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ORIGINAL PAPER

Quantitative evaluation of oxide impurities in bright annealed stainless steels for deep drawing

M. Delucchi · A. Barbucci · R. Ricotti · G. Cerisola

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Abstract Cold rolled SS is suitable for deep drawing operations, however the presence of resilient scales or oxides on the surface can damage the deep drawing punch/die sets and emphasise creep phenomena of the material. These oxides can be formed during the hot rolling process preceding the cold one, or during the bright annealing performed between the steps of thickness reduction of the coil. Then a cleaning of the SS surface before drawing is necessary to have a longer life of the tools. The removal of the surface oxide scale can be performed with electrolytic pickling using neutral electrolytes, but the process parameters can be varied depending on the amount of oxides present on the surface of the starting material. To optimise the process efficiency, then, an univocal scale of the degree of oxidation of the bright annealed SS was determined through microscopical analysis and potentiodynamic tests.

Keywords Stainless steel · Deep drawing · Electrolytic pickling · Polarisation measurements

1 Introduction

Impurities of the inhert gases for bright annealing treatment or impurities carried by the strip in the furnace or oxides deriving from previous operations of rolling may generate some oxide impurities on the surface of SS strips [1]. These impurities, which can be present at different degrees and have dimensions of the order of less than 1 μm, are often extremely resilient and can have negative effects if the SS is used for deep drawing [2]. An example of the morphology of the bright annealed SS strips is reported in Fig. 1, where it is evident that the impurities are present at different degrees and homogeneously or unevenly distributed (particle denuded or enriched regions). Then the production line schedules their removal by electrolytic pickling [3–6].

A rough estimation of the oxide scale which is present can be done during the process of production through surface analysis by optical microscope with a 1,000x magnification. Then, a visual standard to evaluate the so called "Oxidation Number", O.N., before pickling is established. It comprises five classes based on a numerical scale from 0 to 5, in which No. 0 represents no oxides on the surface and 5 the maximum presence of oxides. As an example, some of the classes of oxidation used for the characterisation are reported in Fig. 2.

This classification is based on a subjective evaluation of the operator, while the determination of the surface properties of the material with high reproducibility and reduced subjectivity could help the selection of the appropriate pickling conditions and improve the process control and equipment. Microscopical analysis and potentiodynamic tests have been performed on different 304L and 305 steels to define an univocal scale of degree of oxidation.

2 Experimental

Several strips of stainless steels types 304L and 305 were used as specimens.

The nominal chemical composition of the tested materials is presented in Table 1.

For each grade, specimens were removed at two stages from the standard cold rolled production line:

M. Delucchi (✉) · A. Barbucci · R. Ricotti · G. Cerisola
DIChеP, Università di Genova, P. le Kennedy 1,
16129 Genoa, Italy
e-mail: marina.delucchi@unige.it

