



THE INFLUENCE OF VARIOUS PARAMETERS ON CREVICE CORROSION OF TWO DIFFERENT TYPE GEOMETRY OF 304L STAINLESS STEEL

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ABSTRACT

An investigation was carried out to study the effect of various parameters on crevice corrosion of two different type geometry of (rod, square) 304L stainless steel in 3.4% NaCl solution under static conditions at different temperatures (25, 50) C°, rotation cylinder electrode was used for 100, 200 rpm at the same temperatures. It was found the maximum attack was in square 304L SS at 50 C° under static conditions in account of geometric of specimen whereas slightly effect as the velocity increases due to the passive film is formed on the steel surface. In contrast, the results show the effect of temperature changes and velocity on corrosion rate in rod 304LSS is more pronounced as temperatures and velocities rises enable the migration of chloride ions into the crevice.

KEYWORDS: stainless steel, chloride solution,

تأثير عوامل مختلفة على التآكل التصدي لشكلين مختلفين من الفولاذ المقاوم للصدأ نوع 304L

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الخلاصة

تم في هذا البحث دراسته تأثير عدة عوامل على التآكل التصدي لشكلين مختلفين من الفولاذ المقاوم للصدأ (304LSS) في محلول كلوريد الصوديوم بتركيز 3.4% بدرجات حرارة مختلفة C° (25, 50) في حالة السكون وكذلك استخدم قطب اسطواني دووار بسرعه (100, 200 rpm). وجد ان اعلى معدل تآكل كان للعينة المربعة في حالة السكون بدرجة C° (50) قد يعود السبب الى الشكل الهندسي للعينة في حين كان تأثير السرعة عليها طفيف بسبب تكون طبقة الاوكسيد على السطح (منطقة الخمود) وعلى العكس حيث اظهرت النتائج ان تأثير درجات الحرارة والسرعة واضح على العينة ذات الشكل الاسطواني ويعزى ذلك لتمكن ايونات الكلور الى النفاذ الى داخل الصدع.

1-INTRODUCTION

Crevice corrosion is a localized form of corrosion usually associated with a stagnant solution on the micro-environmental level. Such stagnant micro-environments tend to occur in crevices (shielded areas) such as those formed under gaskets, washers, insulation material, fastener heads, surface deposits, disbonded coatings, threads, lap joints and clamps [Fontana, 2005].

Crevice corrosion generally occurs on the crevice surface while the exterior or bold surfaces are not damaged. However, for copper and its alloys, the opposite is true; the bold surface is corroded while the crevice remains relatively corrosion-free. This unique type of corrosion is referred to as reverse crevice corrosion (RCC). In this research, commercially pure copper was chosen as the target metal to investigate RCC. Based on electrochemical measurements and surface analysis, reverse crevice corrosion was found to occur at room temperature. At elevated temperature only uniform corrosion was observed while under a deoxygenated environment, as expected, no corrosion was observed. [Lin Lu, 2005].

According to [Anees U., 1993] Crevice corrosion tests were carried out to evaluate the performance of some conventional and high alloy stainless steels in Arabian Gulf seawater at 25C and 50C using specimens having three different surface conditions

Immersion tests of 150-180 days duration and accelerated tests were employed to investigate the crevice corrosion behavior. Immersion test results show that crevice corrosion of 3127 hMo, Remanit 4565, 654 SMO, and Monit 44635 initiated as surficial corrosion with virtually no measurable depth of attack; 254 SMO, Duplex 2205, Remanit 4575, 904L and 317L corroded on l-2 sites attack.

Stainless steel is an alloy of iron. According to its definition, stainless steel must contain a minimum of 50% iron. If its contain less iron, the alloy system is named for the next major element. Chromium imparts a special property to the iron that makes it corrosion resistance. When chromium is in excess of 10.5%, the corrosion barrier changes from an active film to a passive film. While the active film continues to grow over time in the cording solution until base metal is consumed, the passive film will form and stop growing. This passive layer is extremely thin, in the order of 10 to 100 atoms thick, and is composed mainly of chromium oxide which prevents further diffusion of oxygen into the base metal [Uhlig, Herbert H, 1951].

When the metal is not in equilibrium with a solution of its ions, the electrode potential differs from the equilibrium potential by an amount known as the polarization. Other terms having equivalent meaning are over voltage and over potential. The symbol commonly used is (η). Polarization is an extremely important parameter because it allows useful statements to be made about the rates of corrosion process. In practical situation, polarization is sometimes defined as the potential change away from some other arbitrary potential and in mixed potential experiments; this is the free corrosion potential [Tretheway, 1996]. The change in the electrode potential from equilibrium potential depends on the magnitude of the external current and its direction. The direction of potential change always opposes the shift from equilibrium and hence opposes the flow of current, whether the current is impressed externally or is of galvanic origin [Uhlig, H., 1984].

