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Sensitization & Corrosion Behaviour of Austenitic Stainless Steel 304 & 316

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ABSTRACT

Austenitic Stainless steels have a wide range of application in the energy industry, but the corrosion resistance of the stainless steel can be reduced by sensitization, which is the formation of chromium carbide precipitates at grain boundaries, causing the formation of a zone of chromium depletion at the grain boundary. Since chromium is the primary alloying element that makes stainless steel corrosion resistant, this chromium depleted zone is susceptible to stress corrosion cracking. Sensitization occurs when the stainless steel is exposed to high temperature for an extended time. The objective of this research is to determine the effect of sensitization & corrosion behaviour of austenitic Stainless steel 304 & 316. Due to the addition of molybdenum SS316 is more preferred over SS304.

In an effort to examine the effect of sensitization & corrosion behavior of SS304 & SS316 various test have been adopted. Test Such as weight loss as per ASTM A262 A to F, Electrochemical Potentiokinetic reactivation (EPR) G108. Both the steel undergoes sensitization when heated in the range of 550^{o}C-850^{o}C.Increasing Sensitization temperature increases corrosion rate SS304& SS316.EPR method was successful in investigating intergranular corrosion of both the steels.TTS diagram is indicating safe holding time of the steel. At the end the results of EPR as well as weight loss as per ASTM 262 C and E closely match.

Keywords: Sensitization, Corrosion rate , heating, Degree of Sensitization, Polaziration

I. INTRODUCTION

Stainless steels are popular construction materials for key corrosion resistant equipments in the chemical, petroleum, process and power industries. Therefore, these have great technological and economic importance. Stainless steels are iron alloys containing a minimum of approximately 11%-12% chromium. This amount of chromium prevents the formation of rust in unpolluted atmosphere. It is this characteristic that their popular designation “Stainless” is derived. Their corrosion resistance is provided by a thin surface film which is self-healing in a wide variety of environments especially in the presence of oxides. Stainless steels are classified as austenitic stainless steels, ferritic stainless steels, martensitic stainless steel and duplex stainless steels as per their microstructure. Out of these austenitic stainless steels are widely used in the process industries. Austenitic Stainless steels are formidable construction material for marine and offshore structure due to their corrosion resistance, high strength, ease of lubrication and moderate cost. After carbon steel, austenitic stainless steels 304 and 316are the most extensively used structural materials for marine installation including desalination plants. SS316 is preferred materials for marine applications due to its outstanding resistance to localized corrosion,

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however the greatest shortcoming is their vulnerability to pitting and crevice corrosion in presence of chloride ions, which subsequently results in the initiations of pits.

In chloride containing environments where stainless steels are prone to localized corrosion under certain conditions, costly nickel-base alloy were used as substitutes up to the late 1960s.Since in the early 1970s it is realized that the addition of larger amounts of chromium or molybdenum (>6%) to steels bring about the same effect as that exhibited by nickel alloys. A new family of stainless steels emerged in the late 1970s and 1980s with superior corrosion resistance .Steels have to be fabricated and welding is one of the process used in fabrication. During welding the steel is heated to variety of temperatures and a zone called Heat Affected Zone (HAZ).

These austenitic stainless steels when exposed to temperature in the range of 538^{o}C to 850^{o}C undergoes precipitation of chromium carbides at the grain boundaries. This precipitation of chromium carbides at the grain boundaries is termed as Sensitization. This Sensitized steel suffers from intergranular corrosion. The presence of nitrogen is thought to improve resistance to intergranular attack due to retardation of carbide precipitation. Sensitization may results from slow cooling annealing temperature or stress relieving .Due to longer time at annealing temperature, It is possible that entire piece of material is sensitized, whereas at shorter time and low temperature the working on stainless steel can result in band type Sensitization of usually 1/8 to 1/4 inch wide, adjacent to the weld. The amount of carbon content in the stainless steel plays important role in precipitation of chromium carbides and is dependent on temperature and time of the process.

II THEORETICAL BACKGROUND OF STAINLESS STEEL

Some elements extend the γ loop in the iron-carbon equilibrium diagram e.g. nickel and manganese. When sufficient alloying element is added, it is possible to preserve the face-centered cubic austenite at room temperature. Chromium addition alone to plain carbon steel tends to close the γ loop and favor the formation of ferrite. However, containing nickel it retards the kinetics of the when chromium is added to a steel $\gamma \rightarrow \alpha$ transformation, thus making it easier to retain austenite at room temperature. The presence of chromium greatly improves the corrosion resistance of the steel by forming a very thin stable oxide film on the surface, so that chromium-nickel stainless steels are now the most widely used materials in a wide range of corrosive environments both at room and elevated temperatures. Simple austenitic steel usually contains 18% -30%Cr, 8% -20% Ni and 0.03%-0.1% Carbon. The binary iron-chromium equilibrium diagram (Fig 1)shows chromium restricts the occurrence of the γ loop to the extent that above 13% Cr the binary alloys are ferritic over the whole temperature range, while their is a narrow ($\alpha + \gamma$)range between 12% and 13 % Cr.

