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PITTING CORROSION RESISTANCE OF ELECTROPOLISHED SEAMLESS STAINLESS STEEL TUBES TYPE EN 1.4404

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ABSTRACT

Seamless tubes type EN 1.4404 produced by hot extrusion have been internally electropolished at a mill that normally produces such tubes from welded tubes made from rolled plate. One or two standard passes have been applied. The short-range surface irregularities are removed by the electropolish, but the long-range waviness, and with that also the Ra value, remains unaffected by the electropolishing. The pitting resistance was evaluated by measurement of pitting potentials in solutions containing 500, 5000, and 50.000 mg/L chloride and temperatures from 10 to 95°C and by the ASTM G150 test. The as-extruded and the once electropolished surfaces have pitting resistance very close to that observed with a rolled and pickled surface. The twice electropolished surface mostly have a much improved pitting resistance, but a few of the test results are no better than the parent material; this is discussed in terms of the number of pit initiation sites.

Keywords: EN 1.4404, tubes, surface condition, pitting potential, critical pitting temperature, ASTM G150

INTRODUCTION

We have previously reported studies of the effect of different surface conditions on the corrosion resistance of stainless steel type 1.4404 tube[1]. That article included a review of the relevant literature.

The main effort in this work has been on commercially available tube surfaces. Our industrial partners have a great interest in the properties of surfaces with a larger roughness than normally accepted in e.g. the diary and pharmaceutical industries. This interest includes hygienic properties as well as corrosion resistance. Such rough surfaces are available with extruded tube, while welded tube produced from plate are obviously not commercially produced to a generally unacceptably large roughness. It follows directly that there is also an interest in improving the roughness of the hot extruded pipe. Our partners have made attempts to achieve this by applying a commercial pipe mill electropolishing process directly to the as-extruded surface.

As part of our previous work, we have observed that most tests made on an electropolished surface produced by a pipe mill show tremendously improved pitting resistance when compared with other surface types. However, a few of the test specimens cut from the electropolished tubes did not show this improvement, and this effect has been studied further.

EXPERIMENTAL PROCEDURES

Roughness measurements were made as *Ra* in µm with a cut-off length of 2.5 mm and 5 such lengths for one individual reading. This is a longer measurement length than used in our previous work, in order to include the longer-range undulations.

Detailed experimental procedures for the corrosion tests were reported previously[1]. In brief, cleaning prior to exposure involved treatment in 2% NaOH and 2% HNO_3 to simulate conventional CIP. A flushed port cell with a specially formed gasket was used for both cyclic polarisation at fixed temperature and for the fixed-potential, increasing temperature procedure of ASTM G150. The exposed tube area was 5 cm^2.

Parameters for the cyclic polarisation tests were: Conditioning at –200 mV SCE for 5 minutes followed by polarisation in the anodic direction at a scan rate of 10 mV/min until either the current exceeds 1 mA/cm^2 or the potential reaches +1000 mV SCE. The return rate was 20 mV/min.

Parameters for the ASTM G150 test were as specified by the standard: Test potential +700 mV SCE, temperature increasing from 0°C at a rate of 1°C/min up to 95°C. The test was ended when the current exceeded 1 mA/cm^2.

Test solutions were neutral solutions of sodium chloride, NaCl, in de-ionised water. The solutions were deaerated by bubbling with nitrogen N95.

MATERIALS

The composition of the hot extruded pipe is shown in table 1.

Joints of the pipe were delivered to an electropolishing mill that usually produces internally electropolished pipe from longitudinally welded pipe made from rolled strip. One pass through the process did not produce a really bright surface, so a number of joints were sent through the electropolishing process once more. This produced a bright surface, but it was still far from flat.

RESULTS

Surface Roughness of Hot Extruded Pipe

For the hot extrusion process, the steel billet is coated with a glass lubricant. The glass is afterwards removed in a pickling process, i.e. the steel surface is for that matter comparable with a hot rolled and pickled or annealed and pickled product. However, the surface of the extruded product has much more topography, and this topography appears on length scales from centimetres to micrometers; the height of the undulations reach towards 10 µm. The electropolishing process is very well able to remove the micrometer-size irregularities, but the 5 to 10 µm high undulations remain largely unaffected. This is shown in figures 1 to 3. Roughness measurements are given in table 2.