2-EXPERIMENTAL WORK

2-1 Experimental Setup

Stainless steel 304L was used for the tests, Table 1 shows that the composition of stainless steel 304L. Two different types geometry of SS 304L specimens were used for exposure tests and electrochemical measurements ((state company of geological survey and mining). One type of specimen was SS304L made from stainless steel rod machined to an outer diameter of 20mm and an inner diameter of 8mm. The other type of stainless steel was a square with a central hole was 8mm,

it was quite thin (thickness=1mm), which allowed many specimens to be onto an insulated stainless steel shaft, separated by Teflon washers, for long term exposure tests at elevated temperature. After each specimen was mechanically formed by cutting, it was wet ground on 600 grit silicon carbide paper, rinsed in distilled water. 3.4% aqueous sodium chloride solution was chosen as the electrolyte because it is close to the concentration of NaCl in sea water. The specimens were rotated using (BARNANT) equipment model (NO.700) which enables the rotation speed to be varied from 50 to 10000 rpm. The process was repeated for 3 speeds, mainly 0, 100 & 200 rpm, almost empirical studies were used this range of speed rotation under 25, 50 C° temperatures.

2-2 Electrochemical instrument:

The experimental apparatus used in this work is consists mainly of :(fig. 1)

- Potentiostat
- Polarization cell(cylindrical glass reaction vessel, lugging capillary probe, reference electrode, counter electrode, the working electrode and thermometer)
- Rotating cylinder electrode assembly
- Digital multi-meters
- Constant temperature bath.

2-3 Electrodes:

An electrochemical experimental system is composed of electrodes and electrochemical instruments. Electrodes are classified into three types by their functions: working electrode; reference electrode; and auxiliary or counter electrode. The working electrode is the sample being studied. The reference electrode provides a relatively fixed potential as a reference to measure the potential of the working electrode. Finally, the auxiliary or counter electrode completes the electrochemical circuit. The crevice assembly was fitted with two grooved washers and the stainless steel specimen was placed in between them. The washers were teflon with a radial groove and a diameter of 16mm. The reference electrode used in this work was a saturated calomel electrode (SCE) with 4 M KCl/ AgCl solution. A carbon rod was chosen as the auxiliary electrode.

2-4 Electrochemical Measurements

The experiments were carried out to determine the polarization curves (cathodic&anodic) in 3.4%NaCl solution at 25&50C of speed, 0,100, 200 r.p.m. electrochemical polarization from - 500mV to + 500mV with scan rate 30 mV/min.

A Potentiodynamic scan is a transient electrochemical method and the scan rate is a key in performing this techniques. If the scan rate is too high, important kinetic data may not be captured, but if the scan rate is too low, the experiment can become very lengthy. A scan rate was chosen such that a small change in scan rate did not significantly affect the shape of the scan for subsequent scans.

Table 1: Composition of stainless steel 304L.

STEEL	% COMPOSITION OF ELEMENTS									
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Fe
	.03	1.0	1.0	0.045	0.02	18	10.1	-	0.23	balance

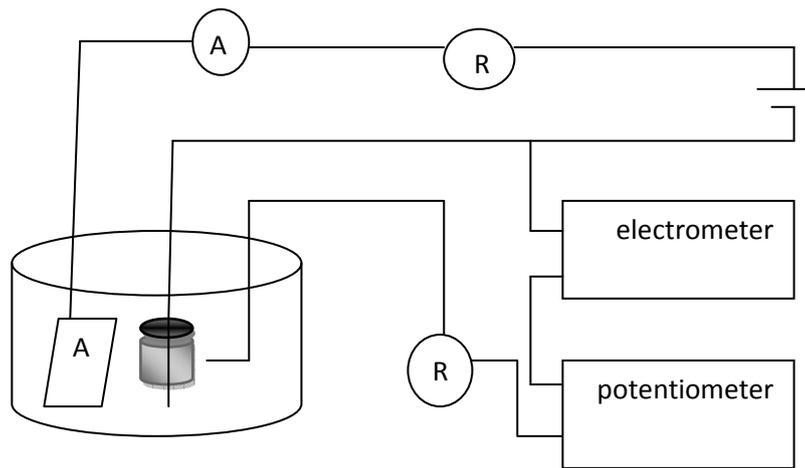


Figure1: Tafel extrapolation

3-RESULT AND DISCUSSION

The results will split into two categories (rod & square) 304LSS. Each one will be grouped into two main parts the first under static conditions, and the second under dynamic conditions.

