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Potentiostatic pickling: a new technique for improving stainless steel processing

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The potentiostatic technique applied to the acid pickling of stainless steels gives remarkable advantages over the ordinary chemical treatment in terms of speed of scale removal and efficiency of restoration of the passivity properties of the pickled surface. Furthermore the potentiostatic control makes descaling and pickling of stainless steels feasible in sulphuric acid baths. Some aspects dealing with the economy of the process, such as weight losses and pickling solution life, have been considered.

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1. Introduction and experimental background

Scales formed on Cr and Cr–Ni steels during hot rolling and solubilization treatments have complex structures because of the high oxidizability of chromium [1, 2]. The oxide layer grows by a succession of low rate (parabolic)-high rate (linear) steps leading to the formation of a stratified scale consisting of Cr-rich and Fe-rich layers on a markedly Cr-depleted base alloy [1, 2]. The extent of Cr depletion beneath the oxide scale depends upon the temperature and the duration of the thermal treatment, as well as the gas composition inside the furnace. The Cr-depleted alloy plays a dominant role in the pickling process as descaling proceeds via dissolution of the Cr-depleted alloy supporting the adherent oxide layer [3].

As the final cold-rolled stainless products achieve their maximum 'passivability' (i.e. resistance to general and localized corrosion) when the Cr-depleted alloy is completely removed, the pickling process must be looked on as a duplex operation: descaling proper and surface restoration of the full Cr content. Therefore, suitable techniques were set up [4] to assess the efficiency of any pickling treatment for both the descaling proper and the surface passivability (i.e. Cr restoration). The descaling efficiency was evaluated visually as well as by measuring the average reflectivity of pickled surfaces on a conventional linear scale ranging from 0–100 [4, 5], where 0 represents the oxidized surface and 100 was assigned to a deeply pickled one.

The Cr restoration, i.e. surface quality, was evaluated by electrochemical methods based on the measurements of the electric charge for passivation [4–6] and/or of the passivity retention properties of the pickled surfaces [6, 7] as the area of the passivation loop in polarization curves and the slope of the depassivation time versus passivation time curves are directly affected by the surface Cr depletion [7, 8].

Our previous papers [3–9] showed that electrochemical control during descaling treatments increases the rate and efficiency of stainless steel acid pickling. The patented working principle [10] of the potentiostatic technique lies in maintaining the steel potential in the acid pickle within the range where the anodic dissolution of the Cr-depleted sub-scale layer is kinetically favoured. The descaling mechanisms involved either in free pickling, intended as a simple dipping in the pickle, or in potentiostatic pickling, were exhaustively explained in the aforementioned papers.

The aim of this work is to single out the advantages allowed by potentiostatic pickling in terms of:

scale removal and surface Cr restoration kinetics in HNO_3-HF solutions;

feasibility of pickling stainless steels in dilute H_2SO_4;

metal losses during pickling treatments;

useful life of pickling solutions.

2. Advantages of the potentiostatic pickling

2.1. *HNO_3-HF solutions*

Pickling experiments were carried out on oxidized AISI 304 steel; the chemical composition of this alloy is given in Table 1. Descaling kinetics of AISI 304 steel are reported in Fig. 1 as reflectivity versus pickling times curves at various polarization potentials. During free pickling the equilibrium potential of the steel ranges from −620 to −660 mV (with reference to the saturated mercurous sulphate electrode). It is clearly shown that by polarizing at −300 to −500 mV the descaling rate is faster than with free pickling.

Table 1. Chemical composition of AISI 304 steel

C	*Cr*	*Ni*	*Mo*	*Mn*	*S*	*Si*	*Cu*
0·055	18·65	9·47	0·35	1·40	0·005	0·61	0·22

Within this potential range, corresponding to the preferential dissolution of the Cr-depleted alloy as could be confirmed by the polarization curve of the oxidized steel in the pickling solution [4, 5], the advantage of the potentiostatic control can be expressed as the shortening of the time required to reach the maximum reflectivity attainable with free pickling. Since descaling is accomplished in 3 min of free pickling and the same reflectivity is reached in about 1.5 min with potentiostatic pickling (−300 and −400 mV), potentiostatic control, in terms of descaling rate, is twice as effective.