Cyclic Polarisation

Cyclic polarisation tests were made at several combinations of chloride concentration and temperature for all three surface types: as-extruded (and pickled), as-extruded and electropolished once, as-extruded and electropolished twice. The test matrix and the pitting potentials recorded are listed in tables 3 to 5. The data are plotted in figures 4 to 6.

ASTM G150

The potential-independent critical pitting temperature was measured according to ASTM G150 for all three surface types. See table 6 for results.

DISCUSSION

When fabricating stainless steel equipment for pharmaceutical or food industry, a limited roughness of the surfaces is most often a part of the specification. This can be specified by referring to comparison with standard surfaces[2], or by specification of an acceptance criterion for roughness measurements[3,4]. A visual comparison standard will preclude any alternative surface preparation method, while the specification of an acceptance limit, e.g. Ra max. 0.8 µm, is incomplete unless a more precise test procedure is also specified. This is illustrated by our roughness measurements. Although the electropolishing greatly reduces the small scale surface irregularities, clearly visible on the surface profile records, the use of a large cut-off length means that the measured Ra values are dominated by the waviness, and the Ra (cut-off 2.5 mm) does not change significantly from as-extruded to twice electropolished.

The CPT results for the as-extruded and extruded plus once electropolished appear to have a sufficiently small scatter to allow a mathematical description like that previously reported for pickled and grinded surfaces.

For the as-extruded surface:

$$E_{pit} = 451\ (\pm 30) - 4.0\ (\pm 0.5) \times Temp - 145\ (\pm 15) \times \log[Cl^-]\ ;\ R^2 = 0.93 \quad (1)$$

For extruded and once electropolished surface:

$$E_{pit} = 492\ (\pm 24) - 4.4\ (\pm 0.4) \times Temp - 158\ (\pm 13) \times \log[Cl^-]\ ;\ R^2 = 0.96 \quad (2)$$

E_{pit} in mV (SCE), Temp in °C, $[Cl^-]$ in g/L. (±XX) reports one standard error.

These parameters obtained here differ less than one standard error from each other, and in fact the difference to those previously observed for a pickled surface is similarly small.

The twice electropolished surface behaves much more erratically, much in line with the observations previously made for welded pipe that had been electropolished in the same mill[1]. It is our opinion that the electropolishing process has the ability to remove pit initiation sites to a large extent, but not completely. When testing a fairly small area in the flushed port cell, there is a good chance that with an electropolished specimen, there will be no obvious pit initiation site inside the test area, and a surprisingly high pitting potential or CPT is recorded. However, occasionally, there are “good” pit initiation sites left also in an electropolished surface, and a more normal Epit or CPT will be recorded. Such “good” pit initiation sites must be expected to be present in a practical piping system, which together with inevitable welds means that a piping system made exclusively from electropolished components cannot be used for more corrosive conditions than a similar system made from pickled pipe. However, we expect the cleanability of the electropolished surface to be superior; results from cleaning tests will be published elsewhere.

The extruded pipe has a slightly leaner composition than the welded pipes used in our previous work[1]. None the less, the ASTM G150 CPT observed here is 4°C higher than that observed with the leanest steel previously tested against an expected reduction of 2°C. However, with a standard deviation of 6°C, the difference is hardly significant. We regard our previous conclusion, that the ASTM G150 CPT is rather insensitive to small parameter variations, as confirmed.

CONCLUSIONS

Electropolishing of extruded pipe is well able to remove short-range irregularities and thus it is able to produce a shiny surface, although it takes more process time than required for pipe produced from pickled plate. However, the longer-range waviness of the extruded surface remains, and the Ra value measured with a cut-off length of 2.5 mm remains unchanged.

The as-extruded (and pickled) surface has very nearly the same pitting resistance as previously observed for a cold rolled, annealed and pickled surface, in spite of very different surface topografies. The dependence of the pitting potential with temperature and chloride concentration is also very similar for the two surfaces.

The ASTM G150 CPT values for the extruded (and leaner) pipe are slightly better than previously recorded for pipe produced from cold rolled, annealed and pickled plate material, but the difference is hardly significant.

