100 h	0.07	0.94	0.04	0.94

Fig. 4.11 shows the comparison of the depth of penetration of corrosion products in the samples coated with salt mixture 2SM for the non-USP and USP treated samples and exposed at 700°C for 100 h. Fig. 4.11 (a) shows that the non-USP treated sample was more prone to corrosion as compared to the USP treated sample.

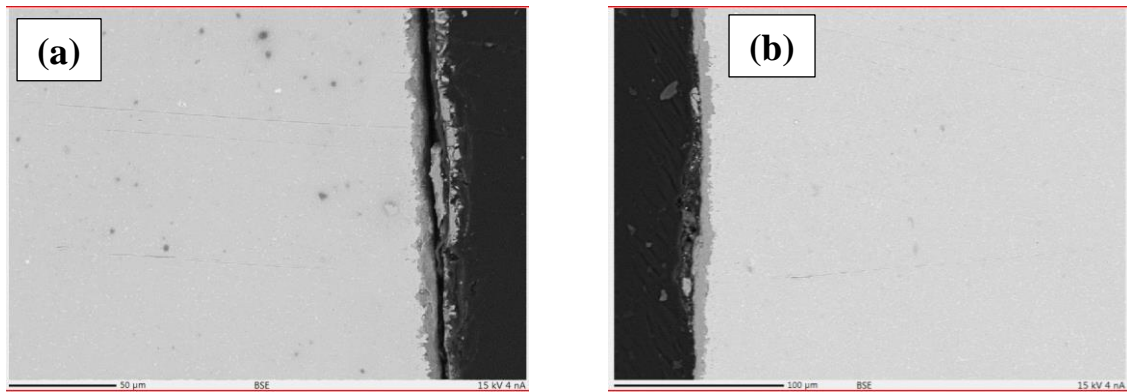


Fig. 4. 11: SEM micrographs showing the comparison of the depth of penetration of corrosion products in the samples coated with salt mixture 2SM and exposed at 700°C for 100 h (a) non-USP and (b) 5 min USP treated.

Wavelength dispersive spectroscopy (WDS) was used for elemental mapping of the corroded samples. EPMA analysis of the coated samples in the highest corrosive state (400 grit ground sample) and the sample USP treated for 5 minutes was performed to examine the elemental distribution in these specimens. The non-shot peened and shot peened samples corroded by 2SM coating, exposed at 700°C for 100 h were sectioned perpendicular to the corroded surface, and the elemental maps show variation of nickel, iron, chromium, oxygen in the hot corroded samples (Fig. 4.12). The diffusion of nickel, iron, and chromium from the base material towards the surface of the substrate resulted in the formation of NiO, Fe₂O₃, Fe₃O₄, Cr₂O₃ oxides.