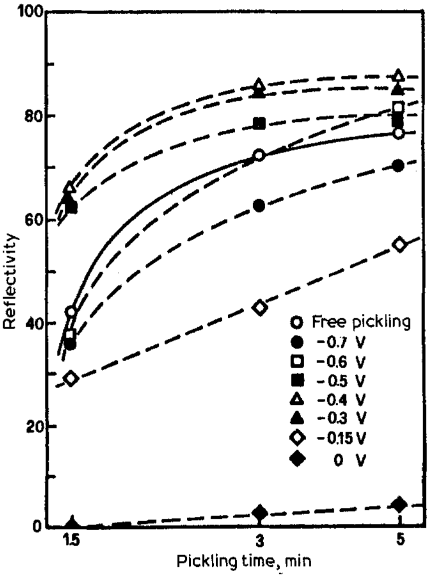

Fig. 1. Reflectivity versus pickling time for surfaces of AISI 304 steel potentiostatically pickled in HNO_3-HF (10:1) at 30° C at different potentials.

As to the removal of the less easy to passivate Cr-depleted alloy, the advantage of potentiostatic pickling over free pickling can be ascertained from Fig. 2, where passivation charge – pickling time curves at different potentials are reported. The time required to reach the maximum passivability using free pickling is 3 min; the same result is obtained in about 1 min with potentiostatic pickling at −300 to −400 mV.

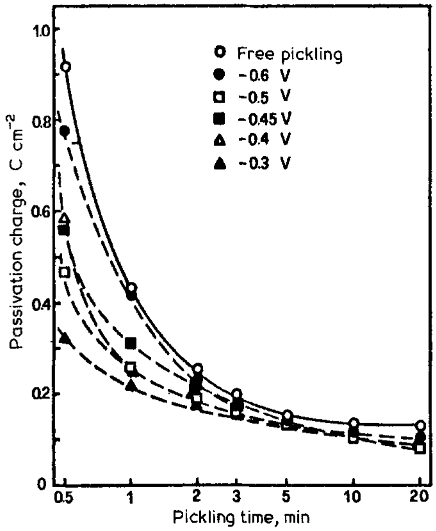

Fig. 2. Time dependence of electrical charge for passivation of specimens of AISI 304 potentiostatically pickled and free pickled in HNO_3-HF at 30° C.

2.2. *Potentiostatic pickling in H_2SO_4*

An attractive potentiality of potentiostatic pickling is the replacement of the usual nitric-hydrofluoric baths with less toxic, cheaper, more stable media such as H_2SO_4 solutions. The role of the potentiostatic control in sulphuric pickling is of vital relevance as it provides the electrochemical conditions usually performed by the use of a appropriate nitric-hydrofluoric mixtures, maintaining the working potential of the steel to be pickled within the range where the anodic dissolution of the Cr-depleted alloy is more favourable.

Potentiostatic pickling experiments were carried out in 20% H_2SO_4 at 80°C on different stainless grades drawn from both hot and cold rolling lines just prior to the pickling tanks. Optimal conditions for the sulphuric potentiostatic pickling were determined for each type of steel and thermal treatment, after a potentiodynamic survey in the sulphuric pickling solution in order to detect the potential ranges corresponding to the rapid dissolution of the Cr-depleted layer [6]. Generally, a sequence of electrochemical polarizations was required to obtain the highest pickling efficiency [6, 9]. The efficiency of each sulphuric pickling test was compared with that of conventional pickling, taken as a reference, the over-all treatment length being the same. Experimental results are exhaustively given in [6].

The following conclusions can be drawn:

potentiostatic pickling in H_2SO_4 gives noticeable advantages in terms of both scale removal kinetics, especially in cold rolled products, and the surface quality of pickled surfaces; when the Cr-depleted layer is completely removed, the scale-free surface assumes promptly a passive state as indicated by the sharp drop of the controlling current.

2.3. *Metal losses*

The metal consumption of the base steel by attack from the acidic environment has a fundamental relevance for the overall economy of the pickling process. Overpickling defects of the final stainless sheets or coils, leading to production rejects, are linked to the aggressiveness of the pickling bath and therefore are included in the study of the metal losses.