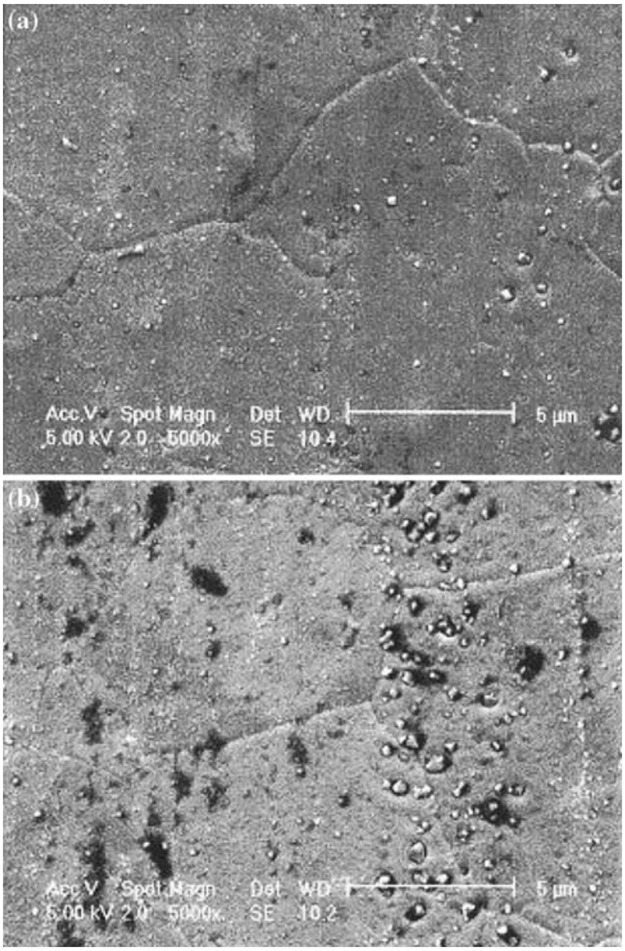


Fig. 1 SEM micrographs showing the morphology of SS type 305 with (**a**) homogeneously distributed particles and (**b**) unevenly distributed particles

- After the bright annealing furnace (in-line continuous sheet anneal in a hydrogen atmosphere).
- After final production line electrolytic pickling (electrolytic pickling in a neutral sodium sulphate solution, 15% w/w, at T = 70 °C), i.e. in the metallically clean or finished state. After this process the strips do not present any impurity on the surface and their O.N. is 0.

The denotation of the samples used in this work is self-explanatory of their status during the production line. The specimens were named with three alpha numeric groups separated by a dash (-). The first group identifies the SS type (304L or 305). The second group of letters defines the status of the sample with respect to the pickling process: IN stays for the bright annealed sample before electrolytic pickling treatment, OUTn for the same sample after electrolytic pickling, where n is the O.N. before pickling. The last group defines the Oxidation Number (only for IN materials). For example the denotation (304L-IN-ox1) stays for a sample of a 304L SS, bright annealed,