Electropolishing, when carried to completion, is mostly able to produce a very marked improvement in the pitting resistance, with a few scattered exceptions. This is seen as a result of reducing the number of pit initiation sites significantly in combination with testing a rather small area in any one test.

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TABLE 1.
Chemical analysis (OES) of extruded pipe.

Material	%C	%Si	%Mn	%P	%S	%Cr	%Ni	%Mo	%N	PRE [a]
Extruded	0.017	0.35	1.79	0.034	0.009	16.3	11.3	2.01	0.057	23.9

a. Pitting Resistance Equivalent, PRE = Cr + 3.3 Mo + 16 N

TABLE 2.
Roughness of extruded and electropolished internal pipe surface. *Ra* values in µm.

Surface	Individual readings						Average	St. Deviation
As Extruded	5.3	5.4	6.5	4.2	5.1	5.6	5.4	0.7
Once Electropolish	6.3	6.7	6.6	6.6	6.5	6.8	6.6	0.2
Twice Electropolish	6.0	6.9	6.4	6.0	6.1	7.5	6.5	0.6

TABLE 3.
Test matrix and pitting potentials (mV SCE) for as-extruded pipe

	Chloride Concentration, mg/L		
Temperature, °C	500	5,000	50,000
10	1000	726	505
15	693		
20	580	476	271
40	463	270	222
60	377	206	70
80	387	163	-5
95	216	162	18

TABLE 4
Test matrix and pitting potentials (mV SCE) for extruded and once electropolished pipe

	Chloride Concentration, mg/L		
Temperature, °C	500	5,000	50,000
10	965	1000	645; 336
15	633	535	491
20	661	388; 496	335
40	491	371	155
60	435	255	88
80	315	253	27
95	262	148	-20

TABLE 5
Test matrix and pitting potentials (mV SCE) for extruded and twice electropolished pipe

Temperature, °C	Chloride Concentration, mg/L		
	500	5,000	50,000
10	1000	646	621
20	478	636	963
40	984	635	383; 291
60	383	295	13
80	315	155	165
95	765	118	68

TABLE 6.
Critical Pitting Temperatures (°C) determined using ASTM G150 (read at 10µA/cm^2)

	As-Extruded	Extruded + Once Electropolished	Extruded + Twice Electropolished
Individual Results	5.7 10.3 10.9 15.8	0.4 3.9 12.9 19.0	4.1 9.6 15.5 25.5
Average	10.7	9.1	16.9
St. Dev.	4.1	8.5	9.2