Descaling kinetics in HNO_3-HF (20 : 2) at 55°C by free pickling and potentiostatic pickling were carried out on AISI 304 stainless steel oxidized in air in a laboratory furnace with the aim to elucidate the effect of potentiostatic pickling on metal losses. By assuming that the oxidation weight gain is due only to the formation of well-adhering oxides of the elements in the steel, the X-ray analysis of the oxide stoichiometry allows the partial contributions of the outer scale and the underlying metal to the total weight losses recorded after pickling to be appraised separately.

In Fig. 3, free pickling kinetics of AISI 304 are displayed as reflectivity and metal losses versus time. The corresponding kinetics for potentiostatic pickling at –200 mV/SMSE are reported in Fig. 4. By comparing Figs. 3 and 4, as well as the aforementioned kinetic advantage, one can observe that in the case of potentiostatic pickling metal losses remain practically constant

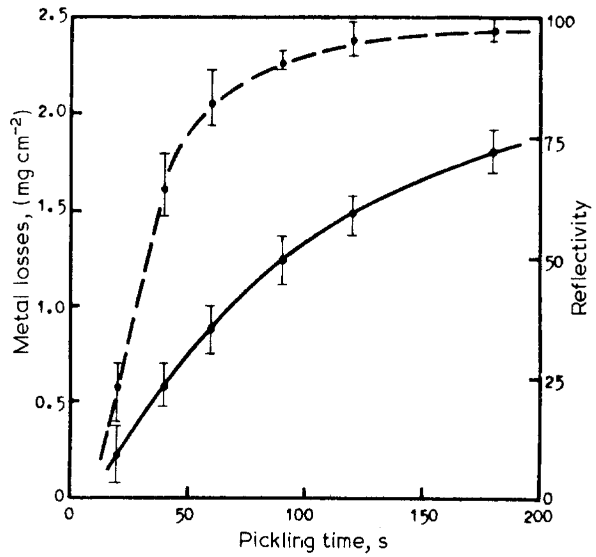

Fig. 3. Reflectivity and weight loss versus pickling time; free pickling in HNO_3-HF (20 : 2) at 55° C on hot rolled AISI 304 steel - - - - - - Reflectivity ——— weight loss.

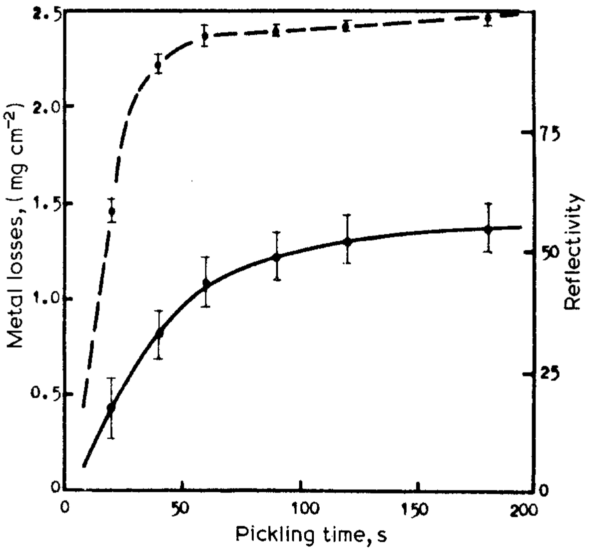

Fig. 4. Reflectivity and weight loss versus pickling time; potentiostatic pickling at –200 mV in HNO_3-HF (20 : 2) at 55° C on hot rolled AISI 304 steel - - - - - - Reflectivity ——— weight loss.

when descaling is completed (reflectivity > 95) because of the passivation of the pickled surface. On the contrary, in the case of free pickling, the dissolution of the base metal proceeds on the scale-free surface. As a consequence, metal losses in potentiostatic pickling are sensibly lowered. In sulphuric potentiostatic pickling too, metal losses practically stop when descaling is accomplished.

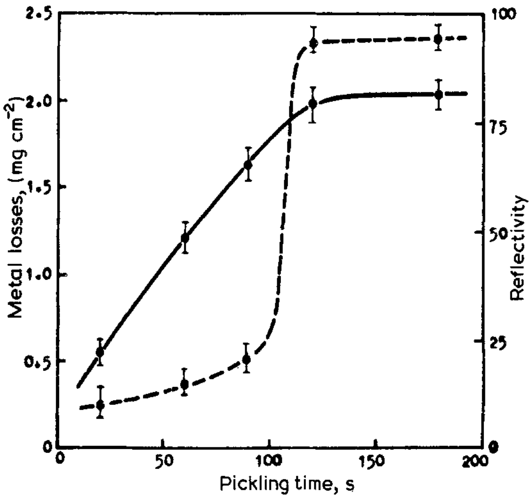

Fig. 5. Reflectivity and weight loss versus pickling time; potentiostatic pickling at –400 mV in 20% H_2SO_4 at 80° C on hot rolled AISI 304 steel - - - - - - Reflectivity ——— weight loss.

