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Summary

A joint corrosion programme is performed at FZK.INE, ENRESA (Subcontractor INASMET), FU Berlin and SCK.CEN on preselected materials for long-lived disposal containers that could be used as a radionuclide barrier in repositories located in rock salt, granite and clay. They are the objectives to investigate the potential effect of essential parameters on the corrosion of the materials carbon steel, stainless steels, Ti99.8-Pd and Hastelloy C4, and to provide more accurate data for a material degradation model that can be used to predict the lifetime of containers. Important parameters to be investigated are: Temperature, pH, Cl^-, $S_2O_3^{2-}$, O_2, salt impurities, strain rate, gamma radiation and welding.

In the present work, long-term immersion tests, electrochemical/radiochemical studies and slow strain rate tests were performed on the container materials in salt and clay environments. Parameters examined were: Temperature (16°C - 170°C), pH (3 - 7), H_2O_2 ($6x10^{-4}$ - $1.7x10^{-1}$ mol/l), Cl^- (16 - 10000 ppm), gamma radiation (10 Gy/h) and strain rate (10^{-4} - $10^{-7}s^{-1}$).

Present results obtained in salt environments (salt brines) indicate that gamma radiation (10 Gy/h) and H_2O_2-concentrations smaller than 10^{-4} mol/l do not influence the corrosion behaviour of Ti99.8-Pd, and that this alloy is resistant to stress corrosion cracking at strain rates up to $10^{-7}s^{-1}$. pH values of the test brine between 3 and 7 do not enhance the corrosion rate of the carbon steel, but at the very slow strain rate of $10^{-7}s^{-1}$ the material shows a slight sensitivity to stress corrosion cracking. First results in oxidizing clay water show that the high alloyed stainless steels, Hastelloy C4 and Ti99.8-Pd are highly resistant to corrosion up to 30°C. However, the stainless steel AISI 316L is susceptible to pitting and crevice corrosion at high Cl^- concentrations in clay water. Finally, the carbon steel undergoes significant general corrosion in the clay water. Further investigations in salt and clay environments are in progress.

Bewertung von metallischen Werkstoffen für langzeitbeständige HAW-Endlagerbehälter im Hinblick auf ihre Korrosionsbeständigkeit

Zusammenfassung

Im Rahmen eines gemeinsamen Forschungsprogramms wird von FZK.INE, ENRESA/INASMET, FU Berlin und SCK.CEN das Korrosionsverhalten ausgewählter Werkstoffe für langzeitbeständige Behälter unter Endlagerbedingungen im Steinsalz, Granit und Ton untersucht. Das Ziel der Untersuchungen ist die Bestimmung des potentiellen Einflusses wichtiger Parameter auf das Korrosionsverhalten von unlegierten/hochlegierten Stählen, Ti99,8-Pd und Hastelloy C4 und die Ermittlung von Daten für ein Korrosionsmodell zur Vorhersage der Standzeit von Behältern. Wichtige Parameter sind: Temperatur, pH, Cl^-, $S_2O^-_3$, O_2, Salzverunreinigungen, Dehnungsrate, Gammastrahlung und Schweißen.

