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(54) RAPID NON-DESTRUCTIVE EVALUATION OF THE DEGREE OF SENSITIZATION IN STAINLESS STEELS AND NICKEL BASED ALLOYS

SCHNELLE ZERSTÖRUNGSFREIE BEURTEILUNG DES ALLERGISIERUNGSGRADES BEI EDELSTAHL UND LEGIERUNGEN AUF NICKELBASIS

ÉVALUATION RAPIDE NON DESTRUCTIVE DU DEGRÉ DE SENSIBILISATION DANS DES ACIERS INOXYDABLES ET DES ALLIAGES À BASE DE NICKEL

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Description

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to an apparatus and a method for evaluation of the degree of sensitization in stainless steels and nickel-based alloys. More precisely, the invention provides an apparatus and a method for detecting depletion of passivating elements, in particular due to formation of sigma phase or other deleterious phases in a stainless steel and nickel-based alloys at least containing one or more of the following alloying elements: aluminium (Al), chromium (Cr), cobalt (Co), molybdenum (Mo), nitrogen (N), nickel (Ni), copper (Cu), titanium (Ti) and tungsten (W). The invention also refers to a portable equipment for *in situ* evaluation of sigma phase content in stainless steel.

BACKGROUND AND PRIOR ART

[0002] WO 01/69198 A2 discloses assessing the presence of undesirable phases in a steel sample by monitoring the rate of increase of an anodising potential.

[0003] As used in this application, stainless steel is the common name for iron (Fe) compositions containing carbon (C) and alloying elements that increase the resistance to corrosion. The dominating alloying element in stainless steel is chromium (Cr) which forms a passivating chromium oxide layer on the surface of the steel when the chromium content amounts to at least about 11 % by weight (any reference to percentage of fractions made herein refers to percentage by weight if not otherwise stated). Beside chromium, other alloying elements are usually added in order to achieve a desired property, such as resistance to acids, malleability and hardening capacity, e.g. Without excluding any potential alloying element from the general definition of stainless steel as it is used herein, some of the typical alloying elements in stainless steel, beside chromium, are molybdenum (Mo), nitrogen (N), nickel (Ni), copper (Cu) and tungsten (W), which can be added in varying amounts and combinations. The present invention can be applied to iron compositions at least containing one or more of the above mentioned alloying elements.

[0004] Further as used in this application, nickel-based alloys refer to solid-solution and precipitation hardened nickel-based alloys and nickel-based super alloys. The nickel (Ni) content typically amounts to about 50% by weight or more in composition with other elements such as chromium (Cr), cobalt (Co), aluminium (Al), titanium (Ti), e.g. Nickel-based alloys provide high temperature strength and oxidation resistance, which makes these alloys useful in parts and components for the oil and gas industry, in pumps, valves, piping and process equipment, in vehicles, spacecraft, ships and submarines, in electric motors, nuclear plants, heat exchangers tubing.

[0005] The present invention can further be applied to steel compositions of different crystalline structure including:

- Martensitic and super martensitic stainless steel (chromium content of about 11-18 % and carbon amounting to 0.1-1.2 %)
- Ferritic and super ferritic (or highly alloyed) stainless steel (chromium content of about 11-30 % and carbon below 0.1 %)
- Austenitic and super austenitic stainless steel (chromium content of about 8-30 %, nickel 4-10%, molybdenum 1-8%, and carbon usually below 0.05 %)
- Ferritic-austenitic stainless steel, also referred to as duplex stainless steel (DSS) and super duplex stainless steel (SDSS) (chromium content 20-25%, nickel content 4-8%, N 0.10-0.30%, Mo 1-4%, W 0-3.5%,Cu 0-3%, and carbon below 0.03 %)
- Precipitation hardening stainless steels: these steels can be matrensitic, austenitic, or a combination. These steels can be hardened by heat treatment.

[0006] Among the stainless steels, the DSS and SDSS steel grades are of special importance in engineering and construction given their good combination of strength and corrosion resistance. The two-phase ferritic-austenitic micro structure composition with a ferrite to austenite ratio of about 35-55 % in the DSS or SDSS steel qualities combines high strength with good workability and welding properties. Together with the ability to resist corrosion in a variety of aggresive environments these engineering qualities make the DSS and SDSS steels suitable for employment in, for example, seawater applications and in subsea engineering structures, vehicles at land and sea, air and space craft, power plants, process industry and in chemical applications.

[0007] Stainless steel, and in particular DSS and SDSS are, however, susceptible to the precipitation of deleterious phases when subjected to a critical temperature for a certain amount of time, such as the temperatures reached during welding. Precipitation of intermetallic phases that are not the matrix or the alloy as it is normally used affect both mechanical properties and corrosion resistance. A high content of chromium and molybdenum can promote the precipitation of intermetallic phases such as sigma phase, chi and chromium nitrides (Cr_2N) when subjected to temperatures in the range of 300-900° C. Among the deleterious phases, sigma phase is considered the most detrimental. Sigma phase is an intermetallic compound rich in chromium and molybdenum with a volume fraction that is larger than that of any other precipitated intermetallic phase. Precipitation of sigma phase depleates chromium and molybdenum from the surrounding ferritic-austenitic matrix, causing locally a weakening of the corrosion resistance ultimately leading to pitting or crevice corrosion.

[0008] Since the phase transformation kinetics of sigma phase is relatively fast, taking less than 1.8 minutes at 870° C for the onset of sigma phase precipitation, the content and volume fraction of sigma phase precipitates can serve as an indicator of the status of the corrosion resistance of a stainless steel structure.

[0009] However, evaluation of sigma phase content in a stainless steel sample using known and standardized methods requires that the microstructure is exposed by sectioning, polishing or etching, such as required in following the international standards ASTM A923 and ASTM E562 which include 24h corrosion tests, impact toughness measurements, and systematic manual point counting procedures for statistically estimating the volume fraction of an identifiable constituent or phase from sections through the microstructure using a microscope and a point grid.

[0010] US2008/179198 discloses a related apparatus using electrochemical impedance spectroscopy to determine corrosion rates in galvanically coupled systems.

SUMMARY

[0011] An object of the present invention is to provide a method and apparatus for non-destructive evaluation of the status of corrosion resistance in stainless steels and nickel-based alloys.

[0012] The object is met in the method and apparatus for detecting depletion of passivating elements, in particular due to the formation of sigma phase or other deleterious phases, in accordance with the accompanying claims.

[0013] The method and apparatus of the present invention can be applied to stainless steel and nickel-based alloys at least containing one or more of the following alloying elements: aluminium (Al), chromium (Cr), cobalt (Co), nickel (Ni), molybdenum (Mo), nitrogen (N), copper (Cu), titanium (Ti) and tungsten (W).

[0014] The method and apparatus of the present invention can be applied in a quality control procedure performed at any stage from the production of a steel ingot to the inspection of a structure or component before or after being put into operation.

[0015] The present invention provides an additional advantage by the fact that it can be applied *in situ* for detection of deleterious phases in the field.

[0016] In a first aspect of the present invention an apparatus in accordance with claim is provided.

[0017] In a second aspect of the present invention a method in accordance with claim 11 is provided.

[0018] Comparative tests have shown that the method and the apparatus of the present invention will unambiguously detect the presence of deleterious phases, in particular the presence of sigma phase which causes severe depletion of passivating elements from solid solution, leading to a sensitized microstructure and low pitting potential at the matrix/particle interface. When a sensitized microstructure is subjected to an acidic and oxidizing environment localized corrosion will initiate at areas with the lowest pitting potential. The open circuit potential Eoc is, then, controlled by the pitting potential of the Cr-Mo depleted region. Below the critical pitting temperature the Eoc of a solution annealed sample free of sigma phase is typically very high - mean value approximately 0.7 V vs. the saturated calomel electrode (SCE) used as reference in the tests. However, the presence of a sigma phase content as low as 0.5 % by volume decreases Eoc dramatically - mean value approximately 0.4 V vs. the SCE reference electrode. The drop in Eoc is a function of the sigma phase content and it is virtually instantaneous. Thus, the range of open circuit potentials Eoc can be used as a fast and accurate indicator for determining the degree of sensitization in a sample of stainless steel. The temperature of the test solution can vary between 20 to 85° C depending on the type of stainless steel in question.

[0019] The correlation between open circuit potential Eoc and, e.g., sigma phase content has been confirmed in cyclic potentiodynamic polarization tests in NaCl solutions and long term Eoc exposure using 6 % $FeCl_3$ (pH 1.10) as electrolyte. The test results are demonstrated in the accompanying diagrammatic drawings.

