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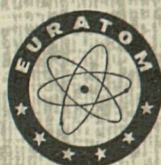
EUROPEAN ATOMIC ENERGY COMMUNITY – EURATOM

**INFLUENCE OF SURFACE TREATMENT
ON VARIOUS TYPES OF STAINLESS STEELS CORROSION**

by

J.-Ph. BERGE

1966



EURATOM/US Agreement for Cooperation

EURAEK Report No. 1709

Directorate General for Research and Training

**Paper presented at the 3rd International Congress on Metallic Corrosion
Moscow, USRR, May 16-25, 1966**

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Geometrical characteristics (roughness).

Chemical characteristics mainly, in this case, "passivation layers". They may be characterized by an electrochemical method involving the coulometric reduction of this oxide layer in sulphuric acid.

Physical or structural characteristics: the superficial cold-work may be assessed by metallographical techniques on sections and by enlargement of the X-ray diffraction lines. The roughness affects considerably the overvoltage in electro-chemical reactions: Pitting corrosion in ferric chloride is greatly influenced by the surface roughness.

The effect of initial passivation is very marked in all corrosive media which are not themselves passivating.

Superficial cold-work may also modify the corrosion behavior very considerably: stress corrosion in magnesium chloride, intergranular corrosion in nitric acid with hexavalent Cr addition, oxidation in superheated steam.

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SUMMARY

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The influence of surface treatment on various types of stainless steels corrosion (*)

Many authors have pointed out that the preparatory treatment of a metallic surface must considerably affect its resistance to corrosion [1, 2]. In spite of this, the surface state of corrosion test specimens is seldom defined in accurate detail. The characteristics to be taken into account in determining a surface state may be classed, according to P.A. Jacquet [3] under three headings:

- a) *microgeometric*, depending on the distribution, number and dimensions of the surface asperities;
- b) *physical*, representing the microscopic, submicroscopic or atomic structure of the surface films, as also their hardness and the internal stresses set up in them;
- c) *chemical*, depending on the nature and composition of the chemical compounds present, other than the actual metal compounds.

Before any consideration of each factor's rôle in different types of stainless steel corrosion, the methods for determining these characteristics should be described.

1. Methods employed to determine surface state characteristics

1.1. *Microgeometry or roughness*

There are a great many of these widely-used methods, and we shall do no more than list them briefly [4]. First, there are the methods which enable surface irregularities to be visualized. When the surface roughness is, on the average, greater than one micron, profilometers are capable of tracing the irregularities with a magnification of 10^3 - 10^4 . Where the average roughness is less than one micron, various optical processes are available (Schmalz optical sections, interferometer, phase-contrast microscopy, etc.). Lastly, replication of the surface and examination with the electron microscope enable very small irregularities, of the order of $0.01 \mu\text{m}$, to be delineated. Also worth noting are the ionic field and electronic field microscopes developed by Muller. For quantitative roughness comparisons a great many methods, based on integration, have been developed. The mechanical integrators associated with the profilometers will give either the absolute mean of the profile deviations from the mean line (CLA) or the root mean square of such deviations (RMS). Pneumatic integrators, such as the SOLEX permit high-accuracy comparison of the surface roughness of machined items. Other types of integrator are optical (photometers, diffusometers, reflectometers), electrical or even acoustic. Finally, certain measuring methods express roughness as the ratio of the actual surface area to the geometric surface area of the specimen. The actual area of a given surface can be measured by gas

(*) Manuscript received on February 9, 1966.

or liquid adsorption. The results must be interpreted cautiously, as they may vary substantially according to the nature of the substance adsorbed [5]. Roughness may also be determined by electrochemical methods, which give the ratio of the capacitance of the specimen to the capacitance of a mercury electrode in the same electrolyte [6]. Thus it is no simple matter to determine a microgeometric state. The choice of method will depend mainly on the size of the asperities liable to influence the corrosion phenomenon being studied. Frequently the microgeometric surface state will be sufficiently defined by using mechanical profilometers and an integrated surface irregularity value.

1.2. *Physical or structural characteristics*

Examination of cross-sections or oblique sections by optical or electron microscope usually reveals the perturbations caused by a surface treatment. It was by this method that L.E. Samuels determined the exact thickness of layers distorted by various mechanical surface treatments of a 18-8 steel [7].

