Effect of Galvanic Coupling on Active - Passive Transition Behaviour of Austenitic Stainless Steels

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Active passive transition behaviour of 18 Cr-8Ni (AISI 304) and 18 Cr 8Ni-2 Mo (AISI 316) steels with and without coupling with nobler metal such as Pt, was studied in sulphuric acid solution, employing potentiodynamic technique. The results indicated considerable variations of passivation potential, passivation current and the range of passive potential between the two systems. Lowering of passivation potential and critical current density requirement for passivation were remarkably noted when AISI 304 & 316 steels were coupled with Platinum. This phenomenon has been attributed to the part played by the cathodic alloying elements to widen the zone of immunity by shifting the hydrogen overpotential on metal surface towards more negative and passivation potential to the more positive values.

Use of stainless steels has increasingly become popular in the process chemical industries primerily for its greater resistance to corrosion. The higher resistance to corrosion is mostly dependent on alloy composition and environmental conditions. As many as 300 varieties of stainless steels having specific physical, mechanical and corrosion resistance properties are known. To achieve higher and higher yields in the industry there is an increasing trend to set process parameters, such as, concentration, temperature and pressure conditions at higher level. This results in greater scope of corrosion attack on the handling equipment and for restoring control of corrosion, development of higher corrosion resistant material is emphasised. There is still demand for exploration of new ideas and further developments. Micro-alloying of stainless steel with nobler element has shown considerable improvement on corrosion resistance (1,2).

Effect of galvanic contact of dissimilar metals was thought to have effect similar to that of the element being in the alloy as constituents. Potentiokinetics of AISI-304 and 316 steels when coupled with Pt was studied to substantiate this. Some of the results in comparison with the performance of Cu & Pd bearing steels are discussed in the present paper.

EXPERIMENTAL

MATERIAL

Test specimen of 2" x 2" size was prepared from the sheet stock supplied by the Alloy steel plant, Durgapur. Chemical compositions of the samples

TABLE 1

CHEMICAL COMPOSITION OF THE TEST SPECIMENS USED IN THE EXPERIMENTS

Steel type	% C	% Cr	% Ni	% Mn	% Si	% P	% S	% Mo	% Cu	% Pd	% N
AISI 430 Steel	0.10	17.70	0.50	1.00	1.00	0.04	0.03	-	-	-	-
AISI 304 Steel	0.12	18.50	9.10	2.00	1.00	0.45	0.03	-	-	-	-
AISI 316 Steel	0.03	18.50	11.10	2.00	1.00	0.04	0.03	2.60	-	-	-
Cu Bearing Stainless Steel	0.07	18.55	5.20	6.80	0.62	-	-	-	3.12	-	0.07
Pd bearing Stainless Steel	0.08	17.0	8.5	-	-	-	-	-	-	0.10	-

are shown in Table - 1. Samples were mechanically polished (up to 400 grit size) and then degreased. An accurate area of 1 cm x 1 cm of the degreased surface was defined with a paraffin mixture and used for the polarisation test. Polarisation measurements were performed in a beaker with the prepared side of the specimen kept vertical and facing the Pt auxiliary electrode of about 6.0 cm^2 . Test media used was 1.0 N and 2.5 N H_2SO_4 solutions and the potential of the working electrode was controlled with a saturated calomel electrode.

TEST METHOD

Polarisation characteristics of the steels was studied at 28 ± 2°C using an electronic potentiostat which delivered polarisation current over 100 mA in both directions with an effective resistance of the polarisation circuit less than 0.5 Ohm.

Before measurement the sample was treated at potentials between -0.5 and -0.6 V for about a minute. This treatment assured a complete activation of the surface and better reproduction of the results. The electrode potential was varied automatically at a scan rate of + 0.05 V/mt. The corresponding change in current was noted approximately 60 reading / mt. Polarisation curves (E vs I) were plotted in a semilog graph paper.