[0020] In the drawings, Fig. 1 illustrates the change in Eoc in effect of a growing content of sigma phase precipitates in a 25Cr super duplex stainless steel test specimen. Fig. 2 illustrates the difference in Eoc over time in a 0.5 vol. % sigma phase test specimen relative to the measured Eoc of a sigma phase free (solution annealed) control specimen. The steel used in the tests was of Figs. 1 and 2 UNS S32750 which is a ferritic-austenitic SDSS grade steel often used, among other components, in subsea pipelines, forged and hot isostatically pressed connectors, as well as small bore tubing and bolting. The test tempeature of this example was 50° C.

[0021] Statistical analysis performed on the same steel shows that the sigma phase free and the 0.5 vol. % sigma phase containing samples display non-overlapping density functions that define two distinctly separated distribution areas, see Fig. 3. The distinctive distributions of Eoc provide further empirical basis for relying on the correlation between open circuit potential Eoc and sigma phase content in the method and apparatus of the present invention.

[0022] Embodiments of the apparatus comprise a number of advantageous features which can be applied separately or in different combinations. Among the features which characterize embodiments of the apparatus are, briefly stated:

An electrolyte including an acidic chloride solution, preferrably ferric chloride ($FeCl_3$) or any other oxidising agent of similar polarization capacity.

[0023] A container wherein the specimen interface is arranged in a lower end.

[0024] A tubular container wherein the container diameter is dimensioned to retain the electrolyte within the tubular container through capillary action.

[0025] A tubular container being a micro-capillary tube having an inner diameter in the range of 0.05-5.0 mm, preferably in the range of 0.05-0.5 mm.

[0026] A specimen interface comprising a perforated or porous membrane in the lower end of the container.

[0027] A positioning means in the form of a circumferential sleeve extending beyond the lower end of the container, a lower end of the sleeve providing a base for standing the container on the surface of a test specimen.

[0028] A perforated or porous membrane arranged inside a surplus length portion of the sleeve of the positioning means.

[0029] A positioning means with a standing base carrying a glue or an adhesive on its lower side that permits temporary attachment to the test specimen.

[0030] A reference electrode in the form of a wire extended into the container/tube from a sealed upper end of the container/tube.

[0031] A reference electrode in the form of a silver wire coated with silver chloride (Ag/AgCl electrode) or a pure tungsten (W) wire.

[0032] A set of containers with reference electrodes individually connected to separate inputs of a multichannel voltmeter via a terminal block and a coupling interface.

[0033] A positioning means arranged as holder for the reference electrodes and preferably also for the terminal block and coupling interface.

[0034] A resistive heating element and a thermocouple may be installed in order to vary and control the temperature of the electrolyte.

[0035] In analogy herewith the present invention also relates to a portable equipment for *in situ* evaluation of deleterious phase content in stainless steels or nickel-based alloys comprising an apparatus according to any previous embodiment, wherein the reference electrode is associated with a positioning means for temporary locating the reference electrode in a measuring point on a test specimen.

[0036] An alternative embodiment of the portable equipment comprises a positioning means arranged for accommodation of a number of reference electrodes for the simultaneous positioning of an array of reference electrodes on the test specimen.

[0037] The portable equipment may further comprise a processing unit, a display and a printer or plotter.

[0038] Embodiments of the method comprises a number of advantageous steps which can be applied separately or in different combinations. Among the steps which characterize embodiments of the method are, briefly stated:

the step of repeating step iv) until the whole test specimen or the area of interest is examined, and generating, based on the sum of readings, an estimate of the amount of deleterious phase content in the test specimen using a calibration curve mapping the correlation between Eoc and deleterious phase content in the material of the test specimen;

- the step of preparing, for the alloy of the test specimen, a calibration curve covering EOC vs. deleterious phase content down to a deleterious phase content of 0.5 % by volume, or less;

- the step of providing a capillary or a micro-capillary tube containing the reference electrode submerged in the electrolyte, and scanning the test specimen for mapping of deleterious phase content at a spatial resolution in the range of 0.05 to 5.0 mm, preferably in the range of 0.5-0.05 mm;

- the step of preparing an electrolyte gel containing ferric chloride ($FeCl_3$) at 1 to 6 % by weight;

- the alternative step of preparing an electrolyte gel containing other acidic and oxidizing chloride solution that produces a potential equal to or above that of ferric chloride ($FeCl_3$);

- the step of providing the reference electrode in the form of an Ag/AgCl wire electrode or a pure tungsten (W) electrode or any other suitable reference electrode;

- the step of forming an array of reference electrodes, and reading and recording a matrix of E_{OC} values through a multichannel voltmeter;

- the step of applying the method in a quality control procedure;

- the step of applying the method *in situ* for sigma phase detection in the field.

SHORT DESCRIPTION OF THE DRAWINGS

[0039] Embodiments of the method and apparatus of the present invention will be further explained in the following with reference made to the accompanying schematic drawings. In the drawings

Fig. 1 is a diagram showing the correlation between Eoc and the fractional amount of sigma phase precipitates in a test specimen,

Fig. 2 is a diagram showing the difference in Eoc over time in a 0.5 vol. % sigma phase 25Cr super duplex stainless steel specimen relative to the measured Eoc of a sigma phase free (solution annealed) control specimen,

Fig. 3 is a diagram displaying non-overlapping distribution areas in statistical analysis of E_{OC} of the sigma phase-free and the 0.5 vol. % sigma phase containing samples of Fig. 2,

Fig. 4 is a diagram showing the difference in Eoc over time in a sensitized nickel-based alloy specimen relative to the measured Eoc of a control specimen,

Fig. 5 illustrates schematically the configuration of an apparatus designed for carrying out the method of the present invention,

Fig. 5b is a partial view showing an alternative embodiment of a positioning means employed in the apparatus of the present invention,

Fig. 6 is a schematic illustration of an alternative configuration of the apparatus,

Fig. 7 is a 2-dimensional plot illustrating the area distribution of sigma phase precipitates in a test specimen, and

Fig. 8 is a 3-dimensional plot illustrating the spatial distribution of sigma phase precipitates in a test specimen.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0040] Figs. 1-3 have been discussed hereinabove under the subtitle Summary of the invention.

[0041] In addition to what is already discussed with reference to Fig. 1 it shall be further noted that the functional correlation between Eoc values and fractions of sigma phase precipitates as confirmed and shown by the plotted diagram of Fig. 1 is used in the invention for calibration of the test equipment and method. For the UNS S32750 steel, the curve connecting the plotted Eoc values in Fig. 1 demonstrates the functional correlation between sigma phase concentration and open circuit potential Eoc down to a sigma phase concentration of 0.5 % by volume (the curve portion connecting the Eoc values of 0.5 vol. % sigma phase with the values of the sigma phase free sample is an estimate).

[0042] In a corresponding way calibration curves can be established for other stainless steel families as well as for other corrosion resistant alloys, and used for reading out sigma phase or other deleterious phase concentrations based on measured Eoc values.

[0043] In this connection, it should be emphasized that the invention can be applied for detection and evaluation of other deleterious phases than sigma phase, such as chromium nitride and carbides etc., all of which deplete Cr and Mo from solid solution and lower the pitting potential of the affected area in the microstructure. The localized Cr and Mo depletion, in turn, lowers the open circuit potential of the test specimen.

[0044] In precipitation hardening nickel-based alloys, precipitation of deleterious phases such as nanometre-sized sigma phase at grain boundaries, leads to a similar drop in open circuit potential as demonstrated above for stainless steel. Fig. 4 illustrates the development of Eoc over time in a sensitized test specimen relative to the measured Eoc of a control specimen free of deleterious phases. The test illustrated in Fig. 4 was performed on nickel-based alloy UNS NO7725 which is a precipitation hardened material of extreme high strength, i.e. 120 Ksi yield strength, containing 50.0-59.0% wt. nickel, 19-22.5% Cr, 7.0-9.5% Mo, 2.75-4.0% Nb, and 1.0-1.7% Ti.

[0045] With reference to Fig. 5 an apparatus for exercising the method of the present invention comprises a reference electrode 1 which is inserted in a container 2 containing an electrolyte 3. The electrolyte 3 comprises a liquid or gelatinized oxidising agent by which the reference electrode 1 can be put in electrochemical contact with a test specimen 4. A voltmeter 5 is electrically connected between the test specimen and the reference electrode via conductors 6 and 7. It should be noted that for ease of reading and understanding the representation of Fig. 5 is not true to scale.