The addition of carbon to the binary alloy extends γ loop to higher chromium contents and also widens the ($\alpha + \gamma$) phase field upto 0.3%.when carbon is progressively added to an 18% Cr steel in the range upto 0.04% C, the steel is fully ferritic (and cannot be transformed. One of the most convenient ways of representing the effect of various elements on the basic structure of chromium-nickel stainless steel is the schaeffler diagram. At its simplest level, the diagram shows the regions of existence of the three phases for iron-chromium-nickel alloys.

In austenitic steels Fig.2 $M_{23}C_6$ is the most significant carbide formed and it can have a substantial influence on corrosion resistance

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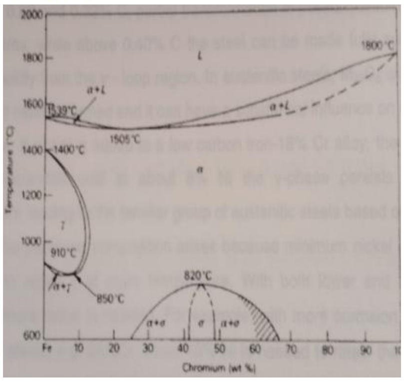

Fig.1 Fe-Cr Equilibrium diagram

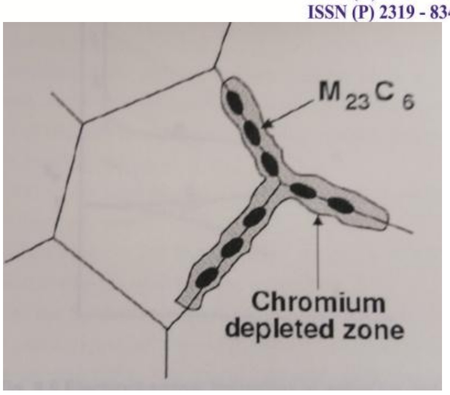

Fig.2 Grain Boundary

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III. EXPERIMENTAL WORK

The overall work is focused at finding out corrosion behaviour of the test steel in received and sensitized condition. Test like weight loss and potentiodynamic polarization were conducted.. Data on weight loss in nitric acid test was used for SS304 for TTS diagram. Data on weight loss in Cu-$CuSO_4$-H_2SO_4test was used for SS316 for TTS diagram. Finally potentiodynamic polarization test was conducted for degree of sensitization. The steel namely SS 304 SS 316 were obtained from local market in the form of sheet. Chemical analyses of test steels carried out by wet chemical analysis technique. Specimen were cut from the sheet in 1.5cmx2cm sizes for weight loss test, 1cmx1cm sizes for potentiodynamic test. Chemical composition of SS304 and SS316 was given in Table 1.

Table 1 Chemical Compositions of Stainless Steel

	Cr	Ni	C	Si	Mn	Mo	S	P	Fe
SS304	18.33	8.32	0.08	0.45	1.09	-----	0.0042	0.013	Balance
SS316	16.12	10.99	0.069	0.69	1.55	2.44	0.0085	0.013	Balance

For weight loss test-

3mm diameter hole was made by drilling for holding the Samples in the solution. Edges were smoothened with emery paper, then all the surface was polished with emery paper 0/0,1/0,2/0,3/0,4/0,5/0 and with cloth smeared with 40µ Alumina Powder.

For potentiodynamic test-

Edges were smoothened with emery paper, then a copper wire (insulated) was soldered with one face of specimen as flat and then the sample was mounted in cold setting resin and the other flat surface was open for exposure. Then the open surface was polished with emery paper 0/0,1/0,2/0,3/0,4/0,5/0 and with cloth smeared with 40µ Alumina Powder. A potentiostat Solartron make model 1285 were used as shown in Fig 3. The cell consisted of the sample used as the working electrode (WE), Reference electrode (RE), and a platinum as Auxiliary electrode (AE). A Sensitized Steel Produces a curve of higher current densities as compared to solutioned steel as showni Fig.4

IJARSE
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Fig.3 Potentiostat

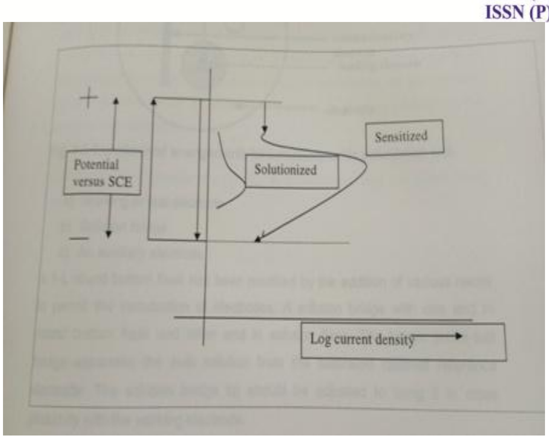

Fig.4 EPR Curves

IV. RESULT AND DISCUSSION

Weight loss test

SS 304 specimens and SS 316 were heated in Muffle Furnace at different temperature 550°C, 650°C,750°C and 850°C for 1 and 2 hour.