Microhardness measurements provide additional data. X-ray diffraction analysis, too, yields information on the surface cold-work of a metal that has undergone mechanical treatment. Experience has shown that diffraction Lines from cold-worked metals exhibit considerable broadening by comparison with those from well crystallized metals. The broadening is due either to lattice parameter variations caused by the heterogeneous stresses to which the deformed grains are subjected, or to the very small dimensions of the crystal fragments produced. In the course of our research on stainless steel oxidation, M. Warzée used this technique to determine the depth of cold-work in 18-10 steel specimens which had undergone various surface treatments [8]. The apparatus consists of an asymmetric focus mounting used for low-angle X-rays. It is connected up to a curved-crystal monochromator employed with the $K\alpha$ Line in copper. Fig. 1 shows the various Line (III) breadth changes in the austenite, measured at mid-intensity above continuous background after successive removals of metal by electropolishing. The specimens had been subjected to three different mechanical treatments: milling, grinding and polishing with 600 paper. It will be noticed that the depth of cold-work differs noticeably for each of these treatments.

When an austenitic 18-8 steel is cold-worked, the metastable austenite is transformed into martensite. The influence of the steel composition and purity on this transformation $\gamma \rightarrow \alpha$ [9, 10] has been demonstrated in numerous instances. In particular the effect of annealing at different temperatures on the amounts of martensite formed was revealed, by the use of X-ray diffraction at high temperature [11]. Thus mechanical polishing with alumina on a 18-8 steel specimen causes a surface layer to form, which, as the electron diffraction diagrams showed, consists almost entirely of martensite [12, 13]. The amount of ferro-magnetic martensite in the austenite can be determined by measuring the magnetic moment of a small bar of the steel [14]. The martensite can also be detected by the Bitter Figure method, which utilizes a colloidal suspension of magnetite that becomes localized on the ferro-magnetic regions of the surface [15, 16]. The chemical and electrochemical behaviour on the stainless steel is, of course, affected by its diphasic structure, so that one or other of the phases can be selectively attacked by means of a potentiostat [17].

1.3. *Chemical characteristics*

The chemical composition of the surface may be altered, in relation to the base metal, by physical or chemical adsorption of matter with which the metal comes in con-

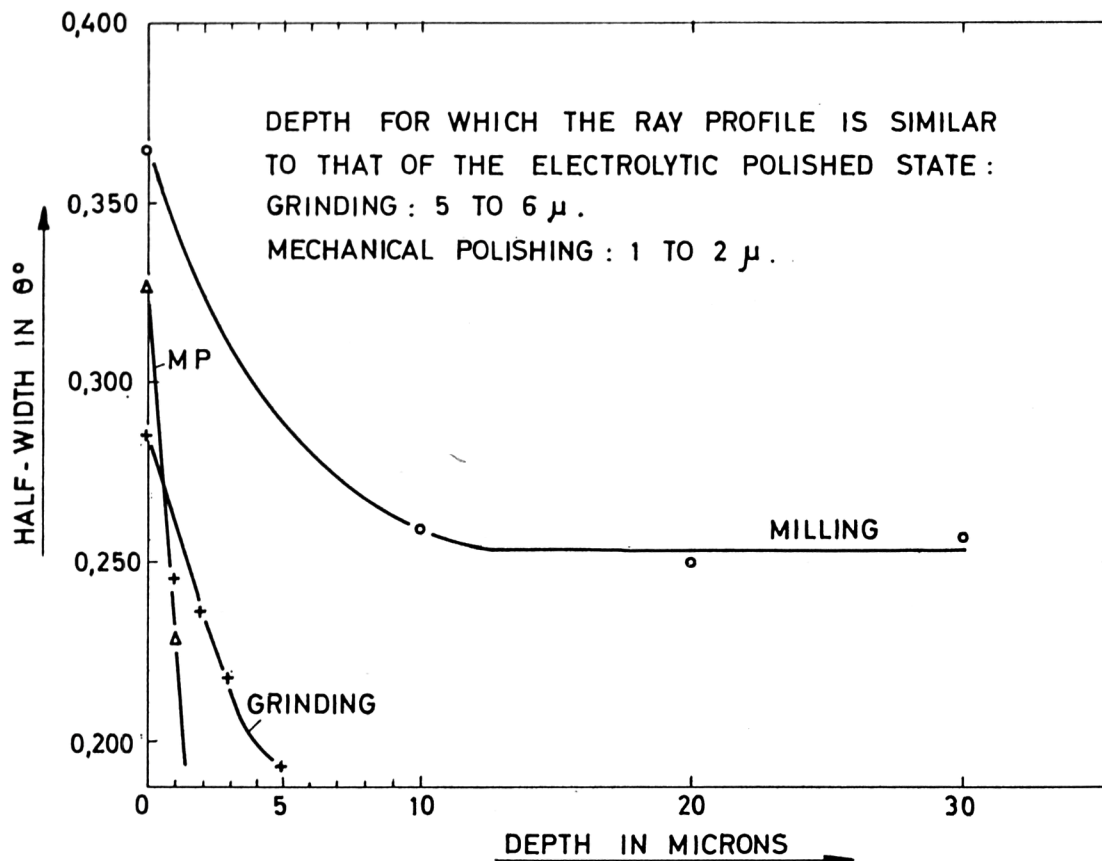


Figure 1

Measure of the cold-working rate of stainless steel, using the half-width of the austenitic ray (111) (given in degrees θ).

tact during or after surface treatment. Contamination of the surface by organic molecules or halogens is common but difficult to detect. Thanks to the remarkable sensitivity of the labelled-molecule technique, adsorbed substances can nevertheless be identified even if present in minute quantities. Surface contamination can also be detected, in certain cases, by measuring electric capacity in an appropriate solution [18].

