A new electrochemical sensor: The ec-pen in industrial applications

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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 was developed that allows 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. Results of investigations in research and development are presented.

Zusammenfassung

In zahlreichen technischen Anwendung ist die Kenntnis des lokalen elektrochemischen Verhaltens erforderlich für das Verständnis der beteiligen Mechanismen. Diese Information hilft das Korrosionsverhalten von Werkstoffen zu verstehen, das Korrosionsrisiko von spezifischen Inhomogenitäten zu bestimmen und Massnahmen für eine verbesserte Korrosionsbeständigkeit zu entwickeln. Es wurde ein elektrochemischer Sensor entwickelt, welcher die schnelle und einfache Bestimmung von lokaler elektrochemischer Information ermöglicht. Einfache Handhabung, kurze Probenvorbereitungszeit und die Möglichkeit Experimente an beliebige grossen Objekten mit unterschiedlichster Oberflächengeometrie auszuführen, eröffnet ein grosses Feld von Applikationen. Ergebnisse von Untersuchungen in Forschung und Entwicklung werden gezeigt.

Résumé

Dans de nombreuses applications des techniques pour la connaissance du comportement électrochimique local sont nécessaire pour la compréhension des mécanismes impliqués. Cette information aide à comprendre le comportement de corrosion des matériaux, à évaluer le risque de corrosion d'inhomogénéité spécifique, et à concevoir des mesures de réduction en vue de l'amélioration de la résistance à la corrosion. Par conséquent, on a développé une sonde électrochimique qui permet l'accès rapide et facile à l'information électrochimique locale. La manipulation facile, le temps court de préparation de

l'échantillon et la possibilité de courir des expériments sur pratiquement n'importe quel objet de taille avec de divers geometries extérieurs ouvre un vaste champ des applications. Des résultats des investigations dans la recherche et le développement sont présentés.

INTRODUCTION

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 inhomogeneities, and to design mitigation measures for the improvement of the corrosion resistance. In recent work locally resolving electrochemical techniques were developed allowing the determination of local electrochemical properties down to the nanometer range [1-5]. A significant improvement of the understanding of the mechanisms involved has been achieved. These techniques are focussed on highest resolution and involve significant experimental effort. Nevertheless, the determination of the lateral distribution of electrochemical properties is also of interest in industrial applications with such as quality control and development. Hence, an electrochemical sensor was developed that allows fast and easy access to local electrochemical information.

The sensor does not require any rubber seal to avoid leaking of the electrolyte. Instead the electrolytic contact is established by a porous polymer body, which prevents the electrolyte from leaking. Therefore, it is possible to scan surfaces with a simple manipulator. 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. Results of investigations in research and development are presented.

EXPERIMENTAL

The electrochemical sensor

The new electrochemical sensor, the so-called ec-pen, was developed for electrochemical testing in industrial applications. This robust device is easy to handle and is equipped with integrated electrodes and the testing solution. Therefore, the ec-pen can be used on large objects for the fast determination of the corrosion resistance. (Fig. 1 and 2). 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 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.

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.). The scanning of the ec-pen over the surface is possible with two computer controlled motors allowing for two-dimensional positioning. A more detailed description of the experimental set-up is given in [6] and [7].

For the on site testing, a mobile electrochemical control unit developed in cooperation with Nitty Gritty GmbH was used. The internal logic of the instrument provides information about the corrosion resistance of the characterized surface.

Sample material

The aluminum samples (machined out of a rolled plate material) were made of AlMg4.5Mn0.7 (EN AW-5083). They were treated with Alodine 1500 and 1200s according

to the procedure of BWB Altenrhein. The electropolished samples consist of stainless steel DIN 1.4301. They were polished according to the procedure of BWB Altenrhein in an electrolyte containing sufphuric acid, phosporic acid and a special additiv.The welded samples were obtained from different sources. The DIN 1.4571 and the welded components in DIN 1.4301 were provided by Nitty Gritty GmbH. The electrochemical cleaning was performed with the Clinox (Nitty Gritty GmbH).

