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## The passivation current density as a parameter for a non-destructive test on plants of the pitting corrosion resistance of welded NiCrMo alloys

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**Abstract** The test methods used so far for the pitting corrosion resistance of weldments of high-alloyed NiCrMo alloys are not suitable for a test directly on plants. Therefore, the passivation current density was qualified as a parameter for the pitting corrosion resistance and its correlation with critical pitting temperatures examined by varying the heat treatment, the weld heat input and the surface treatment. The measuring cell developed for this test can be fitted fast and safely on surfaces with an inclination up to 90° and on cambered surfaces ( $r \geq 750$  mm). Afterwards, it can be loosened again without any deposits.

**Keywords** NiCrMo alloys · Pitting corrosion test · Test on plants

### Introduction

NiCrMo alloys are used for many purposes within the chemical process industry, power engineering and environmental pollution control if a particularly high resistance to the wet corrosion is required. The alloys are especially used in acid solutions with chloride and oxidation agents, which are used, e.g. for environment-friendly treatment of wastewater from the wet scrubbing of flue gas from coal-fired power plants. For the control of such processes materials with high resistance against chloride-induced pitting corrosion are needed for plants in metallic designs. When these materials are welded, intermetallic phases and/or carbides emerge in the heat-affected zone [1], which leads to chromium depletion and molybdenum depletion of

the environment due to the high content of molybdenum in these materials, which explains why the passivation current densities are higher on the sensitised material and on the weldments [2]. In the weld itself segregation defects emerge when the material solidifies, which leads to a rather heterogeneous distribution of the elements of the alloy, particularly of the molybdenum [3, 4]. This reduction of the content of chromium and particularly of molybdenum can lead to local corrosion of the weldments in case of a corrosive load of the weldments to the limit of the corrosion resistance of the unwelded material. Thus, the safety of these plants depends much on the corrosion resistance of the weldments, and it is therefore very interesting to test the pitting corrosion resistance of the weldments.

### Conventional pitting corrosion test of weldments

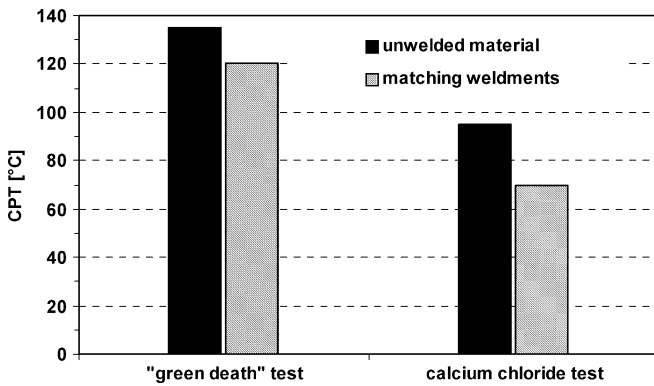
The non-destructive tests for the high-alloyed NiCrMo alloys include, e.g. radiographic measurements and dye penetration tests for pressure vessels [5]. Such tests are, e.g. surface and volume tests, by way of which it is impossible to determine the pitting corrosion resistance of the weldments. To determine this pitting corrosion resistance, test pieces are taken from extra welded test specimens, which are then tested in special solutions. The following tests are possible: (1) “green death” test (11.5% H<sub>2</sub>SO<sub>4</sub>; 1.2% HCl; 1.0% FeCl<sub>3</sub>, 1.0% CuCl<sub>2</sub>), 24 h immersion test at pH -0.27 and  $U_{\text{redox } 25^\circ\text{C}} = 0.642 V_{\text{SCE}}$  [6–8]; and (2) calcium chloride test (4.5 mol/l CaCl<sub>2</sub>), 6 h test at pH 3.2 and  $U = 0.2 V_{\text{SCE}}$  [9].

Comparative examinations with both tests prove the higher aggressiveness of the calcium chloride test, which is a result of the high concentration of chloride and the potentiostatic test control and which leads to lower critical pitting temperatures (Fig. 1).

Contrary to the green death test, which has to be carried out in the autoclave due to the boiling point of this solution at 103°C, the testing can be made at the atmospheric pressure in case of the calcium chloride test because this

Dedicated to Prof. Dr.-Ing. habil Dr. h.c. mult. Kurt Schwabe on the occasion of his 100th birthday.