An important factor in the chemical behaviour of stainless steels is the presence of oxide films. These very thin films, characteristic of the passive state, can be produced by either electrochemical or chemical oxidizing treatment, the latter including simple oxidation in air. Passive stainless steels are particularly notable for their high dissolution potential in sulphuric acid. The oxidation rate of an active specimen in sulphuric acid is rapid. With a passive specimen it is slow but still measurable; the oxidation can then be characterized by an exchange current i_e . The electrochemical equilibrium of this slow oxidation is effected by reduction of the dissolved oxygen, if present in the acid, or by the protective film itself if the solution has been degassed. In the latter case the passivity is not stable. Knowledge of this behaviour of stainless steel in sulphuric acid led to an electrochemical technique, by which the passivation film can be characterized by two values [19, 20]; one is the exchange current i_e of the passive specimen in a given sulphuric solution, the other, q the number of coulombs per cm^2 necessary to reduce the said film,

gives an indication of the film thickness. For the first measurement the passive specimen is depassivated by exposure in a 16 N sulphuric acid solution free of dissolved oxygen. The sharp drop in potential characterizes the transition from the passive to active state after a time t :

$$q = \bar{i}_e t \quad (\text{i})$$

For the second measurement an identical specimen is subjected to a very weak cathodic current i_r (about $5 \mu\text{A}/\text{cm}^2$) the drop in potential occurs after a time t' :

$$q = (\bar{i}_e + i_r) t' \quad (\text{ii})$$

Measurement of t and t' gives the values for q and i_e .

These characteristics differ considerably according to the passivation method used, as may be seen from the results in Table I, relating to an 18-10 steel subjected to anodic passivation treatments (0.5 V/ECS) in 16 N sulphuric acid for periods ranging from 2 to 30 minutes.

TABLE I

Passivation time (in minutes)	2	5	10	30
t (in seconds) ($i_r = 0$)	141	540	1440	2580
t' (in seconds) ($i_r = 5 \mu\text{A}/\text{cm}^2$)	77	108	190	240
q (in microcoulombs per cm^2)	846	675	1100	1290
i_e (in $\mu\text{A}/\text{cm}^2$)	6	1.25	0.76	0.5

2. Surface state and corrosion in stainless steels

With the aid of the foregoing definitions, an attempt was made to discover just what part the initial surface treatment plays in certain cases of stainless steel corrosion. The study of these steels represent a particularly interesting example because in practice stainless steels are subjected to various corrossions, whose effects are triggered by different mechanisms. Furthermore, it is their superficial passivity which accounts for their remarkable behaviour in a wide range of circumstances.

2.1. Roughness

It is not always easy to relate roughness to corrosion in a given medium. In the first place, it must be ascertained that the surface layer structures are identical or play no part in the corrosion process under study. Secondly, the roughness usually changes when the specimen corrodes, either through irregular dissolution of the metal or through the forming of an oxide film. The effect of surface roughness on various possible cases of corrosion has been summarized by B. Le Boucher [21]. Earlier studies had shown that dry corrosion was strongly influenced by the radius of curvature of the exposed surface [22]. The increased corrosion rate for sharply curved areas is attributed by Rebol to an increased adsorption of oxidizing gases.

Electrochemical corrosion is also strongly influenced by roughness. A rough surface not only has a greater actual area than a smooth one, but it also has far greater catalysing power, which may result in a marked decrease in the electrochemical overvoltage.

2.2. Pitting corrosion in ferric chloride

A higher corrosion rate due to such a decrease in electrochemical overvoltage in rough surfaces was observed in the case of pitting corrosion of stainless steels in ferric chloride [23]. Specimens ($50 \times 10 \times 1$ mm) attached to a rotating support were immersed for 2 hours in a 10 % ferric chloride solution at 35° C. The specimens, which we cut from a sheet previously hyperquenched from 1050° C, had undergone the following surface treatments:

milling, grinding, polishing with 600 paper, electropolishing in perchloroacetic acid bath.

The various corresponding roughnesses are shown in Table II, which also gives the test results expressed in weight loss and number of pits visible to the naked eye.

