Electrochemical techniques in quality control in stainless steel manufacturing: Experiences with the ec-pen

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Abstract

In numerous technical applications the knowledge of the local electrochemical behavior is necessary for the understanding of the mechanisms involved. This information helps to understand the corrosion behavior of materials, to evaluate the corrosion risk of specific inhomogeneity, and to design mitigation measures for the improvement of the corrosion resistance. Hence, an electrochemical sensor and a handheld potentiostat were developed that allow fast and easy access to local electrochemical information. Easy handling, short sample preparation time and the possibility to run experiments on virtually any size object with various surface geometries opens a vast field of applications. Moreover the possibility to run non-destructive corrosion tests make it a powerful tool in quality control and process development. Typical applications of the set-up are presented.

Introduction

Stainless steel is increasingly used in civil engineering. In most applications its high corrosion resistance makes it the material of choice. Nevertheless, this property can be easily compromised by manufacturing processes, such as welding and cold work or environmental influences such as scratching and pollution with iron dust to name a few. These effects can severely decrease the corrosion resistance of the stainless steel. Therefore, the high expectations in service life could not be met in numerous cases. This fact demonstrates the need for a quality control. However, the quality control of the corrosion resistance of stainless steel in civil engineering is mostly limited to visual inspection, which only allows the determination of indirect values and depends to a high degree on the experience of the controlling engineer.

In contrast, electrochemical techniques have been developed in corrosion research that allow the reliable determination of the corrosion resistance of stainless steel under laboratory conditions. These techniques have never been used on a routine basis in civil engineering, as they involve cutting out samples and measurements in the lab, making it an expensive and time-consuming procedure. With the development of a new electrochemical sensor [*1, 2*], the so called ec-pen, and a hand held control unit it became possible to run electrochemical tests even in rough environment (Fig. 1 and 2). The ec-pen allows the evaluation of the corrosion resistance of stainless steel on-site and determination of the effectiveness of mitigation measures. Hence, the quality control of stainless steel manufacturing is possible based on the determination of a direct value, resulting in a high reliability. The results obtained in quality control of stainless steels in civil engineering and the scientific background of the test are presented.

Experimental

The electrochemical sensor

The new electrochemical sensor, the so-called ec-pen, was developed for electrochemical testing in industrial applications. It can be used for fast determination of the corrosion resistance of objects of any size and surface geometry (Fig. 1). Electrolytic contact with the surface is established by placing the ec-pen on it. Capillary forces cause electrolyte flow from the reservoir to the surface through a porous polymer body and prevent the leaking of the electrolyte. The incorporated reference electrode is maintenance free and stable. By simply positioning the ec-pen on the sample surface electrolytic contact is established and electrochemical characterization is possible. Unless noted differently the measured area is 1.5 mm^2. A more detailed description is given in [3, 4]

Electrochemical testing

The electrolytes were prepared from distilled water and reagent grade chemicals. All potentials are referred to saturated calomel electrode (SCE). Previous to the measurements the surface was cleaned with ethanol. The surface is locally contacted by the electrolyte contained in a porous body electrochemically controlled by the contained electrodes and a potentiostat (Jaissle 1002 PC.T.). For the on site testing, a mobile electrochemical control unit (Test.Clinox) developed in cooperation with Nitty Gritty GmbH was used. The instrument allows running polarization scans with 10 mV/s and the determination of the pitting potential. A typical calibration measurement is shown in Fig. 3. Running several calibrations results in the averaging of the instrument of the determined pitting potentials. Once calibration is finished the instrument decreases the potential for 140 mV. By running potentiostatic tests for 10s the relative corrosion resistance is determined. Typical results are shown in Fig. 4. If the current shows the typical passive behavior it can be concluded that the tested area exhibits a pitting potential that is comparable or higher than the area where the instrument was calibrated. If the current shows a strong increase, it can be concluded that pitting is initiated. Hence, the tested area exhibits a corrosion resistance that is significantly decreased compared to the area where the calibration was performed. The various possible applications of the instrument are presented.

Sample material

Welds on stainless steel DIN 1.4301 and 1.4432 were investigated. A sheet of DIN 1.4301 was welded without protecting gas. The electrochemical cleaning of the weld was performed with the Clinox Pro (Nitty Gritty GmbH).

A tube of 1.4432 was welded under nitrogen. The welding additive was DIN 1.4430. No post treatment of the weld was performed.

A screw of 1.4404 was subjected to cold work resulting in a surface pollution with iron. For increasing the corrosion resistance it was degreased, subjected to oxidizing cleaning and passivation. The corrosion resistance of the component was characterized electrochemically after each process step.