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**Fig. 1** Critical pitting temperature (CPT) of alloy 59 as unwelded material and as matching weldments

solution does not boil until 115°C. However, in this test, the test potential may not exceed  $0.2 V_{SCE}$  because there is a limit of pitting corrosion in direction to positive potentials for this group of materials in a solution with concentration of chloride more than 2 mol/l. Above this limitation, the so-called pitting corrosion limitations potential, the pit initiation by means is prevented, which is perhaps the result of inactivation of the pitting nuclei due to a high concentration of chloride in the medium and a high concentration of molybdenum in the material [10–12]. On the other hand, the pitting corrosion inhibition potential described in [13] is based on a displacement adsorption of the chloride with nitrate, i.e. it only exists in chloride solutions with nitrate.

The following characteristics conflict with the use of these test procedures for a non-destructive test on plants: (1) increased test temperature; (2) destructive test, irreversible damage on the test surface; (3) demarcation of measuring surfaces leads to crevice corrosion; and (4) long incubation periods are pretending resistance.

The following requirements are to be made for a test on plants: (1) testing at ambient temperature, (2) no generation of local corrosion spots and (3) fast and reproducible measurement of the parameter.

Therefore, parameters, which correlate with the pitting corrosion parameters—and not pitting corrosion param-

eters—have to be determined for a test on plants at the ambient temperature.

The passivation current density as a parameter for the pitting corrosion resistance

The creation of an active point as a starting position for the pitting corrosion due to decomposition or penetration of the passive layer by chloride ions depends on whether the free surface area is passivated again immediately or whether it enters actively into a solution. Thus, the passivation properties of the material are already of decisive importance [14].

Just like the pitting corrosion properties, they are particularly decided by the content of chromium and molybdenum. Then, the pitting corrosion parameters can behave inversely proportional to the degree of the passivation current density (Fig. 2) [15–18].

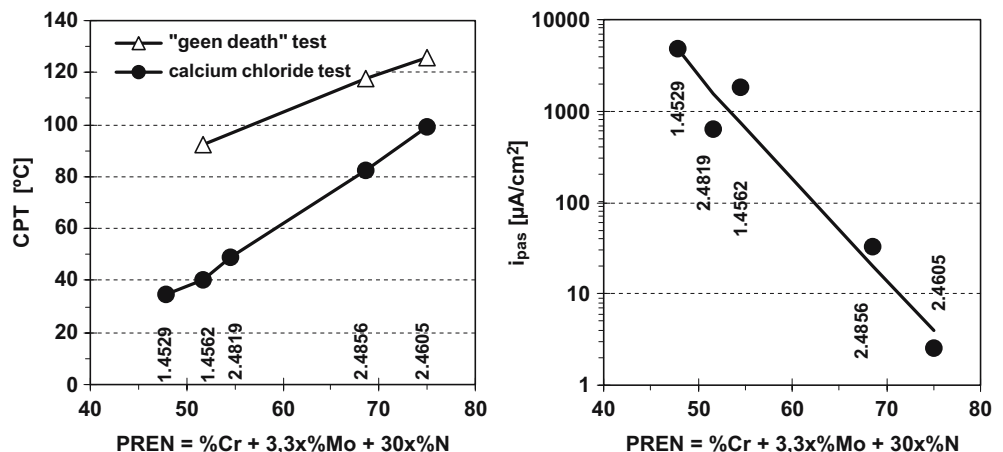
As the content of chromium and molybdenum is reduced during the welding operation in the heat-affected zone and in the weld metal due to the formation of precipitations and segregation defects, it should be possible to prove the involved decrease in the pitting corrosion resistance in the form of increase in the passivation current density.

## Experimental test

The test media and test conditions have to be so selected that it is possible to reproducibly determine the passivation current density on the basis of potentiodynamically measured potential/current density curves on the assumption that the unwelded material is in a passive state and the weldments are in a stably active corrosion state. This succeeds for the weldments of alloy 59 (material no. 2.4605/NiCr23Mo16Al/Nicrofer 5923 hMo) tested here after cathodic activation in a solution with 1.0 mol/l  $H_2SO_4$  + 4.0 mol/l NaCl +  $10^{-4}$  mol/l KSCN.