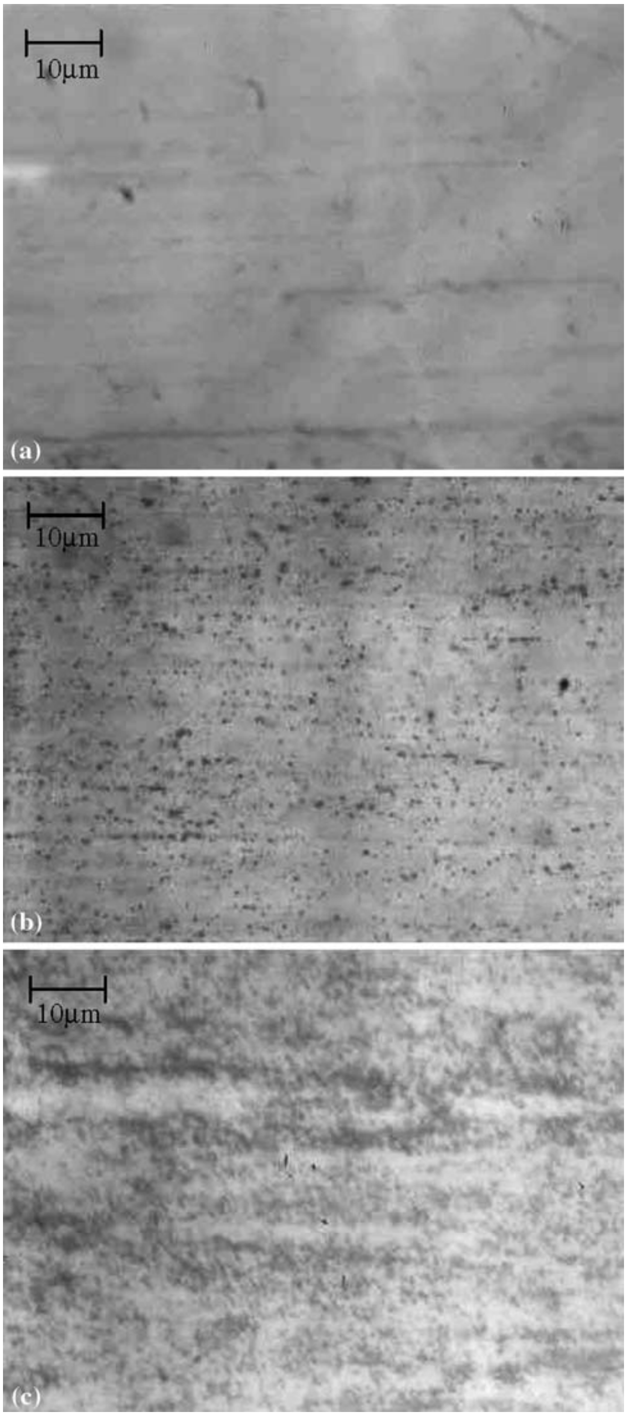


Fig. 2 Visual standard for the definition of the classes of oxidation: (**a**) O.N. 0; (**b**) O.N. 2; (**c**) O.N. 5

Table 1 Nominal chemical composition of the tested materials

AISI	Chemical composition (wt.%)								
	C_{max}	Mn_{max}	P_{max}	S_{max}	Si_{max}	Cr	Ni	Mo	Fe
304L	0.03	2	0.045	0.03	1	18–20	8–10	–	Bal
305	0.12	2	0.045	0.03	1	17–19	10.5–13	–	Bal

Table 2 Sample denotation

Substrate	O.N.	Sample before pickling	Sample after pickling
304L	3	304L-IN-ox3	304L-OUT3
304L	4	304L-IN-ox4	304L-OUT4
304L	5	304L-IN-ox5	304L-OUT5
305	2	305-IN-ox2	305-OUT2
305	3	305-IN-ox3	305-OUT3
305	5	305-IN-ox5	305-OUT5

characterised by an oxidation number equal to 1, while (305-OUT) stays for a sample of a 305 SS, electrolytically pickled. Table 2 shows the materials under investigation.

The electrochemical apparatus was an Avesta cell [7, 8]. The working electrolyte was 1 M Na_2SO_4 aqueous solution. The temperature was maintained at $T = 343$ K by the circulation of the thermostated water through an outer water jacket of the specimen chamber. A three electrode arrangement was used. The counter electrode was a platinum net placed in a separate compartment in contact with the test solution through a fried vitreous membrane. A Luggin capillary was connected to a room temperature $Hg/HgSO_4$ electrode. In the plots the potentials are reported with respect to SHE to allow easier comparison with the literature. The steel samples had a surface area of 0.785 cm^2.

This electrochemical apparatus was used for the comparison of the general electrochemical behaviour of the bright annealed and pickled samples by measuring potentiodynamic polarisation curves (potentiostat-galvanostat Model 273A—EG&G Princeton Applied Research). The tests were started from the open circuit potential. A sweep rate of 60 mV/min was used.

3 Results and discussion

Figure 3 reports some polarisation curves for the IN and corresponding OUT samples for the two considered SSs.

All the bright annealed (IN) samples showed a current peak. It indicates the electrochemical dissolution of the oxides which are present on the surface of the samples before transpassive dissolution region [4]. For the OUT materials, on the other hand, any peaked current-potential curve was found, as expectable for a clean surface. After the peak the current density is about equal in the sample couples, which indicates that both specimens suffer transpassive dissolution by similar mechanism.

A correlation between the dissolution process and the peak development was attempted performing two sequential potentiodynamic polarisation curves on a selected IN material: the first polarisation up to progressively higher