Nitric acid test for SS304 Nitric acid attack rate of alloy in annealed condition was about 0.0457miles per year (MPY). Based on nitric acid rate of alloy the acceptable nitric acid rate for sensitized alloy was arbitrarily fixed at 0.1236 miles per year (MPY). This as per method adopted by R.R.Gaugh for deciding acceptable limit for nitronic 33.The nitric acid rate for SS 304 in sensitized condition is given in table 2 and figure 5.

Table 2 Effect of Time and ageing temperature on corrosion rate

Test method	Ageing Temperature (°C)	Sensitization Treatment Time (hr)	Initial Weight (gm)	Final Weight (gm)	MPY	MDD
Nitric acid test	-	As received	1.6334	1.6314	0.0457	0.2545
	550	1 hr	1.6086	1.6032	0.1236	0.6892
		2 hr	1.6463	1.6406	0.1263	0.7034
	650	1 hr	1.6002	1.4974	0.1580	0.8800
		2 hr	1.6198	1.6126	0.1630	0.9079
	750	1 hr	1.6001	1.5924	0.1750	0.9747
		2 hr	1.6006	1.5923	0.1830	1.0193
	850	1 hr	1.5689	1.5600	0.2038	1.1351
		2 hr	1.4959	1.4863	0.2310	1.2866

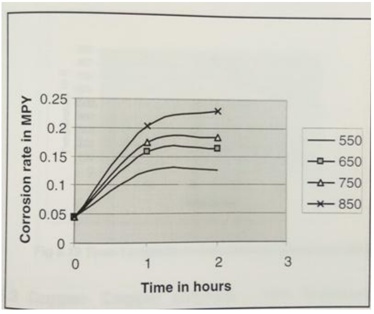

Fig.5 Effect of Time and ageing temperature

The safe holding time for SS 304 is represented in table3 . the data is used to plot fig 6. which is basically TTS diagram. At 550°C nearly 44min of exposure is sustainable. It will not cause intergranular attack. But with increasing temperature in sensitizing range, the safe holding time decreases from 44 min. to 25 min.

Table 3. Safe holding time without sensitization at different temp.

Sensitization Temperature	Holding Time at Temperature without IGC (Min.)
550°C	44
650°C	34
750°C	30
850°C	25

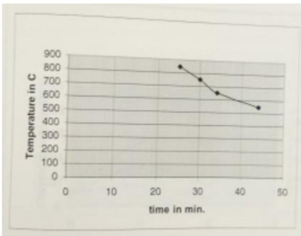

Fig.6 TTS Diagram for SS304

IJARSE
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Copper-Copper Sulphate-16% Sulphuric acid test for SS 316. Nitric acid attack rate of alloy in annealed condition was about 0.0111miles per year (MPY). Based on nitric acid rate of alloy the acceptable nitric acid rate for sensitized alloy was arbitrarily fixed at 0.0167 miles per year (MPY). This as per method adopted by R.R.Gaugh[9] for deciding acceptable limit. Copper-Copper Sulphate-16% Sulphuric acid test for SS 316 is given in table 4 and figure 7.

Table 4 Effect of Time and ageing temperature on corrosion rate

Test method	Ageing Temperature (^{0}C)	Sensitization Treatment Time (hr)	Initial Weight (gm)	Final Weight (gm)	MPY	MDD
Copper-Copper Sulphate-16%Sulphuric Acid	-	As received	16.2035	16.2027	0.0111	0.0618
	550	1 hr	16.2169	1602157	0.0167	0.0930
		2 hr	16.6936	16.6932	0.0054	0.0300
	650	1 hr	14.9690	14.9629	0.0921	0.5129
		2 hr	14.6421	14.6377	0.0683	0.3804
	750	1 hr	16.8797	16.8757	0.0543	0.3024
		2 hr	15.7182	15.7144	0.0540	0.3007
	800	1 hr	15.7085	15.7060	0.0340	0.1893
		2 hr	16.5251	16.5238	0.0177	0.0985