If KSCN is added, the passivation current density can be measured with excellent reproducibility due to the poisoning of the hydrogen electrode because the measurement is no longer impaired by the superimposition of the cathodic partial potential/current density curves [19]. NaCl reduces

**Fig. 2** Critical pitting temperature (CPT) and passivation current density ( $i_{pas}$ ) as a function of pitting resistance equivalent in mass percentage ( $PREN = \%Cr + 3,3x\%Mo + 30x\%N$ ) of CrNiMo steels and NiCrMo alloys



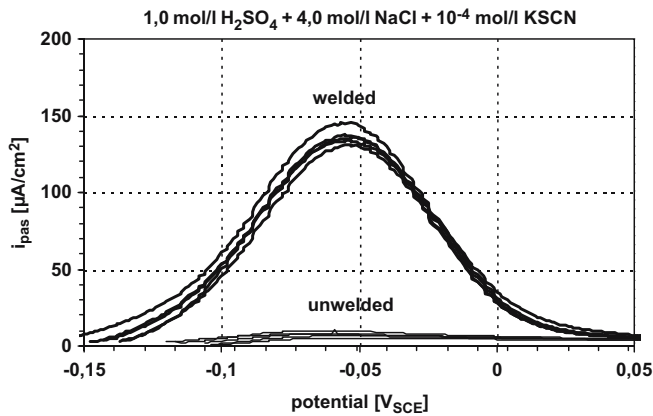


Fig. 3 Potential/current density curves of alloy 59 (unwelded and welded)

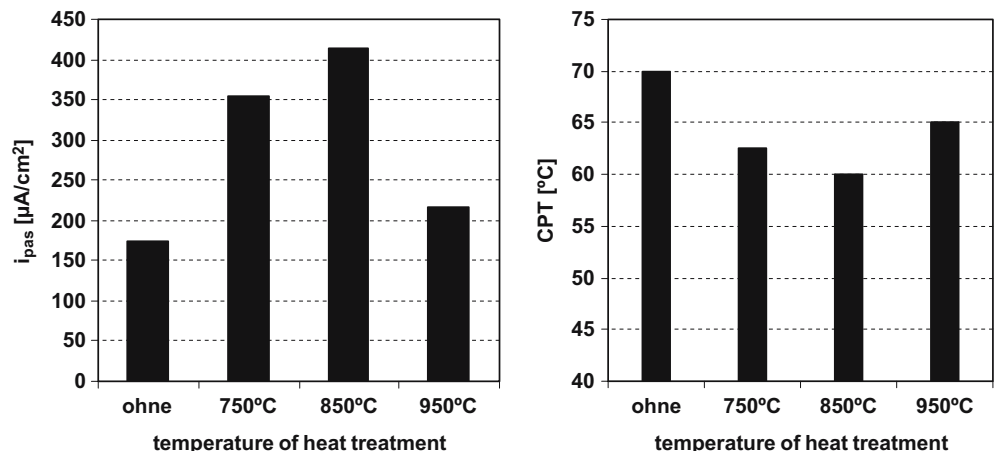
the oxygen solubility, which means that it is not absolutely necessary to remove the oxygen from the solution. This makes it easier to realise the procedure in practice.

The procedure of the measurement is as follows:

1. Galvanostatic activation at  $-5 \text{ mA/cm}^2$  1 min,
2. Measurement of the free corrosion potential 30 min and
3. Recording of the anodic potential/current density curve with  $dU/dt=0.72 \text{ V/h}$ .

Because there is no risk of crevice corrosion during the measurement in the active corrosion, no special test specimens are needed—contrary to the conventional pitting corrosion test. Thanks to a measuring cell with a gasket ring it is possible to use sheets on which a defined measuring surface can be demarcated. By means of this round measuring cell of polytetrafluoroethylene (PTFE) with a volume of  $63 \text{ cm}^3$  and a measuring surface of  $4.9 \text{ cm}^2$ , which comprises a counter-electrode and a capillary tube to the connection with a reference electrode, an electrolyte is led in the circuit by way of a hose pump with  $0.14 \text{ l/min}$  [20]. In that way it is possible to examine the two sides of the weldments independent of each other and without the disturbing influence of the cut surfaces, contrary to the test specimens used for the conventional pitting corrosion test,

Fig. 4 Influence of different heat treatment temperatures on passivation current densities ( $i_{\text{pas}}$ ) in  $1 \text{ mol/l H}_2\text{SO}_4 + 4 \text{ mol/l NaCl} + 10^{-4} \text{ mol/l KSCN}$  and critical pitting temperatures (CPT) in the calcium chloride test for matching weldments of alloy 59



in which the two sides of the weldments and the cut surfaces are measured simultaneously.