TABLE II
Summary of Surface Treatments, Measured Roughness and Corrosion Behaviour

Treatment	Surface Roughness (CLA)		Corrosion Behaviour	
	Longitudinal	Transverse	Weight Loss mg/cm ²	Pit Density in FeCl ₃
1. Milled (cutter movement in longitudinal direction)	11 μm	11 μm	8.1 ± 0.2 mg/cm ²	70
2. Ground	3.9 μm	5.2 μm	3.4 ± 0.3 mg/cm ²	35
3. Mechanical polish through 600 paper (longitudinal)	1 μm	8 μm	2.05 ± 0.05 mg/cm ²	4
4. Electrochemical polish in acetic-perchloric acid bath	1.6 μm	1.6 μm	0.50 ± 0.05 mg/cm ²	0

It was ascertained, by subjecting these specimens to various passivation treatments (passivation in air for 1 hour and for 8 days, oxidation in conc. nitric acid), that the initial passivation had no effect on corrosion in ferric chloride. This finding should not be regarded as applying generally to other pitting corrosion agents. In the present case the non-effect of the initial passivation can be explained by the oxidizing power of the ferric chloride, which forms a passive film independent of the natural film already formed. The graph of the intensity and potential curves showed that the polished specimens' good corrosion resistance was related to a high electrochemical overvoltage in the Fe³⁺ reduction reaction in the steel.

2.3. Chemical State

The stress corrosion cracking of austenitic stainless steel in heavy water at high temperature has been attributed to the adsorption of halogens during pickling. S.P. Rideout [24] has shown that after pickling in a hydrofluoric nitric acid bath 18-8 steels

are liable to become very sensitive to stress corrosion in hot water containing no more than a few ppm of chloride.

Furthermore, we were able recently to demonstrate the serious effect of surface contamination by chlorine, during the stress corrosion test in a boiling 42 % solution of magnesium chloride. Even so-called pure magnesium chloride may contain traces of impurities (probably chlorate) which decomposes into chlorine. This chlorine is released when the salt is heated and attacks the stainless steel specimen if the latter is in contact with the salt. We found that if the specimen, previously passivated in nitric acid or electropolished in acetic perchloric bath, was put in a magnesium chloride solution, which had been boiling for some minutes, the delaytime, associated with a very negative electrochemical potential of the specimen in the solution was completely eliminated (Fig. 2) [25].

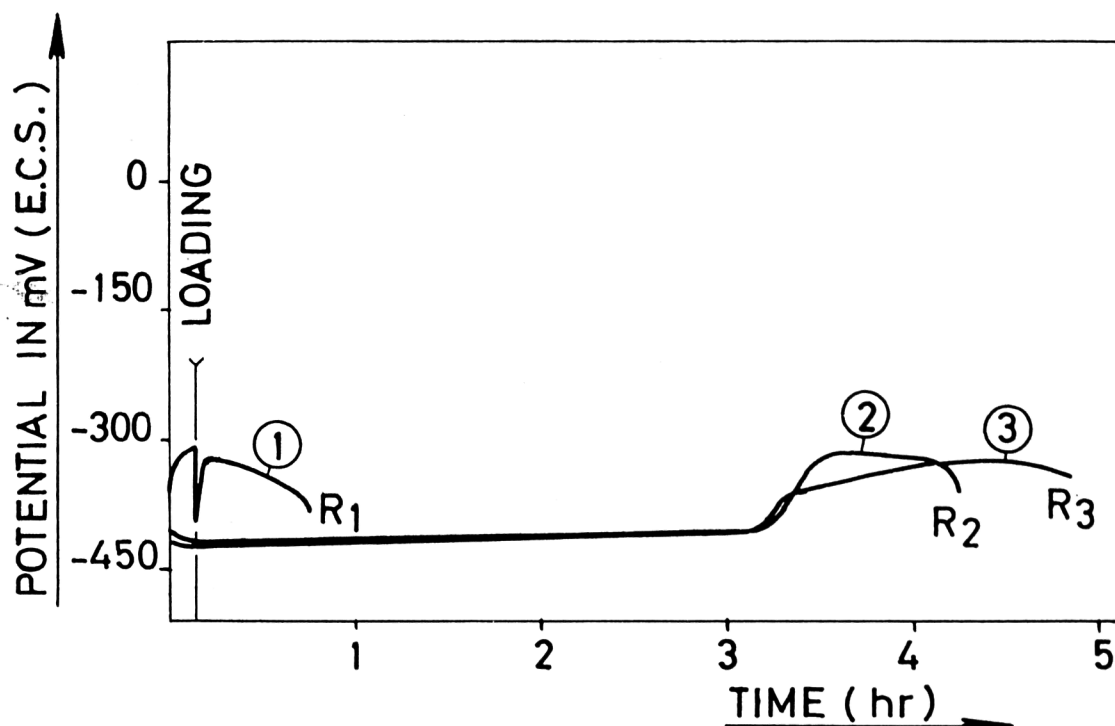


Figure 2

Curves showing 18-8 steel wire dissolution potential during stress corrosion tests in magnesium chloride (load: 30 kg/mm²).