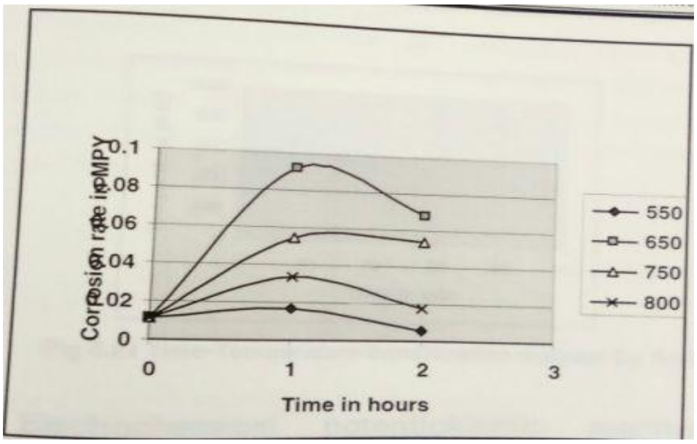

Fig.7 Effect of Time and ageing temperature on corrosion rate

The safe holding time for SS 316 is represented in table 5 .the data is used to plot fig 8. which is basically TTS diagram. At 550^{o}C nearly 80min of exposure is sustainable. It will not cause intergranular attack. But with increasing temperature in sensitizing range, the safe holding time decreases from 80 min. to 39 min in 800^{o}C .

Table 5. Safe holding time without sensitization at different temp

Sensitization Temperature	Holding Time at Temperature without IGC (Min.)
550^{0}C	80
650^{0}C	15
750^{0}C	25
800^{0}C	39

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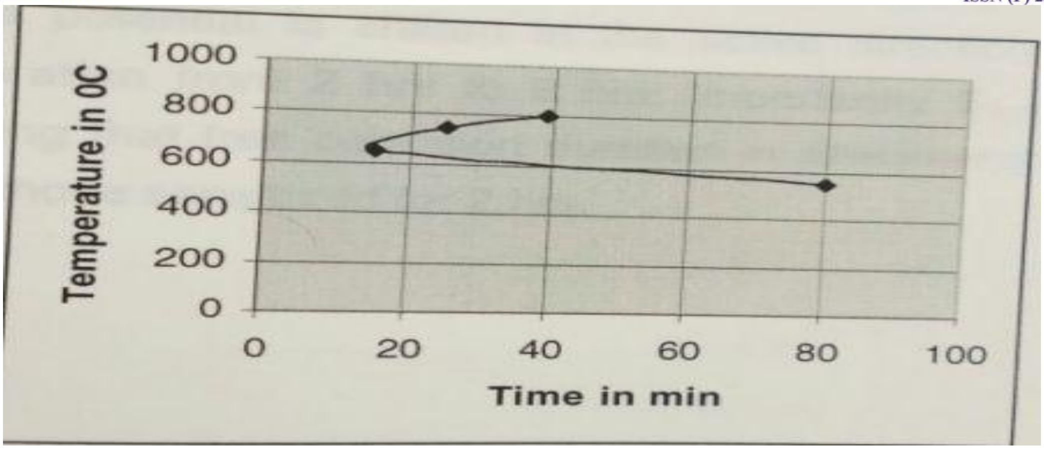


Fig.8 TTS for SS316

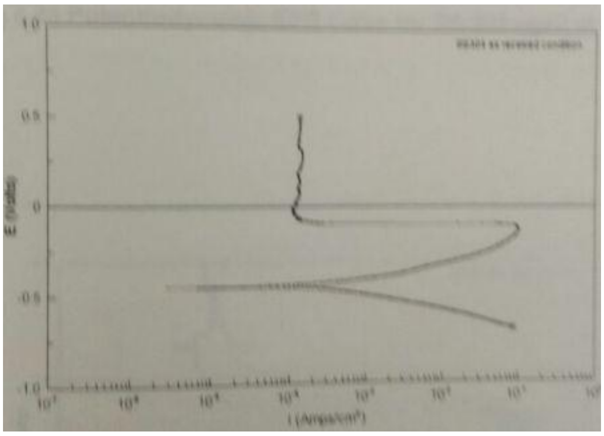
Electrochemical potentiokinetic reactivation(EPR)

The Polarization Behavior of SS304

EPR test were conducted in 0.5 M H_2SO_4 + 0.01M KSCN both for SS304 and SS316.

A potentiodynamic polarization curve for sample SS304 aged for various time and temperature at 500^{o}C to 850^{o}C is shown in fig 9 to17 . The current density then decreases to a lower value than i_{corr} obtained from cathodic part of the plot. This indicates that the metal is passivating.

It is also evident that Passivation current Density increases marginally on increasing sensitization duration in almost all the cases. In all the cases the critical current density doesnot vary much on increasing on increasing duration for a given sensitization temperature. E_{corr} is not affected thereby, indicating that free corrosion duration in specimens sensitized for 8 hr is less than those sensitized for 2 hr.



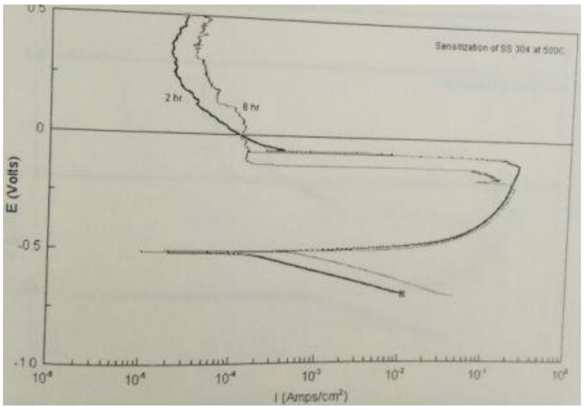


Fig. 9 Potentiodynamic EPR Curve (Received) **Fig.10 Potentiodynamic EPR Curve (500^{o}C)**

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ISSN (P) 2319 - 8346

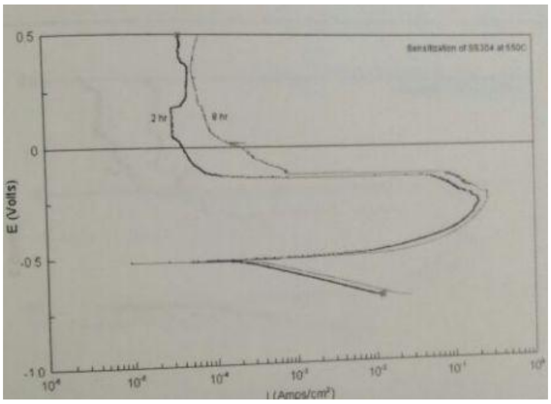

Fig.11 Potentiodynamic EPR Curve (550°C)

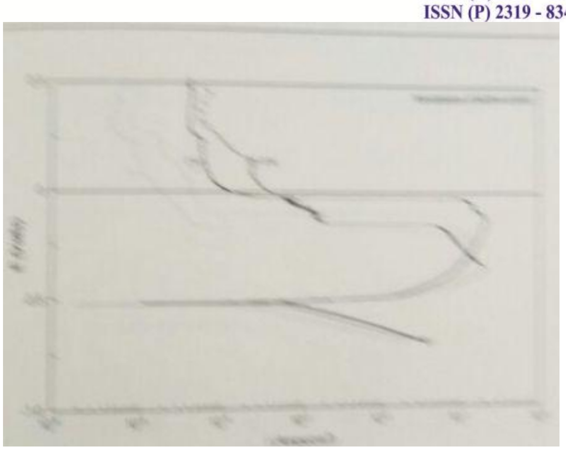

Fig.12 Potentiodynamic EPR Curve (600°C)

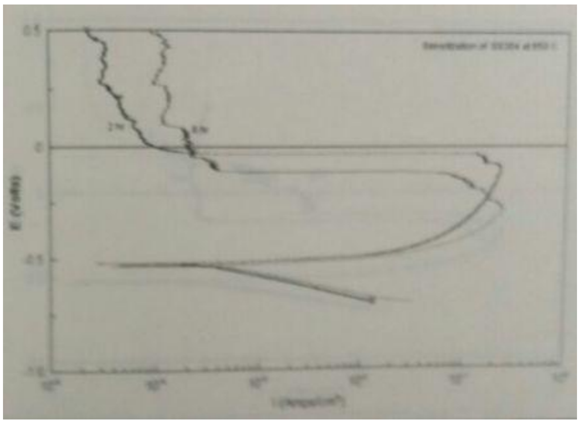

Fig.13 Potentiodynamic EPR Curve (650°C)

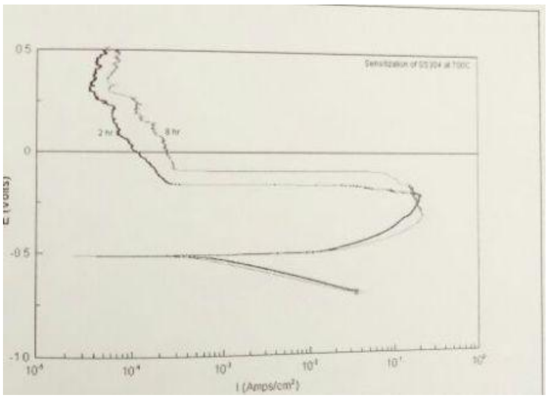

Fig.14 Potentiodynamic EPR Curve (700°C)

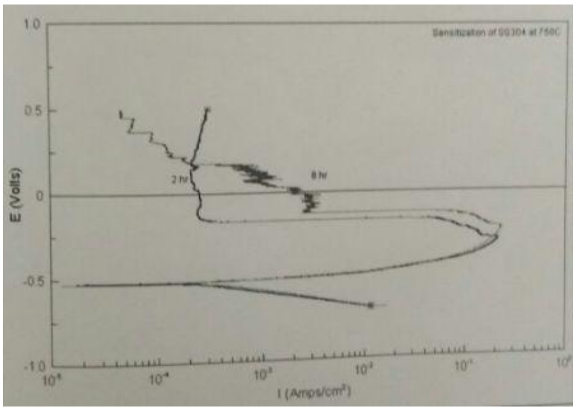

Fig.15 Potentiodynamic EPR Curve (750°C)

