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Anodic pickling of stainless steels in sulphuric acid

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Potentiostatic pickling in 20% aqueous H_2SO_4 was investigated on hot- and cold-rolled strips of stainless steels from industrial lines, in order to assess the potentiality of this technique. Experimental evidences for AISI Types 202, 304, 316, 410 and 430 are given. Optimum pickling conditions were defined on the basis of the potentiodynamic behaviour of oxidized specimens.

Visual and electrochemical evaluation of pickled surfaces showed that:

(i) The potentiostatic technique makes descaling and pickling of stainless steels quite feasible in sulphuric baths;
(ii) remarkable advantages result over ordinary chemical treatments in terms of speed of scale removal;
(iii) a higher efficiency of restoration of passivity properties also results.

Introduction

The selective character of dry oxidation of stainless steels has been widely recognized [1, 2]. Therefore any industrial heat treatment in oxidizing atmospheres causes a remarkable Cr-depletion beneath the oxide scale, to an extent depending upon the temperature and the duration of treatment, as well as the gas composition inside the furnace.

Since Cr-depleted alloy is electrochemically more noble than that unaffected, the polarization curve of an oxidized surface in a pickle presents an enlarged anodic current peak at a potential shifted by some hundred mV in the positive direction with respect to a well-pickled surface [3]. The larger peak results from the anodic dissolution of the base alloy plus a number of contributions by more noble Cr-impoverished zones. This is clearly demonstrated by the splitting of the initial peak into at least two current maxima on repeating the potential sweeps [4].

Considering Cr-depletion and the fact that descaling occurs essentially via subscale metal dissolution [3, 4], a technique has been envisaged [5] for improving pickling by potentiostatically polarizing the steel at a potential favouring the dissolution of the impoverished alloy, as shown schematically in Fig. 1. Accordingly, pickling of stainless steels must be looked on as a duplex operation [4], namely descaling proper and surface restoration of the full chromium content.

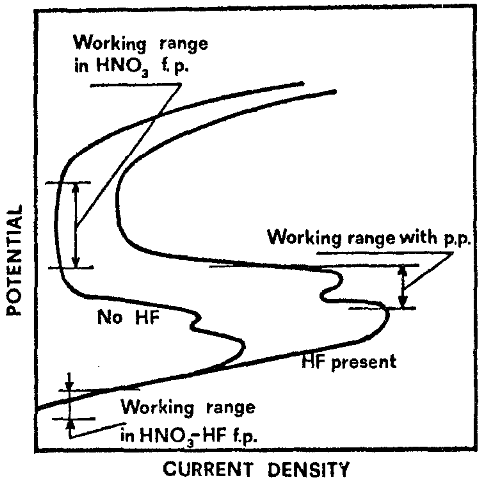

Fig. 1. Potential ranges of free and potentiostatic pickling in HNO_3–HF mixtures.

A previous work of ours [6] showed a number of advantages of potentiostatic pickling over a free one in ordinary HNO_3–HF mixtures:

(i) quicker scale removal;
(ii) more rapid restoration at the surface of the base Cr content;
(iii) possible replacement of nitric–hydrofluoric baths by cheaper and less toxic sulphuric baths.

In connection with this last point, this work reports on tests in H_2SO_4 carried out on stainless strips from industrial rolling lines, in order to assess the feasibility and convenience of this new technique.

Experimental and results

Materials

Annealed strip specimens were drawn from both hot- and cold-rolling lines just prior to pickling sections. Various steel grades were considered, as follows:

(i) hot-rolled strip: Types 202 and 304 (4 mm thick); 316 (5 mm); 410 and 430 (4 mm);
(ii) cold-rolled strip: Type 202 (1·2 mm thick); 304 (0·8 and 2 mm); 410 (2 mm); 430 (0·5 and 2 mm).

Hot-rolled products had undergone the usual shot-peening soon after the annealing treatment. 40 × 30 mm specimens were used for potentiostatic tests carried out with an AMEL apparatus model 555/SU.

Pickling tests

Conditions for potentiostatic pickling (p.p.) must be determined for each type of steel and thermal treatment. Indeed, chromium depletion and scale properties depend, besides the steel composition, upon the oxidation duration and temperature.