[0046] The voltmeter 5 can be an off-the-shelf instrument known as a potentiostat or galvanostat by which the potentials of the reference electrode and test specimen can be frequentially monitored and varied by application of a current through the electrolyte in a polarization scanning procedure as is known *per se.* The voltmeter is associated with a data processing unit 8 via a data bus. The data processing unit 8 is operational for receiving, processing, storing and displaying data recorded by the voltmeter. The voltmeter 5 and processing unit 8 form parts of a network, by wire or wireless, including at least a display 9 and a printer or plotter 10 by which the results of the scanning procedure can be presented in the form of plots, tables, data maps etc., as desired. Some or all of the operational units such as the voltmeter, the processor, the display and the printer/plotter can be integrated in a portable equipment if convenient. Software and mobile applications can interface with the device as well as record and report the results.

[0047] The containerized electrolyte 3 is prepared from an acidic and oxidizing chloride solution, preferably including ferric chloride, $FeCl_3$, at a concentration of 1-6 % by volume and a pH value of about 1.0 to 1.20. Other oxidising agents may alternatively be used as the electrolyte in container 2, preferably any other oxidising agent which will polarize the test specimen to a potential similar to that of 1-6 wt. % $FeCl_3$.

[0048] In a preferred embodiment the reference electrode 1 is a miniaturized silver/silver chloride (Ag/AgCl) electrode or a pure tunsgten wire. Other electrodes with a stable and well-known electrode potential relative to the standard hydrogen electrode may be used as reference electrode in the apparatus of the invention. The preferred reference electrode 1 is prepared from a silver wire coated with silver chloride and inserted in the electrolyte 1 in a tubular glass or plastic container 2 of capillary or micro-capillary dimensions. In this context, the expressions capillary and micro-capillary refer to a tube with an inner diameter capable of retaining the electrolyte in the tube through capillary action. Depending on the viscosity of the liquid or gelatinized electrolyte the inner diameter d of a tubular container 1 may be in the range of about

0.05-5.0 mm, preferably in the range of 0.05-0.5 mm. For electric connection with external equipment the reference electrode is extended through a cap 11 which seals a first and upper end 12 of the container.

[0049] The container 2 has an open second and lower end forming a specimen interface 13 in the mouth of the container, through which the electrolyte with oxidising agent comes to contact with the surface of the test specimen. A perforated or porous membrane 14 covers the specimen interface in said lower end. The membrane 14 may be realized as a sintered ceramic, glass or silica element, e.g.

[0050] A key feature of the present invention is the mobility of the apparatus for evaluation of sigma phase content and other deleterious phases in stainless steel and nickel-based alloys,thus mapping the status of corrosion resistance inthe material. The mobility makes the apparatus equally suitable for quality control procedures on bulk material as for evaluation of deleterious phase content in material and welded structures in the field.

[0051] For the purpose of temporary positioning and optionally attaching the container 2 onto the test specimen during a polarization test the container is equipped with a positioning means 15. Similar to the container 2, the positioning means 15 can be made in glass or plastic material insensitive to the acidic electrolyte 3. In the embodiment of Fig. 5 the positioning means 15 comprises a sleeve 16 with a circumferential wall and an inner periphery 17 that mates with the outer periphery 18 of the container. In mounted position on the container the sleeve extends beyond the lower end 13 of the container for a length l of a few mm, such as from about 5-15 mm. A radial shoulder 19 may be formed on the inner periphery of the sleeve to define the length of insertion of the container into the sleeve. The surplus length l of the sleeve may serve as a seat for fixation of the porous membrane 14.

[0052] The sleeve 16 may be shaped as a straight cylinder, in its lower end connected to a flange 20 that extends radially outside the sleeve as illustrated in Fig. 5. An alternative sleeve may have a conical wall, the larger radius of which forms a bottom end face 21 of the sleeve as illustrated in Fig. 5b. In both cases the positioning means 15 forms a standing base that provides added stability to the container when positioned on the test specimen.

[0053] The flange 20 and the bottom end face 21 each provides a base which can be formed planar for positioning the container on planar test surfaces as illustrated. This base can alternatively be curved for positioning the container on pipes, rods or other non-planar surfaces as shown in dash-dot lines in Fig. 5b.

[0054] A repositionable glue or adhesive 22 may advantageously be applied to the base of the positioning means for detachably attaching the positioning means and container with the reference electrode to the test specimen.

[0055] Albeit being disclosed as a separate element for mounting on the container 2, it will be understood that the positioning means 15 may optionally be realized as a structural part that is formed integrally with the container.

[0056] A heating element such as heat resistance wire e.g., may be wrapped about the container or inserted in the electrolyte in order to vary the temperature of the electrolyte if appropriate. A thermocouple may be arranged to control the temperature.

[0057] An alternative embodiment of the apparatus is schematically shown in Fig. 6. It should be noted that for ease of reading and understanding the representation of Fig. 6 is not true to scale. In the embodiment of Fig. 6 the reference electrode 1 is multiplied in a set of sensors, each sensor comprising a reference electrode in a container containing a liquid or gelatinized electrolyte. The reference electrodes 1 are individually connected to a multichannel voltmeter with a corresponding number of input terminals (voltmeter not shown).

[0058] The containers 2 and electrodes 1 are supported in a positioning means arranged as a holder 23 carrying a terminal block 24 that collects the electrode wires 25 and provides a coupling interface 26 towards the voltmeter. Feet 27 in the lower side of the holder 23 form a standing base that provides stability to the set of sensors when supported on the surface of a specimen during testing. In order to ensure electrolytic contact between the test specimen and each reference electrode, the containers are adjustable and movable in relation to the holder in the length direction of the containers. To this purpose the holder 23 is formed with a respective guiding slot 28 that provides a seat for accommodation of a container. Slide bearings 29 may be arranged in connection with the slots 28 in order to arrest the containers in mounted position through frictional engagement.

[0059] The holder 23 may be sized to provide an array of sensors/reference electrodes arranged in one row or in several parallel rows permitting simultaneous reading and recording of a matrix of Eoc values. Sensor arrays of other configurations than rectangular are of course possible.

[0060] The voltmeter records the Eoc vs time for a given time interval until a stable reading is obtained. By successively moving the apparatus over the area to be examined the degree of sensitization and distribution of sensitized areas of the test specimen can be mapped with a resolution determined by the diameter dimensions of the container and standing base of the positioning means, or by the diameter of the container and the interspace between adjacent containers in the sensor array. With regards to the sizes of micro-capillary tubes available for the purpose, embodiments of the invention comprise mapping of deleterious phase content at spatial resolutions in the range of 0.05 to 5.0 mm, preferably in the range of 0.5-0.05 mm.

[0061] For visual representation of the test result, the collected data can be presented in 2- or 3-dimensional plots. Fig. 7 is one example of a 2-dimensional plot illustrating the area distribution and concentration of sigma phase precipitates in a test specimen based on the range of recorded Eoc values. Fig. 8 is an example of a 3-dimensional plot illustrating the spatial distribution and concentration of sigma phase precipitates in a test specimen based on the range of Eoc values as recorded through the method and apparatus of the present invention.

[0062] The invention as illustrated and described provides the advantage of rapid and non-destructive testing of stainless steel and nickel-based alloys for detecting the occurrence of deleterious phases and for evaluation of the status of the corrosion resistance. Although the major benefits reside in the mobile application it should be noted that in alternative use a test sample may be exposed to the electrolyte in a quality control evaluation using test specimens in a destructive way. The listing below includes a majority of the corrosion resistent alloys to which the present invention can be applied:

1) Austenitic and super (also known as highly alloyed) austenitic stainless steels

UNS S31600 and S31603
UNS S30400 and S30403
UNS S31700
UNS S34500
UNS S32100
UNS S20910
Type 6Mo Stainless Steel (e.g. UNS S39254, J93254, N08367, N08925)
Type 7Mo UNS S32654
N08926
J95370

2) Duplex and super duplex stainless steels

Type 22Cr duplex stainless steels (UNS S31803, S32550)
Type 25Cr DSS or SDSS (UNS S32750, S32760, S39274, S39277)
Lean DSS (UNS S32101, S32304)

3) Ferritic and super (or highly alloyed ferritic) stainless steels

UNS S44400
UNS S43000
UNS S40900
UNS S40500
UNS S44700

4) Martensitic and super martensitic stainless steels

UNS S41000
UNS S41425
UNS S41426
UNS S41500
UNS S42500
UNS J91540
SM17CRS-12

5) Precipitation hardened stainless steels

UNS S66286
UNS S15500
UNS S17400
UNS S45000
UNS S15700

6) Solid-solution nickel based alloys

UNS N06625
UNS N06022
UNS N06059
UNS N06686
UNS N07022
UNS N08026
UNS N10276
CW12MW

7) Precipitation hardenable nickel based alloys

UNS N07718
UNS N07725
UNS N07716
UNS N09925
UNS N09945
UNS N06625
UNS N07626

[0063] Although it will be realized that in alternative use a test sample may be exposed to the electrolyte in a quality control using test specimens in a destructive way, the major benefits provided by the present invention reside in the mobile and non-destructive implementation.