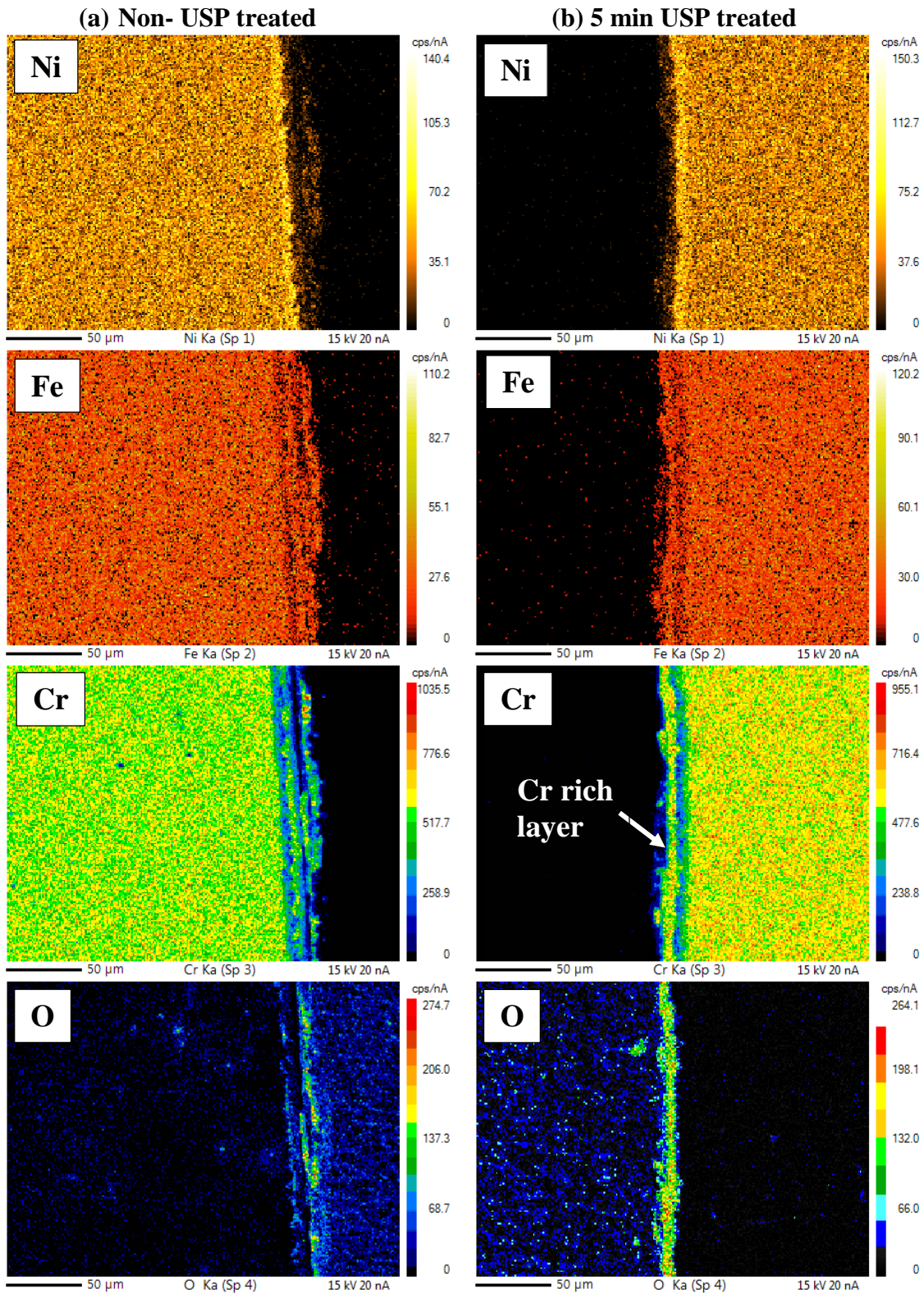


Fig. 4. 12: EPMA/SE X-ray mapping of cross sections of the specimens coated with the salt mixture 2SM and exposed at 700°C for 100 h, showing distribution of different elements: Nickel, Chromium, Iron and Oxygen for (a) non-USP and (b) 5 min USP treated.

4.3 DISCUSSION

There is little gain in the weight of the uncoated sample exposed at 700°C, and small gain in the weight of the samples coated with the three salt mixture 3SM, from exposure at 700°C. This may be attributed to formation of an intact and protective oxide layer on the uncoated sample. On the other hand, there is significant gain in weights of the samples coated with the salt 1S, followed by that coated with the dual salt mixture 2SM, from the exposure at 700°C for 100 h. It may be seen that there are dual slopes in the plots of the square of weight gain per unit area versus the time of exposure in the samples coated with the salt 1S and the three salt mixture 3SM (Figs. 4.2 b and 4.4 b respectively). This behavior is attributed to spalling of scales in these samples due to the stresses induced by the oxide films during their growth. At some point, the increased thickness of the scale is unable to sustain the associated stress and leads to breakage of the scale and subsequent spallation of the oxide scale [Khanna (2002)]. The partial spallation of scale in some regions exposes the subsurface of the sample to air environment to cause oxidation at the exposed subsurface and thus the overall corrosion kinetics slows down. However, in the samples coated with the salt mixture 2SM, and exposed at 700°C for 100 h, the coating was found to be adherent and there was no spallation of scale; therefore, there is a single slope for this condition (Fig. 4.3 b).

