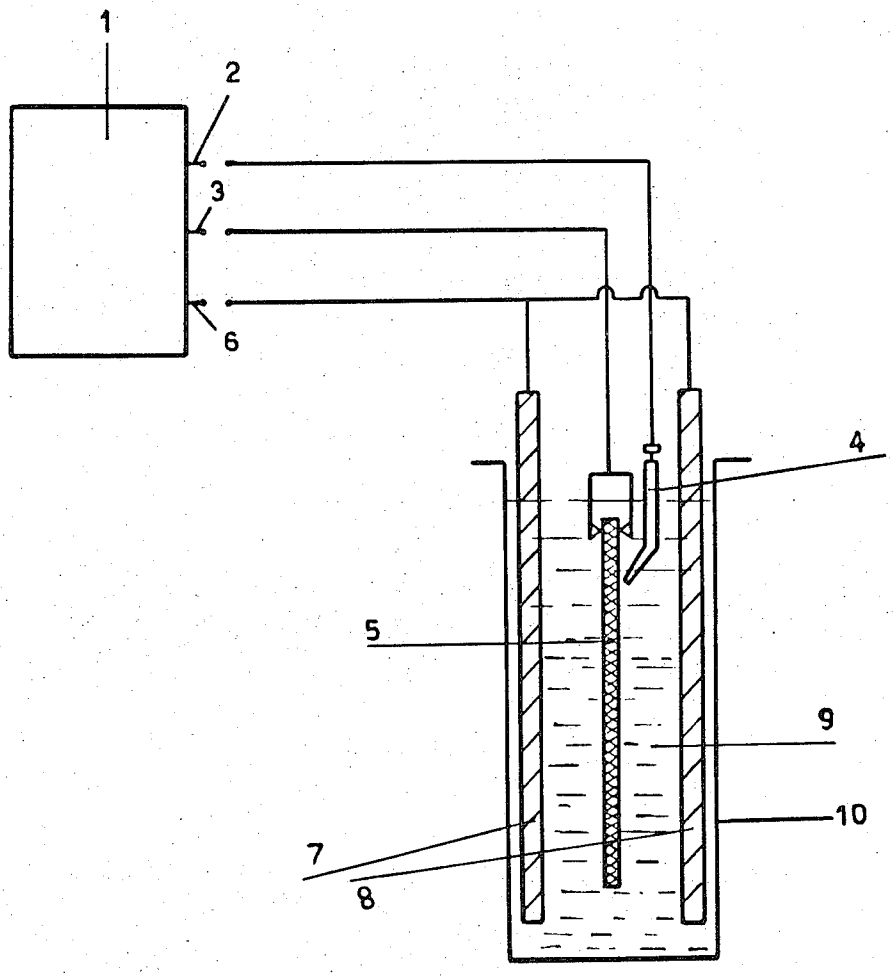
Sept. 26, 1972 G. A. BOMBARA 3,694,334

ACID PICKLING OF STAINLESS STEELS

Filed April 10, 1969

Fig. 1



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ACID PICKLING OF STAINLESS STEELS

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ABSTRACT OF THE DISCLOSURE

A process for electrostatically pickling stainless steel having a chromium-depleted layer beneath the scale formed during hot-rolling.

The present invention relates to the pickling of stainless steels and, more particularly, to an electrochemical method of scale removal from hot-rolled stainless steels.

It is common knowledge that scales formed during the hot-rolling of alloy steels and especially of stainless steels are compact and adherent and therefore difficult to remove.

The pickling of the above mentioned steels is carried out by means of a mixture of nitric and hydrofluoric acids, with possible presence of specific oxidizing, complexing and inhibiting agents, and moreover by means of external electric power.

Furthermore it may be realized that in chromium stainless steels, apart from differences in chemical and chemico-physical composition according to the zones of the rolled product, there is a difference in chemical composition inside the scale itself. In fact a chromium-depleted layer forms beneath the scale in these chromium and chromium-nickel stainless steels.