For the preparation of thermally sprayed coating commercially available Ni powders in a size range appropriate for each spraying technique were used as feedstock materials. As substrates quadratic pieces of mild steel with the dimensions 25 x 25 x 5 mm were used for all samples. After chamfering the edges and grit blasting the substrates were coated by vacuum plasma (VPS) - and flame spraying (FS). In order to obtain comparable results during the salt spray test and the electrochemical investigations, all coatings were ground on a magnetic table to a uniform thickness of approx. 350 µm resulting in a flat surface of a uniform waviness. Subsequently, the samples were polished and ultrasonically cleaned to open up pores, which may be smeared during the grinding process. The substrate and the borders were sealed by an epoxy resin in such a way that only a well defined, square shaped area of 20 x 20 mm of the coating is exposed to the atmosphere. In between the preparation steps mentioned above samples were cleaned in ethanol in an ultrasonic bath and dried in a vacuum oven to avoid to choke the open connected porosity. Detailed microstructural characterization of the obtained systems are given in [8] and [9].

RESULTS AND DISCUSSION

Characterization of aluminum surface treatments

A common surface treatment to increasing the corrosion resistance of aluminum alloys is based on chromates. However, there are increasing environmental concerns regarding the use of chromates and restrictions are expected. Hence, industry requires techniques for the fast control of the corrosion resistance of components and the efficiency of the used procedures. Some processes in surface treatment show a significant influence of sample geometry and therefore it is crucial that the characterization of the corrosion resistance is performed on the original working piece and not on specifically prepared samples.

The result of a surface treatment with two Alodine solutions is shown in Fig. 3. It is clear that the Alodine 1200s, which has a high chromate content results in a significantly decreased passive current density over a wide potential range. Even at elevated potentials, where additional growth of the passive film is observed, no pitting corrosion is initiated. In comparison, the Alodine 1500 shows a significantly higher passive currrent density demonstrating the less passivating effect of this solution. At slightly elevated potentials pitting corrosion is observed. The resistance against localized corrosion is not significantly higher than the one of the non-treated surface. Hence, the Alodine 1500 treatment does not represent a possible replacement for the Alodine 1200 treatment. Based on the obtained results it is clear that the ec-pen allows for fast testing of the susceptibility against pitting corrosion. It is therefore used for optimizing process parameters and quality control during production.

Electropolishing of stainless steel

Electropolishing is a well-known procedure for increasing not only the optical properties of stainless steel, but also its corrosion resistance. In order to adjust the process parameters and optimize polishing time a series of polarization curves was run on stainless steel DIN 1.4301. The summary of the obtained results is shown in Fig. 5, while Fig. 4 shows single polarization curve. It is clear from Fig. 5 that an increasing polishing time results in an increased pitting potential. From the single curves (Fig. 4) it can be concluded that the

increased polishing time decreases the height of the metastable pitting events. Additionally the open circuit potential is shifted to higher values. Apparently the increased polishing time results in an increased dissolution of heterogeneities on the surface, as e.g. MnS inclusions, which can function as initiation sites of the metastable pitting. Based on the obtained results it can be concluded that already short polishing times can improve the corrosion behavior. Nevertheless, for maximum improvement longer times are required. Based on the obtained results the primary cause might be the decreased number of inclusions that function as initiation sites for pitting corrosion [4].

Pickling of stainless steel

Pickling is a common procedure for removing oxide layers, which formed on the stainless steel surface during the welding process. The use of the pickling paste involves highly aggressive acids as HF. Insufficient cleaning and neutralization of these acids prevents the formation of a protective new passive film. Corrosion problems after pickling showed clearly that the process had to be modified. The polarization curve of the stainless steel DIN 1.4571 1 week after pickling showed clearly (Fig. 6) that the open circuit potential is very low and that the passive current density is extraordinary high. Both effects demonstrate the lack of a protective passive film on the surface. In order to form a stable passive film the sample was treated in 5% HNO_3. This resulted in a significant decrease in the passive current density showing the formation of a significantly more protective passive film. However, the treatment of the weld with tap water of a carbonate hardness of 14.6 °f resulted in an even better behavior. Based on this observation it can be concluded, that the neutralization of the acids present in the pickling paste with the calcium bicarbonate buffer present in ordinary tap water in combination with the dissolved oxygen is significantly more efficient than the passivation in HNO_3. Therefore, the optimization of the process parameters is possible based on a few simple measurements.