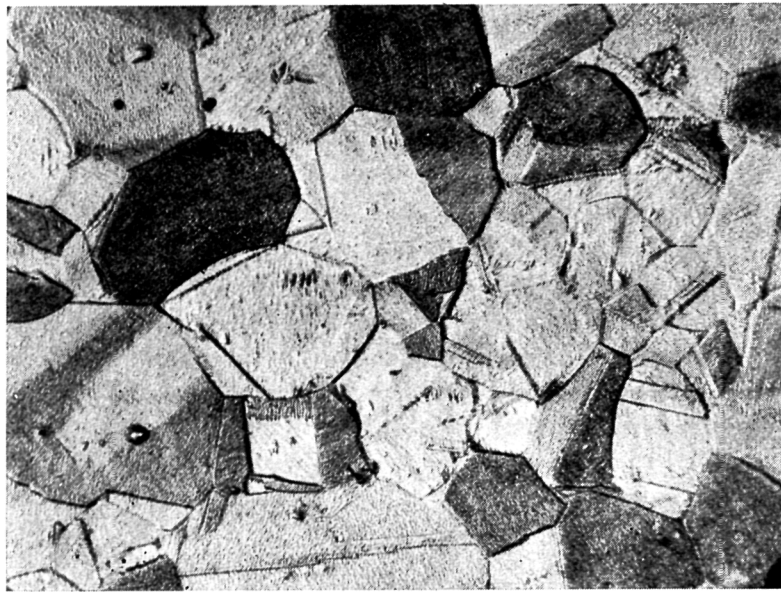
Curve 1: steel immersed in chlorine free solution

Curve 2: steel immersed in solution from which chlorine has not been removed. The rise in potential indicates the end of the incubation period

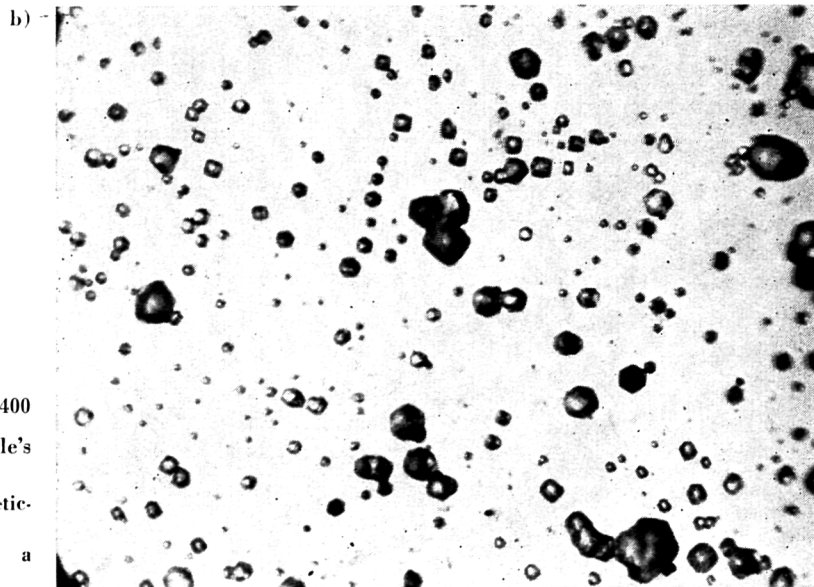
Curve 3: steel subjected to action of chlorine gas and then to corrosion test in a chlorine-free solution.

The protective film which forms in oxidizing media is responsible for the superior resistance of stainless steels to chemical corrosion. Wherever the corrosive medium is not itself sufficiently oxidizing to form a passive film, the passivity conferred by the initial

surface treatment will afford protection. A standard experiment consists in taking a plate of ferritic stainless chrome steel and placing on it a drop of solution containing sodium chloride and a colour indicator for iron ions. If the passivity is destroyed by scratching the plate, colouring appears at the scratch and spreads rapidly outwards. In the same way, stainless steel generally cannot long withstand attack in a aerated sulphuric acid solution unless it has first been passivated. P.A. Jacquet has shown that directly after an 18-8 austenitic steel had been electropolished in a perchloracetic acid bath, its micro-structure was completely revealed by a few seconds' immersion in Marble's reagent [26]. But if the same steel is polished in a sulphuric-phosphoric acid bath, which possesses passivating properties, this reagent fails to reveal the structure and, as will be seen in Fig. 3, local fracture of the protective film causes pitting.



a)



b)

Figure 3 × 400
Etching of a AISI 304 in Marble's reagent:
a. After electropolishing in acetic-perchloric acid bath
b. After electropolishing in a sulfuric-phosphoric acid bath.