Therefore during an usual acid pickling, notwithstanding the oxidizing character of acid mixtures usually employed, the electrode potential of stainless steel, owing to hydrogen developed during the corrosion, is always very low (near the one of the hydrogen electrode) and in any case lower than the potential of primary passivation of chromium depleted layer. Under said conditions, not only the corrosion rate of the above mentioned chromium-depleted layer is very much lower than the highest one, but the base alloy, which is not chromium-depleted, is also substantially corroded thus producing waste of metal and less efficacious pickling.

An object of the present invention is to provide an improved method of scale detachment and removal by means of acid pickling with or without impressed current. A further object of the present invention is to provide a more rapid and suitable pickling process for stainless steels.

Further, another object is to provide a method of pickling being also efficacious for hot-rolled stainless steels which have particularly adherent and compact scales.

A further object is to provide a method of scale removal which avoids any pretreatment or conditioning of the scale itself, said pretreatment or conditioning being carried out in the conventional processes according to the state of the scale.

A further object is to provide a method of pickling wherein the reaction with the base metal is kept under control in order to obtain only the wanted effect which is to complete scale detachment.

A more specific object of the invention is to provide an apparatus for the pickling of stainless steels according to the process of the present invention.

The process of the present invention consists in controlling the working potential of steel during the pickling by means of a potentiostat and in maintaining said potential at a suitable value (more electropositive than spontaneous potential) in order to have the highest corrosion rate of the chromium-depleted alloy and the lowest corrosion rate of the base alloy. More precisely there is no corrosion of the base alloy because the working potential is in the passivation area. In this way, by means of any kind of acid bath, a quicker pickling, a more uniform scale removal and a smaller total metal waste are obtained.

In accordance with the present invention, the steel piece is dipped in an acid pickling solution; the output voltage of a potentiostat is applied between the steel piece and one or more counter-electrodes dipped in the same bath, said voltage being controlled by the potential difference between the steel to be pickled and a reference electrode. In this way the steel can be maintained during the pickling at the wanted potential which corresponds to the highest anodic corrosion rate of the chromium-depleted layer.

To this end an apparatus of the type reported as a cross section in FIG. 1 can be utilized, it being understood that many other alternative embodiments are possible and it is not intended herein to limit the scope of the invention to the case illustrated.

In said figure, **1** is a conventional potentiostat having the output **2** connected with a calomel electrode **4** and the output **3** connected with the steel piece **5** to be pickled; two counter-electrodes **7** and **8** also dipped in the electrolyte **9** contained in the pickling tank **10** are connected in parallel to the output **6**. According to the invention, as above mentioned, the potentiostat steadily keeps the potential of the steel compared with the reference electrode at a suitable value in order to have the highest anodic corrosion rate of the chromium-depleted layer.

Although theoretically the method could be applied to all alloys which during oxidation produce a surface depletion of the passivating element, the process can more specifically be applied to the following standard stainless steels according to "American Iron and Steel Institute."

Austenitic steels 301, 302, 304, 309, 310, 316, 322, 347;
Ferritic steels 403, 410, 430;
Martensitic steels 420, 431.

The process can be applied to pickling solutions based on mixtures of nitric, hydrofluoric, hydrochloric and sulphuric acids, with possible additions of alkaline salts, iron salts and ammonium salts. The percentages can range within large bounds, as in the following typical compositions wherein the percentages are by weight:

	Percent
Nitric-hydrofluoric mixtures:	
NHO_3 (65%)	5–20
HF (40%)	1–6
Sulphuric-hydrochloric mixtures:	
H_2SO_4 (98%)	10–30
HNO_3 (65%)	0.5–10
Sulphuric-hydrochloric mixtures:	
H_2SO_4 (98%)	10–30
HCl (36%)	1–10

The polarization potential of the steel piece corresponding to the highest pickling rate can be established, for any mixture, by means of potentio-dynamic determinations, that is by plotting the anodic polarization curve of a small oxidized steel electrode dipped in the selected solution and by reading in said curve the potential of primary passivation of the chromium-depleted alloy.

In any case, according to the types of steel and acid bath, the optimum potential can range from −150 up to +150 mv. as to a saturated calomel electrode (S.C.E.).