Welds on stainless steel

A unique property of the ec-pen is the possibility to scan it over surfaces. Hence, the lateral distribution of the corrosion properties can easily be determined. The possibilities of this technique are demonstrated in a few examples.

In Fig. 7 the potentiostatic linescan over a weld of a storage tank of C2 nickel base alloy is shown. It is clear that pitting corrosion is initiated within the heat affected zone of the weld, while the weld itself and the base material exhibit a good corrosion resistance. These tanks indeed turn out to be susceptible to local corrosion attack in the heat affected zone when used for storage of sulfuric acid in chemical industry. Hence, it is possible to optimize welding parameters based a fast test.

Another example is the linescan over a weld of DIN 1.4301 (Fig. 8). The potentiostatic linescan reveals the initiation of local corrosion attack on the oxide layers, which formed in the heat affected zone. These were removed and the surface passivated by an electrochemical treatment with ac-current on part of the sample surface. Then the scanning was repeated in a two dimensional scan showing the lateral distribution on the entire sample surface (Fig. 9). The result of the two dimensional scan demonstrates clearly that the lower left side of the sample which has been treated shows passive behavior, while the non treated upper right side shows pit initiation along the weld.

Characterization of thermally sprayed coatings

The possibility of determining the lateral distribution of electrochemical properties on a two dimensional surface offer a vast field of applications.Thermally sprayed coatings are often used for corrosion protection. However, local defects in the coating, such as irregularities in pore size, cracks and delamination result in the formation of a low resistant electrolytic path to the substrate, where corrosion reactions can occur. These areas with

electrolytic contact to the mild steel substrate can readily be detected with the scanning electrochemical technique. This is illustrated by the results obtained on Ni coatings sprayed on mild steel with different spraying techniques. It is clear, that the Ni coating prepared by flame spraying shows a comparably low background current (Fig. 10). Additionally, areas with increased current density are observed. They consist of rather spread areas with an average current density and highly localized peaks with a current density exceeding the detection limit of 5 µA of the data acquisition system in the given experimental configuration. These findings are compared with the Ni coating prepared by vacuum plasma spraying. This different preparation technique resulted in an altered electrochemical behavior. Besides the low and homogeneous background current only single localized maxima were found (Fig. 11). No spread out areas with increased current density were observed, demonstrating both a different structure and distribution of the defects in the coating.

The ec-pen not only allows to obtain information about the distribution of defects and their position on sprayed coatings within a few tens of minutes, but also the easy and fast quantitative evaluation and comparison of the results obtained with different systems. Hence, the new characterization technique allows for fast and easy comparison of different systems prepared with different parameters and efficient differentiation between the various systems. Optimization can easily be performed as the time for characterization is short allowing for a fast feedback and significantly decreased development times.

In order to establish the ec-pen for the characterization of spray coatings the investigated samples were exposed to the salt spray test. The results were evaluated by photographs recorded after 700 hours and by the accumulated damage distribution acquired according to DIN 50 021. The results of 700 hours of salt spray test are compared to the data obtained with the scanning electrochemical cell and a good correlation was found [7].

The use of the ec-pen in field applications

Up to now the quality control of the corrosion resistance of welded components was generally limited to visual inspection. The welding process results often in a decrease of the corrosion resistance of the material and the weld itself. However, the desired corrosion resistance can only be achieved with the correct choice of material and a high quality in welding and cleaning. Otherwise, failure of the stainless steel component can occur within short time. In order to guarantee the required corrosion resistance, a quality control is necessary with suitable testing procedures. The look of the weld, the presence of defects and discolorations are the essential criteria used so far. In some cases the determination of the δ-ferrite content was used to obtain information about the possible corrosion resistance. However, 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. Especially on safety relevant components in the chemical industry the corrosion resistance of the weld is critical. Nevertheless, the durability of installations has to be assured also in numerous other applications to justify the high investments. Up to now there was no testing procedure available, which allowed for a direct, quantitative, and non-destructive characterization of large components under industrial conditions.