Figure 3 shows examples of the potential/current density curves of an unwelded material and a weldment, which were determined on the basis of the above-mentioned conditions.

Whereas only passive currents are measured on the unwelded material, the passivation current density of the weldments is easily reproducibly accessible and can be used as a parameter for the pitting corrosion resistance of the weldments. For the proof of a correlation between this passivation current density and the pitting corrosion values, the material parameters (1) heat treatment, (2) surface treatment and (3) weld heat input were varied. Thereafter, the passivation current densities determined in the above-mentioned test medium were compared with the critical pitting temperatures determined in the calcium chloride test.

Moreover, priority was on the development of a measuring cell for the measurement of the passivation current densities directly on plants.

## Results

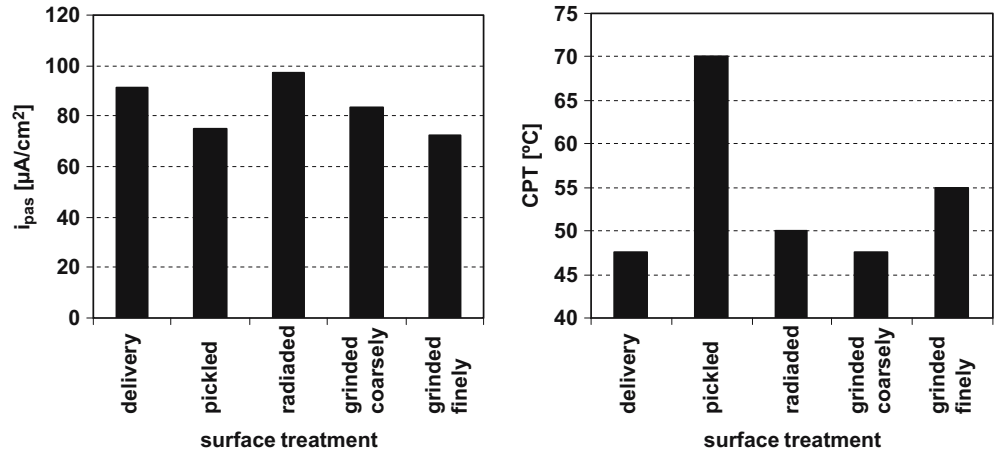
Welded test specimens with the dimension  $500 \times 300 \text{ mm}$ , with a longitudinal welded seam in the middle, were subjected to the following heat treatment: (1)  $750^{\circ}\text{C}/30 \text{ min Ar/water}$ , (2)  $850^{\circ}\text{C}/30 \text{ min Ar/water}$  and (3)  $950^{\circ}\text{C}/30 \text{ min Ar/water}$ .

To remove the scale layer, which develops during the heat treatment, the test specimens were radiated with glass pearls and pickled in  $\text{HNO}_3/\text{HF}$ . Figure 4 shows the results.

At a heat treatment temperature of  $750\text{--}850^{\circ}\text{C}$  high passivation current densities and low critical pitting corrosion temperatures point out to a maximum of susceptibility, which is in line with the examinations of alloy 59 by way of the ASTM G28A test [21].

To determine the influence of different surface treatments, an examination was made for matching weldments of alloy 59 in their state for delivery, pickled with  $\text{HNO}_3/\text{HF}$ , radiated as well as grinded coarsely and finely, respectively (Fig. 5).

**Fig. 5** Influence of different surface treatment on passivation current densities ( $i_{pas}$ ) in 1 mol/l  $H_2SO_4$  + 4 mol/l NaCl +  $10^{-4}$  mol/l KSCN and critical pitting temperatures (CPT) in the calcium chloride test for matching weldments of alloy 59



Pickling and fine grinding reduce the passivation current densities of the weldments, whereas they are increased a little by radiation. The critical pitting temperatures also show these changes in resistance. This relatively low influence of different surface treatment is also mentioned in other examinations [12, 13] and cannot be explained by the influence of the roughness of the surface because it only differs a little [20].