Claims

1. An apparatus for detecting depletion of passivating elements, in particular due to formation of sigma phase and/or other deleterious phases, in stainless steels or nickel-based alloys at least containing one or more of the following alloying elements: aluminium (Al), chromium (Cr), cobalt (Co), nickel (Ni), molybdenum (Mo), nitrogen (N), copper (Cu), titanium (Ti) and tungsten (W), the apparatus comprising:

a container (2) containing a liquid or a gelatinized electrolyte (3),
a specimen interface (13) on the container, the specimen interface (13) in providing contact between the electrolyte and the surface of a test specimen,
a reference electrode (1) in the container, the reference electrode (1) in use being in electro-

chemical contact with the test specimen via the electrolyte,
a voltmeter (5), in use being electrically connected between the reference electrode and the test specimen, and whereby the apparatus is **characterised in**
a data processing unit (8) for reading and recording open circuit potential (Eoc) values at each testing point of the specimen and comparing the Eoc values of the test specimen with the open circuit potential of a sigma phase free sample of the steel of the test specimen

2. The apparatus of claim 1, wherein the electrolyte is an acidic chloride solution.

3. The apparatus of claim 2, wherein the electrolyte is ferric chloride ($FeCl_3$).

4. The apparatus of any previous claim, wherein the container (2) is a tube and the specimen interface (13) is arranged in a lower (second) end of the tubular container.

5. The apparatus of claim 4, wherein the container diameter (d) is dimensioned to retain the electrolyte within the container through capillary action.

6. The apparatus of claim 4 or 5, wherein the container is a micro-capillary tube having an inner diameter (d) in the range of 0.05-5.0 mm, preferably in the range of 0.05-0.5 mm.

7. The apparatus of any of claims 4 to 6, wherein the specimen interface (13) comprises a perforated or porous membrane (14) covering the specimen interface (13) in said lower end of the container.

8. The apparatus of any of claims 4 to 7, further comprising a positioning means (15) in the form of a circumferential sleeve (16) extending beyond the lower end of the container, a lower end (20; 21) of the sleeve (16) providing a base (20; 21) for standing the container (2) on the surface of the test specimen.

9. The apparatus of any of claims 4 to 8, wherein the reference electrode (1) is a wire extended into the tube from an upper (first) end (12) of the tube.

10. The apparatus of any preceding claim, comprising a set of reference electrodes (1) separately connectable to individual inputs of a multichannel voltmeter via a terminal block (24) and a coupling interface (26).

11. A method for detecting depletion of passivating elements, in particular due to formation of sigma phase or other deleterious phases, in stainless steels or nickel-based alloys at least containing one or more of the following alloying elements: aluminium (Al), chromium (Cr), Cobalt (Co), nickel (Ni), molybdenum (Mo), nitrogen (N), copper (Cu), titanium (Ti) and tungsten (W), the method comprising:

i) providing a container containing a liquid or gelatinized electrolyte (3),
ii) providing a reference electrode (1) in electrochemical contact with a test specimen via the liquid or gelatinized electrolyte (3),
iii) electrically connecting (6, 7) the reference electrode with the test specimen over a voltmeter (5),
iv) reading and recording open circuit potential (Eoc) values at each testing point of the specimen,
v) comparing the E_{OC} values of the test specimen with the open circuit potential of a sigma phase free sample of the steel of the test specimen.

12. The method of claim 11, further comprising:

repeating step iv) until the whole test specimen or the area of interest is examined, and
generating, based on the sum of readings, an estimate of the amount of deleterious phase content in the test specimen using a calibration curve mapping the correlation between E_{OC} and sigma phase content in the steel of the test specimen.

13. The method of claim 11 or 12, further comprising:

providing a container in form of a micro-capillary tube (2) containing the reference electrode (1) submerged in the liquid or gelatinized electrolyte, and
scanning the test specimen for mapping of deleterious phase content at a spatial resolution in the range of 0.05 to 5.0 mm, preferably in the range of 0.5-0.05 mm.

14. The method of any of claims 11 to 13, further comprising:
preparing an electrolyte gel containing ferric chloride ($FeCl_3$) at 1 to 6 % by weight.

15. A portable equipment for *in situ* evaluation of deleterious phase content in stainless steels and nickel-based alloys comprising an apparatus according to any of claims 1 to 10, **characterized in that** the reference electrode (1) is associated with a positioning means (15; 23) for temporary locating the reference electrode (1) in a measuring point on a test specimen.

Patentansprüche

1. Einrichtung zum Erkennen einer Depletion von Passivierungselementen, insbesondere aufgrund der Bildung einer Sigma-Phase und/oder anderer schädlicher Phasen, in Edelstählen oder Legierungen auf Nickelbasis, die mindestens eines der folgenden Legierungselemente enthalten: Aluminium (Al), Chrom (Cr), Kobalt (Co), Nickel (Ni), Molybdän (Mo), Stickstoff (N), Kupfer (Cu), Titan (Ti) und Wolfram (W), wobei die Einrichtung Folgendes umfasst:

einen Behälter (2), enthaltend eine Flüssigkeit oder einen gelatinierten Elektrolyten (3),
eine Prüfkörperschnittstelle (13) auf dem Behälter, wobei die Prüfkörperschnittstelle (13) während der Verwendung einen Kontakt zwischen dem
Elektrolyt und der Oberfläche eines Prüfkörpers bereitstellt,
eine Referenzelektrode (1) in dem Behälter, wobei die Referenzelektrode (1) während der Verwendung mit dem Prüfkörper
über den Elektrolyten in elektrochemischem Kontakt steht,
ein Spannungsmessgerät (5), das während der Verwendung
zwischen der Referenzelektrode und dem Prüfkörper elektrisch verbunden ist, und wodurch die Einrichtung **gekennzeichnet ist durch**
eine Datenverarbeitungseinheit (8) zum Lesen und Aufzeichnen von Werten eines offenen Schaltungspotenzials (E_{OC}-Werten) an jedem Prüfpunkt des Prüfkörpers und Vergleichen der E_{OC}-Werte des Prüfkörpers mit dem offenen Schaltungspotenzial einer Sigma-Phasen-freien Probe des Stahls des Prüfkörpers

2. Einrichtung nach Anspruch 1, wobei der Elektrolyt eine saure Chloridlösung ist.

3. Einrichtung nach Anspruch 2, wobei der Elektrolyt Eisenchlorid ($FeCl_3$) ist.

4. Einrichtung nach einem der vorstehenden Ansprüche, wobei der Behälter (2) ein Rohr und die Prüfkörperschnittstelle (13) in einem unteren (zweiten) Ende des rohrförmigen Behälters angeordnet ist.

5. Einrichtung nach Anspruch 4, wobei der Behälterdurchmesser (d) so bemessen ist, dass er den Elektrolyten durch Kapillarwirkung innerhalb des Behälters hält.

6. Einrichtung nach Anspruch 4 oder 5, wobei der Behälter ein Mikrokapillarrohr ist, das einen Innendurchmesser (d) im Bereich von 0,05-5,0 mm, vorzugsweise im Bereich von 0,05-0,5 mm aufweist.

7. Einrichtung nach einem der Ansprüche 4 bis 6, wobei die Prüfkörperschnittstelle (13) eine perforierte oder poröse Membran (14) umfasst, welche die Prüfkörperschnittstelle (13) in dem unteren Ende des Behälters abdeckt.

8. Einrichtung nach einem der Ansprüche 4 bis 7, ferner umfassend ein Positionierungsmittel (15) in Form einer Umfangshülse (16), die sich über das untere Ende des Behälters hinaus erstreckt, wobei ein unteres Ende (20; 21) der Hülse (16) eine Basis (20; 21) zum Aufstellen des Behälters (2) auf der Oberfläche des Prüfkörpers bereitstellt.

9. Einrichtung nach einem der Ansprüche 4 bis 8, wobei die Referenzelektrode (1) ein Draht ist, der sich von einem oberen (ersten) Ende (12) des Rohrs in das Rohr erstreckt.

