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Influence of surface treatment on the hysteresis effect in anodic polarization of stainless steels

N. AZZERRI AND G. BOMBARA

Centro Sperimentale Metallurgico, 00129, *Rome, Italy*

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The hysteresis effect in the anodic passivation of a series of stainless steels in acid solutions has been evaluated coulometrically from the polarization curves obtained by forward and reverse potential scanning.

Based on such effects, an index of passivity retention has been drawn differentiating the stainless grades and reflecting the surface preparation.

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1. Introduction

The corrosion behaviour of stainless steels depends upon the speed of formation, the degree of imperfection, chemical instability and ease of healing of the passive film. These properties, described by self-explanatory terms such as ‘passivability’, ‘degree of passivity’, ‘passivity retention and repairability’, are principally functions of the chemical composition of the steel, but are also markedly affected by the surface condition. This was demonstrated in a previous investigation [1] on passive potential breakdown times [2], measured for different surface treatments. In the same context it seems of interest to consider the hysteresis effect in the anodic polarization of passivable alloys, that is to say, the substantial difference, in the active dissolution and passivation ranges, between the polarization curves obtained by forward and reverse potential scanning. Such an effect has been already observed in relation to the susceptibility of stainless steels to localized corrosion [3].

In the work reported in this paper, the hysteresis effect has been studied on a series of stainless steels to produce a method of practical use for the evaluation of different surface preparations.

2. Experimental

2.1 *Materials*

Commercial sheets 1 mm thick with a standard finish, 2B, were used for two austenitic grades (304L and 316), a ferritic grade (430) and a martensitic grade (410). The chemical compositions are given in Table 1. As previously reported [1] electron probe examination of these flat-rolled products showed a 10 to 20% chromium-depletion in the surface alloy.

With particular reference to such depletion the following surface preparations were tested:

(i) simple degreasing in an ethyl alcohol-ether mixture;

(ii) chemical passivation by dipping for 24 h in 30% w/w HNO_3 aqueous solution at room temperature;

(iii) pickling in HNO_3 (density 1·4) 20% vol. + HF (density 1·15) 4% vol. as follows:

10 min at 60C for Types 304L and 316,
5 min at 60C for Type 430,
5 min at 25C for Type 410;

(iv) metallographic polishing with emery papers and diamond pastes to 0·25 microns.

Strip specimens, sheared from the sheets were

Table 1. Alloy compositions

Alloy	*C*	*Mn*	*Si*	*P*	*S*	*Cr*	*Ni*	*Mo*
				Composition %				
304 L	0·018	1·42	0·53	0·017	0·010	18·85	10·53	0·02
316	0·045	1·40	0·51	0·021	0·012	16·68	10·70	2·03
430	0·068	0·52	0·45	0·018	0·007	17·08	0·42	0·07
410	0·055	0·52	0·54	0·018	0·010	12·22	0·12	0·01

employed, with an exposed circular test area of 5 cm^2. The experimental cell was as described [4].

2.2 *Procedure*

The anodic polarization of the steels was determined by potentiodynamic scanning in 4·5 N H_2SO_4 aqueous solution. Type 410 steel was tested also in 0·1 N H_2SO_4. Experiments were performed at 30C in electrolytes deaerated with high purity nitrogen by a Hersch apparatus [5]. A model 557 AMEL potentiostat was employed together with an electrometer and a strip chart recorder. A Hg/Hg_2SO_4 electrode in saturated K_2SO_4 solution was used as reference and the potentials quoted below are those obtained experimentally.

Polarization curves in the positive potential direction were obtained after a 5 min cathodic activation at $-1·1$ V and subsequent freeing of the working electrode until it reached a steady corrosion potential. Starting from this active value the potential was then scanned at a rate of 40 mV min^{-1} up to the passive value of 0·0V, while recording the polarization current continuously. Reverse curves were obtained by first polarizing the steel electrode for 5 min at 0·0V and then scanning the potential in the negative direction at the same rate as in the forward scan. Some curves are shown in Fig. 1.