In contrast, there is a large amount of experience with electrochemical testing from research work under laboratory conditions. However, the application of these techniques in industrial applications failed because of the high experimental effort involved in setting up the electrochemical cell. With the ec-pen the direct determination of the corrosion behavior of complete components of any size and surface geometry is possible as is shown in the figures 4 to 9. Nevertheless, not only an electrochemical sensor, but also an electrochemical control device is required in order to run electrochemical tests in field applications. Therefore, a potentiostat was developed with a controlling processor, that allows to

determine the pitting potential of stainless steel components and to run comparative tests (Fig. 12). Hence, the direct determination of the corrosion resistance of stainless steel components is possible, allowing for detection of non visible defects in the weld which affect the corrosion resistance.

CONCLUSIONS

The ec-pen opens a new field to electrochemical investigations. Its extraordinary easy handling significantly decreases the experimental effort for running electrochemical tests resulting in significantly increased throughput and decreased costs. The measurements are independent on sample size, orientation and surface geometry. Therefore, sample preparation is obsolete and experiments can be run in a nondestructive way. A significant improvement compared to conventional electrochemistry is the possibility to scan the ec-pen over surfaces to obtain information about the lateral distribution of the electrochemical properties. Contrary to other scanning techniques the sample is not completely immersed in the electrolyte and the wetting of the surface is only restricted to a comparably small surface area.

Currently the system is not suited for the use of concentrated acids and bases. Modification of the currently used components is subject of current work.

The combination of the ec-pen with a portable electrochemical control device offer new perspectives in the quality control. The evaluation of the corrosion resistance of welds, the efficiency of mitigation measures, the quality of surface treatments and the optimization of process parameters is possible by means of a comparably small and simple instrument.

ACKNOWLEDGEMENTS

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

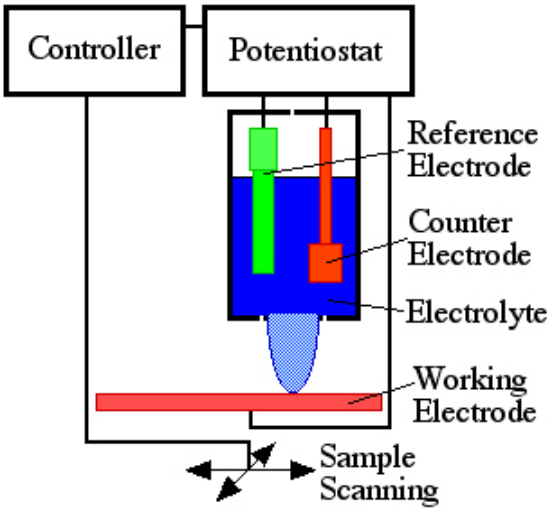

Fig. 2: Scheme of the experimental setup for the electrochemical mapping

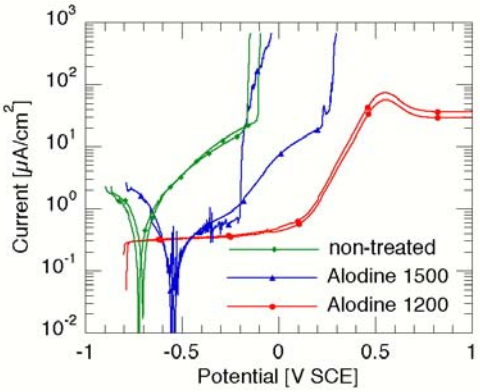

Fig. 3: Polarization curves at rate of 10 mV/s of AlMg4.5Mn0.7 in 0.1 M Na_2SO_4, 0.01 M NaCl.