The electrochemical coulometry measurements described on an earlier page confirmed that the specimens polished in a perchloroacetic acid bath had no protective film against the sulphuric acid immediately after polishing, the film being formed by subsequent exposure to air. On the other hand, the passivity was measured by this method directly after electropolishing the sulphuric-phosphoric acid bath [26, 27].

There have been reports from industry of corrosion in items that had not received initial passivation treatment. For example, chrome steel knife-blades, which had been covered with grease after machining, corroded after being washed in hot water, whereas identical blades which had been passivated by air-exposure remained undamaged.

Similarly, the behaviour of chrome steels in oxygen at 1100° C may be influenced by the presence of very thin oxide films resulting from chemical surface treatments. D. Caplan and al. have observed that the barely perceptible films formed by electropolishing in a perchloroacetic bath appeared to have an adverse effect on the oxidizing kinetics in high-temperature oxygen [28].

2.4. Structural State

2.4.1. Anodic passivation in sulphuric acid

Intensity-potential curves are widely employed for studying the behaviour of stainless steels in sulphuric acid solutions [29]. If the curve for an 18-10 steel in the milled state is compared with that for the same steel electropolished in a perchloroacetic acid bath, it will be seen that in the latter case the passivated region is more extensive and that the intensity needed to maintain passivity in that region is distinctly lower (Fig. 4). It has been shown that these differences are due not only to the greater surface roughness of

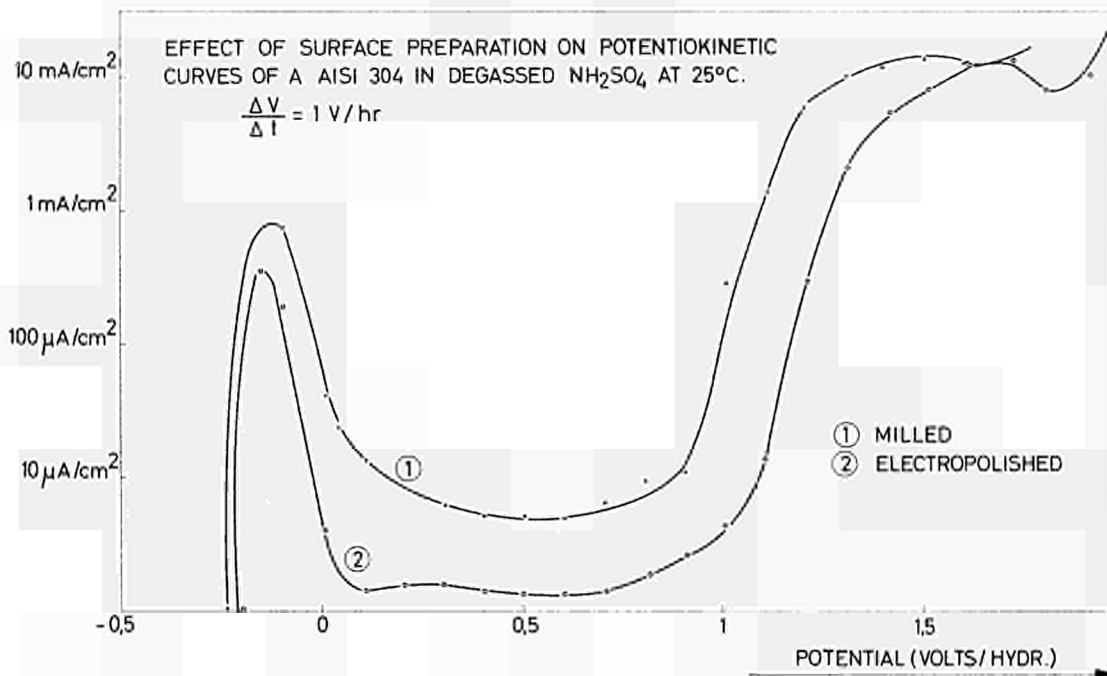


Figure 4

the mechanically treated specimens, but also to the structure conferred by cold working [30].

2.4.2. Stress Corrosion

Hochmann has shown that surface treatment may be a paramount factor in the stress corrosion resistance of austenitic stainless steels in magnesium chloride [31, 32]. The 18-8 steel specimens were subjected to 20 kg/mm² bend stress. The pickled and mechanically polished test-pieces broke after a period ranging from 2 to 24 hours. The electro-polished test-pieces proved more resistant, while no cracking had appeared in the sand-blasted specimens after 150 hours. The beneficial effect of sand blasting is due to the fact that it induces surface compression stresses which, being contrary to the external stresses, cancel out their effect. A similar phenomenon is found in test-pieces subjected to cyclic stresses (fatigue) [33].