EXAMPLE 1

Specimens 10 x 250 mm. obtained from AISI type 316 austenitic stainless steel sheets (1 mm. thick), were treated by means of air flow (3 liters/min.) at 1095° C. for 30 minutes and then were water-quenched. So oxidized

specimens were dipped for the pickling in a solution containing 2% by volume of a 40% hydrofluoric acid and 10% of a 65% nitric acid, thermostatically maintained at 65° C.

Without potentiostatic polarization on 10 specimens was observed what follows:

After 5 minutes from the dipping there was no scale removal; after 10 minutes the descaled area was ranging from 20 up to 50% of total area.

In the same pickling bath with a 0 mv. vs. S.C.E. potentiostatic potential impressed to any steel specimen, after 5 minutes from the dipping the descaled area was ranging from 30 up to 40% of the total area and after 10 minutes from 65 up to 95%.

EXAMPLES 2, 3 AND 4

Other tests were carried out on AISI type 321 austenitic stainless steel using different treatments and different pickling baths. The operating conditions and the obtained results are summarized in Tables I and II, wherein all percentages of pickling bath are by volume, except for $Fe_2(SO_4)_3$ whose percentage is by weight on volume.

TABLE I

Ex.	Material used	Heat treatment, ° C.	Pickling bath
1	AISI 316	[1] 1,050	HF (40%) 2%+ plus HNO_3 (65%) 10% temp. 65° C.
2	AISI 321	[2] 1,050	HF (40%) 4%+ plus HNO_3 (65%) 10%, temp. 65° C.
3	AISI 321	[1] 1,050	HF (40%) 2%+ plus $Fe_2(SO_4)_3$ 6%, temp. 75° C.
3	AISI 321	[1] 1,050	HF (65%) 2%+ plus NH_3 liq. 1%+ plus $Fe_2(SO_4)_3$ 6% temp. 75° C.

[1] 30 minutes in air by cooling in water.
[2] 30 minutes in N_2 containing 1% O_2 by cooling in water.

TABLE II

	Descaled area (percent) without polarization after—				Descaled area (percent) without polarization (0 mv.) after—			
Ex.	1 min.	2 mins.	5 mins.	10 mins.	1 min.	2 mins.	5 mins.	10 mins
1				20-50			30-40	65-95
2			90-95	100			100	100
3	0	40-50	90-95		30-40	80-85	100	
4	4-6	10-15	30-40		20-25	35-40	55-60	

What I claim is:

1. In a process for electrochemically pickling in an acid solution chromium stainless steel from the group comprising austenitic chromium steels, ferritic steels and martensitic steels to remove scales therefrom wherein chromium-depleted alloy exists under the scale, the improvement comprising the steps of: applying the output voltage of a potentiostat between the chromium stainless steel and a counter-electrode immersed in the acid solution; maintaining the voltage between the chromium stainless steel and the counter-electrode at the highest corrosion rate of the chromium-depleted alloy under the scales and the lowest corrosion rate of the base alloy by maintaining the potential difference between the steel to be pickled and a saturated calomel reference electrode, which reference electrode is immersed in the acid solution and connected to an output of the potentiostat, by means of external polarization at a uniform value ranging from −150 mv. up to +150 mv.

2. A process according to claim 1 wherein the acid bath is constituted by nitric, hydrofluoric, hydrochloric and sulphuric acids or by mixtures of said acids.

3. A process according to claim 2, wherein alkaline salts, iron salts and ammonium salts are added to the acid bath.

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U.S. Cl. X.R.

204—231

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,694,334 Dated September 26, 1972

Inventor(s) Giuseppe A. Bombara

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, between lines 5 and 6, insert the following line

--Claims priority, application Italy,

April 12, 1968, 15,167A/68 --.

Column 2, line 48, change "NHO_3" to read --HNO_3--.

line 50, change the line to read --Nitric-sulphuric

mixtures--.

line 71, "1095°C" should read --1050°C--.

Signed and sealed this 4th day of June 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents