

CHAPTER 7
COMPARISON OF CYCLIC AND
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7.1. INTRODUCTION

In the previous chapters the oxidation and hot corrosion behavior of the super austenitic stainless steel 904L has been presented in detail. The various aspects such as the rate of oxidation/hot corrosion, scale formation and surface morphology have been discussed. This chapter presents comparison of the isothermal and cyclic oxidation and also of hot corrosion behavior of SASS 904L over the temperature range from 500-650 °C.

Barrett and co-workers [111] investigated oxidation behavior of twenty five commercial alloys with Cr and Cr+Al additions, at 1150 °C for 100 h under cyclic and isothermal exposures. It was observed that there was hardly any difference in their weight change in both the processes. The major phases formed in both the processes were based on alloy composition and were NiO and Cr₂O₃/chromite spinels. During cyclic oxidation, the alloys containing up to 16 wt% Cr were more likely to form Cr₂O₃ and its spinels which in general are more prone to spall due to vaporization. This vaporization is caused due to thermal cycling, which further gives rise to decrease in Cr-content in the alloy. Moreover, during isothermal exposure the vaporization rate of Cr₂O₃ was less, due to which the rate of spallation was also less. It was found that k_p value was more under cyclic oxidation than that in isothermal exposure.

Table 7.1: Comparison of cyclic and isothermal oxidation of important structural materials.

Material	Environment			Cyclic		Isothermal		Observations/Remarks
	Time	Temp (°C)	Condition	ΔW (mg/cm ²)	k_p (mg ² -cm ⁻⁴ h ⁻¹)	ΔW (mg/cm ²)	k_p (mg ² -cm ⁻⁴ h ⁻¹)	
Ti-48Al-2Cr [112]	3000 h	700	Flowing and Static air	No change in weight from 0-100 hrs. Incubation from 0-500 h. $\Delta W=6-8$ (3000 h)		$\Delta W=0.1$ mg(150 h), 1.2 mg(1500 h)		No spallation in both the processes. Thicker scale during cyclic than isothermal process. Most Detimental: Cyclic proces. Kinetics: Parabolic rate law
Ni-10Cr [113]	100 h	1000	81 vol. % N ₂ , 16 vol % O ₂ , 3 vol % O ₂ .	-		$\Delta W=5.2$ mg(25 h), 7.3 mg (50 hrs), 8.3 mg(75 h), 9.5 (100 h), $k_p=3.68 \times 10^{-2}$ (80 hrs)		Cyclic: Massive spallation. Isothermal: Moderate spallation. Most Detimental: Cyclic proces. Kinetics: Parabolic rate law.
AISI 304, Alloy 800 [114]	30-3000 h	650	In air	$\Delta W=0$ mg(25 h), 0 mg (50 h), 0.022 mg (75 h), 0.025 mg (100 h),		$\Delta W=0$ (25h), 0 mg (50h), 0.01 mg (75h), 0.02 mg (100 h), 1-0.2 mg (0-3000 h)		Cyclic: Increases Cr to deplete. Isothermal: Resists Cr to deplete. Most Detimental: Both has harmful effects.
T91 [115]	14-329 h	575-650	under Steam at 70% relative humidity	-		575 °C ($k_p=3 \times 10^{-5}$) $\Delta W=9$ mg(25 h), 10 mg(50 h), 15 mg(75 h), 22 mg (100 h), 600 °C ($k_p=5.32 \times 10^{-5}$) $\Delta W=20$ mg(25 h), 29 mg(50 h), 31 mg(75 h), 37 mg (100h), 650 °C ($k_p=3.14 \times 10^{-4}$) $\Delta W=40$ mg(25 h), 51 mg(50 h), 68 mg(75 h), 75 mg (100h),		Isothermal oxidation process is more damaging than cyclic process. Kinetics: Parabolic rate law.