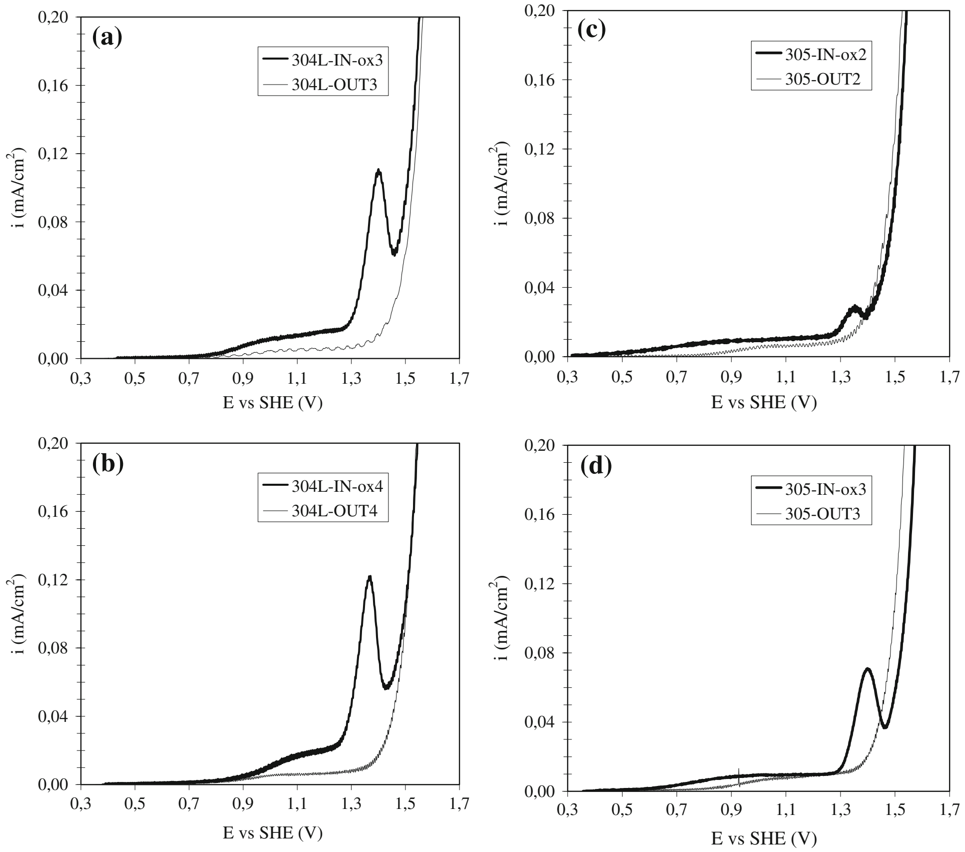


Fig. 3 Polarisation curves for (**a**) 304L-IN-ox3, (**b**) 304L-IN-ox4 (**c**) 305-IN-ox2, (**d**) 305-IN-ox3

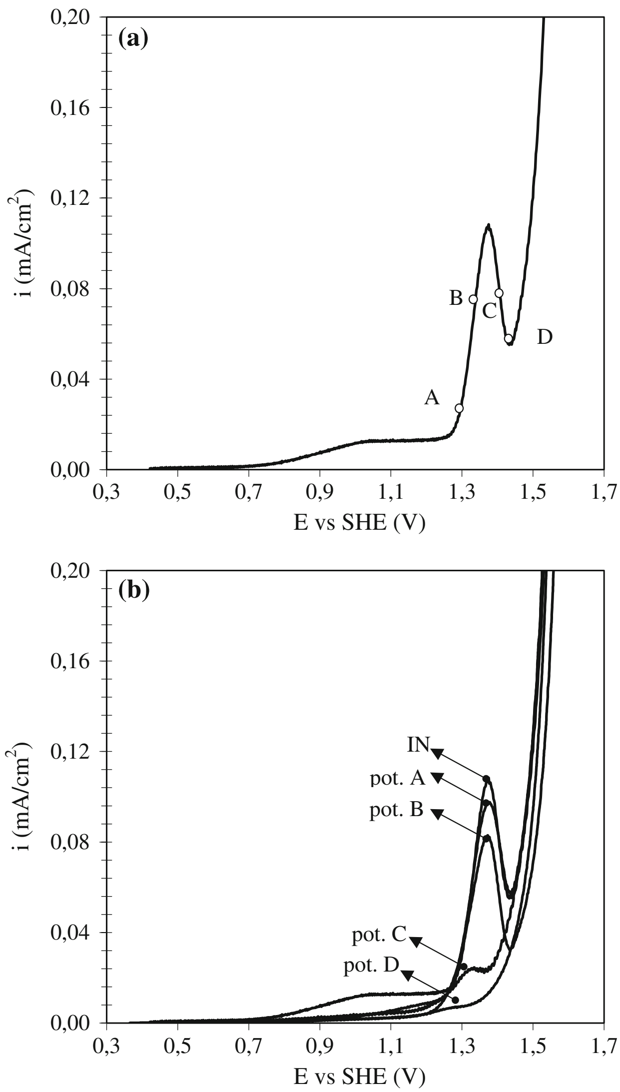


Fig. 4 (**a**) Steps of polarisation; (**b**) Peaked polarisation curves after different degrees of polarisation for 304L