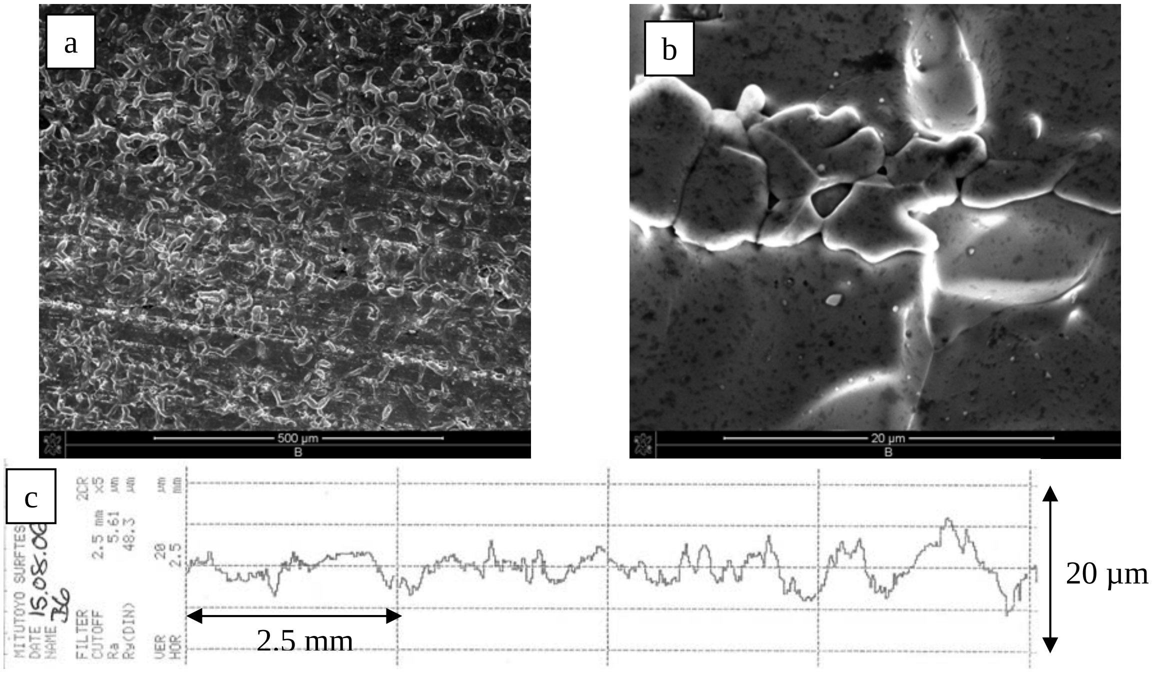

Figure 1. Inner surface of as-extruded (and pickled) pipe.
a and b: SEM- pictures. c: example of surface profile.

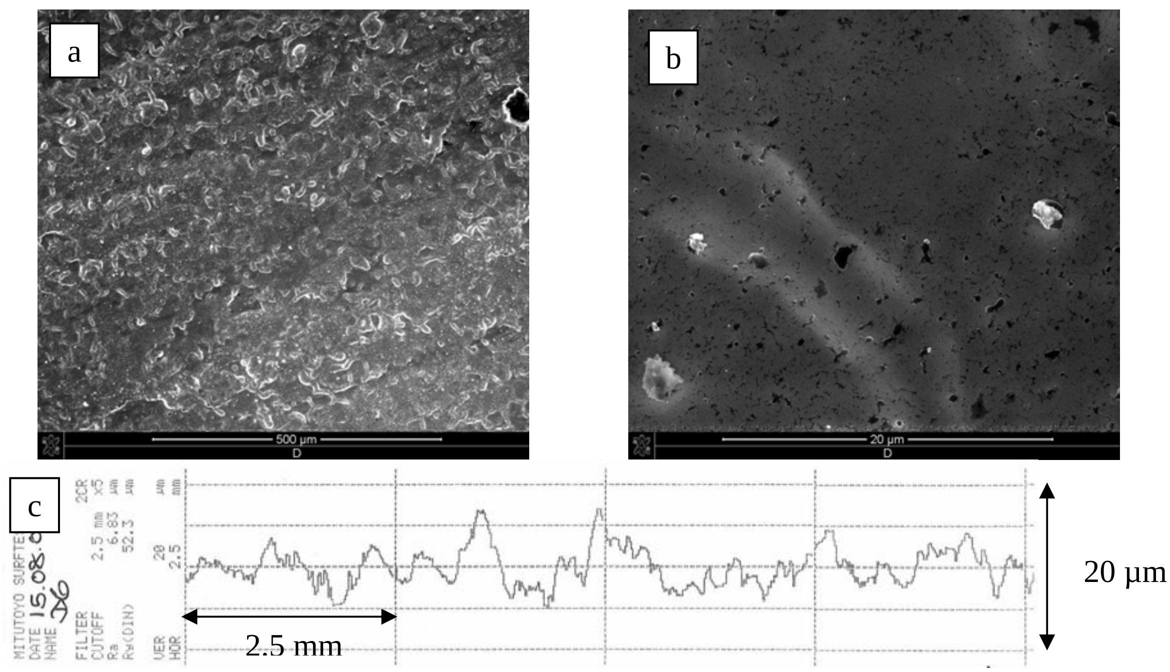

Figure 2. Inner surface of extruded and once electropolished pipe.
a and b: SEM- pictures. c: example of surface profile.