3-1Effect of temperature

The effect of temperature on atmospheric corrosion rates is also quite complex. Figure 3 shows the effect of temperatures on the electrochemical behaviour of square 304LSS under static conditions. It indicates that increasing in temperatures leads to increases in corrosion current density due to an increase in temperature will tend to stimulate corrosive attack by increasing the rate of electrochemical reactions and diffusion processes. As temperature rises, diffusion increases. Increased diffusion enables more dissolved oxygen to reach a cathodic surface, thereby depolarizing the corrosion cell. But this behaviour is not pronounced with rod304LSS, as shown in figure 1 due to design or geometric of specimen.

3-2Effect of geometric of specimen

The results of the exposure tests carried out on rod and square 304 LSS at 25& 50C° are summarized in Tables 2-4. At static conditions, the maximum attack was in square 304LSS at 50 C°. the corrosion resistance of a stainless steel is dependent on the presence of a protective oxide layer on its surface, but it is possible under certain conditions for this oxide layer to break down. Areas where the oxide layer can break down can also sometimes be the result of the way components are designed, in sharp re-entrant corners or associated with incomplete weld penetration or overlapping surfaces. These can all form crevices which can promote corrosion. To function as a corrosion site, a crevice has to be of sufficient width to permit entry of the corrodent, but sufficiently narrow to ensure that the corrodent remains stagnant. Accordingly crevice corrosion usually occurs in gaps a few micrometres wide, and is not found in grooves or slots in which circulation of the corrodent is possible. This problem can often be overcome by paying attention to the design of the component, in particular to avoiding formation of crevices or at least keeping them as open as possible.

3-3Effect of rotation speed

Potentiodynamic polarization curves of rod and square 304LSS at 25 & 50 C and rotation speed of 100 &200 r.p.m are shown in figures 2&3. It can be seen that as velocity is increased from 100 to 200 r.p.m, corrosion rate increases at 25C in rod 304L SS as shown in figure 1, due to the

migration of chloride ions into the crevice. This results in an increased concentration of metal chloride within the crevice, thus



However, as velocity is increased further, the reduction reaction becomes activation-controlled. As a consequence, the corrosion rate becomes independent of velocity at high velocities at 50 C. Solution velocity affects the corrosion rate of diffusion – controlled system. Velocity has no effect on activation – controlled system.

Figure 2 shows the apparent that the change in the rotation speed influences the corrosion behaviour of square 304LSS. However, as rotation speed is increased from 100 to 200 rpm, the corrosion rate remains constant at 25 & 50C, which means that the reduction reaction becomes activation controlled. Since velocity has no effect on activation controlled system. It shows that passive film is formed on steel surface.

Figures 4&5, show the surface after potentiostatic polarization on rod and square 304 LSS in solution containing 3.5% NaCl at 50C°.

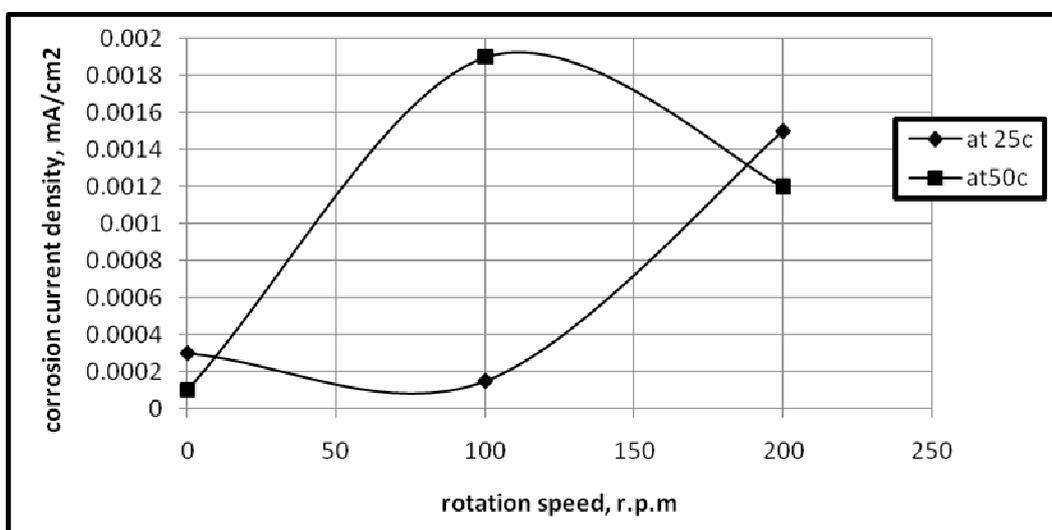


Fig.2: Effect of rotation speed on the corrosion current density of rod 304 L SS at different temperatures.