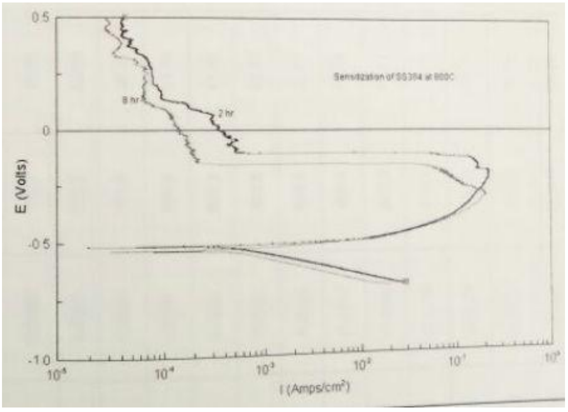

Fig.16 Potentiodynamic EPR Curve (800°C)

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ISSN (P) 2319 - 8346

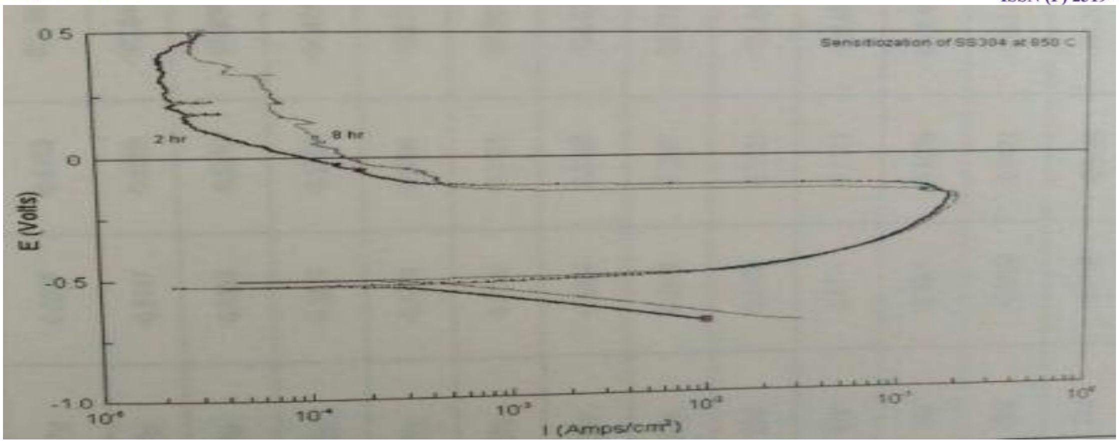

Fig.17 Potentiodynamic EPR Curve (850°C)

The Polarization Behavior of SS316

A potentiodynamic polarization curve for sample SS316 aged for various time and temperature at 500°C to 850°C is shown in fig 18 to25. It is evident that sensitization duration affects the passivation current density . However ,SS316 Sensitized at 800°C shows reverse effect as to higher passivation current density for 2 hr as compared to 8 hr duration.

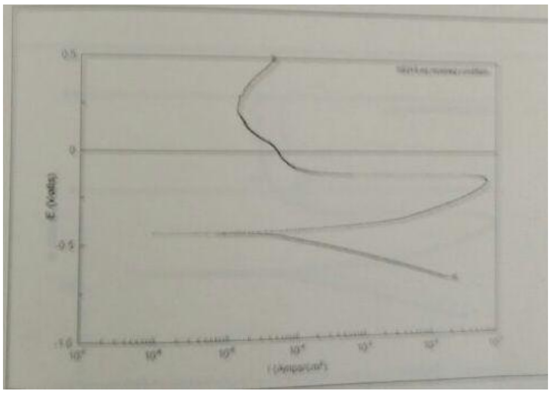

Fig. 18 Potentiodynamic EPR Curve (Received)

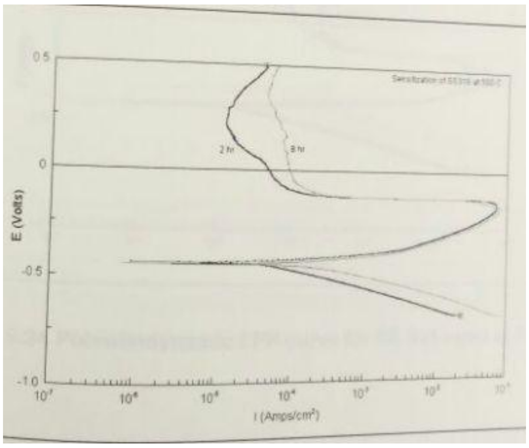

Fig.19 Potentiodynamic EPR Curve (500°C)