2.4.3. Intergranular Corrosion

If 18-8 steels are cold-worked before testing for sensitization to intergranular corrosion, their resistance in the standard copper sulphate/sulphuric acid reagent is greatly improved [34]. This behaviour may be explained by the presence in the cold worked metal of a large number of slip planes on which the carbides precipitate. The chromium-depleted zones, which are responsible for this type of corrosion, are thus small well distributed. The cold-working of the surface may therefore account for its improved behaviour in the sensitization test.

The mechanisms that cause intergranular corrosion in nitric media containing hexavalent chromium are as yet little-known, but are certainly not the same as that which produces the typical intergranular corrosion revealed in the copper sulphate reagent [35, 36]. Surface cold-working by milling, for instance, will considerably delay intergranular attack in this medium (Fig. 5) but if the specimen is subsequently treated at 750° C this favourable effect disappears [37].

Figure 5

Effect of superficial cold-work on intergranular corrosion of 18-8 (quenched from 1100 °C) in boiling 70 % HNO₃ + 5 g/l Cr⁶⁺ (2hrs) [37].

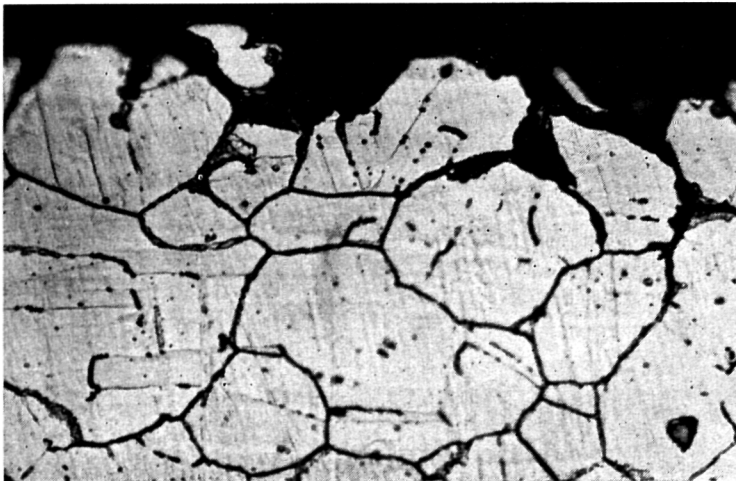


Figure 5 a Electropolish in acetic perchlore solution

× 400



Figure 5 b Milled

× 400

2.4.4. Corrosion in Steam at High Temperature

The considerable influence of surface treatment of stainless steel on its corrosion behaviour in high temperature steam was demonstrated recently [38-40]. In an early stage of our study a number of 18-10, 20-25 and Fe-13 Cr stainless steel specimens were studied in an autoclave over a wide temperature range. Table III gives a summary of the results, from which the following conclusions can be drawn [41]:

— In dry steam up to 350° C, the surface treatment has practically no effect on oxidation.

— From 400° C upwards, mechanical treatment (*) gives distinctly better resistance than pickling or chemical or electrolytic polishing. This improvement was observed in all three steels studied, becoming particularly noticeable at temperatures of 500 and 600° C.

TABLE III
Total Corrosion Values in mg.dm⁻² after 1000 hr in autoclaves [41]

Stainless Steel % Compositions	Surface Treatment	Superheated Steam					
		Temperature and Pressure					
		250° C	350° C	400° C	450° C	500° C	600° C
		15 kg/cm ²	35 kg/cm ²	70 kg/cm ²	70 kg/cm ²	70 kg/cm ²	70 kg/cm ²
AISI 304 C 0.04 Si 0.5 Ni 11.0 Mn 1.1 Cr 18.8	Milled	3.0	4.5	7.5	27.2	34.2	18.7
	Electro-polished	3.1	4.5	11.4	78	160	1100
Stainless 25 (Yddeholm) C 0.075 Si 2.0 Ni 21.5 Mn 2.6 Cr 23.5 P 0.03 S 0.025	Milled	—	—	3.8	—	8.4	—
	Electro-polished	—	—	5	—	79	—
AISI 410 C 0.07 Cr 13.4 Mn 0.38 Si 0.32 P 0.021 S 0.006	Milled	—	—	6.8	—	83	—
	Electro-polished	—	—	55	—	460	—

Using Bloom's technique (**), we showed that with a suitable treatment this improved oxidation rate still persisted after 2000 hours (Fig. 6).

We proved that this improvement was due to the presence of a cold-worked surface layer, since neither roughness nor initial passivation was involved. Furthermore, examination by electronic microscope and microprobe revealed that at the test temperatures the chromium was able to diffuse through the cold-worked layer, so that the oxide film which formed was rich in chromium and highly protective.