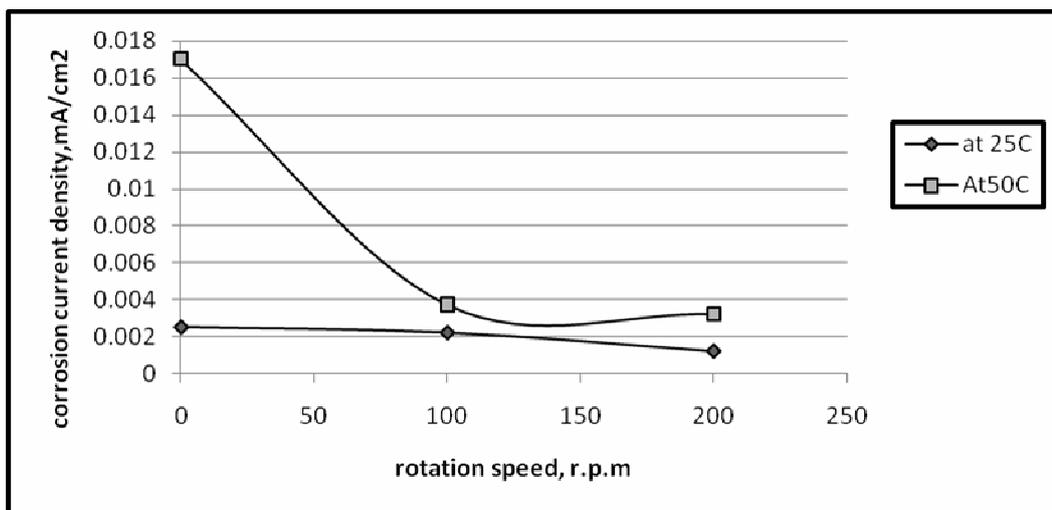


Fig. 3: Effect of rotation speed on the corrosion current density of square 304 L SS at different temperatures.

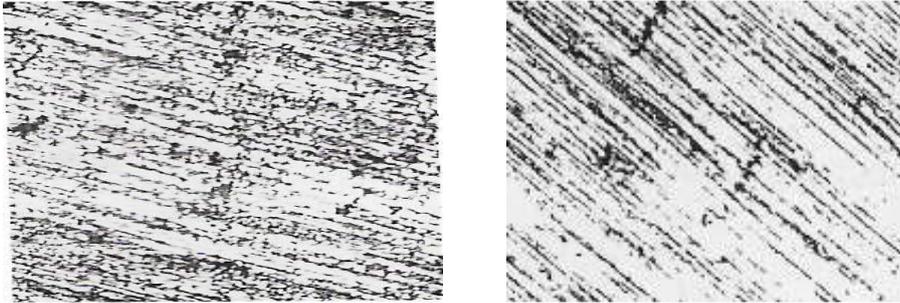


Fig.4: square & rod 304LSS after potentiostatic polarization in 3.4% NaCl at 50C°

4-CONCLUSIONS

1. The corrosion rate of a metal in diffusion – controlled system becomes independent of solution velocity at very high velocities (100 & 200) r.p.m.
2. At static conditions, the maximum corrosion rate was in square 304L SS at 50 C°.
3. It can be seen that the corrosion current density is almost constant or in other word it increases slightly as the velocity increases from (0.00015 to 0.0015) mA/cm² at 100 & 200 r.p.m. respectively.
4. No clear effect of rotation speed and temperatures on the corrosion current density of square 304 L SS
5. The effect of temperature changes and velocity on corrosion rate in rod 304LSS is more complex than square 304 LSS.

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Table2: Potential static polarization of square-red 304L SS At 25 C temp.