10. Einrichtung nach einem der vorstehenden Ansprüche, umfassend einen Satz von Referenzelektroden (1), die getrennt mit einzelnen Eingängen eines Mehrkanalspannungsmessgeräts über einen Anschlussblock (24) und eine Kopplungsschnittstelle (26) verbindbar sind.

11. Verfahren zum Erkennen einer Depletion von Passivierungselementen, insbesondere aufgrund der Bildung einer Sigma-Phase oder anderer schädlicher Phasen, in Edelstählen oder Legierungen auf Nickelbasis, die mindestens eines der folgenden Legierungselemente enthalten: Aluminium (Al), Chrom (Cr), Kobalt (Co), Nickel (Ni), Molybdän (Mo), Stickstoff (N), Kupfer (Cu), Titan (Ti) und Wolfram (W), wobei das Verfahren Folgendes umfasst:

i) Bereitstellen eines Behälters, der einen flüssigen oder gelatinisierten Elektrolyten (3) enthält,
ii) Bereitstellen einer Referenzelektrode (1) in elektrochemischem Kontakt mit einem Prüfkörper über den flüssigen oder gelatinisierten Elektrolyten (3),
iii) elektrisches Verbinden (6, 7) der Referenzelektrode mit dem Prüfkörper über ein Spannungsmessgerät (5),
iv) Lesen und Aufzeichnen von Werten eines offenen Schaltungspotenzials (E_{OC}-Werten) an jedem Prüfpunkt des Prüfkörpers,
v) Vergleichen der E_{OC}-Werte des Prüfkörpers mit dem offenen Schaltungspotenzial einer Sigma-Phasen-freien Probe des Stahls des Prüfkörpers.

12. Verfahren nach Anspruch 11, ferner umfassend:

Wiederholen von Schritts iv), bis der gesamte Prüfkörper oder der Bereich von Interesse untersucht ist, und

Erzeugen, basierend auf der Summe von Messwerten, einer Schätzung der Menge des Gehalts an schädlichen Phasen in dem Prüfkörper unter Verwendung einer Kalibrierungskurve, welche die Korrelation zwischen Eoc und Sigma-Phasengehalt im Stahl des Prüfkörpers abbildet.

13. Verfahren nach Anspruch 11 oder 12, ferner umfassend:

Bereitstellen eines Behälters in Form eines Mikrokapillarrohrs (2) mit der Referenzelektrode (1), die in den flüssigen oder gelatinierten Elektrolyten eingetaucht sind, und

Abtasten des Prüfkörpers zum Abbilden des schädlichen Phasengehalts bei einer räumlichen Auflösung im Bereich von 0,05 bis 5,0 mm, vorzugsweise im Bereich von 0,5-0,05 mm.

14. Verfahren nach einem der Ansprüche 11 bis 13, ferner umfassend:
Herstellen eines Elektrolytgels, das Eisenchlorid ($FeCl_3$) bei 1 bis 6 Gew.-% enthält.

15. Tragbare Ausrüstung zur In-situ-Beurteilung des schädlichen Phasengehalts in Edelstahl und Legierungen auf Nickelbasis, umfassend eine Einrichtung nach einem der Ansprüche 1 bis 10, **dadurch gekennzeichnet, dass** die Referenzelektrode (1) einem Positionierungsmittel (15; 23) zum temporären Lokalisieren der Referenzelektrode (1) in einem Messpunkt auf einem Prüfkörper zugeordnet ist.

Revendications

1. Appareil permettant de détecter un appauvrissement en éléments de passivation, en particulier dû à la formation de phase sigma et/ou d'autres phases préjudiciables, dans des aciers inoxydables ou des alliages à base de nickel contenant au moins un ou plusieurs des éléments d'alliage suivants : aluminium (Al), chrome (Cr), cobalt (Co), nickel (Ni), molybdène (Mo), l'azote (N), cuivre (Cu), titane (Ti) et tungstène (W), l'appareil comprenant :

un récipient (2) contenant un électrolyte liquide ou gélatinisé (3),

une interface échantillon (13) sur le récipient, l'interface échantillon (13) lors de l'utilisation fournissant un contact entre l'électrolyte et la surface d'un échantillon de test,

une électrode de référence (1) dans le récipient, l'électrode de référence (1) lors de l'utilisation étant en contact électrochimique avec l'échantillon de test par le biais de l'électrolyte,

un voltmètre (5), lors de l'utilisation étant électriquement connecté entre l'électrode de référence et l'échantillon de test, et moyennant quoi l'appareil est **caractérisé en ce que**

une unité de traitement de données (8) permettant de lire et d'enregistrer des valeurs de potentiel en circuit ouvert (E_{OC}) au niveau de chaque point de test de l'échantillon et de comparer les valeurs d'E_{OC} de l'échantillon de test avec le potentiel en circuit ouvert d'un échantillon exempt de phase sigma de l'acier de l'échantillon de test

2. Appareil selon la revendication 1, dans lequel l'électrolyte est une solution de chlorure acide.

3. Appareil selon la revendication 2, dans lequel l'électrolyte est du chlorure ferrique ($FeCl_3$).

4. Appareil selon l'une quelconque revendication précédente, dans lequel le récipient (2) est un tube et l'interface échantillon (13) est agencée dans une (seconde) extrémité inférieure du récipient tubulaire.

5. Appareil selon la revendication 4, dans lequel le diamètre de récipient (d) est dimensionné pour retenir l'électrolyte à l'intérieur du récipient par effet capillaire.

6. Appareil selon la revendication 4 ou 5, dans lequel le récipient est un tube micro-capillaire ayant un diamètre interne (d) dans la plage de 0,05 à 5,0 mm, de préférence dans la plage de 0,05 à 0,5 mm.

7. Appareil selon l'une quelconque des revendications 4 à 6, dans lequel l'interface échantillon (13) comprend une membrane perforée ou poreuse (14) couvrant l'interface échantillon (13) dans ladite extrémité inférieure du récipient.

8. Appareil selon l'une quelconque des revendications 4 à 7, comprenant en outre un moyen de positionnement (15) sous la forme d'un manchon circonférentiel (16) s'étendant au-delà de l'extrémité inférieure du récipient, une extrémité inférieure (20 ; 21) du manchon (16) fournissant une base (20 ; 21) permettant de maintenir le récipient (2) debout sur la surface de l'échantillon de test.

9. Appareil selon l'une quelconque des revendications 4 à 8, dans lequel l'électrode de référence (1) est un fil étendu dans le tube à partir d'une (première) extrémité supérieure (12) du tube.

10. Appareil selon l'une quelconque revendication précédente, comprenant un ensemble d'électrodes de référence (1) pouvant être connectées séparément à des entrées individuelles d'un voltmètre multicanal par le biais d'un bornier (24) et d'une interface de couplage (26).

11. Procédé permettant de détecter l'appauvrissement en éléments de passivation, en particulier dû à la formation de phase sigma ou d'autres phases préjudiciables, dans des aciers inoxydables ou des alliages à base de nickel contenant au moins un ou plusieurs des éléments d'alliage suivants : de l'aluminium (Al), chrome (Cr), cobalt (Co), nickel (Ni), molybdène (Mo),
l'azote (N), cuivre (Cu), titane (Ti) et tungstène (W), le procédé comprenant :

i) la fourniture d'un récipient contenant un électrolyte liquide ou gélatinisé (3),
ii) la fourniture d'une électrode de référence (1) en contact électrochimique avec un échantillon de test par le biais de l'électrolyte liquide ou gélatinisé (3),
iii) la connexion électrique (6, 7) de l'électrode de référence avec l'échantillon de test en passant par un voltmètre (5),
iv) la lecture et l'enregistrement de valeurs de potentiel en circuit ouvert (E_{OC}) au niveau de chaque point de test de l'échantillon,
v) la comparaison des valeurs d'E_{OC} de l'échantillon de test avec le potentiel en circuit ouvert d'un spécimen exempt de phase sigma de l'acier de l'échantillon de test.

12. Procédé selon la revendication 11, comprenant en outre :

la répétition de l'étape iv) jusqu'à ce que la totalité de l'échantillon de test ou la zone d'intérêt soit examiné, et
la génération, en fonction de la somme de lectures, d'une estimation de la quantité de teneur en phases préjudiciables dans l'échantillon de test à l'aide d'une courbe d'étalonnage établissant une carte de la corrélation entre Eoc et la teneur en phase sigma dans l'acier de l'échantillon de test.