RESULTS AND DISCUSSION

Polarisation behaviour of ferritic (17% Cr) and austenitic (18 Cr - 8Ni - 2Mo) steels with and without coupling with Pt has been shown in Figs. 1,2 & 3. Table - 2 indicates the values for critical current density (I crit), passivation potential (Ep), and the corrosion current (I pass) in the passive state for each system. It has been broadly observed that when AISI-304 & 316 steels were coupled with platinum and subjected to anodic polarisation, the passivation current is lowered in both cases and the potential zone persistent with lower current is extended. Introduction of the cathodic elements such as Mo, Cu & Pd into the Fe - Cr - Ni system has shown to have similar effect.

GENERALISED VIEW OF POLARISATION

The earlier results (1,2,3) have been reproduced schematically in Fig 4. This figure shows distinctive features of zones of A,P and T characteristically interrelated with the composition of the alloy and the environmental conditions of testing.

ACTIVE REGIONS

For example, the A zone represents as active zone and have three subdivision. The portion A_2 which shows very little corrosion is termed as immunity of the metal in the active region. The boundary potentials of the immunity area are overpotential of hydrogen on a given metal (E_H) and the potential for anodic dissolution (E_R). If the region of immunity is very small or not present at all, the polarisation curve cuts the zero axis of the current during the transfer from the area A_1 to A_3 sharply. E_R may also exist at more negative potential than E_H (not shown in figure) and in that case, corrosion with

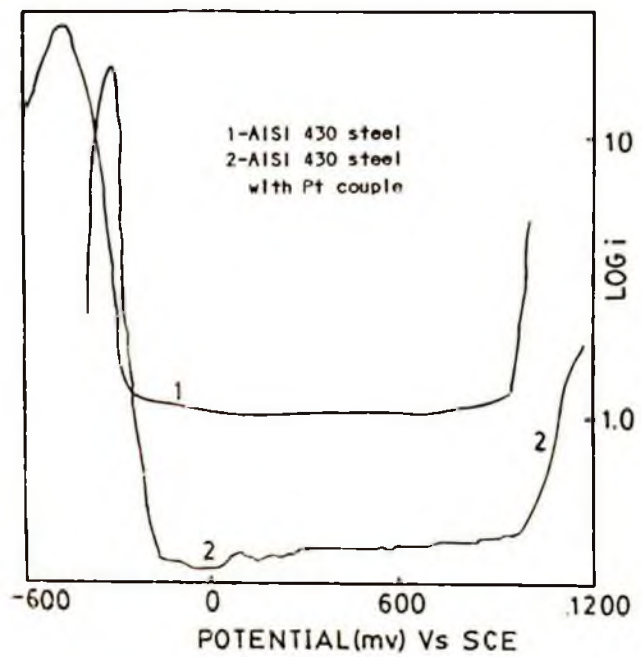


Fig. 1 Anodic Polarization of AISI 430 Steel + Pt Couple in (N) Sulphuric Acid Solution

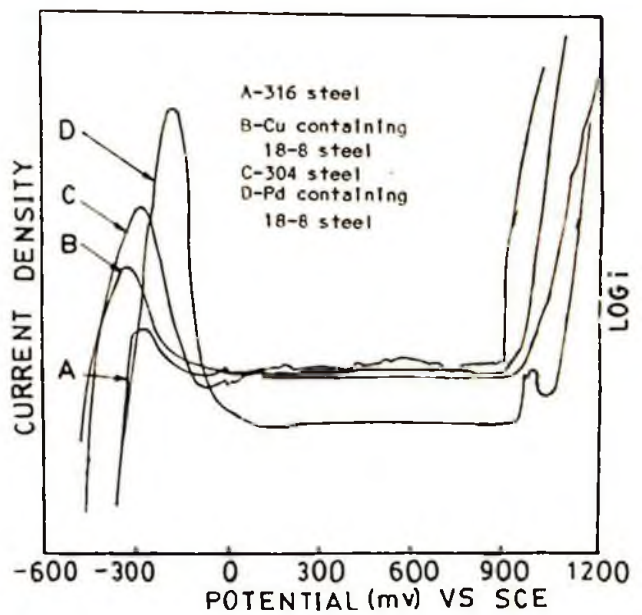


Fig. 2 Anodic Polarization curves in H_2SO_4 Solution

hydrogen depolarisation can take place more vigorously in the active zone. Materials with similar polarisation curve, for example chromium or chromium-manganese steels, do not show good corrosion resistance in the active state.