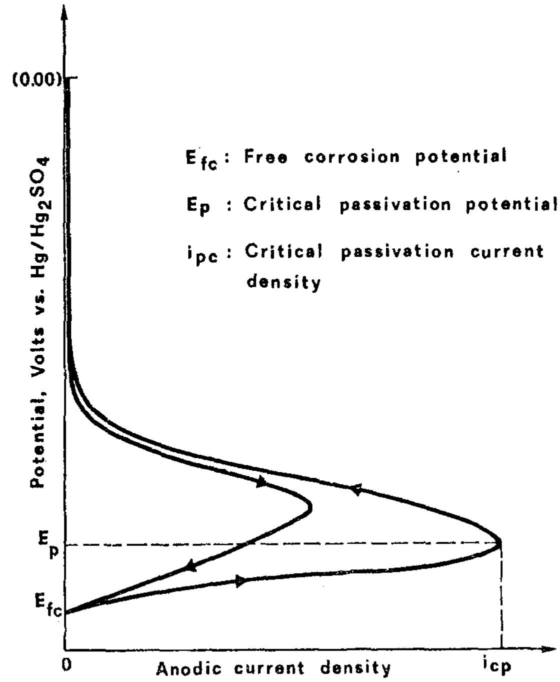

Figure. 1. Typical polarization curves

3. Results and discussion

Polarization parameters for the differently prepared steels are listed in Tables 2 and 3. The number of coulombs, Q_p, required (at the given scanning rate) for the anodic passivation, was drawn from the area of the anodic peak recorded in the forward scan. Q_d, analogously, was obtained from the peak area in the reverse scan. Since the total coulombs in each scan results from a combination of electrochemical and non-faradaic processes, the bulk of the anodic current density going to metal dissolution, the scanning rate is of considerable importance in determining the relative kinetic behaviour of the various associated anodic reactions. This means that Q_p and Q_d, as well as the other polarization parameters, must be strictly referred to the chosen scanning rate.

For Type 304L steel some differences result among the various finishes but only in i_{cp} and Q_p and Q_d.

Table 2. Polarization parameters in 4·5 N H_2SO_4

Alloy	*Surface condition*	*Free corrosion potential (after cathodic activation)* E_{fc} (mV versus Hg/Hg_2SO_4)	*Critical passivation potential* E_p (mV versus Hg/Hg_2SO_4)	*Passivation c.d.* i_{cp} (mA cm^{-2})	*Passivity c.d.* ($\mu A\ cm^{-2}$ *at* −0·4 V versus Hg/Hg_2SO_4)	*Total coulombs in the forward scan* Q_p (C cm^{-2})	*Total coulombs in the reverse scan* Q_d (C cm^{-2})
304 L	As received	−810	−745	2·1	8·0	$3{\cdot}07.10^{-1}$	$41{\cdot}3.10^{-3}$
	Passivated	−800	−725	1·3	8·0	$2{\cdot}07.10^{-1}$	$0{\cdot}36.10^{-3}$
	Pickled	−795	−750	0·8	8·0	$1{\cdot}19.10^{-1}$	$2{\cdot}34.10^{-3}$
	Polished	−805	−750	1·0	10·0	$1{\cdot}54.10^{-1}$	$3{\cdot}46.10^{-3}$
316	As received	−740	−655	0·30	5·0	$6{\cdot}07.10^{-2}$	$3{\cdot}15.10^{-3}$
	Passivated	−740	−690	0·29	13·0	$5{\cdot}10.10^{-2}$	0
	Pickled	−750	−715	0·09	1·0	$1{\cdot}74.10^{-2}$	0
	Polished	−750	−720	0·09	0·8	$1{\cdot}92.10^{-2}$	0
430	As received	−930	−800	18	40	2·74	2·50
	Passivated	−930	−810	16	32	2·46	2·12
	Pickled	−940	−810	18	15	2·82	1·08
	Polished	−935	−810	16	—	2·59	1·31
410	As received	−930	−750	30	170	6·49	6·40
	Passivated	−920	−720	37	90	8·22	4·70
	Pickled	−930	−745	32	170	6·93	4·66

Table 3. Polarization parameters for Type 410 steel in 0·1 N H_2SO_4

Surface condition	E_{fc} (mV)	E_p (mV)	i_{cp} (mA cm^{-2})	i_p ($\mu A\ cm^{-2}$)	Q_p (C cm^{-2})	Q_d (C cm^{-2})
As received	−950	−780	2·8	22	0·87	0·45
Passivated	−930	−730	3·2	36	1·12	0·95
Pickled	−960	−810	2·6	20	0·72	0·16
Polished	−965	−800	2·4	21	0·71	0·24

Considering that i_{cp} is an index of the difficulty in anodic passivation, the removal from the surface of the Cr-depleted layer through pickling or polishing appears to increase the passivability consistently with the restoration of the base Cr-content. The passivating treatment in nitric acid seems to work in a similar manner. The values of Q_p and Q_d reflect the effects on i_{cp}.