13. Procédé selon la revendication 11 ou 12, comprenant en outre :

la fourniture d'un récipient sous forme d'un tube micro-capillaire (2) contenant l'électrode de référence (1) immergée dans l'électrolyte liquide ou gélatinisé, et
le balayage de l'échantillon de test permettant d'établir une carte de teneur en phases préjudiciables à une résolution spatiale dans la plage de 0,05 à 5,0 mm, de préférence dans la plage de 0,5 à 0,05 mm.

14. Procédé selon l'une quelconque des revendications 11 à 13, comprenant en outre :
la préparation d'un gel d'électrolyte contenant du chlorure ferrique ($FeCl_3$) à raison de1 à 6 % en poids.

15. Équipement portable pour l'évaluation *in situ* de teneur en phases préjudiciables dans des aciers inoxydables et des alliages à base de nickel comprenant un appareil selon l'une quelconque des revendications 1 à 10, **caractérisé en ce que** l'électrode de référence (1) est associée à un moyen de positionnement (15 ; 23) permettant de placer temporairement l'électrode de référence (1) dans un point de mesure sur un échantillon de test.

Fig. 1

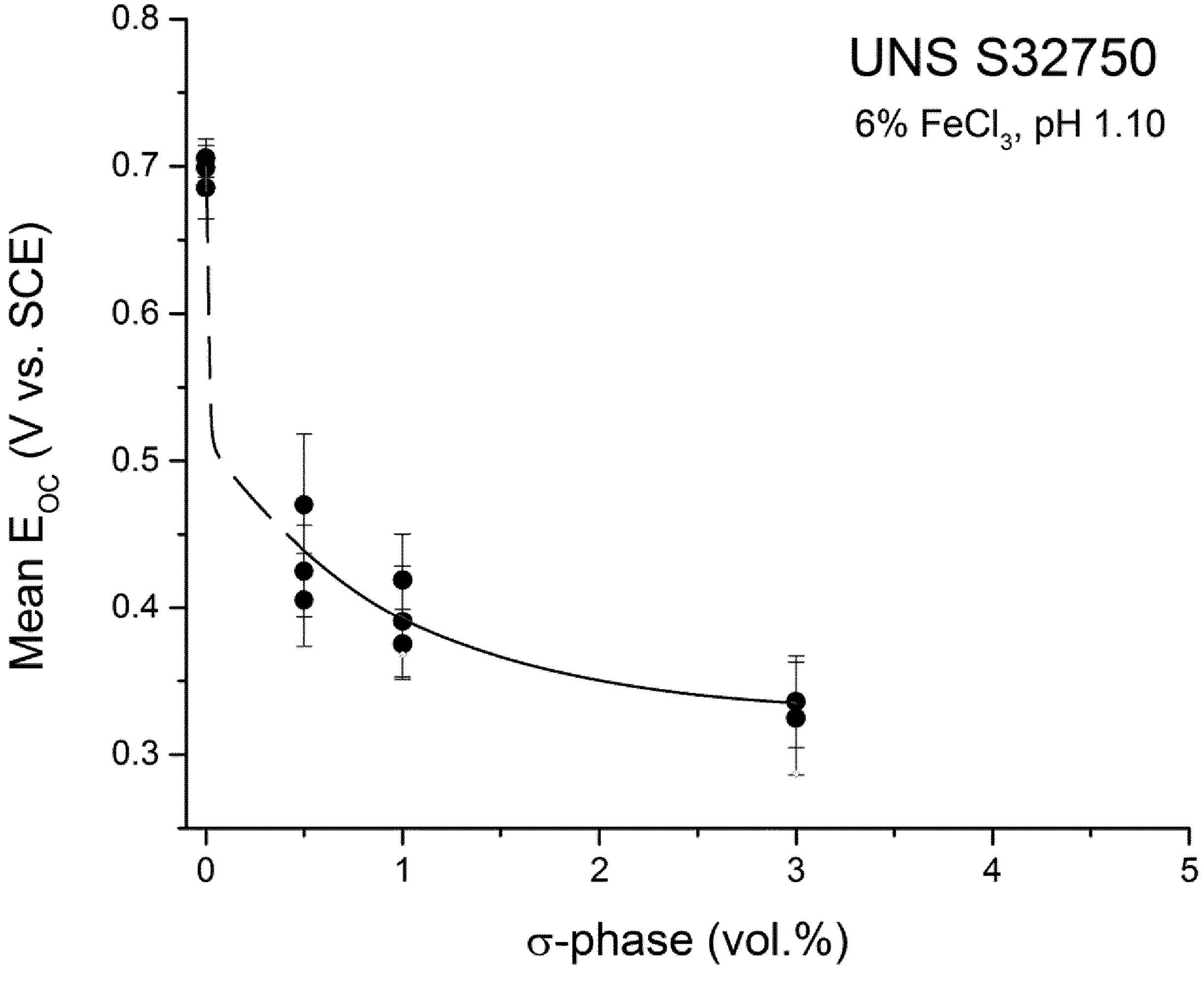

UNS S32750
6% $FeCl_3$, pH 1.10
Mean E_{OC} (V vs. SCE)
0.8
0.7
0.6
0.5
0.4
0.3
0
1
2
3
4
5
σ-phase (vol.%)

Fig. 2

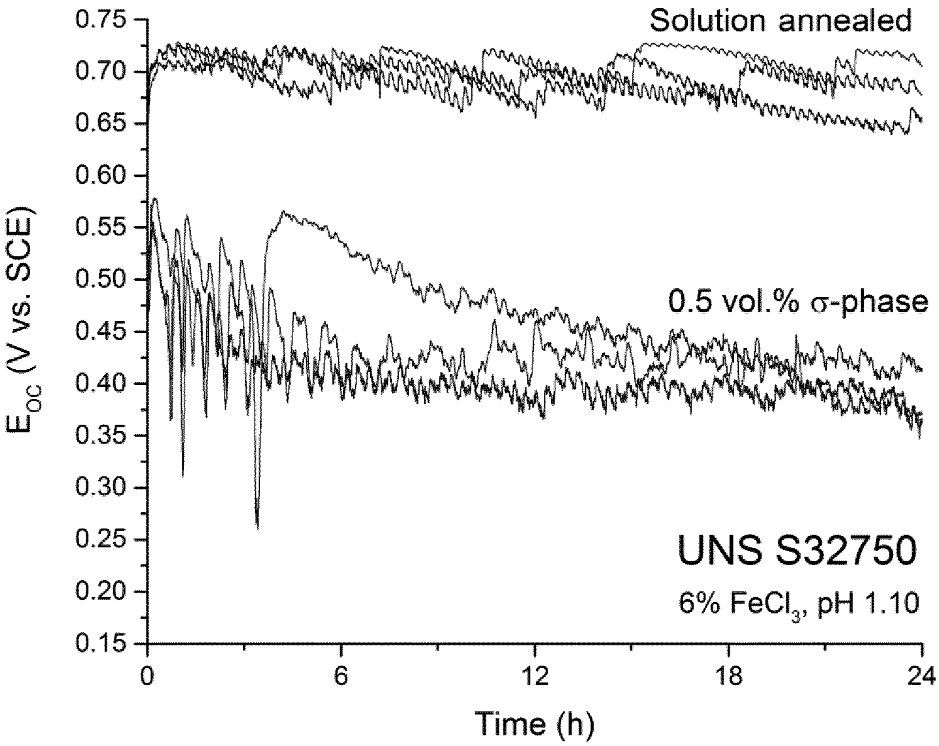

Solution annealed
0.5 vol.% σ-phase
UNS S32750
6% FeCl3, pH 1.10
E_OC (V vs. SCE)
Time (h)
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0
6
12
18
24