Material	Environment			Cyclic		Isothermal		Observations/Remarks
	Time	Temp (°C)	Condition	ΔW (mg/cm ²)	k_p (mg ² -cm ⁻⁴ h ⁻¹)	ΔW (mg/cm ²)	k_p (mg ² -cm ⁻⁴ h ⁻¹)	
Ni-BASE ALLOY (738X) [111]	100 h	1000, 1100	In still air	<i>Weight gain at 1000 °C;</i> $\Delta W=1.4$ mg (25 h), 2.3 mg(50 h), 2.7 mg(75 h), 2.7 mg (100h), <i>Weight loss at 1100 °C;</i> $\Delta W=0.1$ mg(25 h), 12.8 mg(50 h), 18.5 mg(75 h), 27 mg(100h),		<i>Weight gain 1000 °C;</i> $\Delta W=0.5$ mg (25 h), 0.85 mg (50 h), 1.25 mg (75 h), 1.75 mg (100 h), 1100 °C; $\Delta W=1.75$ mg(25 h), 2.5 mg(50 h), 3.5 mg(75 h), 4.5 mg(100h),		Cyclic process is more damaging than Isothermal process
Ni-20Cr [116]	50-100 h	1100, 1200	In still air	<i>Weight loss 1100 °C,</i> $\Delta W= 27$ mg(25 h), 70 mg(50 h), 195 mg (100h), 1200 °C, $\Delta W= 165$ mg(25 h), 340 mg (100h),		<i>Weight gain 1100 °C,</i> $\Delta W=1.4$ mg(25 h), 2.1 mg(50 h), 2.6 mg(75 h), 3 mg (100h), 1200 °C, $\Delta W=3.05$ mg(25 h), 4 mg(50 h), 4.5 mg(75 h), 4.8 mg (100h)		Cyclic process is more damaging than Isothermal process

Note : Table 7.1:continued

Riffard and co-workers [117] investigated the influence of *yttrium* sol-gel coating on 304L stainless steel during air exposure at 1000 °C under cyclic and isothermal condition. During cyclic exposure, the *yttria* coated sample exhibited spallation after 10 cycles in which iron oxide was found in the spalled layer. However, during isothermal exposure coated *yttria* inhibited formation of iron oxide in the scale and was adherent due to which the weight gain under isothermal exposure was less than that in cyclic oxidation.

Laverde et al. [115] conducted continuous and cyclic oxidation tests on T91 ferritic steel grade under steam at 575-700 °C for 329 h. During isothermal exposure parabolic rate law was followed from 575-650 °C where the passivated layer consisted of three zones; the

outermost Fe_2O_3 , innermost Fe_2O_3 and the substrate $(\text{Fe,Cr})_3\text{O}_4$. There was continuous growth of thick oxide layer. Under cyclic exposure, the oxide scales were irregular and cracked due to thermal expansion at 600 and 700 °C.

Lowell [116] made additions of 3wt% Mn and 3wt% Si to Ni-20Cr and Ni-40Cr and generated new alloy Ni-20Cr-3Si. He performed oxidation test under cyclic and isothermal exposures at 1100-1200 °C for up to 100 h. Cyclic oxidation exposures resulted in much more severe attack compared with those of isothermally exposed samples. Another important observation was that during cyclic test the samples showed slight loss in weight whereas during isothermal exposure there was weight gain and formation of a thick scale. During cyclic oxidation there was spallation of scale. Addition of Si was found to be more protective than that of Mn. Si addition was more effective in case of cyclic exposure than isothermal exposure.

Barnard et al. [118] showed the effect of applied tensile stresses on the isothermal and cyclic oxidation behavior of nickel-based super alloys. The influence of applied stresses was investigated through measurements of specific mass change, oxide morphology and thickness, degree and depth of internal oxidation as well as compositional changes, in and around the oxide scales. It was observed that an applied tensile stress generally led to larger Cr/Ni ratios in the oxide scales, greater chromium depletion under the oxide as well as lower specific mass change and thinning of oxide scales. These affects are attributed to a greater concentration of dislocations, defects, etc. in the materials caused by the applied stresses. These defects acted as fast diffusion path for the Cr atoms to diffuse to the surface and thus caused a reduction in the duration of the less protective transient oxidation period, and promoted a faster formation of the protective Cr_2O_3 layer.

7.2. RESULTS

In the previous Chapters oxidation and hot corrosion behavior of the SASS 904L under both the isothermal and cyclic exposures at 500, 550, 600 and 650 °C for the various exposures from 0-100 h was observed by variation of weight change per unit area (ΔW). In this chapter the variation of weight gain with the duration of exposure is shown by bar diagrams. **Figure 7.1** shows bar diagram for isothermal and cyclic exposure of the SASS 904L for 25, 50, 74 and 100 h for the samples exposed at 500-650 °C. It may be noted that data for cyclic oxidation are obtained from the ΔW vs t plots corresponding to exposures of 25, 50, 75 and 100 h.

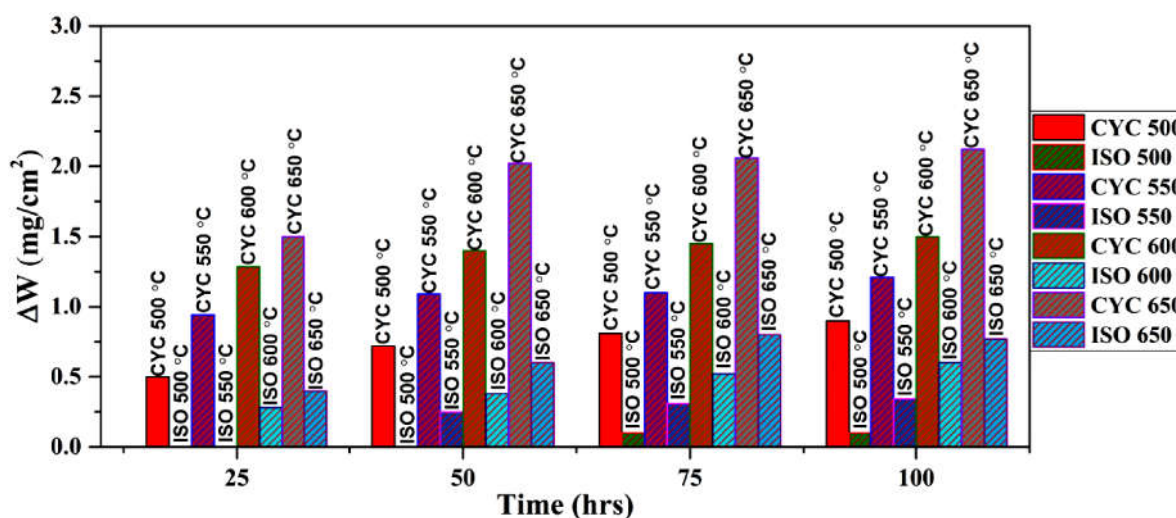


Figure 7.1: Bar representation of the weight gain/area (ΔW) from exposure under cyclic and isothermal condition from 500-650 °C for 25, 50, 75 and 100 h.

It may be seen from **Figure 7.1** that during oxidation in static air up to 25 h of exposure while weight gain at 500 and 550 °C under isothermal exposure, was not detectable, ΔW for cyclic oxidation at 500 and 550 °C was 0.5 and ≈ 0.75 mg/cm² respectively. At 600 °C, ΔW for cyclic exposure was ≈ 1.25 mg/cm² whereas, it was ≈ 0.25

mg/cm², which is nearly five times higher under cyclic oxidation as compared with that in isothermal oxidation. The weight gain during oxidation at 650 °C for 25 h of exposure under cyclic and isothermal oxidation was 1.5 and 0.3 mg/cm² respectively, as expected the weight gain at 650 °C in both isothermal as well as cyclic exposures is higher as compared to that at 600 °C.

At 50 h of exposure there was no weight gain at 500 °C under isothermal condition whereas there was ≈ 0.75 mg/cm² under cyclic exposure. Weight gain under isothermal exposure starts at 550 °C and increases with rise in temperature up to 650 °C, on the other hand there was appreciable increase in ΔW (≈ 0.75 mg/cm²) under cyclic oxidation even at 500 °C. There was progressive increase in ΔW under cyclic exposure with increase in temperature. It may be seen that weight gain starts under isothermal exposure at 600 °C and it was ≈ 0.2 mg/cm². The increase in ΔW under cyclic oxidation was quite appreciable (≈ 0.75 mg/cm²) even at 500 °C and progressively increased up to 650 °C. A similar trend was seen in variation of ΔW under isothermal and cyclic exposure at 75 h and also at 100 h of exposure. The damaging effects of SM1 and SM2 coatings on hot corrosion behavior of the material with the duration of exposure under cyclic and isothermal condition is shown by bar diagrams in **Figures 7.2 and 7.3** respectively. It is evident that increase in ΔW of SM2 coated samples was much higher in respect to those of SM1 coated samples under respective conditions of exposures in terms of temperature and the duration of exposures, both under isothermal and cyclic conditions. The increase in ΔW at 650 °C under cyclic exposure, even after 25 h of duration, was almost comparable to those observed from exposures at 50, 75 and 100 h.

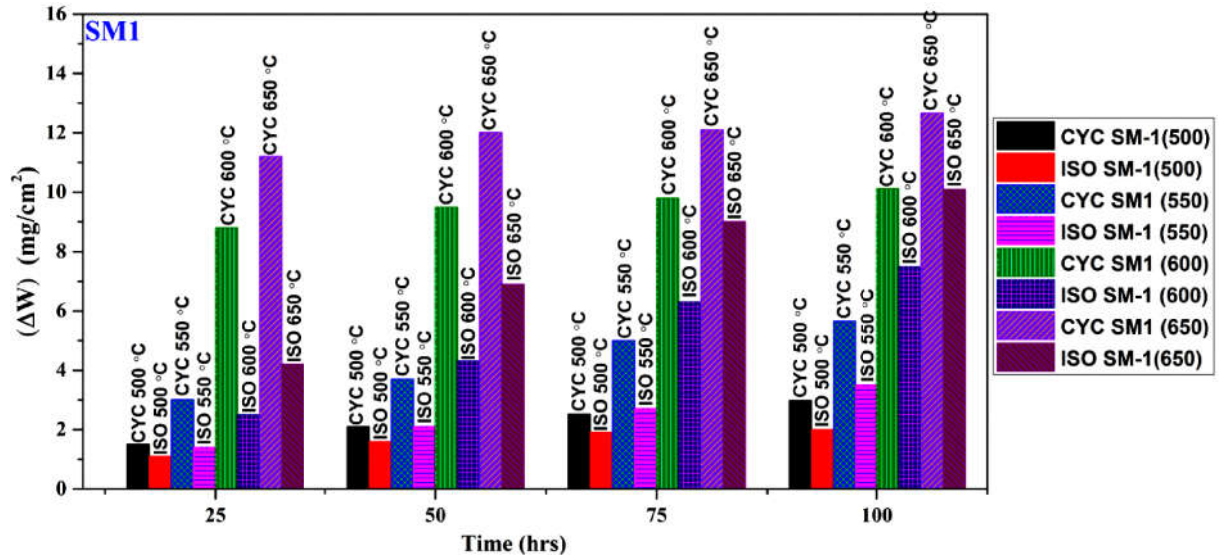


Figure 7.2: Bar data representation of the weight gain/area (ΔW) for the corroded samples exposed cyclically and isothermally under SM1 salt coated at 500 to 650 °C, at 25, 50, 75 and 100 h.

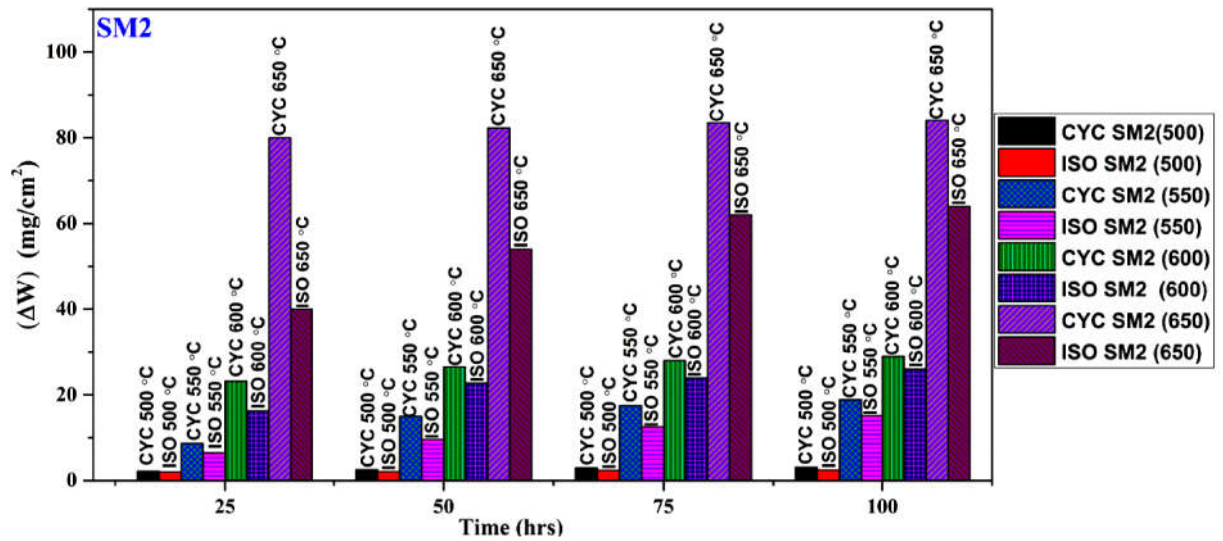


Figure 7.3: Bar data representation of the weight gain/area (ΔW) for the corroded samples exposed cyclically and isothermally under SM2 salt coated at 500 to 650 °C, at 25, 50, 75 and 100 h.

7.2. DISCUSSION

It is evident from the bar diagram data of ΔW as a function of the duration of exposure of the SASS 904L at different temperatures of 500, 550, 600 and 650 °C that ΔW is quite different from one to other condition of exposure. It is also evident that the increase in weight gain is significantly more in cyclic exposure in air without any salt coating, and also with salt mixture (SM1) coating and salt mixture (SM2) coating. The different aspects of oxidation/hot corrosion such as rate controlling law, parabolic rate constant k_p , stability of the applied salt at elevated temperature, spallation/cracking of the scale, surface morphology of the oxidized surfaces, thickness of the oxidized/corroded layer are presented in **Table 7.2** for the cyclic and isothermal exposure of SASS 904L. There are significant differences in these aspects between the cyclic and isothermal exposures of the material. Though near parabolic rate law was followed in both the conditions, there were marked differences in the k_p values. These aspects have been discussed in the previous chapters for the cyclic and isothermal exposures at different temperatures.

It is important to mention that the scales of ΔW shown in **Figures 7.1, 7.2 and 7.3** are quite different while the scale is smallest in **Figure 7.1**, larger in **Figure 7.2** and largest in **Figure 7.3**. Thus, it is obvious that the severity of damage was lowest from exposure in air and it was highest in the samples coated with salt mixture SM2. It is important to understand the major reasons for the observed differences in resistance of the material against oxidation/hot corrosion under isothermal and cyclic exposures. The important factors affecting the oxidation/hot corrosion are the environment, the material and its alloying elements, oxygen potential/partial pressure, temperature, stresses generated during exposure, nature of the scale formed on the surface, barrier action of the scale for diffusion