(*) The mechanical surface treatments employed were milling, grinding and polishing with 600 paper; the respective cold-working depths are given in Fig. 5.

(**) This consists in evaluating the corrosion rate by measuring the volume of hydrogen formed in the metal/water oxidation reaction, which is effected in small capsules heated up to test temperature [42]. The hydrogen thus released diffuses through the capsule walls and is measured daily. Used in combination with a chromatograph, which provides very accurate determination of the quantity of hydrogen and thus of the corrosion rate, this method was successfully applied to the steam corrosion study [41].

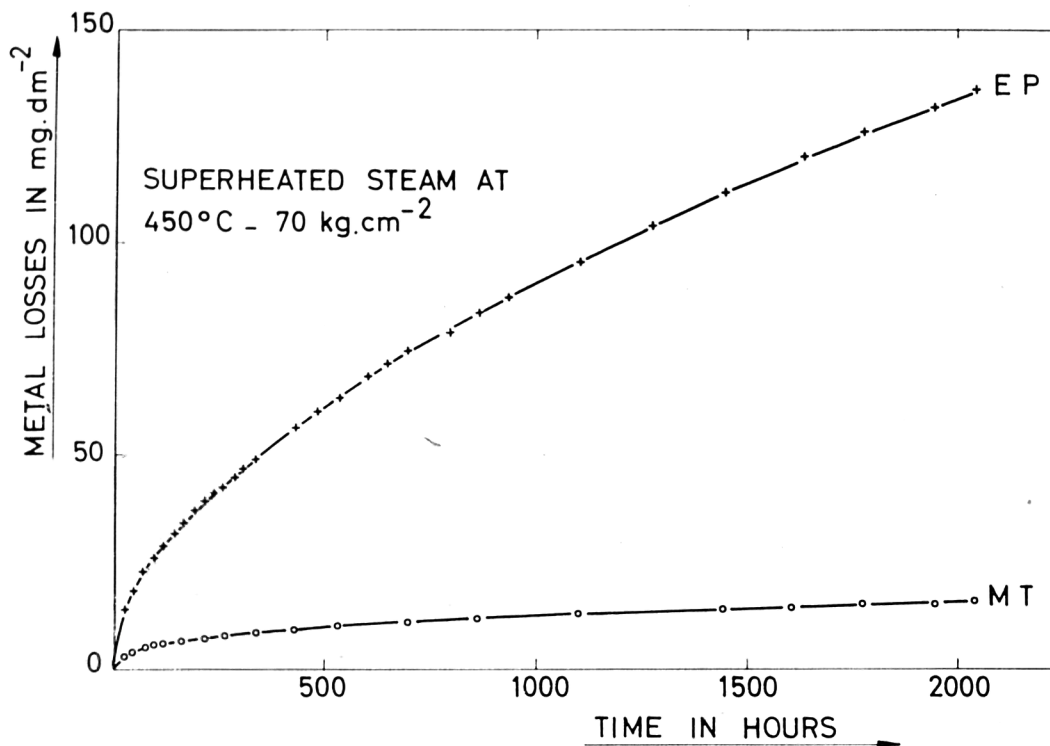


Figure 6

Total corrosion of AISI 304 in superheated steam at 450° C 70 kg/cm² measured by hydrogen evolution.

EP electropolished.

MT mechanically treated (lathe-turned).

3. Conclusion

The examples cited were limited to a few cases of stainless steel corrosion. In similar fashion it would be possible to demonstrate the importance of the initial surface state as a factor governing the corrosion of many other metals and alloys. The foregoing examples also show that, generally speaking, a surface state cannot be adequately determined by the roughness value alone.

The case of electropolishing, which so notably advanced the studies of metal surfaces, clearly demonstrates the complexity of the problem. The photographs in Fig. 3 show that two surfaces which have been electropolished in different baths may differ widely in behaviour. Again the study of oxidation in steam showed that two specimens electropolished in the same solution may differ in behaviour if in one of them the electropolishing process has not wholly dissolved the cold-worked layer formed by prior mechanical treatment.

To sum up, whenever a corrosion study is undertaken, all the surface-state characteristics of the test pieces must be defined as fully and accurately as possible.

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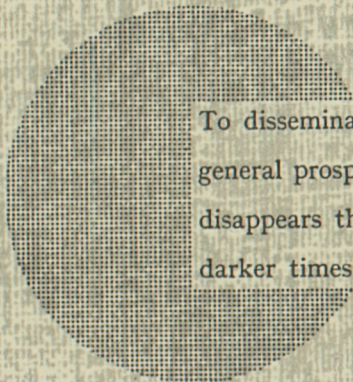
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