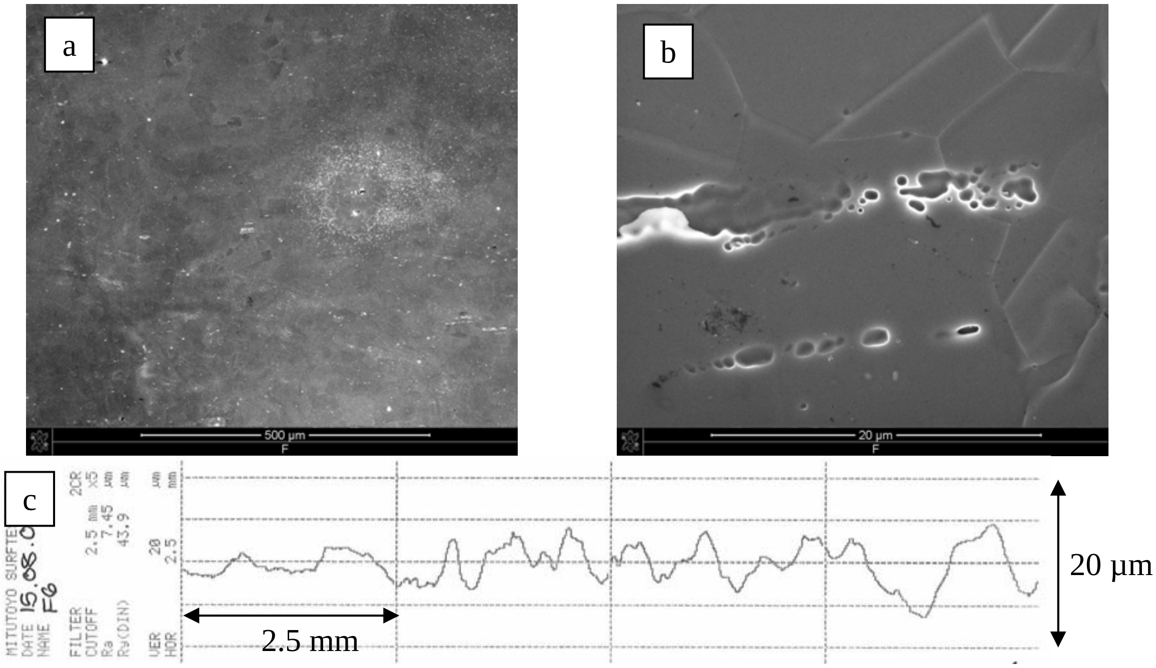

Figure 3. Inner surface of extruded and twice electropolished pipe.
a and b: SEM- pictures. c: example of surface profile.

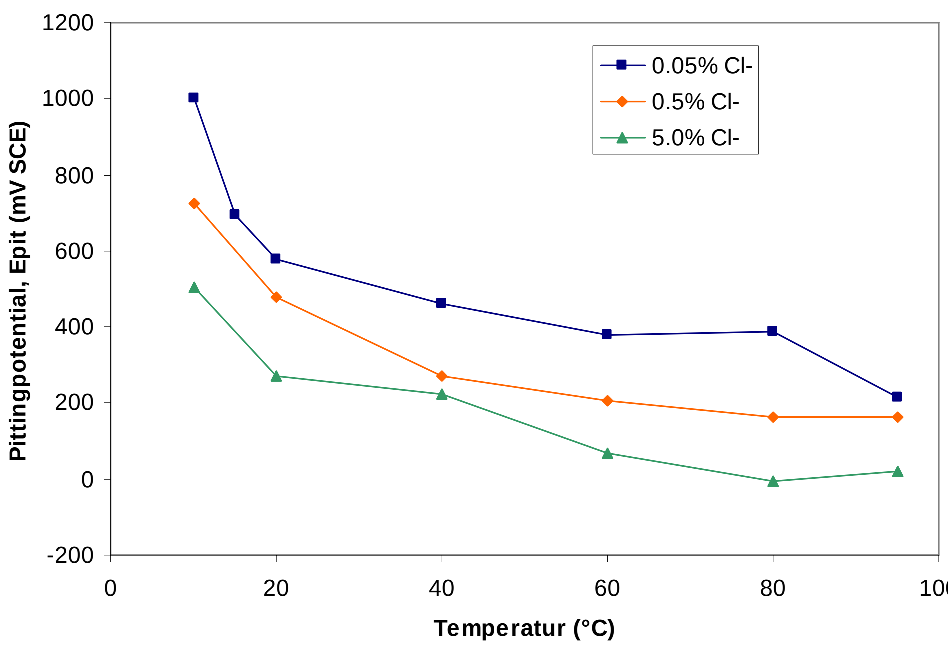

Figure 4. As-extruded pipe: Relationship between pitting potential and temperature.