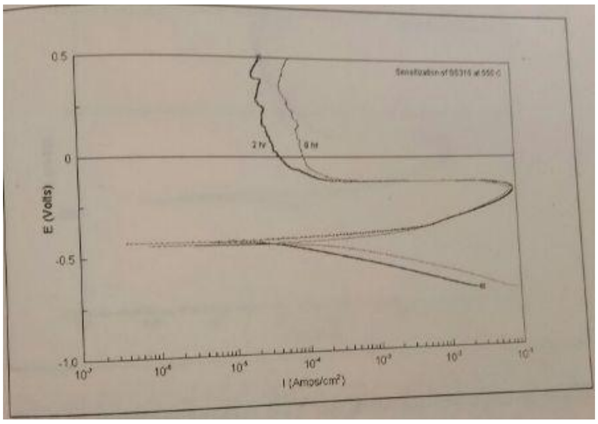

Fig.20 Potentiodynamic EPR Curve (550°C)

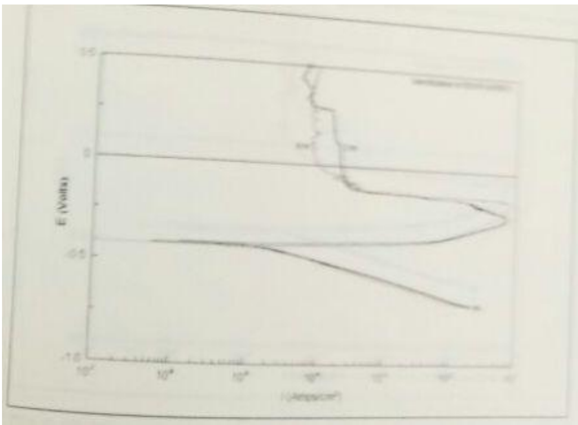

Fig.20 Potentiodynamic EPR Curve (600°C)

IJARSE
ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346

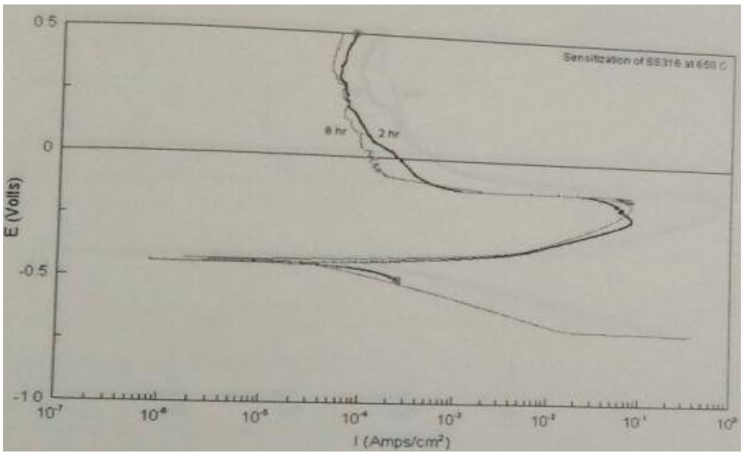

Fig.21 Potentiodynamic EPR Curve (650°C)

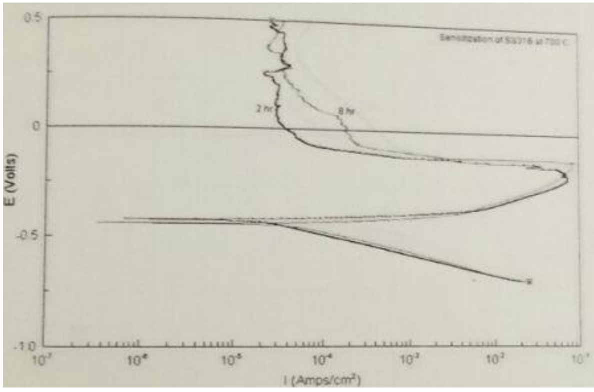

Fig.22 Potentiodynamic EPR Curve (700°C)

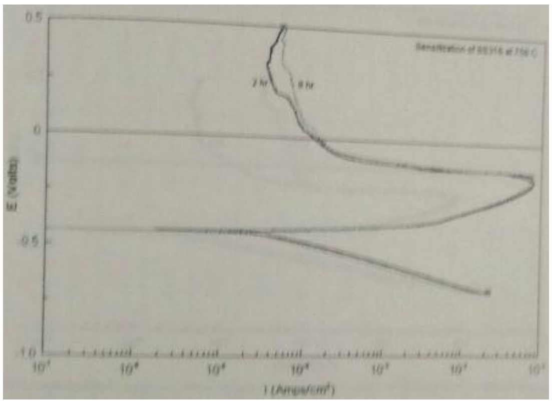

Fig.23 Potentiodynamic EPR Curve (750°C)