In a hot rolling line, the soaking time at elevated temperatures (900–1100°C) during rolling and annealing is relatively long. Consequently, an adherent scale is formed only a few microns thick but rather microcracked owing to the rapid growth through alternately parabolic (protective) and linear (non-protective) oxidation stages. In the plant, scale cracking is usually completed by shot-peening for an easier subsequent pickling.

In contrast, cold-rolled strip undergoes a

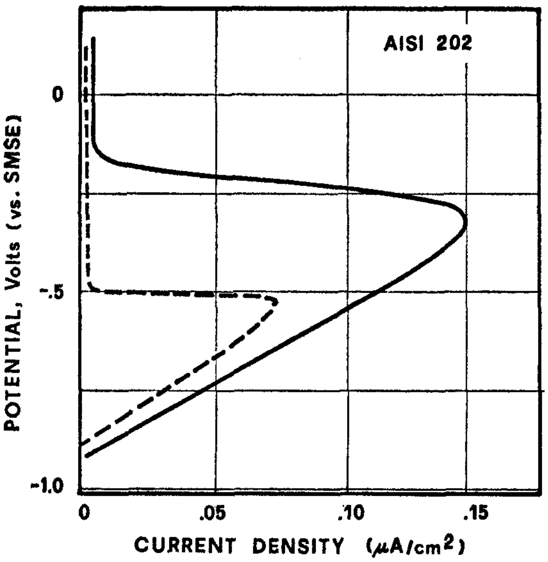

Fig. 2. Anodic polarization curves of oxidized Type 202 steel in 20% H_2SO_4 at 80°C (scanning rate: 1·5 V/min). Hot rolled ——; cold rolled – – –.

Table 1. Pickling cycles for hot rolled strips

		*Sulphuric p.p.**		*Reference pickling*
AISI steel designation	*Strip thickness* (mm)	*Polarization potentials‡* (V)	*Time* (s)	*Time* (s)
202	4	−0·4	75	75
304	4	f.p. −0.1 −0.4	5 10 5	20
316	5	−0.6	40	40
410	4	−0.7 +0.6	5 3	10
430	4	−0.7 +0.4	15 10	25

* 20% H_2SO_4 at 80°C.
† HNO_3 (d 1·4) vol 20%+HF (d 1·15) vol 2% at 55°C.
‡ Potentials referred to Hg/Hg_2SO_4 electrode (+0·641 V versus NHE).

solubilization treatment only a few minutes long, leading to an extremely thin and compact oxidation patina. In this case pickling requires a drastic preconditioning of the strip consisting of either an alternate anodic–cathodic treatment in aqueous HNO_3 or a dipping in molten salts.

However, cold-rolled strips in the annealed condition show a Cr-depletion much lower than in hot-rolled ones as is evident from substantial differences in the potentiodynamic behaviour (Fig. 2). These lie mainly in larger passivation peaks and more noble peak potentials for hot-rolled products [6].

As indicated in Fig. 1, the potentiodynamic curve in the pickling solution gives for each material the optimum conditions for p.p. This latter should be over when the initially high anodic current density decreases to negligible values corresponding to the passive state of the base alloy.

Tables 1 and 2 summarize the p.p. conditions singled out from the polarization curves for the various steels and heat treatments. As it can be seen, generally a sequence of electrochemical operations is required rather than a single one, in order to obtain the highest pickling efficiency.

Pickling evaluation

The efficiency of each sulphuric pickling test was compared with that of conventional pickling taken as reference, the overall duration being the same. Reference pickling for shot-peened hot-rolled strips consisted of dipping in the mixture HNO_3 (d 1·4) vol 20%+HF (d 1·15) vol 2% at 55°C, whilst for cold-rolled products a duplex

Table 2. Pickling conditions for cold-rolled strips

		*Sulphuric p.p.**			*Reference pickling‡*	
AISI steel designation	*Strip Thickness* (mm)	*Polarization†*	*Time* (sec)	*Bath temp.* (°C)	*Treatment‡*	*Time* (sec)
202	2	−0·9 V	40	80	e.p.	30
		−0.5 V	15		f.p.	30
304	0·8	−20 A/dm_2§	5	80	e.p.	30
		−0·65 V	25			
		−0·55 V	15−35		f.p.	35
	2	−0·6 V	75	80	e.p.	60
		−0·55 V	5−25		f.p.	40
316	1	−0·55 V	170	80	e.p.	90
					f.p.	90
	2	−0·475 V	130	80	e.p.	90
					f.p.	90
410	2	±20 A/dm^2§	30	25	e.p.	30
430	0·5	f.p.	5	80	e.p.	10
	2	+10 A/dm^2§	1			

* 20% H_2SO_4.