Results and discussion

Comparative quality control of welds

Constructing with stainless steel in many cases involves welding. The welding process strongly alters and affects the microstructure of the metal, its phase composition, and the distribution of the alloying elements by the melting and freezing. However, even the increased mobility of the atoms due to the high temperature in the heat-affected zone (HAZ) can compromise the corrosion resistance of the metal. Additionally, the high temperature during welding results in a surface oxidation of the metal causing changes in the composition of the stainless steel at the surface and strongly decreasing its corrosion resistance. Although this oxidation only affects the very surface of the metal it is detrimental to the durability of the stainless steel component.

Up to now the quality control of the corrosion resistance of welded components was generally limited to visual inspection. The look of the weld, the presence of defects and heat tint were the essential criteria used. The correct interpretation of the visual inspection depends on the experience of the expert. Additionally, there is a high degree in uncertainty, as the visual inspection is not a direct measure for the corrosion resistance of the material. The ec-pen in combination with the handheld control device offers the possibility of determining the corrosion resistance directly. Its application is demonstrated on the weld on a DIN 1.4301. At first the instrument is calibrated on the base material not affected by the welding process. The instrument determines the pitting potential (Fig. 3). As this value is subject to a certain scatter caused by the statistical distribution of the corrosion initiation sites in the metal, it is useful to run several calibrations. Of those pitting potentials the instrument calculates the average, which allows compensating for the scatter. Once the calibration is finished the instrument decreases the testing potential for 140 mV. By performing potentiostatic tests, it is readily determined whether the investigated spot exhibits comparable corrosion resistance as the base material or whether the corrosion resistance is significantly decreased (Fig. 4). Hence, uncertainties in the visual inspection can easily be excluded, resulting in an increased reliability of the quality control in field applications or in the testing of sample weldings. In the present example, it was clearly shown that the corrosion resistances of the discolored area in the heat affected zone strongly affects the corrosion resistance (Fig. 4 and 5). The cleaning with the Clinox pro (Nitty Gritty GmbH) resulted in an increase of the corrosion resistance in the same range.

Process optimization by determining the pitting potential

While the comparative evaluation of the corrosion resistance is an efficient way of characterizing the corrosion resistance for controlling the quality of welds in field applications, the determination of the pitting potential is helpful for optimizing process parameters. Contrary to a good/bad response, it allows determining the effect of single parameters on obtaining an optimal corrosion resistance. This possibility is illustrated with the post treatment of a weld on DIN 1.4432. The visual inspection of the weld yielded slight yellow oxides (Fig. 6). According to DIN 50930 the yellow would have been acceptable for this application in drinking water. However, the characterization of the weld with the ec-pen showed clearly that the corrosion resistance in the areas with the yellow oxides was strongly compromised. In order to quantify this effect and finding mitigation measures the pitting potentials were determined with the ec-pen. The results are shown in Fig. 7. Contrary to the visual inspection, strongly decreased pitting potentials were also found in the entire HAZ even on the clean surface up to 1.5 cm away from the weld. In order to improve the corrosion behavior the exposure to water for 24 hours and the passivation in 5% HNO_3 for 3 hours were investigated. It is clear from the obtained pitting potentials, that the water treatment improved the corrosion resistance of the clean areas in the heat-affected zone. However, a passivating treatment is required to obtain a pitting potential above 300 mV SCE in the areas with the yellow oxides.

Based on a few tests with the ec-pen the evaluation and optimization of the post treatment of the weld was possible, while the visual inspection used so far would have resulted in an erroneous evaluation of the corrosion resistance.

In order to obtain more detailed information about the corrosion behavior of the weld, additional investigations with a potentiostat that allowed the measurement of the current were performed. The result is shown in Fig. 8. It is clear, that the zone with the yellow oxides does not exhibit a passive behavior. The treatment in water results in a certain improvement, but the passivation with HNO3 is required to obtain comparable pitting potentials as the bulk material (Fig. 9). It is interesting to note that even this strong passivation treatment was not sufficient to obtain comparable passivity as on the bulk, as the passive current density is still significantly higher in the HAZ.

In the present example it was found that the essential conclusions obtained with a standard electrochemical set-up was possible to obtain with the handheld instrument on site.

<u>Quality control of stainless steel with standard calibration</u>

The use of a relative calibration of the instrument is useful for on site quality control, as it allows compensating for external effects such as temperature. For the optimization of process parameters the determination of the pitting potential turned out to be efficient in order to obtain absolute values. However, the influence of temperature of the obtained values has to be considered. Hence, the evaluation of the data and the correct use of the instrument require certain electrochemical knowledge.

Nevertheless, there is a large field of problems related to quality control in surface treatment of stainless steel components of smaller size that can easily be handled in the laboratory. Under these well-controlled temperature conditions it is possible to use the ec-pen with a standard calibration. This is illustrated with the surface treatment of a screw for application in corrosive environment.