In general, corrosion kinetics of the rough samples is found to be higher than those of the smoother ones. Also, the weight gain per unit area and k_p values are relatively higher for the samples exposed to salt 1S and the salt mixture 2SM. Square of weight gain per unit area versus time plot show that corrosion rate is slow for the initial 5 h and increases rapidly till 25 h and remains almost constant up to 100 h, for the samples coated with salt 1S and the salt mixture 3SM. The exposure of the first 25 h is more aggressive because of continuous formation of corrosion products over the substrate; however, the

corrosion rate is slowed down after 25 h for the samples coated with salt 1S and the salt mixture 3SM. Oxide layer was formed due to initial corrosion reaction and acted as a barrier against further penetration of the remaining salt/salt mixtures. On the other hand, samples coated with 2SM salt mixture shows increasing trend of weight gain/area up to 100 h. Parabolic nature of hot corrosion is exhibited by all the samples coated with 1S, 2SM and 3SM.

The effect of surface roughness on corrosion behavior of different alloys has been discussed by different researchers and various mechanisms have been proposed. The deleterious effect of surface roughness can be explained in terms of electron work function (EWF), the minimum energy required for release of an electron from the surface of the alloy. Electron release is reported to be easier from the rougher surface with high density of defects and exhibiting higher corrosion rate [Li et al. (2006), Wan et al (2012), Saito et al. (1994)]. In the case of rough surface, involvement of larger area of the surface should be another cause of the high rate of corrosion. It is known that cold deformation occurs due to mechanical grinding and it increases the density of dislocations in the upper most surface layer of the material and the state of energy is increased which enhances the rate of diffusion of metallic atoms towards the surface. Defects like dislocations, kinks and ledges enhance the nucleation and growth of oxides on the rough surface [Seo et al. (2014)].

A schematic presentation of the probable mechanism of hot corrosion, based on the effect of surface roughness is shown in Fig. 4.13. The ground surface exhibits various peaks and valleys at the surface of the sample (Fig. 4.13 a). All the valleys get filled with deposition of salt/salt mixtures, whereas the peaks have much less amount of salt/salt mixtures for the reaction (Fig. 4.13 b); therefore, the surfaces with deeper

valleys undergo severe corrosion. Diffusion of salt/ salt mixture starts at 700°C towards interior of the specimen and diffusion of alloying elements towards the surface of specimen (Fig. 4.13 c and d). Penetration of corrodants in the bulk of the specimen occurs through the valley (Fig. 4.13 e). Fig. 4.13 (f) shows broadening of valley due to corrosive reactions taking place and the formation of oxides and pits at the interface of the alloy and corrodant.