† Potentials referred to Hg/Hg_2SO_4 electrode (+0·641 V versus NHE).

‡ e.p. = Alternative anodic (10s)—cathodic (5s) pickling in 30% HNO_3 at 55°C.
f.p. = Free pickling (dipping) in HNO_3 (d 1·4) vol 20%+HF (d 1·16) vol 2% at 55°C.

§ Cathodic (−) or anodic (+) electrolytic treatment.

operation was adopted; namely, an alternate anodic–cathodic treatment at 20 A/dm^2 in 30% HNO_3 at 55°C followed by an immersion in the same solution used for hot-rolled strips.

The evaluations of experimental and reference picklings were made in two ways:

(i) visual assessment of scale removal;

(ii) electrochemical determination of passivity parameters, as discussed in previous works [6, 7, 10] such as the anodic passivation charge and the passivity retention.

As to descaling, Figs. 3 and 4 show photographically the results obtained with sulphuric and reference picklings on hot- and cold-rolled specimens, respectively. The superiority of p.p. is quite evident especially for cold-rolled strips. No photographic evidence can be given for cold-

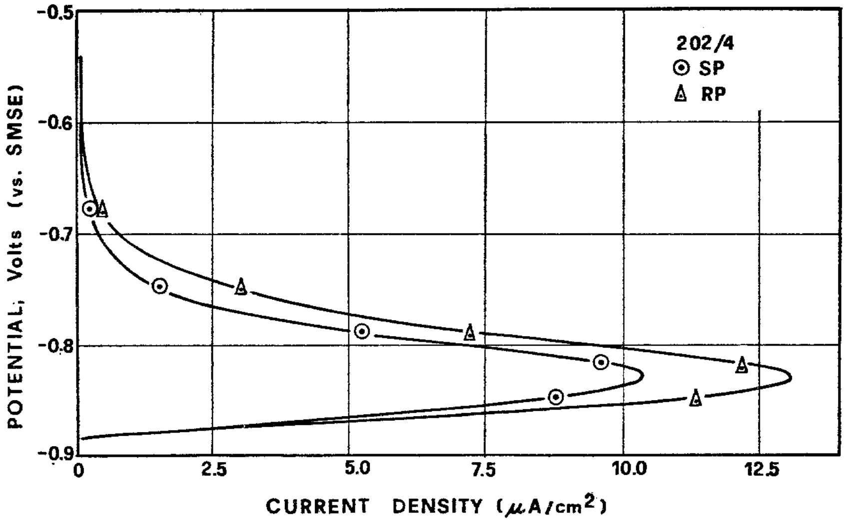

Fig. 5. Anodic polarization curves of hot-rolled Type 202 steel in 20% H_2SO_4 at 30°C. SP—Sulphuric pickled specimen; RP—Conventionally pickled specimen.

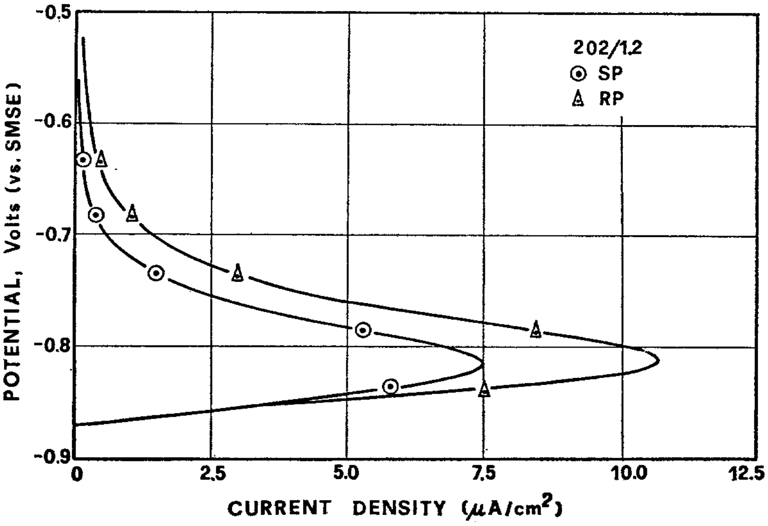

Fig. 6. Anodic polarization curves of cold-rolled Type 202 steel in 20% H_2SO_4 at 30°C. SP—Sulphuric pickled specimen; RP—Conventionally pickled specimen.