potentials—points A, B, C and D of Fig. 4a—and the second polarisation (before removing the sample from the Avesta cell) till potentials characteristic of transpassive dissolution. The "second polarisation" curves are reported in Fig. 4b: it is evident that the curve peak reaches lower current densities as the first polarisation is performed up to higher potentials, while the potential of the maximum remains almost fixed.

A second series of samples of the previous material was prepared to analyse the surface after the first polarisation; the morphological inspection performed through the optical microscope indicated a variation of the content of oxide particles with the increased polarisation of the sample.

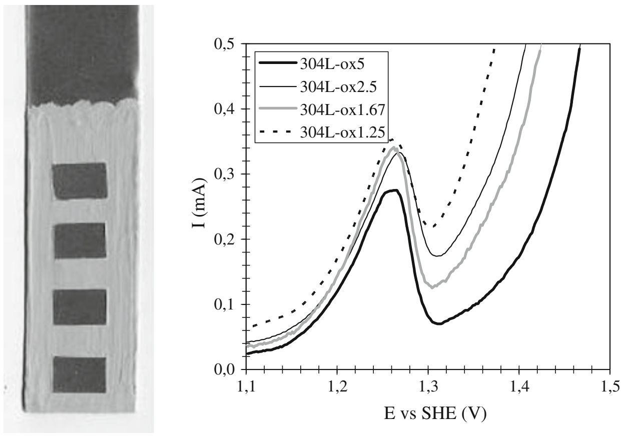
The surface of the specimen after bright annealing was characterised by dark spots, in form of islands or generally distributed, representing the oxides which are present on the surface. As the potential of the first polarisation was increased (points A–B–C of Fig. 4), the oxide presence on the surface decreased. A further increase of potential (point D) resulted in a surface without particles but with some holes.

After this qualitative analysis, a quantitative evaluation of the presence of oxides on the bright annealed samples was attempted: it was performed calculating the charge associated with the dissolution process, corresponding to the total area of the peak.

The first step for this evaluation was the analysis of the repeatability of the obtained data. The oxide-coverage of the IN materials, in fact, is unevenly distributed and it could be the cause of different results depending on the area selected for the testing. Then, five potentiodynamic measurements were performed on different areas of a strip of the same material (then with the same O.N.) and the area subtended to each peak of the obtained curves was calculated. As an example, the value obtained for specimen 304L-IN-ox3 was 11.67 mC/cm^2. The repeatability of the data was good, with a maximum difference between the calculated area and the mean value of 3.9%.

Therefore the analysis was carried on. In order to have a controllable oxide coverage variation, a particular geometry of the samples was devised: a small strip of the 304L SS characterised by the highest O.N., 5, was selected and insulated with a high build two-pack epoxy coating, leaving four "windows" of the bright annealed sample (Fig. 5a). Depending on the big dimensions of the sample (area of a "window" about 1.5 cm^2), a simple becker was used as specimen cell instead of the Avesta cell. The platinum counter electrode and Hg/HgSO$_4$ reference electrode were maintained as in the previous polarisation experiments.

Since the orientation of the working electrode was different in the two cell arrangements, an examination of the



(a) (b)

Fig. 5 (**a**) Geometry of the test sample; (**b**) Polarisation curves for different degrees of oxidation for 304L cell geometry influence on the polarisation curves was performed. As an example the curves obtained for 305-IN-ox4.5 resulted almost identical, even if there was a little shift at higher potentials for the curve obtained with the Avesta cell; on the other hand the subtended areas to the peaks resulted practically equal: 13.7 and 13.8 mC/cm^2 for the experiment in the Avesta cell and in the becker, respectively. In addition, a careful analysis of the sample edges after polarisation was performed to verify possible problems of crevice. All the tested samples, analysed by optical microscope, did not display signs of crevice corrosion.