Fig. 3

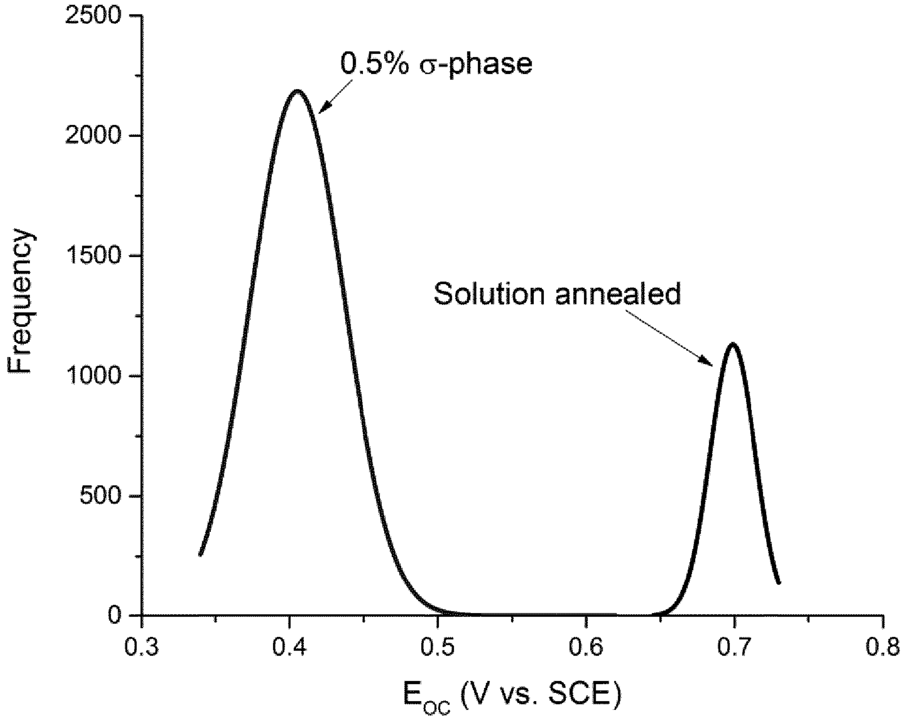

0.5% σ-phase
Solution annealed
Frequency
E_OC (V vs. SCE)
2500
2000
1500
1000
500
0
0.3
0.4
0.5
0.6
0.7
0.8

Fig. 4

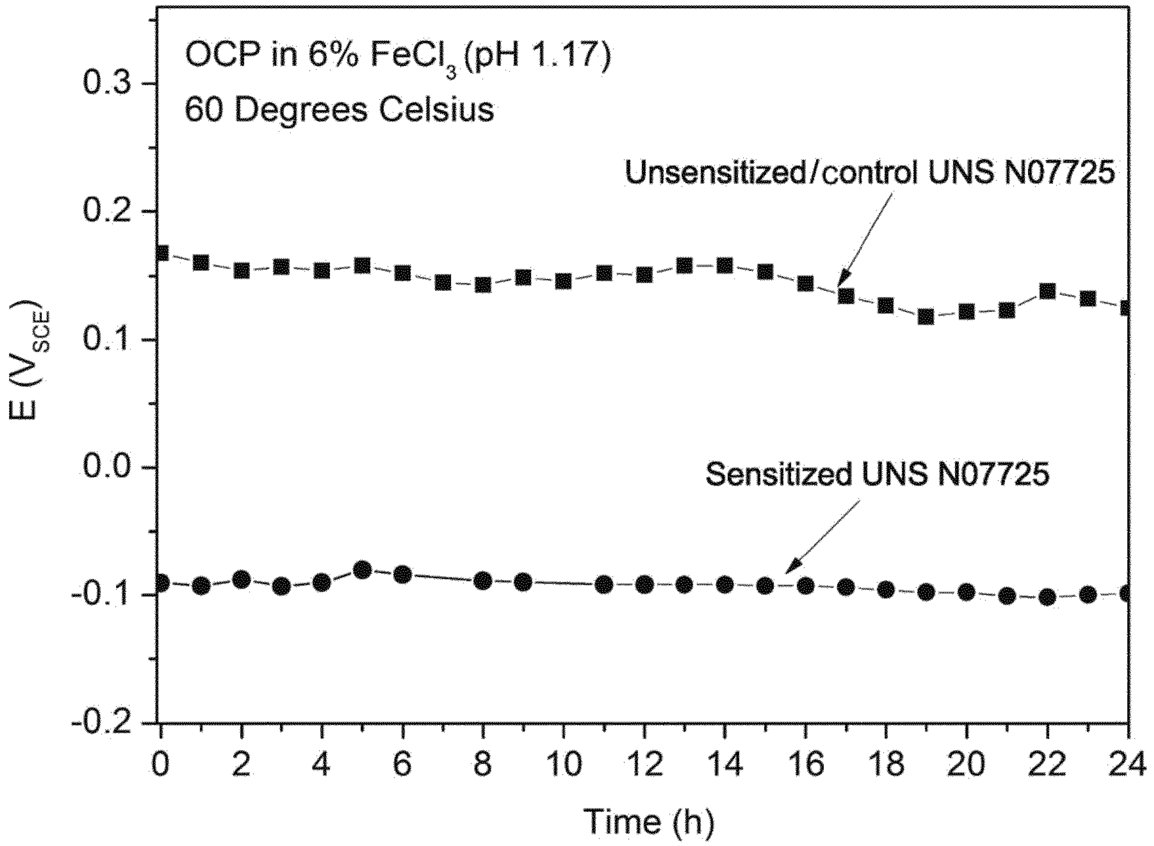

OCP in 6% $FeCl_3$ (pH 1.17)
60 Degrees Celsius
Unsensitized/control UNS N07725
Sensitized UNS N07725
E (V_{SCE})
0.3
0.2
0.1
0.0
-0.1
-0.2
0
2
4
6
8
10
12
14
16
18
20
22
24
Time (h)