Table 1: Test results obtained with the Test.Clinox after calibration at 0.46 V SCE. X stands for corrosion initiation and O stands for passive behavior.

Treatment	Test result
none	XXXXXX
degreased	XXXXXX
oxidizing cleaning	XXXXOO
passivation	OOOOOO

After the cold work process the screw is polluted with iron particles. Subsequent degreasing, oxidizing cleaning, and passivation the corrosion behavior is increased, as can be concluded from the increasing pitting potential found in the polarization scans (Fig. 10). Additionally, the passive current density is decreased demonstrating the improvement of the passive layer. Determining the pitting potential with the Clinox Tester shows a clear increase of the pitting potential with the passivation procedure. Based on the obtained results it is clear that the components exhibit a pitting potential above 0.46 V SCE after a successful surface treatment. The potential can be set at this value by running the calibration with an external calibration box. Once the value is set a large number of tests can run in a very efficient and straightforward way as is shown in Table 1. The easy way of running the test and the short testing time offers a fast and reliable way of keeping track of the efficiency of the surface treatment.

Conclusions

The possibilities offered by the new electrochemical sensor are illustrated with various practical applications. The robust design, the lack of any maintenance, and the fast applicability allow for the evaluation of the corrosion resistance of stainless steel components of any size and virtually any surface geometry on site. Cutting out samples for laboratory characterization is therefore obsolete, making the technique virtually nondestructive. During the test the metal surface is polluted with chlorides, which have to be washed off afterwards to avoid possible problems. In case of highly aggressive applications it is recommended to passivate the surface after the test. Contrary to visual inspection it is possible to determine the corrosion resistance directly, making the quality control independent on the experience of the executing engineer. On the other hand it offers a good alternative to the time consuming salt spray test. Three different ways of applications are possible:

- Comparative test with calibration of the sensor on the base material. This operation is optimal for field applications and yields a simple fail/pass response. Effects of temperature or also variations of base material properties can be excluded to a significant degree. Moreover, the test does not require any electrochemical knowledge of the operator. Contrary to previous visual inspections, the new technique allows the direct measuring of the corrosion resistance. Hence, it is an ideal complementation for the visual inspection.
- Determination of the pitting potential. This application makes it possible to differentiate clearly among different process parameters. This way of operation requires keeping control of the temperature of the environment and the interpretation of the date requires certain electrochemical knowledge. Nevertheless it allows for detailed investigation of the corrosion resistance. Process optimization or failure analysis can readily be performed.
- Testing with calibration on an external calibration box. Once the critical potential value is determined, the test can be performed in a simple fail/pass mode. In order to obtain reliable results the temperature of the investigated surface has to be controlled. This operation mode is perfectly suited to monitor the efficiency of surface treatments or automatic weldings under industrial conditions.

Acknowledgements

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Fig. 1: Electrochemical measurement with the ec-pen on a stainless steel tube.

Fig. 2: Handheld instrument for quality control on stainless steels.

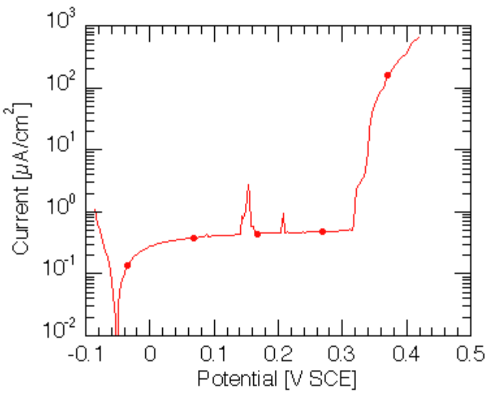

Fig. 3: Polarization curve at rate of 10 mV/s on 1.4301 in 1 M NaCl.

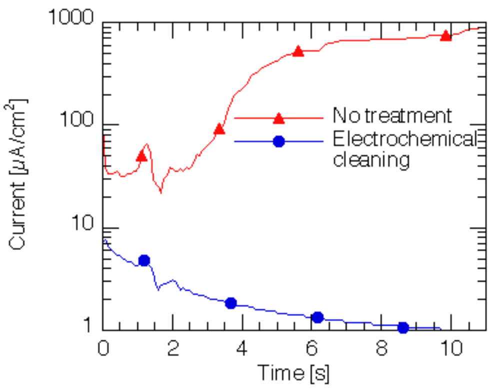

Fig. 4: Potentiostatic test of a weld on 1.4301 at 0.2 V SCE in 1 M NaCl. One part of the weld was untreated and the other was electrochemically cleaned.