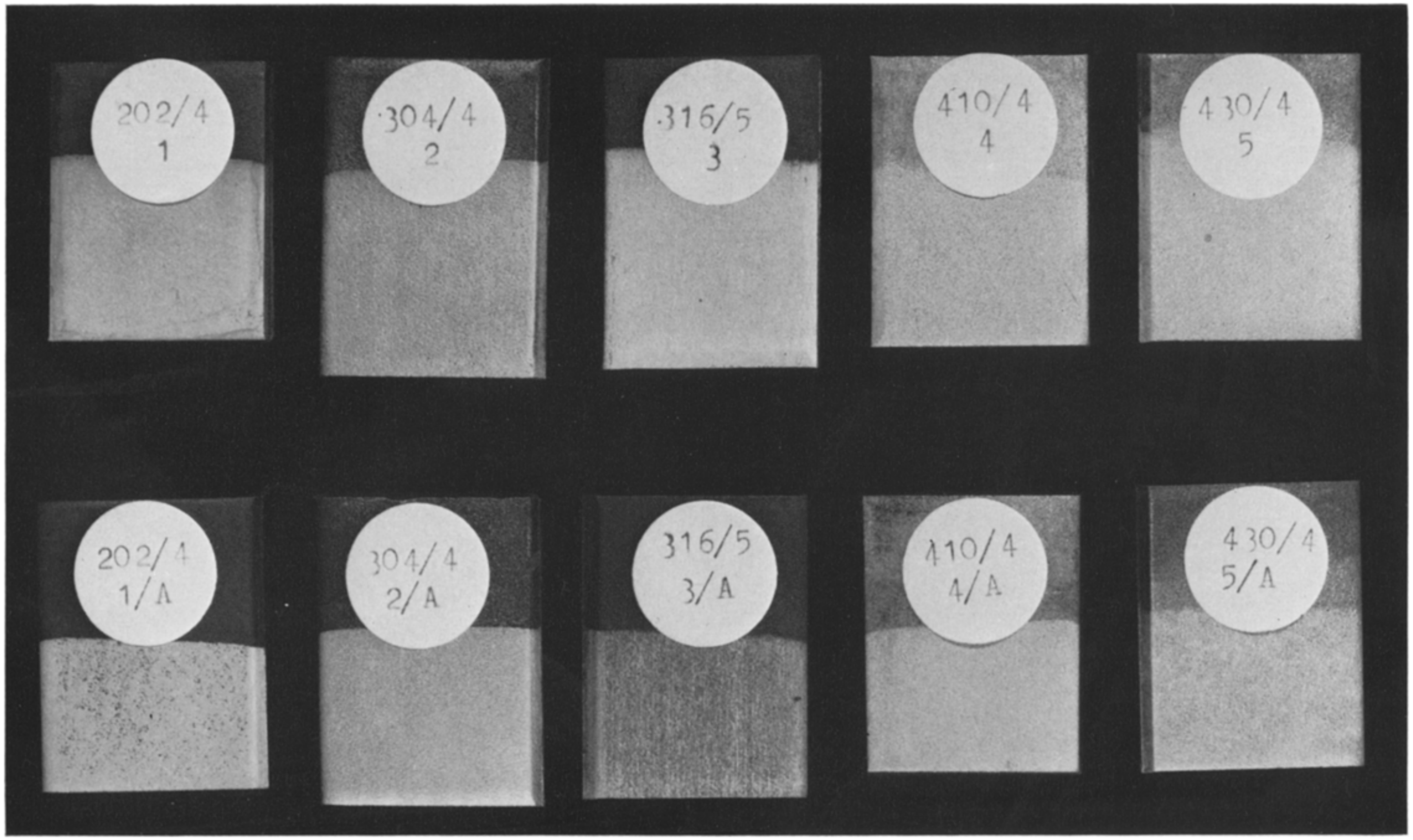

Fig. 3. Descaling obtained with sulphuric (specimens 1 – 5) and reference HNO_3–HF pickling (specimens 1A – 5A) on hot-rolled specimens. Pickling conditions reported in Table 1.