In this case it is interesting to observe the typical stepwise trend of reflectivity correspondingly to the completion of scale removal and surface passivation (Fig. 5).

Pickling losses, looked on as scale plus dissolved underlying metal, were also evaluated on hot and cold-rolled stainless grades drawn from industrial lines just before entering the pickling vats. As the scale weight can be considered to be practically the same on specimens of the same steel type, differences resulting from applying different pickling techniques to each specimen set can be attributed to the way the base steel is attacked.

A comparison between the losses during potentiostatic pickling using the experimental conditions summarized in Table 2 and the losses resulting by applying the usual industrial pickling cycle is given in Table 3 for AISI 304 steel. Treatment times and temperatures vary according to the different pickling kinetics.

The results of this investigation on metal losses can be summarized as follows:

potentiostatic pickling applied to AISI 304 steel oxidized in the laboratory lowers the metal losses by about 15–20% in the HNO_3-HF bath, whereas in H_2SO_4 the losses appear to be equivalent to those in the conventional treatment;

when potentiostatic pickling in H_2SO_4 is

Table 2. Experimental conditions for the potentiostatic pickling of AISI 304 steel in both sulphuric and nitric-hydrofluoric solutions

Thermal treatment	*Potentiostatic pickling in 20% H_2SO_4 at 80° C Polarization potentials, Volts**	*Potentiostatic pickling in 20% HNO_3 + 2% HF at 55° C Polarization potentials, Volts**
Oxidized in laboratory (20 min at 1050° C in air)	210 s at – 0·55 V	65 s at – 0·20 V
Oxidized and shot-peened in industrial lines (hot rolled 4 mm thick)	° 5 s not polarized 10 s at – 0·10 V 5 s at – 0·40 V	30 s at – 0·20 V
Oxidized in industrial lines (cold rolled 0·8 mm thick)	° 5 s not polarized 25 s at – 0·65 V 15 s at – 0·55 V	–
Oxidized in industrial lines (cold rolled 2 mm thick)	° 75 s at – 0·65 V 5 s at – 0·55 V	–

* Electrode potentials referred to mercurous sulphate electrode (+ 0·641 V versus N.H.E.)

° Sequence of electrochemical polarizations

Table 3. Weight losses after pickling

Thermal treatment	*Pickling treatment designation*	*Over-all pickling time s*	*Total weight loss mg cm^{-2}*
Oxidized in laboratory (20 min at 1050° C in air)	A B C	210 65 165	1·44 ± 0·14 1·55 ± 0·10 1·88 ± 0·13
Oxidized and shot-peened in industrial lines (hot-rolled 4 mm thick)	A B C	20 30 40	1·75 ± 0·18 1·80 ± 0·05 2·30 ± 0·15
Oxidized in industrial lines (cold rolled 0.8 mm thick)	A D	45 90	0·57 ± 0·09 1·28 ± 0·03
Oxidized in industrial lines (cold rolled 2 mm thick)	A D	80 120	1·53 ± 0·08 2·59 ± 0·05

A: Potentiostatic pickling in 20% (w/v) H_2SO_4 at 80° C (see Table 2).
B: Potentiostatic pickling in 20% (v/v) HNO_3 + 2% (v/v) HF at 55° C (see Table 2).
C: Reference pickling for hot rolled steel consisting of free dipping in 20% HNO_3 + 2% HF at 55° C.
D: Reference pickling for cold rolled steel consisting of cyclic electrolytic treatment at ± 20 A dm^{-2} (5 s cathodic and 10 s anodic in each cycle) in 30% (w/v) HNO_3 at 55° C followed by free dipping in 20% HNO_3 + 2% HF at 55° C.