REGION OF IMMUNITY

The region of immunity is widened if the potential E_R moves towards more positive and E_H to the more negative values. These requirements are met with either by metals which are electrochemically more noble or by metals with higher hydrogen overpotentials. Alloying with such metals therefore have a beneficial effect on the corrosion resistance of the alloys in the active state and the zone of potential for which the corrosion current is maintained minimum is extended.

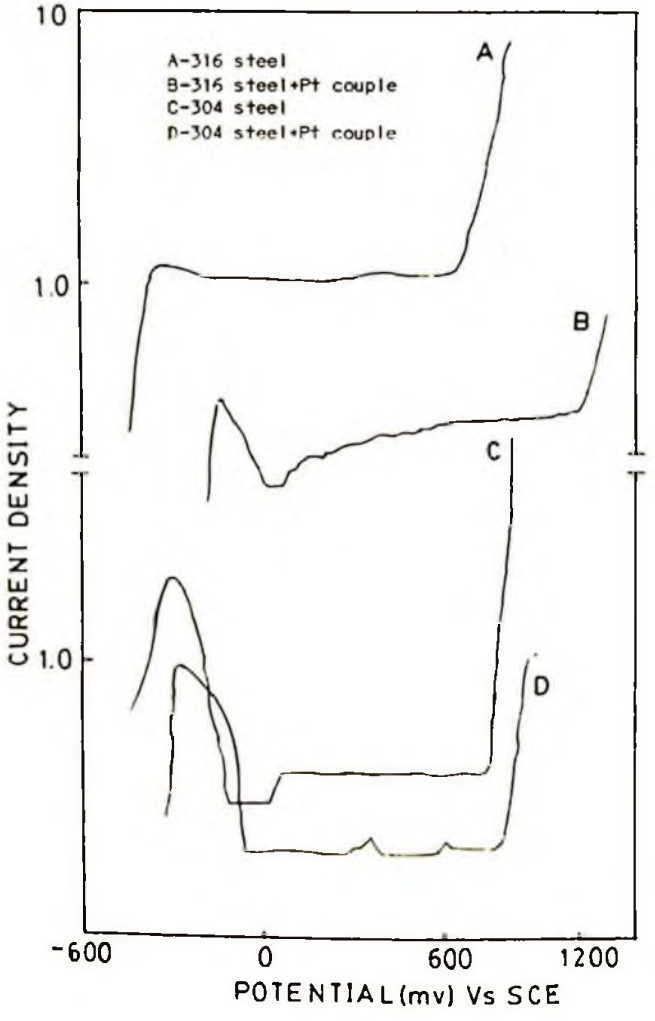


Fig. 3 Anodic Polarization of AISI 304 Steel and AISI 316 Steel & Pt Couple in 1(N) Sulphuric Acid Solution

PASSIVATION POTENTIAL AND CRITICAL CURRENT DENSITY

Potential dependent transition from the active to passive state or vice-versa is known since long (Flade potential). When the Flade value is crossed, the corrosion state of the system is also changed. The dependency of activation potential of the iron-chromium alloys has been studied in greater detail and it has been observed (4) that the activation potential of iron decreases with the increase of chromium content from a value of +0.70 V to -0.20 V in acid solutions of unit hydrogen ion activity. And as a result, the tendency of the steel towards passivity also increases.