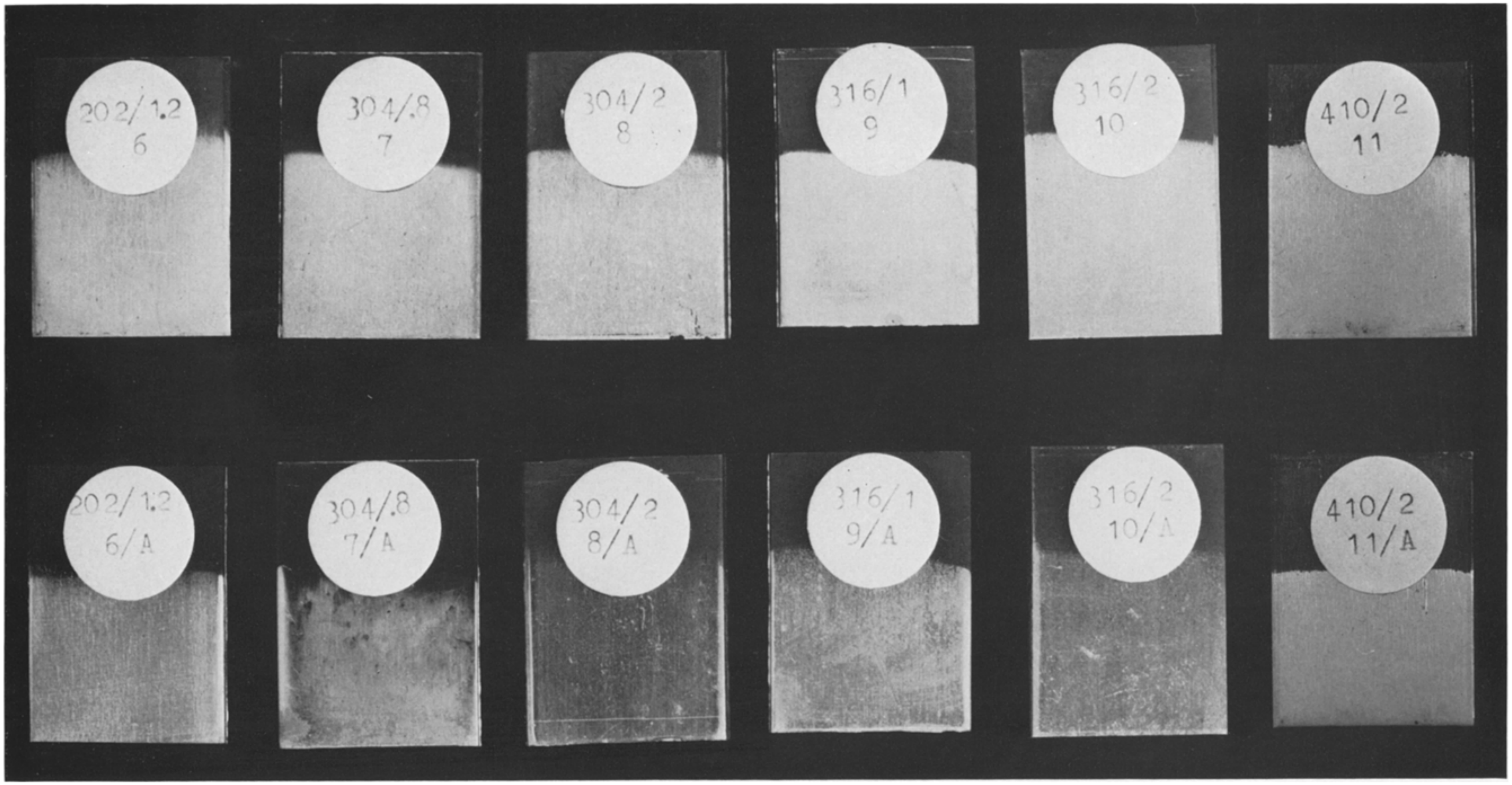

Fig. 4. Descaling obtained with sulphuric (specimens 6 – 11) and reference pickling (specimens 6A – 11A) on cold-rolled specimens. Pickling conditions reported in Table 2.

rolled Type 430, owing to the high surface reflectivity.