of cations and anions. Apart from these factors also the flow rate of air and humidity in air play important role on oxidation resistance [114]. In steels containing Cr, usually protection is achieved by formation of chromia layer on the surface, however, in such materials Cr content is very important for the formation of protective chromia layer. Usually 10-12 wt% Cr is a border line for the formation of protective layer. In the steel like SASS 904L there is sufficient Cr content to form protective oxide layer. In some cases, in humid air, chromia layer has been reported to volatilize above 600 °C [17, 119]. The duration of exposure is also a very important factor affecting oxidation resistance. Following the formation of chromia on the surface, material remains protective against oxidation till the concentration of Cr below the substrate does not fall below the equilibrium content of Cr with chromia [51].

Table 7.1 compares oxidation behavior of important metallic materials. It is evident from the data of this Table that in general, the damage caused by cyclic exposure is more than that from isothermal exposure in these materials. Also, the relevant details are included for each material listed, in the **Table 7.1**.

Thus, the findings of the present investigation are in line with those in the earlier investigations, that damage from cyclic exposure is more severe than that from isothermal exposure.

Table 7.2: Comparison between results obtained from cyclic and isothermal exposures.

	Cyclic	Isothermal
Weight Change	Parabolic	Parabolic
Trend of Change in	Dual segments	Single segment
k_p - value	Value increases upto initial stage of cyclic exposure from 5-15 h. Later, the value decreases and tends to increase with increased temperature in both oxidation and hot corrosion.	Values are less than cyclic exposure in both the cases. However, the weight change is very low at lower temperature of 500-550 °C and further at 600-650 °C weight change was observed to be nominal during oxidation. In case of corrosion k_p values increase, with an increase in temperature and time.
Partial melting of salt composition	At 500 °C with SM1 only	at 500 and 550 °C with SM1 and SM2 upto 25 h of exposure
Spallation/Cracks	Only during corrosion at 600-650 °C	Initiated after 50 h from 600-650 °C with SM1 and from 550-650 °C with SM2. No such effect was during oxidation
Surface morphology	During oxidation, surface is smooth and has less effect at 500-600 °C, and at 650 °C lamellar and cubic crystals were observed, whereas during corrosion, globular morphology was observed with SM1 and globular+needle like structures with SM2 salt mixture.	During oxidation, surface showed formation of pits/pore on the surface. Size of pits increased with increase in temperature, whereas density of pits decreased with increase in time of exposure. During hot corrosion, the effect of salt corrosion was less with SM1 than that with SM2. Moreover the effect of time showed rise in large sized globular morphology with SM1, whereas with SM2 uniform corrosion and complete melting of salt resulted in uniform corrosion, forming small sized nodules all over the surface.
Cross section thickness of oxide/corroded layer	Oxide layer increases with increase in temperature. Higher non-uniformity during corrosion at 550-650 °C with SM2 than SM1.	Oxide layer increases with increase in temperature. Effect of time is less significant for rise in thickness. During corrosion, internal oxidation from at 550-650 °C was observed.

7.3. CONCLUSION

This chapter presents comparison of isothermal and cyclic exposure in air and with coatings of two salt mixtures (SM1 and SM2) at 500-650 °C on the SASS 904L.

1. Bar diagram of the weight gain per unit area (ΔW) for the cyclic and isothermal oxidation and hot corrosion of SASS 904L corresponding to different temperatures of exposure from 500-650 °C, for the durations of 25, 50, 75 and 100 h, clearly show much larger weight gain from cyclic exposure than that from isothermal exposure.
2. While the severity of damage from oxidation is seen to be lowest, it is highest from that resulting from hot corrosion due to SM2 salt mixtures. Hot corrosion due to SM1 is much less than that from SM2.
3. The observation of present investigation that cyclic exposure of the SASS 904L at elevated temperature is more detrimental than isothermal exposure, is in line with the observations made earlier on many structural alloys.