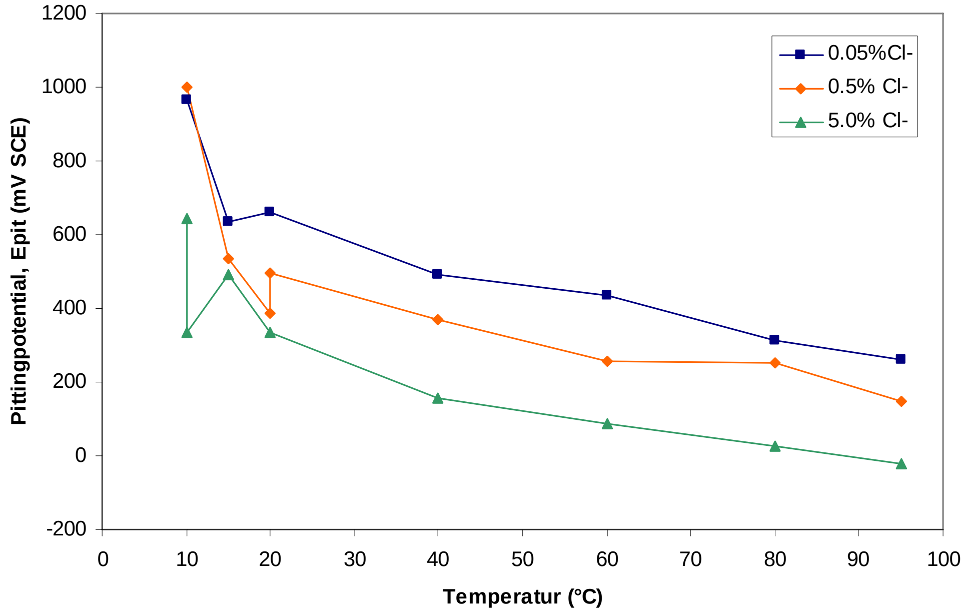

Figure 5. Extruded and once-electropolished pipe: Relationship between pitting potential and temperature.

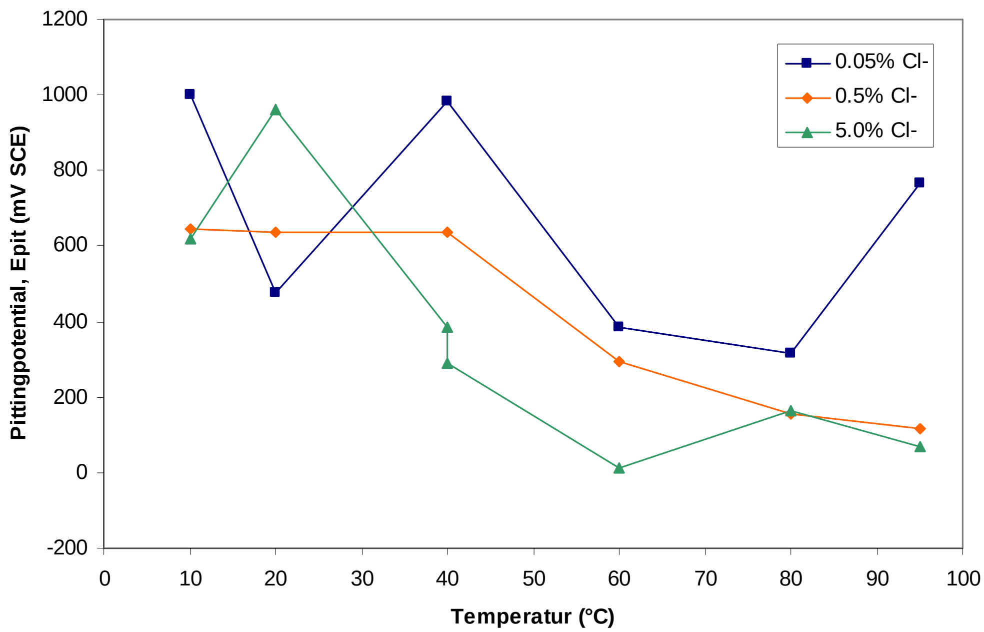

Figure 6. Extruded and twice-electropolished pipe: Relationship between pitting potential and temperature.