Two different methods were used for the electrochemical evaluation. One was based on the anodic polarization curve obtained by scanning at a rate of 40 mV/min the potential of the pickled specimen in deaerated 20% H_2SO_4 at 30°C. As explained in previous works [4, 6] the area of the anodic peak, being inversely related to the passivability, indicates the residual Cr-depletion at the metal surface. In Figs. 5 and 6 the curves of hot- and cold-rolled Type 202 steel show the kinetic superiority of sulphuric p.p. over reference pickling.

The second method consisted of evaluating the passivity retention through break-down times [8, 9] of the passive film. Namely, the steel electrode was allowed to assume the free active corrosion potential in a deaerated solution of H_2SO_4 whose concentration was chosen as a function of steel reactivity: 0·01 N for Type 410, 4·6 N for Type 430 and 18 N for the austenitic grades. Once a steady state was reached in free corrosion, the specimen was polarized at a passive potential (+630 mV/NHE) for a fixed time. The potentiostat was then switched off and the steel potential recorded up to a prefixed active potential. Linear relationship obtained by plotting depassivation times vs. passivation times give a measure of the passive film stability. The sharper the passivity retention curve, the higher the passivity stability. As pointed out in a recent work [10], the slope of this curve is directly affected by the surface Cr-depletion. As an example, in Figs. 7 and 8 such a relationship is shown for hot- and cold-rolled Type 202 steel after sulphuric p.p. and reference pickling.

All the parameters drawn from the curves are collected in Table 3, showing an overall superiority of sulphuric p.p., as to passivity recovery.

The convenience of integrating the coulometric evaluation of passivability with passivity retention measurements came out from the poor reproducibility in microgeometry of oxidized surfaces leading in some cases to uncertainties with methods based on current measurements. By recording passivity breakdown through simple potential measurements, any uncertainty from differences in effective areas was eliminated.

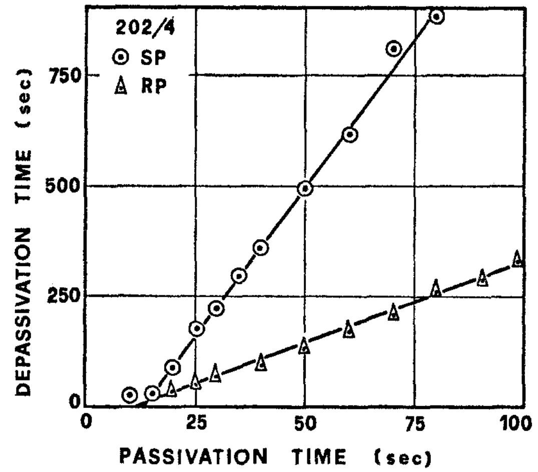

Fig. 7. Depassivation times versus passivation times for hot-rolled Type 202 steel in 18 N H_2SO_4 at 30°C. SP— Sulphuric pickled specimen; RP—Conventionally pickled specimen.

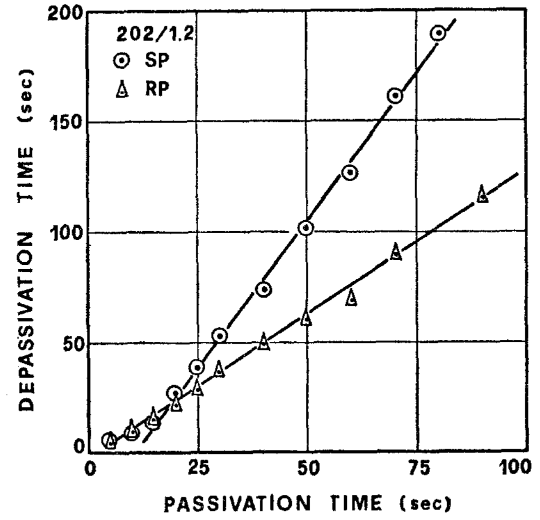

Fig. 8. Depassivation times versus passivation times for cold-rolled Type 202 steel in 18 N H_2SO_4 at 30°C. SP—Sulphuric pickled specimen. RP—Conventionally pickled specimen.