To examine the influence of the weld heat input, manufactured welded test specimens were examined by way of the tungsten inert gas (TIG) procedure. The test specimens were welded with a heat input of 6 and 12 kJ/cm (Fig. 6).

If the heat input is increased from 6 to 12 kJ/cm, the passivation current densities of the two sides of the weldment increase, whereas the critical pitting temperatures decrease. Both factors announce the reduction of pitting corrosion resistance.

**Measuring cell**

The pitting corrosion resistance of weldments is to be determined by measuring the passivation current density directly on plants. For that purpose a measuring cell was developed, which can be fitted quickly and safely directly on the test object and loosened again quickly and without

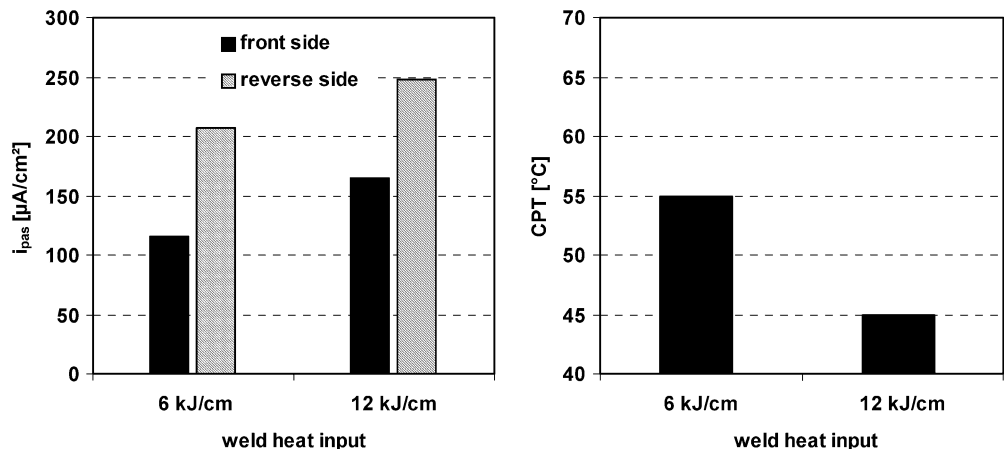
any deposits [20, 22]. The cell is fastened on the object with the help of suckers with air-operated vacuum pumps. Due to ball-and-socket joints on the suckers and washers between the measuring box and the support, it can also be fitted on cambered surfaces. Due to the gasket the measuring surface is demarcated, and due to the pins with spring bearing, there is electrical connection with the object measured (Fig. 7). The measuring box also has a platinum wire because the counter-electrode as well as a capillary tube with a suction ball and three-way tap for the accommodation of the reference electrode.

Moreover, the following has been fitted on the cell: (1) inlet and outlet for the pumping of the electrolyte; (2) compressed air connection; (3) electrical connection of object to be measured, reference electrode and counter-electrode; and (4) adjusting screws for adjustment of the measuring box.

The technical data for these measuring cells are as follows:

1. Required surface, 280×280 mm;
2. Compressed air connection 0.314 MPa, 120 l/min;
3. Minimum radius of object to be measured, 750 mm (inside or outside dimension);
4. Measuring surface, 490 mm<sup>2</sup>; and
5. Amount of electrolyte, approximately 0.25 l.

**Fig. 6** Influence of different weld heat input on passivation current densities ( $i_{pas}$ ) in 1 mol/l  $H_2SO_4$  + 4 mol/l NaCl +  $10^{-4}$  mol/l KSCN and critical pitting temperatures (CPT) in the calcium chloride test for matching weldments of alloy 59