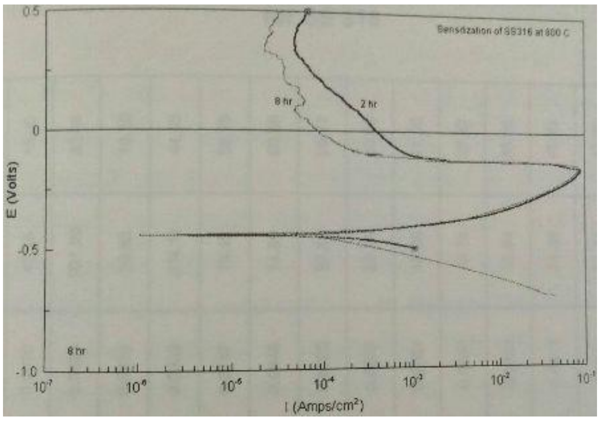

Fig.24 Potentiodynamic EPR Curve (800°C)

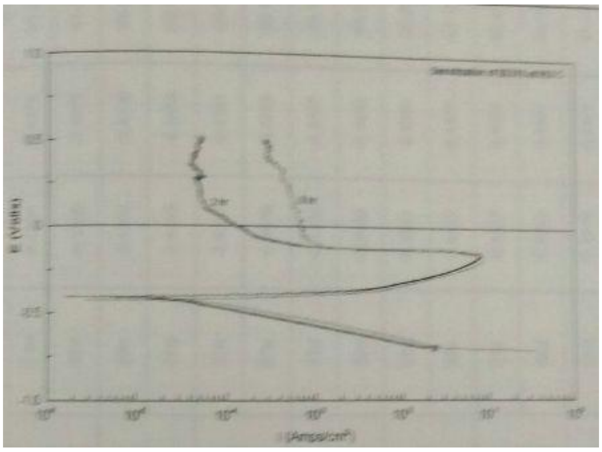

Fig.25 Potentiodynamic EPR Curve (850°C)

Degree of Sensitization

Effect of ageing time and temperature on Degree of sensitization of SS304 and SS316 was studied using Electrochemical Potentiokinetic reactivation(EPR)technique.

Table6 and figure26 shows effect of ageing time and temperature on Degree of sensitization of SS304.This indicates that 2 hours at 750°C is most damaging.

Table 6 Effect of Time and ageing temperature on Degree of sensitization

Sensitization Temperature (^{0}C)	Ageing Time (hr)	Degree of Sensitization (C/cm^2)
500	2	2.73
	8	4.83
550	2	2.96
	8	6.68
600	2	4.28
	8	8.77
650	2	6.41
	8	14.11
700	2	3.51
	8	11.41
750	2	23.41
	8	9.18
800	2	5.94
	8	7.31
850	2	3.17
	8	3.94

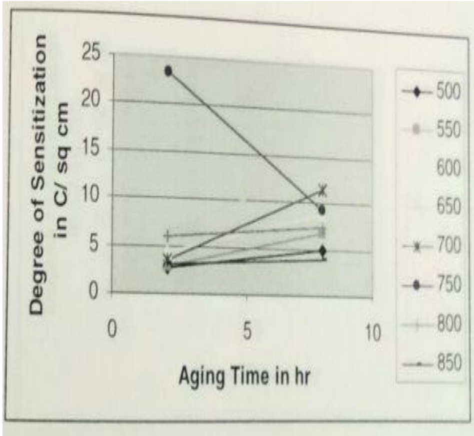

Fig. 26 DOS Vs Ageing Time

Table7 and figure 27 shows effect of ageing time and temperature on Degree of sensitization of SS316.This indicates that 8 hours at 850^{o}C is most damaging.

Table 6 Effect of Time and ageing temperature on Degree of sensitization

Sensitization Temperature (^{0}C)	Ageing Time (hr)	Degree of Sensitization (C/cm^2)
500	2	1.23
	8	3.98
550	2	2.73
	8	5.14
600	2	6.42
	8	9.58
650	2	9.71
	8	6.16
700	2	2.36
	8	5.10
750	2	3.97
	8	9.64
800	2	7.42
	8	3.69
850	2	3.49
	8	32.60

Fig. 26 DOS Vs Ageing Time

Effect of sensitization duration

For SS304 the increasing sensitization duration from 2hr to 8 hr increases $I_{passive}$ for all temperature except those at 750^{o}C to 800^{o}C. it is clear that holding duration of 2 hr and 8 hr is too much more than the safe holding time and therefore increasing corrosion rate with increasing holding duration.

For SS316 the increasing sensitization duration from 2hr to 8 hr increases $I_{passive}$ for all temperature except those at 650^{o}C to 800^{o}C.

V. CONCLUSION

Increasing sensitization temperature from 550^{o}C to 850^{o}c increase the corrosion rate for both the steel .EPR method was used successfully in investigating IGC of SS304 and SS316.Degree of sensitization for SS 304 is highest at 750^{o}C for 2 hr. Degree of sensitization for SS 316 is highest at 850^{o}C for 8 hr.

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