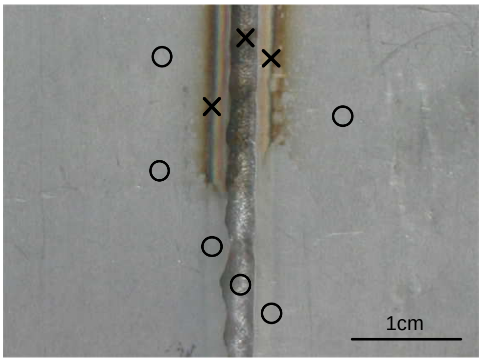

Fig. 5: Potentiostatic test on 1.4301 at 0.2 V SCE in 1 M NaCl. O indicates passive behavior, X indicates corrosion initiation.

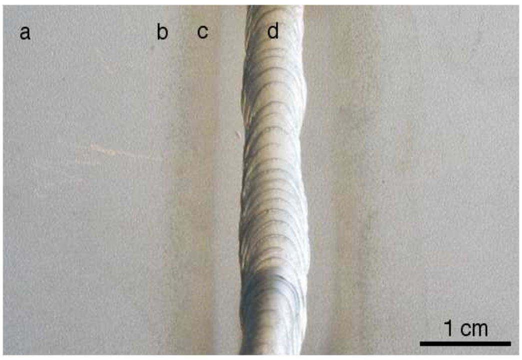

Fig. 6: Stainless steel 1.4432 with slight yellow heat tint (c). Measurements were performed on the bulk (a), the clean HAZ (b), the yellow HAZ (c) and the weld (d).

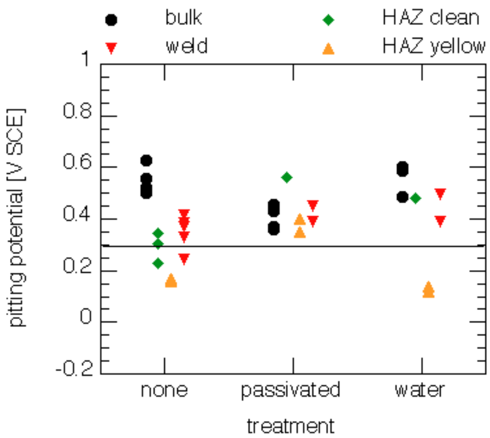

Fig. 7: Pitting potentials determined with the Test.Clinox on 1.4432 in 1 M NaCl on different areas after different post treatments.

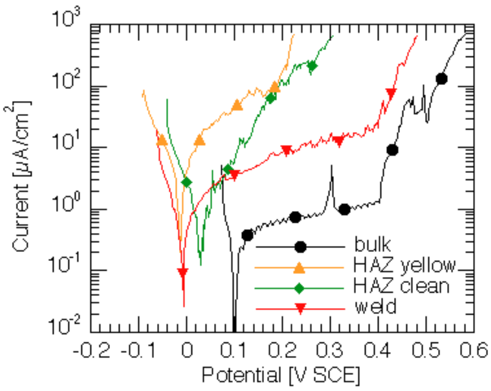

Fig. 8: Polarization scans on different areas on 1.4432 in 1 M NaCl recorded with the potentiostat.

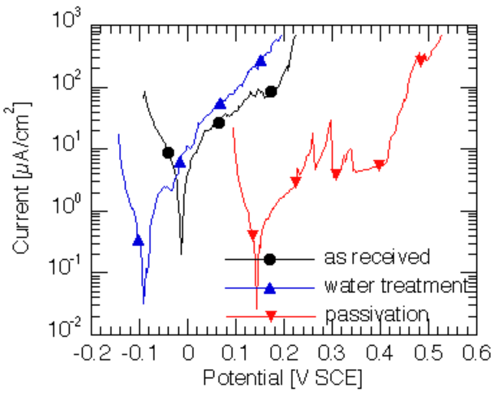

Fig. 9: Polarization scans on the yellow heat tint in the HAZ on 1.4432 in 1 M NaCl recorded with the potentiostat.

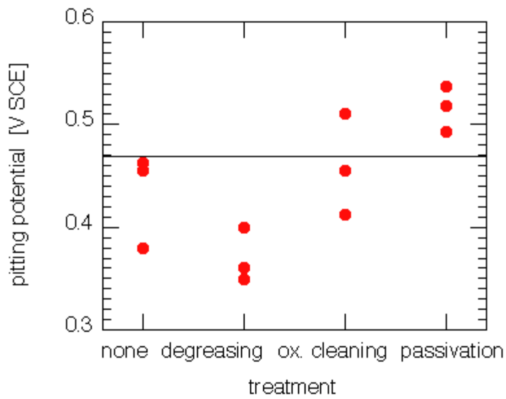

Fig. 10: Pitting potentials determined with the Test.Clinox on 1.4401 in 1 M NaCl on different areas after different post treatments.