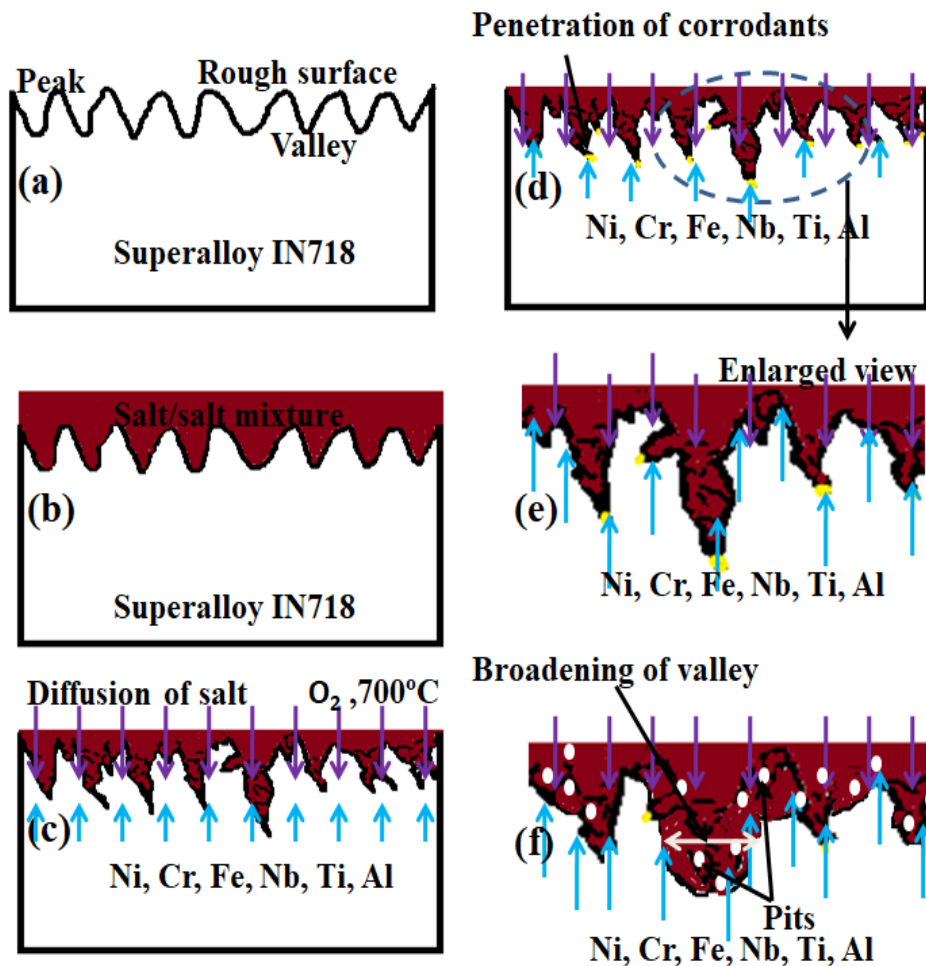


Fig. 4. 13: Schematic showing the effect of surface roughness on hot corrosion of the superalloy IN718 at 700°C.

The samples ground by the most rough emery paper (#400) with the average surface roughness $R_{a4} \approx 0.46 \mu\text{m}$ [Chapter 3], showed highest weight gain and the most deleterious effect is observed in the samples coated with 2SM, from exposure at 700°C for 100 h. The depth of penetration of the corrosive species is found to be 7.2 μm , 9.9 μm , 12.1 μm and 17.5 μm corresponding to average roughness of R_{a1} , R_{a2} , R_{a3} , and R_{a4} from Figs. 4.7 (a-d), respectively.

It was found that the severity of hot corrosion at 600°C was in decreasing order from the coatings of salt 1S, followed by that of the salt mixture 3SM and was lowest in the salt mixture 2SM. On the other hand this sequence is changed as 1S>2SM>3SM at 700°C. Since the salt mixture 2SM undergoes eutectic melting at 603°C [Otero et al. (1987)], corrosion resistance of the sample coated with 2SM salt mixture at 600°C was not much affected at 600°C and the Cr_2O_3 layer formed was quite protective [Cuevas-Arteaga (2008)]. The mechanism of hot corrosion of the sample coated with the 2SM, the most corrosive one with roughness R_{a4} , was studied in detail.

Out of the four samples with different surface roughnesses exposed in the salt mixture 2SM; the sample with the maximum surface roughness of R_{a1} showed much higher weight gain as compared with that exposed at 600°C for 100 h. The surface with higher roughness was more susceptible to corrosive attack than the smoother ones due to its greater surface area. Oxygen penetrated the substrate and formed oxides of Cr, Fe, and Ni which led to weight gain. Some possible oxidation reactions with this salt mixture are reported in the Chapter 3. The solubility of the protective oxides in the molten salt mixture 2SM is higher than that in Na_2SO_4 , therefore the dissolution of the protective oxide layer took place [Porcayo-Calderon et al. (2015)]. V_2O_5 reacted with Cr_2O_3 , Fe_2O_3 , and NiO and formed vanadate compounds at the oxide salt interface along with

the formation of $\text{Na}_2\text{Cr}_2\text{O}_7$. Dissociation of sodium sulfate to attain equilibrium at oxide/salt interface takes place. Basic fluxing process leads to formation of different products as per the following reactions (4.1-4.4):



Sulfur ions react with Cr, Fe and Ni or with their oxides and form following sulfides which break the protective chromia layer [**Mannava et al. (2016)**].