In der vorliegenden Arbeit wurden Langzeit-Immersionsexperimente, elektrochemische/radiochemische Untersuchungen und Spannungsrißkorrosionsuntersuchungen bei langsamen Dehnungsraten an den o.g Behälterwerkstoffen unter den Bedingungen der Endlagerung in Steinsalz und Ton durchgeführt. Die Untersuchungsergebnisse in endlagerrelevanten Salzlösungen (T=25°C-170°C) zeigen, daß Gamma-Dosisleistungen von 10 Gy/h und H_2O_2-Konzentrationen in den Salzlösungen bis 10^{-4} mol/l keinen nennenswerten Einfluß auf die Korrosion von Ti99,8-Pd haben. Darüber hinaus ist diese Legierung bei Dehnungsraten bis 10^{-7} s^{-1} beständig gegenüber Spannungsrißkorrosion (SpRK). Im Falle des unlegierten Stahls TStE355 führen pH-Werte der Testlösung zwischen 3 und 7 zu keiner Erhöhung der Korrosionsrate, jedoch zeigt dieser Stahl bei der sehr langsamen Dehnungsrate von 10^{-7} s^{-1} eine leichte Empfindlichkeit gegenüber SpRK. Erste Ergebnisse in oxidierendem Tonwasser bis 30°C zeigen, daß hochlegierte Stähle, Ti99,8-Pd und Hastelloy C4 beständig gegenüber allen Korrosionsarten sind. Allerdings ist der rostfreie Stahl AISI316L bei hohen Cl^--Konzentrationen (1000 und 10000 ppm) im Tonwasser anfällig gegenüber Loch- und Spaltkorrosion. Schließlich zeigt der unlegierte Stahl TStE355 im Tonwasser eine starke Flächenkorrosion. Weitere Korrosionsuntersuchungen an Stählen, Ti99,8-Pd und Hastelloy C4 sind im Gange.

TABLE OF CONTENTS

A. OBJECTIVES AND SCOPE

In previous corrosion studies [1,2,3], two approaches were identified for the manufacture of long-lived HLW/Spent Fuel disposal containers that could act as a radionuclide barrier in repositories in rock salt, granite and clay. These are the corrosion allowance concept and the corrosion-resistant concept. For corrosion-allowance, carbon steels are the most promising material for all three rock formations. For corrosion-resistant, the strongest candidates are the alloy Ti99.8-Pd (Ti/0.2 Pd, TiGr-7) for rock salt, and stainless steels for granite and clay.

In the present research programme, further in-depth corrosion studies will be performed on the abovementioned materials in rock salt, granite and clay environments. These include: long-term immersion tests, electrochemical/ radiochemical studies and slow strain rate tests. The objectives of the studies are:

- to investigate the potential effect of essential parameters on corrosion.
- to gain a better understanding of corrosion mechanisms.
- to provide more accurate data for a material degradation model that can be used to predict the lifetime of such containers.

B. WORK PROGRAMME

B.1 Corrosion studies on candidate container materials in salt environments

1.1 Long-term immersion tests are performed on the TStE355 carbon steel (0.17 wt.% C) and Ti99.8-Pd in salt brines aimed at evaluating the effect of essential parameters on their corrosion behaviour. Such parameters are: the pH of the brines, the content of salt impurities, gamma-radiation, and welding (FZK.INE).

1.2 Combined electrochemical and radiochemical studies are performed on Ti99.8-Pd in salt brines in order to get a detailed insight into corrosion kinetics and especially into the potential influence of the radiolytic product H_2O_2 on corrosion. Both unwelded and welded specimens are examined (FU Berlin).

1.3 The resistance of Ti99.8-Pd (TiGr-7) and TStE355 carbon steel (0.17 wt.% C) to stress corrosion cracking (SCC) is investigated in a NaCl brine (25.9 wt.% NaCl) at 170°C and strain rates of 10^{-4}-$10^{-7}s^{-1}$ by means of the slow strain rate technique

(SSRT). For comparison, additional investigations are conducted in argon as inert reference medium (ENRESA).

B.2 Stress corrosion cracking studies in granite environments

The resistance of the AISI 316L stainless steel and TStE355 carbon steel to stress corrosion cracking (SCC) in a bentonite buffered granitic groundwater is investigated at 90°C at various slow strain rates (ENRESA).

B.3 Corrosion studies in clay/bentonite environments

Electrochemical corrosion studies are performed on candidate container materials aimed at investigating the influence of important environmental parameters on corrosion. Such parameters are: the temperature (16°C and 90°C) and the content of O_2, Cl^- and $S_2O_3^{2-}$ of the corrosion medium (SCK.CEN).