For Type 316 steel, there is a clear differentiation between results for the various surface preparations. Free-corrosion potentials as well as critical passivation potentials for polished or pickled surfaces are more active than for untreated or chemically passivated surfaces. This is consistent with the removal of the depleted chromium surface layer which is the most active of the alloy elements. Polished and pickled specimens show, accordingly, easier passivation and a less defective passivity (lower i_p). Analogous conclusions can be drawn from Q_p and Q_d.

Type 430 steel also shows a slight shift of E_{fc} and E_p in the active direction produced by pickling and polishing, as well as a lower i_p for pickled specimens. Values of Q_d indicate a higher passivity retention in the reverse scan for pickled or polished surfaces.

For Type 410 in 4·5 N H_2SO_4, which is too aggressive a medium for this steel, a difference among the surface treatments results only from Q_d which indicates a lower anodic reactivity in the reverse scan for pickled and polished specimens. A higher differentiation results in less aggressive 0·1 N H_2SO_4, as shown in Table 3. More active free corrosion and passivation potentials and lower Q_d were recorded on pickled and polished specimens.

3.1 *Passivity retention*

In order to draw from the available polarization data an index of electrochemical stability of the passive state, the kinetic significance of Q_p and Q_d must be considered. Q_p indicates quantitatively the amount of metal dissolution involved in the anodic passivation. Bearing in mind the dependence of Q_p on the scanning rate in connection with the anodic polarizability of the alloy, it is a measure of the relative ease of passivation by an anodic potential sweep of a previously activated surface. Unless the existence of a non-protective pre-passive film is assumed which cannot be cathodically reduced, cathodic activation would produce a bare metal surface and Q_p would involve the entire metal area exposed.

On the other hand, Q_d indicates the amount of anodic dissolution permitted by the previously formed passive film while undergoing breakdown in the active potential range. Therefore, the difference between Q_p and Q_d would reflect the hindering action of non-conductive products of passivation virtually decreasing the electrode area. Q_d also depends largely on the polarizability of the alloy, i.e., on the scanning rate. However, in relation to the chosen rate, Q_d is a measure of the relative ability of the passive film to prevent the alloy from undergoing anodic dissolution during the reverse scan across the active range.

Should the passivity be completely retained during the reverse scan, Q_d would consist of only a very few coulombs allowed by the high polarizability of the filmed surface. If instead the anodically produced passivity be totally lost, Q_d should be nearly equal to Q_p.

An index of relative stability of anodic passivity can be given accordingly by the expression

$$P_r = \frac{Q_p - Q_d}{Q_p} \times 100\%$$

Table 4 shows the values of P_r so calculated for the various steels and surface treatments. The following decreasing order of passivity retention results for the steels investigated: Type 316>304L>>430>410. In the received condition, the superiority of Types 300 over Types 430 and 410 is of one and two orders of magnitude, respectively.

As far as surface preparation is concerned it appears that both polishing and pickling remarkably increase the stability of the passive film with respect to the standard finish. It is suggested that this is due to the restoration of the bulk chromium concentration to the alloy surface. In this connection the beneficial effect of removing the Cr-depleted layer is more marked for the steels with a weaker passivity, namely Types 430 and 410. Pre-treatment in HNO_3 is clearly beneficial only for Types 300, while it is harmful for Type 410 [6].

Table 4. Passivity retention, P_r(%)

Surface condition	Solution: 4·5 N H_2SO_4				0·1 N H_2SO_4
	Alloy				
	Type 304 L	Type 316	Type 430	Type 410	Type 410
As received	86·5	93·7	8·7	1·4	48·3
Passivated	99·8	100	13·8	—	15·2
Pickled	98·0	100	61·7	42·8	77·8
Polished	97·7	100	49·4	32·7	66·2

4. Conclusion

The criteria described, based on simple coulometry of polarization curves, appear to be of use for assessing the relative stability of anodic passive films on stainless steels. The index P_r, clearly differentiating the steels and the finishes tested, appears to be applicable to the comparative evaluation of passive films produced otherwise than by anodic polarization in aqueous solutions.

References

[1] N. Azzerri, L. Giuliani and G. Bombara, *Corrosion*, **26**, (1970) 381.

[2] E. A. Lizlovs, *Corrosion*, **22,** (1966) 297.

[3] B. E. Wilde and E. Williams, *Electrochimica Acta*, **16,** (1971) 1971.

[4] G. Bombara, N. Azzerri and G. Baudo, *Corrosion Science*, **10,** (1970) 847.

[5] D. Gilroy and J. E. O. Mayne, *J. Appl. Chem.*, **12,** (1962) 382.

[6] J. M. Defranoux, Paper presented at 23rd Meeting C.I.T.C.E., Stockholm, August 1972.