Time (min)	Potential (mV/min)	r.p.m=0		r.p.m=100		r.p.m=200	
		Current density (mA/cm ²) (square)	Current density (mA/cm ²) (rod)	Current density (mA/cm ²) (square)	Current density (mA/cm ²) (rod)	Current density (mA/cm ²) (square)	Current density (mA/cm ²) (rod)
1	-500	0.061	0.0466	0.094	0.061	0.1	0.055
2	-470	0.044	0.0201	0.062	0.0401	0.07	0.038
3	-440	0.031	0.0098	0.046	0.0198	0.038	0.016
4	-410	0.024	0.0068	0.029	0.0161	0.022	0.0081
5	-380	0.016	0.0026	0.017	0.009	0.013	0.0046
6	-350	0.007	0.0008	0.01	0.005	0.008	0.0018
7	-320	0.004	0.0027	0.008	0.001	0.0051	0.0001
8	-290	0.0022	0.0055	0.0054	0.0033	0.0033	0.001
9	-260	0.0001	0.0087	0.0032	0.0055	0.0018	0.0021
10	-230	0.0061	0.012	0.00089	0.0089	0.001	0.0029
11	-200	0.002	0.022	0.00044	0.0013	0.0029	0.0038
12	-170	0.0024	0.171	0.0019	0.0088	0.0052	0.0093
13	-140	0.0025	0.877	0.0042	0.022	0.0071	0.017
14	-110	0.0025	2.131	0.0061	0.092	0.0089	0.053
15	-80	0.0025	2.817	0.0077	1.121	0.0141	0.099
16	-50	0.0026	3.677	0.0092	2.211	0.0172	0.203
17	-20	0.0047	5.899	0.015	2.588	0.018	0.751
18	0	0.0081	7.121	0.024	2.987	0.02	2.122
19	30	0.012	9.871	0.041	4.123	0.021	2.988
20	60	0.017	11.339	0.053	5.212	0.0273	3.116
21	90	0.025	14.521	0.069	5.717	0.0332	4.362
22	120	0.039	18.629	0.088	6.212	0.0388	5.122
23	150	0.052	21.211	0.121	6.719	0.0421	5.501
24	180	0.083	24.712	0.153	7.442	0.0756	6.198
25	210	0.11		0.197	8.199	0.0931	6.787
26	240	0.198		0.366		0.161	7.389
27	270	0.301		0.721		0.257	7.778
28	300	0.621		1.321		0.501	
29	330	0.955		1.887		0.588	
30	360	1.751		3.116		0.821	
31	390	3.922		3.882		1.391	
32	420	11.321		4.661		1.751	
33	450	18.811		5.198		2.473	
34	480	29.99		6.245		4.116	
35	510	35.177		8.421		6.221	

Table3: Potential static polarization of square-rod 304L SS at 50 C temp.

Time (min)	Potential (mV\min)	r.p.m=0		r.p.m=100		r.p.m=200	
		Current density (mA\cm ²) (square)	Current density (mA\cm ²) (rod)	Current density (mA\cm ²) (square)	Current density (mA\cm ²) (rod)	Current density (mA\cm ²) (square)	Current density (mA\cm ²) (rod)
1	-500	0.0912	0.0601	0.092	0.097	0.0887	0.091
2	-470	0.0821	0.0522	0.078	0.069	0.0802	0.079
3	-440	0.061	0.0388	0.066	0.048	0.0633	0.061
4	-410	0.022	0.0301	0.041	0.031	0.0349	0.042
5	-380	0.011	0.0255	0.022	0.017	0.0211	0.011
6	-350	0.0088	0.00078	0.011	0.0061	0.0082	0.0072
7	-320	0.0071	0.006	0.0051	0.005	0.0046	0.0053
8	-290	0.0058	0.0098	0.0027	0.01	0.0019	0.0001
9	-260	0.0013	0.022	0.0018	0.0201	0.00055	0.0056
10	-230	0.0006	0.038	0.0032	0.0481	0.0032	0.01
11	-200	0.00051	0.0466	0.0051	0.0701	0.0022	0.0221
12	-170	0.00059	0.171	0.0091	0.0977	0.0041	0.0361
13	-140	0.00093	0.833	0.0162	0.335	0.0056	0.0452
14	-110	0.0028	2.011	0.022	1.12	0.0063	0.0721
15	-80	0.0082	3.129	0.026	2.678	0.0071	0.278
16	-50	0.031	3.331	0.0281	2.911	0.0089	0.988
17	-20	0.0601	4.177	0.0388	3.121	0.016	2.11
18	0	0.0933	4.838	0.044	3.661	0.0187	2.548
19	30	0.1221	5.219	0.051	4.399	0.0269	3.179
20	60	0.1431	6.288	0.064	5.203	0.0466	3.455
21	90	0.301	6.455	0.091	5.811	0.0671	4.521
22	120	0.711	7.288	0.15	6.552	0.0921	5.287
23	150	1.398	7.448	0.31	7.11	0.181	5.621
24	180	3.1	9.011	0.621		0.336	6.301
25	210	5.319		0.921		0.556	7.122
26	240	9.871		1.811		0.962	
27	270	15.521		2.333		2.445	
28	300	21.121		2.921		4.129	
29	330	27.711		4.613		6.677	
30	360	33.821		6.772		9.321	
31	390			7.12		13.101	
32	420			7.788		17.211	
33	450			8.299		33.601	
34	480			8.891			
35	510			9.522			