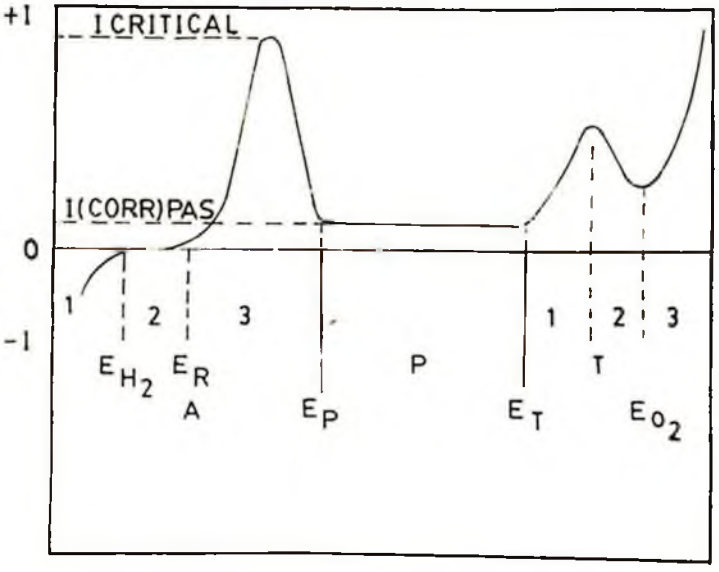


Fig. 4 Schematic Polarisation Curve for Active Passive- Transpassive transition A-Active; P-Passive and T-Transpassive

TABLE 2

Steel type	E mV SCE	I Crit mA/Cm^2	I Pass
17 Cr	-180	26.1	1.10
18 Cr-8Ni	-150	1.94	0.49
18Cr-8Ni-3.12 Cu	-015	1.13	0.46
18Cr-8Ni-2 Mo	-120	0.69	0.47
18Cr-8Ni-0.1Pd	+060	4.40	0.31
18Cr-8Ni+Pt coupling	-60	0.94	0.21
18Cr-8Ni-2Mo+Pt coupling	-75	0.39	0.32

From the view point of passivation tendency of the alloy, the critical current density requirement for passivation is most important. On a polarisation curve, this is indicated as the maximum current value of the region A_3 . Lower value of the I (Critical) is advantageous, since, even lower concentration of passivating agent in the environment shall be able to produce passivation.

PASSIVATION CURRENT AND THE ZONE OF PASSIVITY

Since passivation current is the measure of corrosion rate, its lower value is desirable for obvious reasons. Therefore, the alloying addition that brings down the passivation current is a definite advantage. It should also be considered that the passivation current is significantly affected by the complex formation. Therefore, the passivation as observed with one media, e.g. sulphric acid may not be applicable for other acids, namely HF or HCl.

Another important aspect in passivation is the potential zone covered by the portion P of the polarisation curve. It should be as wide as possible to cover up a greater range of oxidising conditions that may eventually arise in service environments.

DIFFERENTIATION AND EXPLANATION OF THE RESULTS

Ferritic chrome steel showed relatively high value of I Crit (Table-2) compared to 18Cr-8 Ni and 18Cr-8Ni-2 Mo steels. This is obviously the reason for its high corrosion losses in the active state and less easy change to passive state, even though the passivation starts at more negative potential compared to 18.8 steel as evident in Fig.5.

The effect of nickel addition in iron chromium alloys for better corrosion resistance is evident from the shape of the polarisation curve. Nickel reduces the value of, I crit and I pass and both of these factors are inductive for easy transformation from active passive state. The presence of molybdenum as a further alloying addition supresses the area of activity with additional advantage of increased corrosion resistance properties of the material.

Polarisation behaviour of 18Cr-8Ni and 18Cr-8Ni-2 Mo steels coupled with a piece of platinum showed considerable reduction of corrosion in the active area, reduction of I crit and thus greater ease for the transformation from active to passive state. Effect of galvanic contact of platinum with the stainless steels is mostly confined in the active region of the polarisation behaviour of the couple. It has effect on widening of A_2 region i.e. the immunity zone by shifting the dissolution potential E_R towards more positive direction and the hydrogen evolution potential E_H to more negative direction (Hydrogen overpotential on platinum surface being minimum).