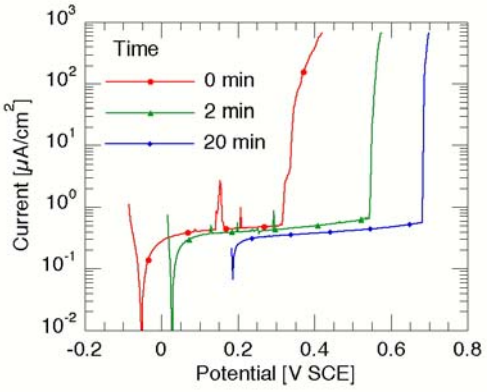

Fig. 4: Polarization curves at rate of 10 mV/s of stainless steel DIN 1.4301 electropolished for various times in 1 M NaCl.

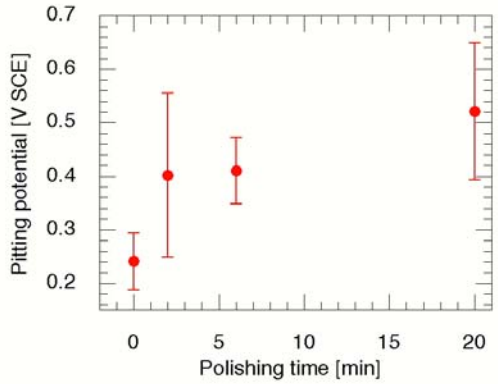

Fig. 5: Pitting potential of stainless steel DIN 1.4301 as a function of polishing time in 1 M NaCl.

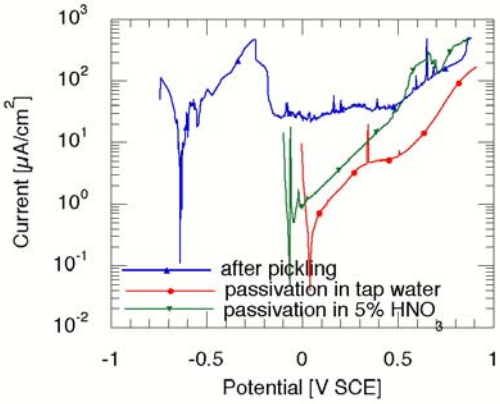

Fig. 6: Polarization curves at rate of 10 mV/s of stainless steel DIN 1.4571 electropolished for various times in 0.1 M NaCl.

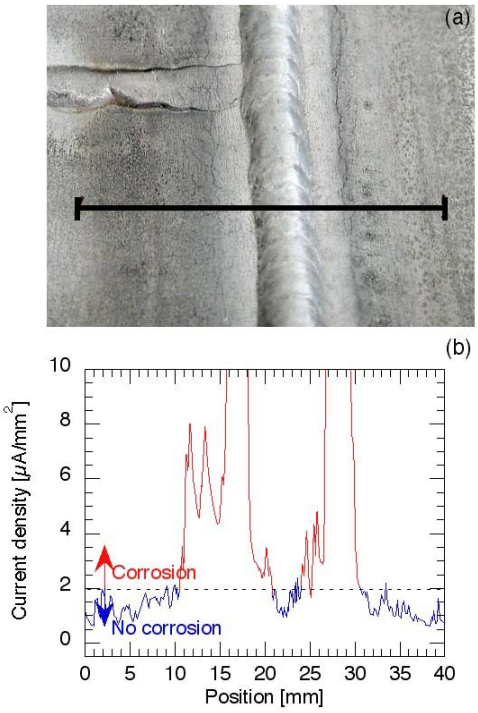

Fig. 7: Potentiostatic line scan over a weld of a nickel base alloy (C22) in 0.1 M NaCl at 360 mV SCE. (a) investigated area of 40 mm length; (b) result.

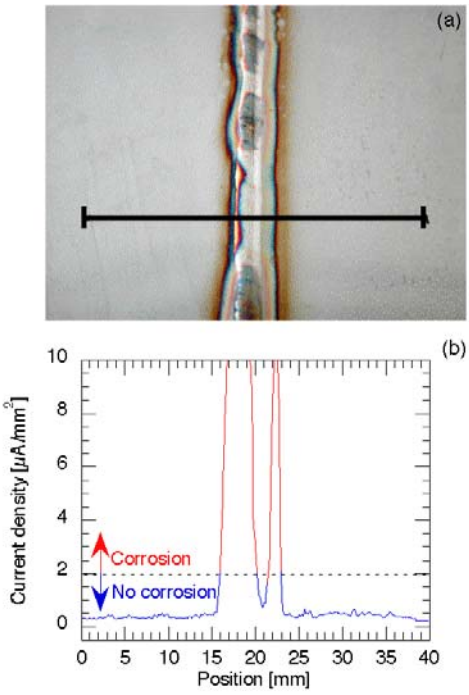

Fig. 8: Potentiostatic line scan over a weld of a stainless steel (DIN 1.4301) in 0.1 M NaCl at 260 mV SCE. (a) investigated area of 40 mm length; (b) result.