Table4: Effect of rotation speed on corrosion current density of square – rod 304L SS at different temperatures.

r.p.m	square 25C		Square 50C		Rod 25C		Rod 50C	
	i _{corr} mA/cm ²	E _{corr}						
0	0.0003	-230	0.0001	-200	0.0025	-390	0.017	-330
100	0.00015	-200	0.0019	-260	0.0022	-330	0.0037	-330
200	0.0015	-240	0.0012	-260	0.0012	-280	0.0032	-330

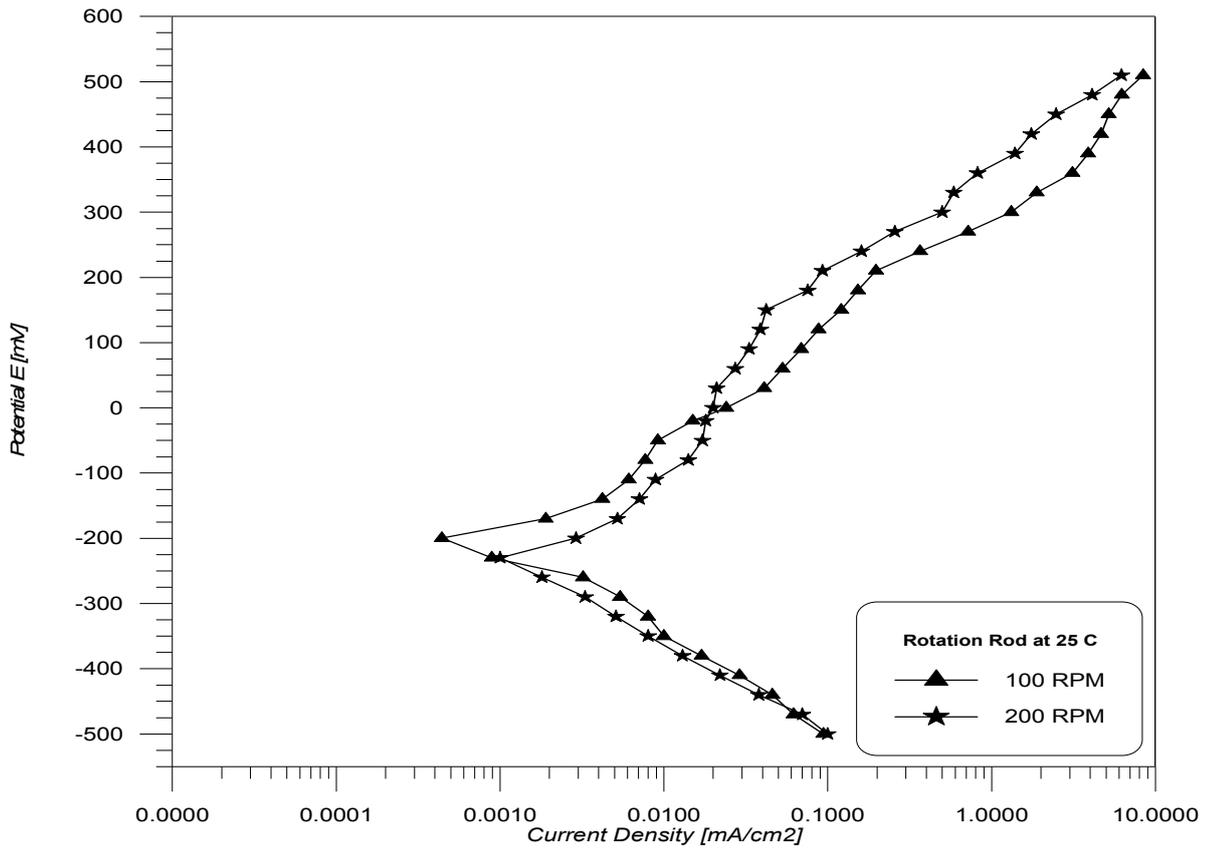


Fig.5: Polarization curves of rod at 100&200 r.p.m in 25 C

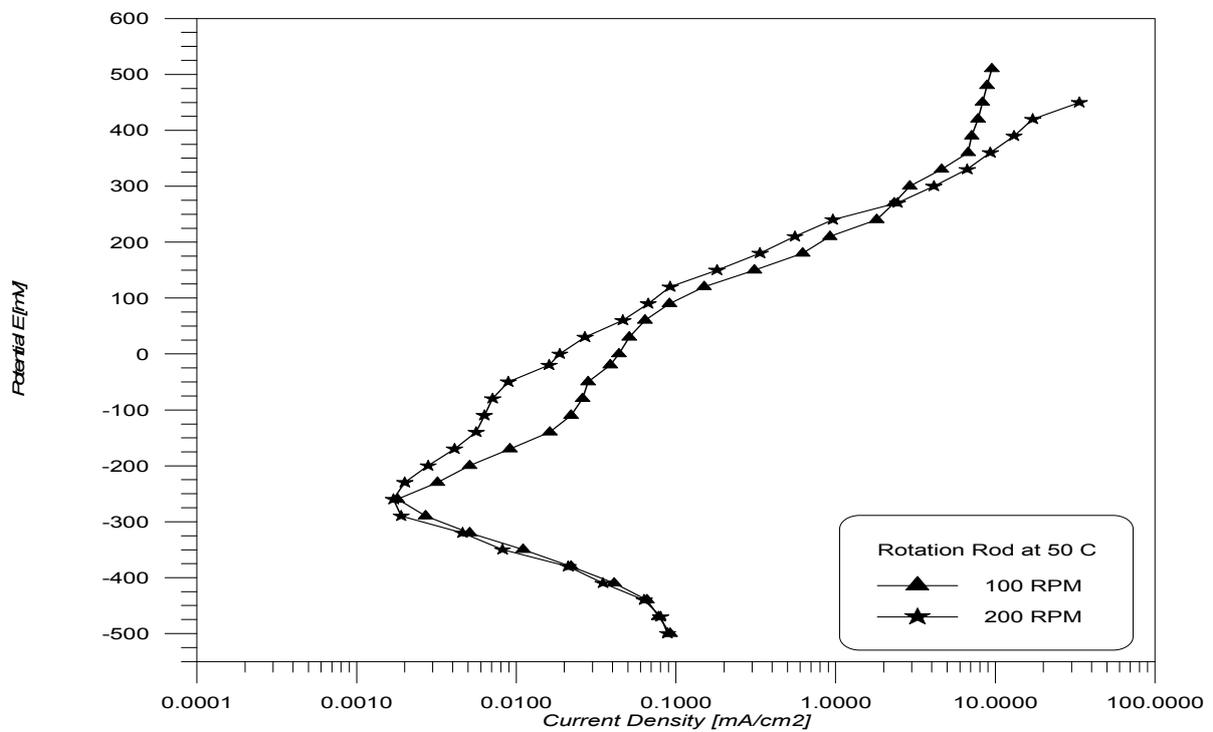