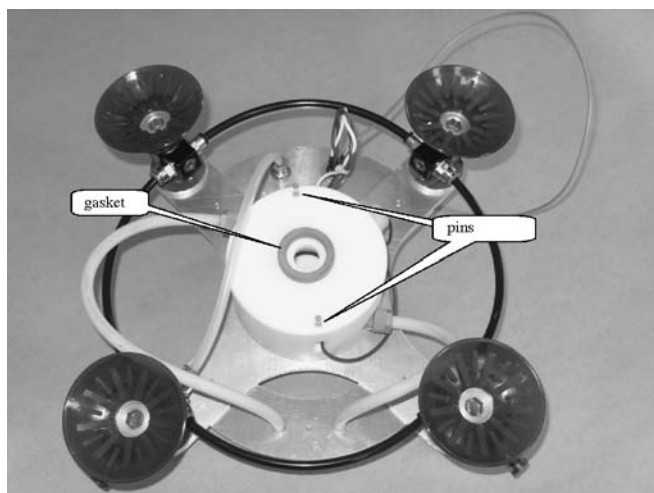


Fig. 7 Measuring box for the cell with suckers, pins and gasket ring

The measuring system is completed by containers for the electrolyte and the flushing liquid, a hose pump and the electrochemical measuring facility. First measurements confirm the reliable performance of the measuring cell.

## Conclusions

The passivation current density is suitable for a non-destructive test of weldments of high-alloyed NiCrMo alloys as a parameter for their pitting corrosion resistance. It behaves more or less inversely proportional to the critical pitting temperature determined during the destructive test used up to now. This passivation current density is reproducibly measurable for weldments of the alloy 59 in a test medium with 1.0 mol/l  $\text{H}_2\text{SO}_4$ , 4.0 mol/l NaCl and  $10^{-4}$  mol/l KSCN. It is not necessary to vent the medium. The measuring cell, which has been made for measurements on plants, can be fitted quickly and safely on surfaces with an inclination up to  $90^\circ$  and on cambered surfaces with an inside or outside radius of at least 750 mm, and it can be loosened again without any deposits.

The test of other welded NiCrMo alloys is practicable. However, the concentration of sulphuric acid is dependent on the composition of alloy.

For the operational use calibration has to be made in the form of a comparison of the results of the passivation current density measurements with the results of the destructive test procedures used so far on test specimens manufactured especially for this purpose. It is the objective to determine still-permissible characteristic values as a function of the material for designs to be used.

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## References

1. Heubner U, Köhler M (1992) *Werkst Korros* 43:181
2. Riedel G, Voigt C, Werner H, Heubner U (1999) *Werkst Korros* 50:452
3. Bäuml A (1976) *Werkst Korros* 27:682
4. Heubner U, Hoffmann Th, Rudolph G (1990) *Weldability of Materials. Proceedings of the Materials, Weldability Symposium, Detroit*, p 175
5. AD-Merkblatt HP5/3
6. Uhlig HH, Asphahani AI (1979) *Mater Perform* 11:9
7. Kirchheiner R, Köhler M, Heubner U (1992) *Werkst Korros* 43:388
8. Wallen B, Liljas M, Stenvall P (1993) *Werkst Korros* 44:83
9. Riedel G, Voigt C, Werner H (1997) *Werkst Korros* 48:518
10. Werner H, Riedel G, Voigt C (1995) *GDCh-Monographie Elektrochemie und Werkstoffe*, vol 2, p 163
11. Werner H, Voigt C, Riedel G (1996) *Werkst Korros* 47:383
12. Werner H, Riedel G, Eckstein C (2001) *Werkst Korros* 52:619
13. Brauns E, Schwenk W (1961) *Arch Eisenhüttenwesen* 32:387
14. Riedel G, Werner H, Friedrich S (2003) *Werkst Korros* 54:940
15. Voigt C, Riedel G, Werner H, Günzel M, Erkel KP (1987) *Werkst Korros* 38:725
16. Riedel G, Voigt C, Werner H, Günzel M, Skuin K, Erkel KP (1988) *Korrosion (Dresd)* 19:122
17. Werner H, Voigt C, Riedel G, Günzel M, Simmchen R (1990) *Korrosion (Dresd)* 21:135
18. Arlt N, Gillessen C, Heimann W, Heuser H, Ladwein Th (1991) *TEW Tech Ber* 17:29
19. Riedel G, Voigt C (1985) *Werkst Korros* 36:156
20. Werner H (2005) 3 Kolloquium des Kuratoriums Korrosionsschutz-KKF, Stahl-Zentrum, Düsseldorf, 3 March 2005
21. Köhler M (1997) *Werkst Korros* 48:528
22. Utility model application no. 20 2004 011 357.0