Once verified that the new geometry had negligible influence on the results, four different polarisations, up to 1.5 V vs OCP, were performed on the specimen. At first only one “window” of the sample was polarised; the oxidation number of this surface is 5 and in this case an oxidation rate equal to 100% was assumed. Then two “windows” of the sample were polarised; with this kind of sample a 50% oxidation rate was obtained, in fact the first “window” resulted without oxides (the total dissolution of the oxides occurred during the first polarisation), corresponding to O.N. 2.5. The third and the fourth windows were progressively immersed to obtain 33 and 25% oxidation rates, corresponding respectively to O.N. 1.67 and 1.25.

The polarisation curves, reported in a E (V vs SHE)—I (mA) plot, are shown in Fig. 5b.

It is worth noticing that all the curves present almost the same current peak: the curves are only slightly shifted towards higher currents. Calculating the charge associated with each dissolution (or, equivalently, polarisation of the selected areas of the specimen), it is possible to draw the graph of Fig. 6, which indicates a linear dependence of the charge for oxides dissolution with their presence on the surface of the 304L stainless steel. The linear regression of the experimental data gives a good fitting, since R Square is very near to 1.

Since our purpose was to define a standard scale for the objective evaluation of the presence of oxides on a generic IN SS, the same experimentation was performed also on the grade 305, in particular on the strip with the highest O.N., 305-IN-ox5. The linear regression that interpolates the experimental data is reported in Fig. 6.

It has the same slope of that obtained for 304L SS, then the general Q–oxidation% relationship is validated; the difference in the value of the y intercept clearly depends on the subjective initial O.N.; on the basis of these results, the oxidation grade attributed to the 305SS by optical microscopy and used as starting value for the 100% oxidation rate of the material was, in reality, slightly underestimated.

For simplicity, supposing that the highest amount of oxides characteristic of any SS could be less or equal to that found for the tested 304L, the general law can be written as follows:

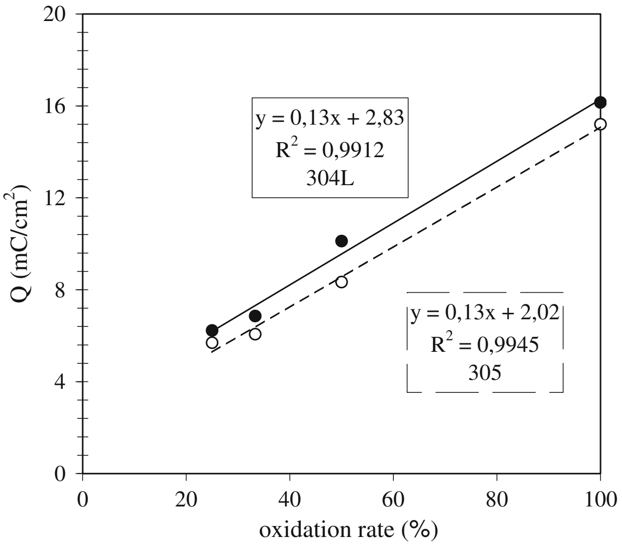


Fig. 6 Relationship between the oxidation rate and the charge of dissolution

$$Q(\mathrm{mC/cm^2}) = 0.13 * \text{oxidation rate } (\%) + 2.83.$$

4 Conclusions

Bright annealing of cold rolled 304L and 305 SS in an H_2 atmosphere cannot avoid the formation of resilient oxide impurities on the steel surface. If the SSs are used for deep drawing, the oxide removal is necessary to allow the deep drawing punch/die sets not to be worn. It can be done through electrolytic pickling in neutral sodium sulphate solution. Adjustment of the process parameters to optimise the pickling process (fast pickling rate and reduced over-pickling) depends on the properties of the starting material, then an univocal scale of degree of oxidation of SS was determined. Its validity was confirmed analysing two different stainless steels, grade 304L and grade 305, obtained from different SS coils.

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