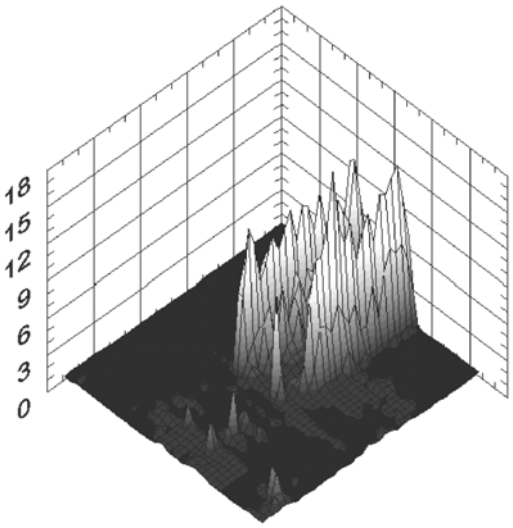

Fig. 9: Potentiostatic current [µA] distribution on a weld on DIN 1.4301 at 0.3 V SCE in 0.1 M NaCl over an area of 30 x30 mm.

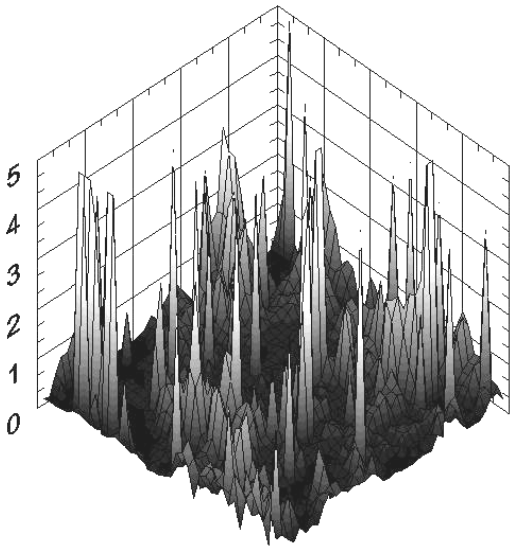

Fig. 10: Potentiostatic current [µA] distribution on FS Ni coating recorded at 0.16 V SCE in 0.1 M $NaNO_3$ over an area of 18 x18 mm. The tip area was 0.1 mm^2.

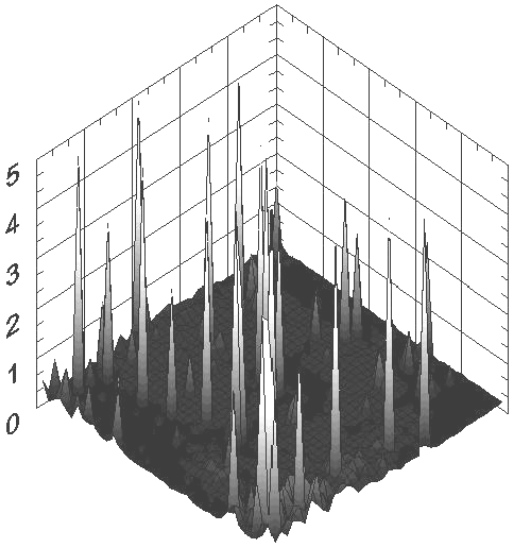

Fig. 11: Potentiostatic current [µA] distribution on VPS Ni coating recorded at 0.16 V SCE 0.1 M $NaNO_3$ over an area of 18 x18 mm. The tip area was 0.1 mm^2

Fig. 12: Handheld instrument for quality control of welds on stainless steels.