Fig.6: Polarization curves of rod at 100&200 r.p.m in 50 C

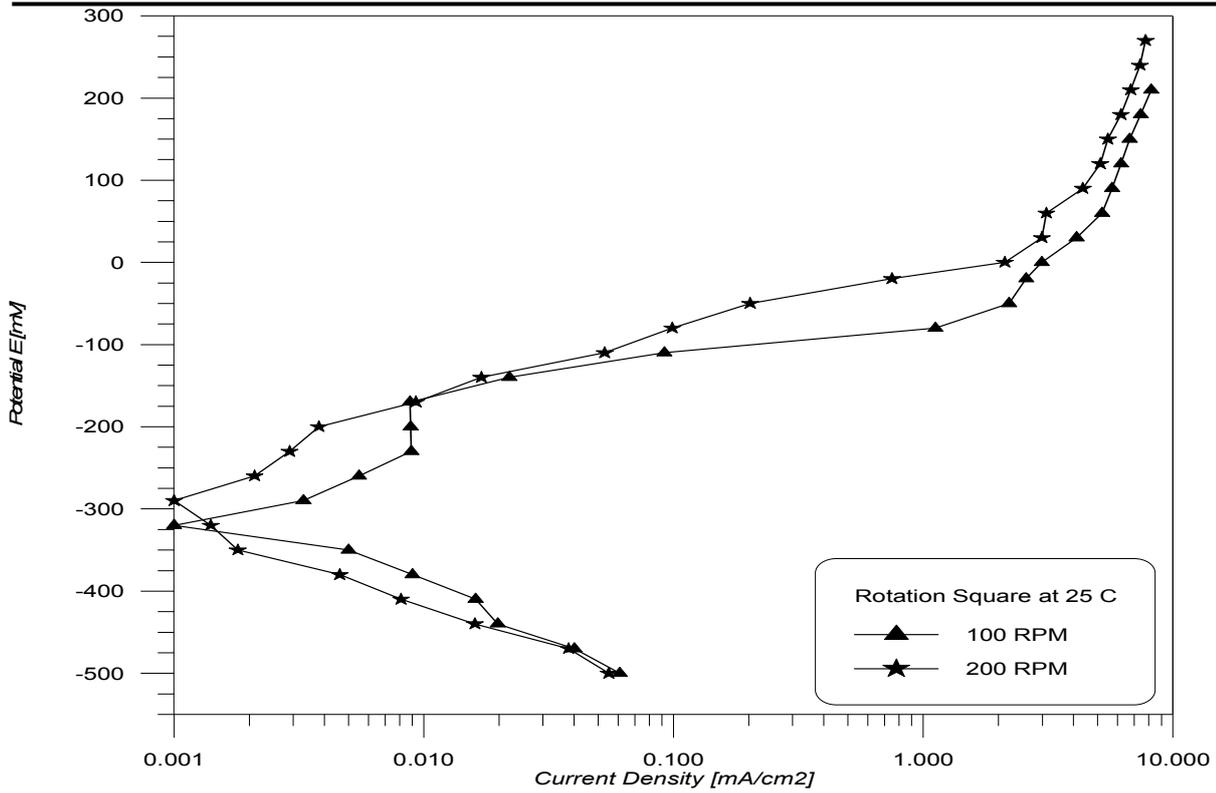


Fig.8: Polarization curves of square at 100&200 r.p.m in 25 C

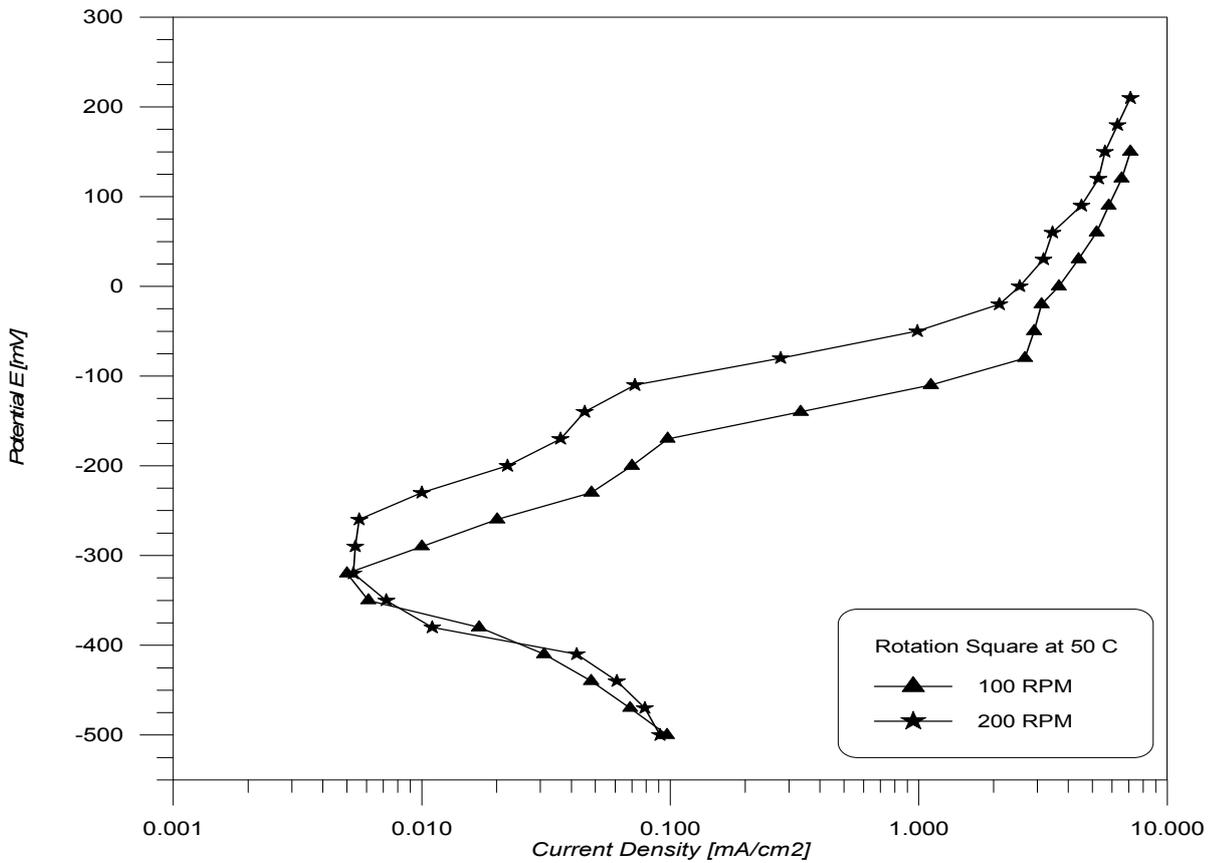


Fig.8: Polarization curves of square at 100&200 r.p.m in 50 C