As an example, the case of cold-rolled Type 304 steel can be cited. For this product an essential equivalence resulted as to passivation charge between sulphuric p.p. and reference pickling (see Table 3) in spite of the remarkable difference observed in descaling efficiency (see Fig. 4). Instead, the slopes of the depassivation–passivation time curves were much higher with sulphuric pickling, in agreement with the visual examination.

Table 3. Electrochemical evaluation of pickled surfaces

AISI steel designation	*Thickness* (mm)	*Passivation charge after sulphuric pickling* (C/cm²)	*Passivation charge after ordinary pickling* (C/cm²)	*Slopes of depassivation–passivation time curves after sulphuric pickling*	*Slopes of depassivation–passivation time curves after ordinary pickling*
202	1·2	1·05	1·62	2·67	1·28
	4	1·34	1·83	13·50	3·71
304	0·8	0·67	0·65	8·34	1·56
	2	0·49	0·48	7·15	1·39
	4	1·11	1·18	1·04	0·97
316	1	0·03	0·07	35·7	5·88
	2	0·07	0·21	5·00	1·00
	5	0·27	0·50	3·84	0·91
401	2	21·97	22·99	0·67	0·29
	4	21·24	20·16	1·25	1·02
430	0·5	9·32	9·32	0·66	0·66
	2	4·56	6·43	1·22	1·09
	4	12·06	17·85	1·67	0·36

Conclusions

The sulphuric p.p. tests carried out on oxidized strips from industrial lines lead to the following conclusions.

(a) the potentiostatic technique makes pickling in sulphuric acid quite feasible and efficient;
(b) noticeable advantages are given by this technique in terms of scale removal kinetics;
(c) a kinetic improvement over conventional treatments results also in the recovery of passivity properties, leading to a superior surface quality.

The function of the potentiostat in sulphuric pickling lies in achieving the activating action, usually developed by hydrofluoric acid in nitric baths, by maintaining the working potential in a range where the anodic dissolution of the Cr-depleted alloy is favoured. When the depleted layer is completely removed, the scale-free surface assumes promptly a passive state as indicated by a sharp drop in the controlling current.

The replacement of nitric–hydrofluoric mixtures by sulphuric solutions would allow substantial lowering in direct costs for chemicals and in indirect costs for abating nitrous vapours from the baths and treating exhausted pickles, especially as regards hexavalent chromium ions. Lower evaporation losses would also result and many problems connected with such a toxic chemical as hydrofluoric acid could be avoided.

Finally, the potentiostatic control is expected to reduce metal losses so as to extend the bath life. The results of a systematic investigation on this aspect will be dealt with in a later paper.

Acknowledgments

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References

[1] D. P. Whittle and G. C. Wood, *J. Electrochem. Soc.* **114** (1967) 986.
[2] T. Ericsson, *Oxidation of Metals*, **2** (1970) 173.
[3] B. Vicentini and G. Bombara, *Electrochim. Metall.*, **3** (1968) 313.
[4] A. Tamba, N. Azzerri and G. Bombara, Paper presented to I.C.S.T.I.S. Conference, Tokyo, September (1970), *Suppl. Trans. Iron Steel Inst. Japan.* Vol 11 (1971) 790.

[5] Italian Patent no. 829.174 (1969). Belgian Patent no. 731296 U.K. Patent no. 1.242761 Luxemb. Patent no. 58417 Pat. pending in W. Germany, Japan, U.S.A., Netherland, Sweden.

[6] G. Bombara, A. Tamba and N. Azzerri, *J. Electrochem. Soc.* **118** (1971) 676.

[7] N. Azzerri and G. Bombara, to be published.

[8] H. Uhlig and P. F. King, *J. Electrochem. Soc.*, (1959) **106** 1.

[9] H. G. Feller and H. H. Uhlig, *J. Electrochem. Soc.*, **107** (1960) 864.

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