The salt mixture 2SM with 60 wt% Na_2SO_4 and 40 wt% V_2O_5 forms a very hazardous and low melting phase of sodium meta vandate (NaVO_3) with melting point of 610°C [**Doolabi et al. (2017)**] which significantly enhances the oxygen activity [**Porcayo-Calderon et al. (2015)**].



At 700°C, the fluidity of the molten eutectic increases [**Cuevas-Arteaga (2008)**] and the increase in severity of hot corrosion led to weight gain per unit area of the 2SM

coated samples. Vanadates are known to cause severe damage to protective oxide of Cr_2O_3 [Porcayo-Calderon et al. (2015)].

EPMA analysis also supports the above statement (Fig. 4.12 a). Here, it is worth mentioning that the weight gain per unit area from the 2SM coating is nearly 153% more at 700°C as compared with that at 600°C [Chapter 3]. The EPMA results show the extent of diffusion of alloying elements from the substrate to surface and that of salt elements from the surface into the substrate. It may be seen that Cr was involved more in corrosion reaction during hot corrosion, as it is depleted more from the base alloy. The corrosion of the superalloy IN718 with the 2SM salt mixture coating, at 700°C, is primarily by the oxidation process followed by sulfidation reactions as indicated above.

Furthermore, corrosion resistance is found to be enhanced by the novel process of ultrasonic shot peening. The presence of Cr_2O_3 layer on the shot peened samples resulted in improved corrosion resistance of the alloy because of extensive grain refinement at the surface. As discussed in Chapter 3, here also the diffusivity of chromium increases with increase in the population of grain boundary which leads to formation of highly protective Cr_2O_3 as compared to that in the un-shot peened one [Tan et al. (2008)]. The diffusivity of oxygen is enhanced on the shot peened before the formation of protective layer and decreased after the formation of protective layer by covering the grain boundaries on the modified surface [Kumar et al. (2016), Wang et al. (2003)]. The more protective effect of the oxide layer of Cr_2O_3 formed at 700°C on the USP treated surface is quite evident from the much better uniformity and higher thickness of the compact Cr_2O_3 layer formed on the USP treated sample (Fig. 4.12 b).

4.4 CONCLUSIONS

The following conclusions are drawn from this study:

- (a) Hot corrosion of the superalloy IN718 coated with salt 1S and salt mixtures 2SM and 3SM exhibited parabolic kinetics at 700°C. The weight gain analysis showed that IN718 had higher oxidation resistance at 700°C without any coating and the salt 1S coated sample exhibited higher weight gain at 700°C from exposure of 100 h as compared with the samples coated with the salt mixtures 2SM and 3SM, in respect of that observed earlier at 600°C.
- (b) The relative increase in weight gain/area from exposure at 700°C as compared with that at 600°C, from the salt 1S is only 49%, whereas it is 153% from 2SM, and only 8% from the 3SM coating.
- (c) The solubility of the protective oxides in the molten salts of sulfate-vanadate mixture at 700°C is higher than in Na_2SO_4 , therefore, there was dissolution of the protective oxide layer.
- (d) The highly damaging low melting compound of NaVO_3 increased the severity of corrosion of the sample coated with 2SM, enhancing the activity of oxygen.
- (e) Higher surface roughness increased the rate of corrosion due to nucleation and growth of oxides at the surface and penetration of corrosion products through the surface to the bulk of the alloy. Also, the sample with higher roughness had higher dislocation density and exhibited higher rate of corrosion.
- (f) Ultrasonic shot peening improved the hot corrosion resistance of the superalloy IN718 in the salt mixture 2SM at 700°C, promoting formation of highly protective layer of Cr_2O_3 .