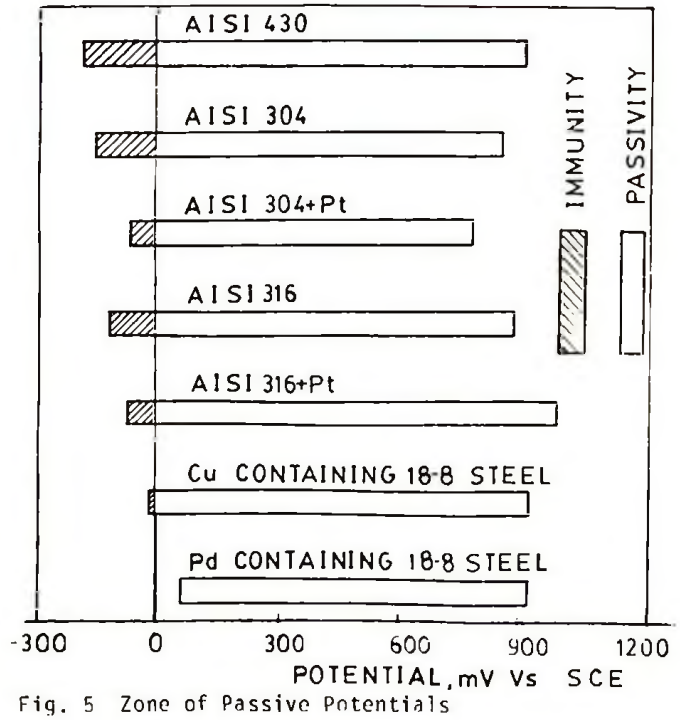


Fig. 5 Zone of Passive Potentials

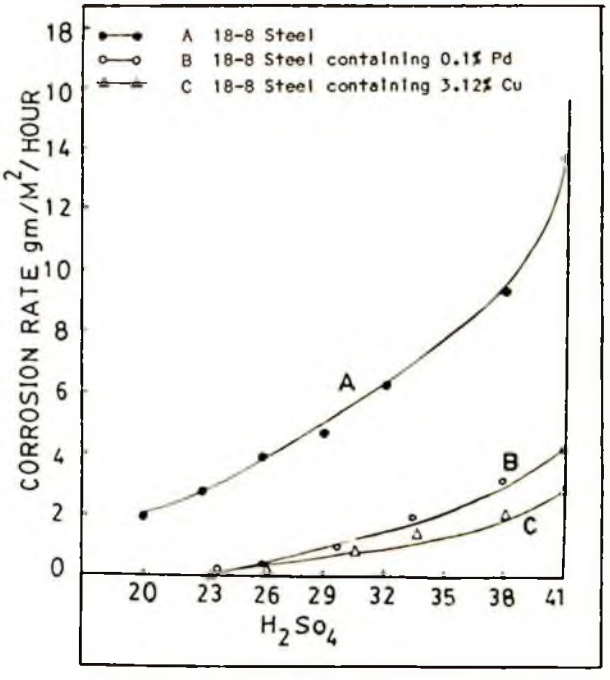


Fig. 6 Corrosion rate of 18-8 Chrome-Nickel Steels additionally alloyed with Cu and Pd.

Polarisation behaviour of Cu and Pd containing steels showed less passivation current which corroborates the results reported by Chernova (5) as shown in Fig.6. Suppression of critical current density due to the presence minor cathodic element is attributed to the shift of passivation potential E_P into positive direction as evident in the present investigation (Fig.5). These additives accumulate on the surface due to the selective dissolution of base metal and induce similar effect of potential enrichment as it happenes when the metal is galvanically coupled with a more cathodic metal e.g. Pt.

High critical current density requirement of Pd bearing steel appears to need clarification. On this point further basic study is necessary.

CONCLUSIONS

Improvement in corrosion resistance of stainless steel in acid media by additionally cathodic alloying is possible.

Part played by the cathodic elements is mostly confined in the active zone of the polarisation behaviour of the metal environment system, Preferential dissolution of the base metal enriches the surface with respect of the cathodic elements which in turn under conducive conditions widen the zone of immunity by shifting the E_H towards negative and E_P to the positive directions.

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