applied to hot rolled AISI 304 steel, the metal losses are about 25% less than when this steel is free-pickled in HNO_3-HF mixture; metal losses can be reduced by up to 50–60% when potentiostatic pickling in H_2SO_4 is applied to cold-rolled products;

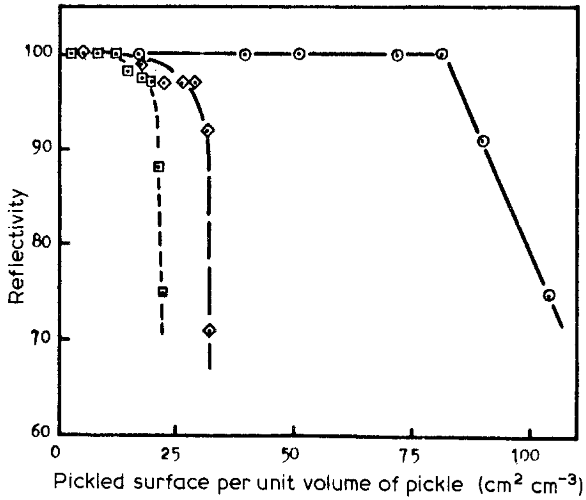

Fig. 6. Reflectivity versus pickled surface per unit volume of pickle for hot rolled AISI 304 steel □ Free pickling in HNO_3-HF at 55° C; ◇ Potentiostatic pickling in HNO_3-HF at 55° C; ○ Potentiostatic pickling in H_2SO_4 at 80° C.

in any case potentiostatic pickling is accompanied by a drastic reduction of metal losses when the descaling is over. Therefore, potentiostatic pickling could be a promising method to avoid overpickling problems in the working of stainless steels.

2.4. *Useful life of pickling solutions*

Three different pickling techniques were applied to hot-rolled AISI 304 steel:

free pickling in HNO_3-HF (20 :2) at 55°C;
potentionstatic pickling in HNO_3-HF (20 :2) at 55°C and −200 mV/ESMS;
potentiostatic pickling in 20% H_2SO_4 at 80°C according to the optimum cycle for this stainless grade [6, 9], given in Table 2.

The useful pickling solution life was determined, for each pickling technique, by descaling, in a given volume of solution, a large number of specimens whose surface reflectivity was also measured. When the reflectivity value dropped below 95, the pickling bath was considered exhausted.

The results are outlined in Fig. 6 as reflectivity versus surface pickled per unit volume of pickling solution (useful life of pickle). In HNO_3-HF (20:2) mixture at 55° C the useful life of the bath rises from 20 to 30 cm^2 cm^{-3} by applying the potentiostatic treatment. Potentiostatic pickling in the sulphuric bath extends the pickling solution life up to 80 cm^2 cm^{-3}, which corresponds to an improvement of about four times compared to the conventional treatment in HNO_3-HF (20:2) at 55° C.

3. Conclusions

Stainless steel pickling carried out by driving the working potential of the steel into the potential range where the dissolution rate of the Cr-depleted alloy beneath the oxidation scale is increased, leads to a number of advantages over the conventional treatments.

In HNO_3-HF mixture, higher efficiency and speed of descaling as well as better surface quality in terms of passivability result from the application of the potentiostatic control. Quantitatively, overall improvements of 100% in descaling rate and of 200% in terms of surface Cr restoration could be achieved.

Replacement of HNO_3-HF mixtures with cheaper, less toxic, more stable H_2SO_4 solutions is made feasible by the potentiostatic technique. The potentiostat plays the activating role usually exhibited by appropriate HNO_3-HF mixtures, allowing the surface to be pickled at potentials where the active dissolution of the Cr-depleted alloy is kinetically favourable. This pickling technique also improves the rate of descaling proper and passivability restoration, leading to better surface quality with respect to conventional treatments.

Owing to the highly selective character of potentiostatic pickling, metal losses, an important aspect in determining the over-all economy of the pickling process, are appreciably reduced. Moreover, troublesome over-pickling problems can be minimized as surfaces pickled under potentiostatic control become passivated immediately and further metal dissolution by acid attack is stifled.

The potentiostatic control enables the useful life of HNO_3-HF pickling solutions to be extended by about 50%; utilization of simple H_2SO_4 solutions for pickling stainless steels, using potentiostatic control also extends the useful life of the pickling bath.

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