Fig. 5

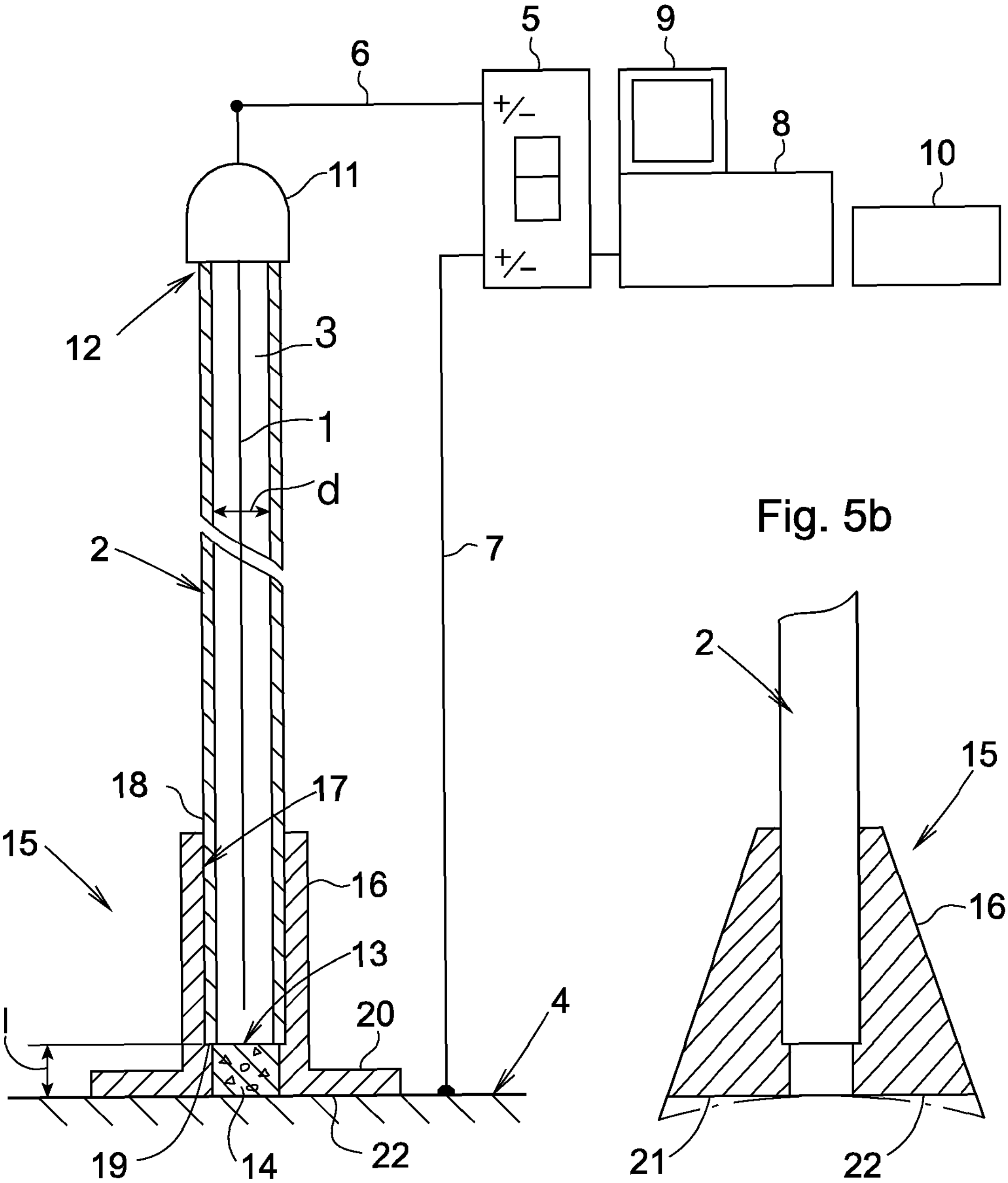


Fig. 5b

Fig. 6

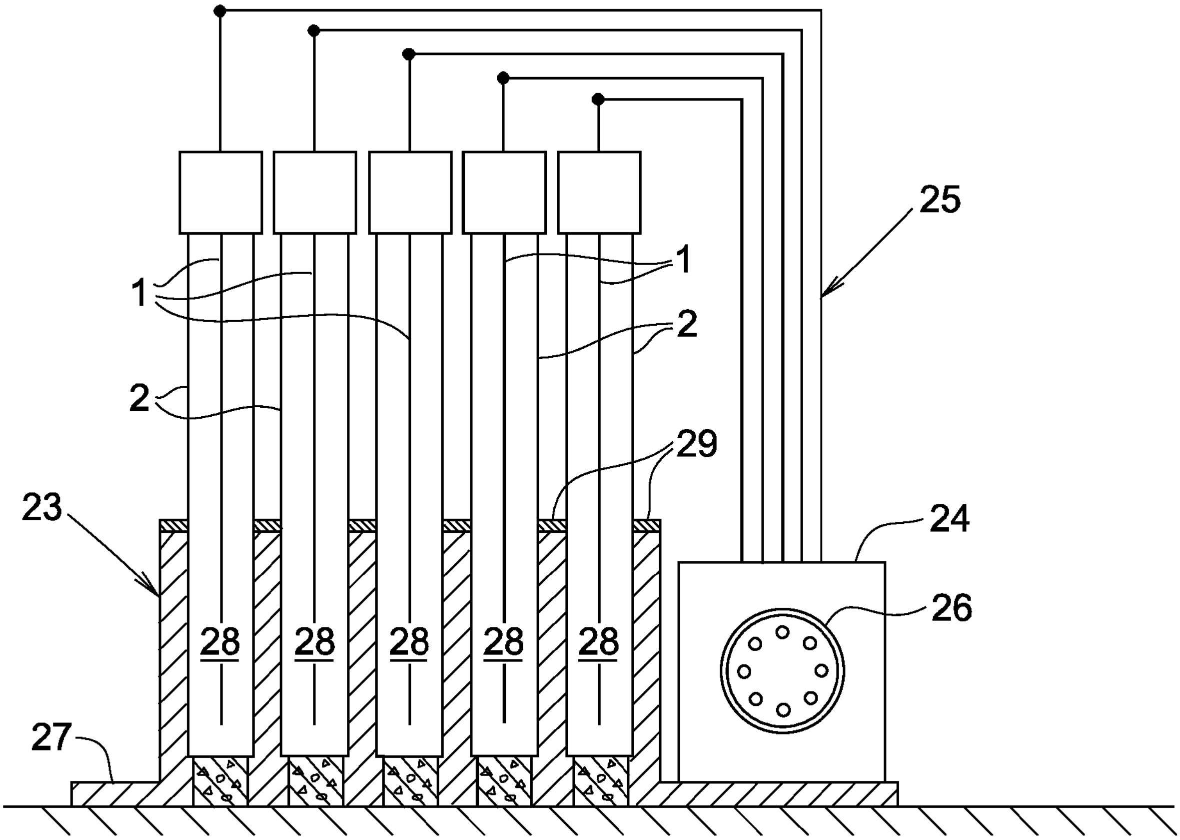


Fig. 7

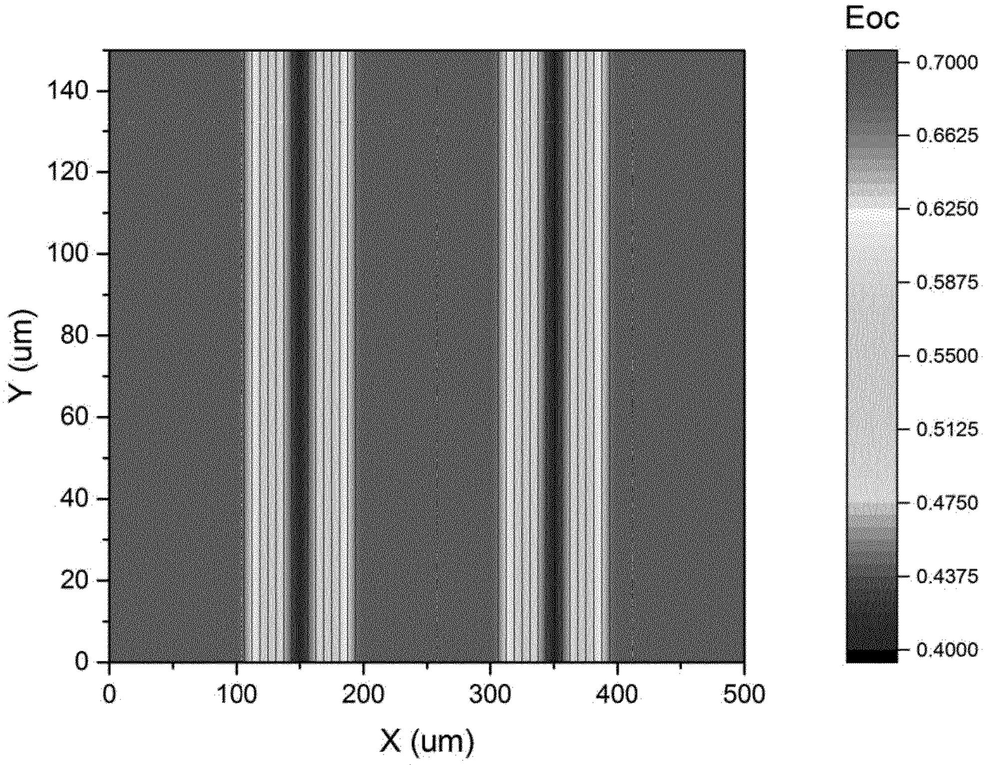
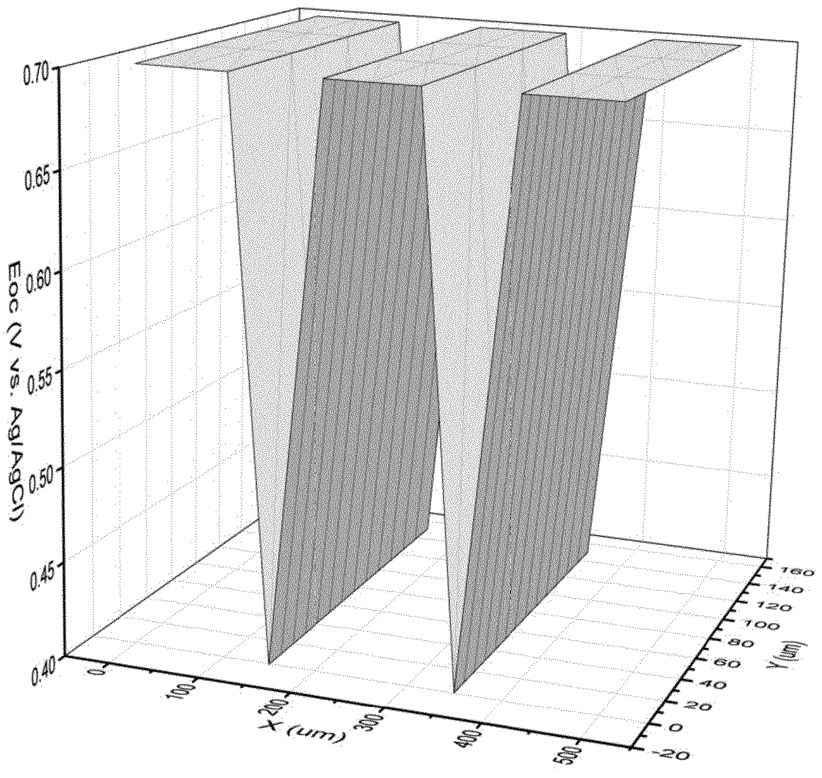

Eoc
0.7000
0.6625
0.6250
0.5875
0.5500
0.5125
0.4750
0.4375
0.4000
Y (um)
0
20
40
60
80
100
120
140
X (um)
0
100
200
300
400
500

Fig. 8


Eoc (V vs. Ag/AgCl)
0.40
0.45
0.50
0.55
0.60
0.65
0.70
X (um)
0
100
200
300
400
500
Y (um)
-20
0
20
40
60
80
100
120
140
160

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 0169198 A2 **[0002]**
- US 2008179198 A **[0010]**