C. PROGRESS OF WORK AND RESULTS OBTAINED

C.1 Corrosion studies on candidate container materials in salt environments

C.1.1 Long-term immersion tests (FZK.INE) (B.1.1)

Long term immersion tests are performed on the TStE355 carbon steel (0.17 wt.% C) and Ti99.8-Pd in salt brines aimed at evaluating the effect of essential parameters on their corrosion behaviour. Such parameters are: the pH of the brines, the content of salt impurities, gamma radiation, and welding.

In the period under review, work has been concentrated on the investigation of the:

- Influence of pH value on corrosion of the TStE355 carbon steel in the disposal-relevant $MgCl_2$-rich Q-brine
- Effect of gamma radiation on corrosion of the alloy Ti99.8-Pd in the Q-brine.

Influence of pH on corrosion of the TStE355 carbon steel in Q-brine

The influence of pH values between 3 and 7 on the corrosion of the TStE355 carbon steel in the $MgCl_2$-rich Q-brine was investigated at 170°C. The steel was examined in the hot-rolled and annealed condition. For the investigations plane specimens having the dimensions 40mm x 20mm x 4mm were used. The steel had the following composition in wt.%:

0.17 C; 0.44 Si; 1.49 Mn; bal. Fe.

The composition of the Q-brine (wt.%) at 55°C was:

26.8 $MgCl_2$; 4.7 KCl; 1.4 NaCl; 1.4 $MgSO_4$; 65.7 H_2O (pH (55°C) = 4.6).

The various pH values were adjusted by addition of HCl or NaOH to the brine. The experimental setup is described elsewhere [4]. Shortly, for the experiments stainless steel pressure vessels with corrosion resistant PTFE inserts were used. After tightly closing the inserts, the vessels were stored in heated chambers at the 170°C test temperature.

The results indicate that the steel is resistant to pitting corrosion in the sense of an active-passive corrosion element. At all pH values of the brine, a non-uniform general corrosion is observed, and the thickness reduction of the specimens increases linearly with the corrosion time. Figures 1 and 2 show by way of example optical micrographs of steel specimens after exposure to the brine at pH values of 3 and 7. The linear time-dependence of the general corrosion of the steel in the brine at 170°C and pH = 3 is shown in Figure 3.

The general corrosion rates of the steel at the various pH values (177 μm/a - 209 μm/a) differ among one another only about 18% at the maximum (Figure 4). As such differences are within the statistical variations of the measured values, it can be concluded that initial pH values of the brine between 3 and 7 have no significant influence on the steel corrosion. This can be explained by the fact that after termination of the exposure time, the same pH value of 4.5 - 4.8 was measured in all brines independent of their initial pH. It appears that the pH of the brine will be buffered by the reaction of corrosion products with brine constituents.

Effect of gamma radiation on the corrosion of Ti99.8-Pd in Q-brine

Irradiation corrosion-studies up to 1 year were performed on the alloy Ti99.8-Pd in the $MgCl_2$-rich Q-brine at 150°C and a gamma dose rate of 10 Gy/h which is relevant for the thick-walled container discussed (steel containers with Ti99.8-Pd corrosion protection). For comparison, experiments without radiation have been also conducted in the brine. The alloy was examined in the hot-rolled and annealed condition and had the following composition in wt.%:

0.18 Pd; 0.05 Fe; 0.01 C; 0.04 O_2; bal. Ti

The irradiation-corrosion experiments were performed in the spent fuel storage pool of KFA Jülich. The radiation source were spent fuel elements. For the experiments, autoclaves made of Ti99.8-Pd with insert vessels of Duran glass were used. The autoclaves were placed into heated stainless steel containers (irradiation containers), which were positioned at the bottom of the 6 m deep water-filled spent fuel element storage pool. A detailed description of the test facilities can be found in [5].

After removal from the brine, the specimens were examined for general and pitting corrosion. The general corrosion was calculated from the gravimetrically determined weight losses and the material density. Evaluation of the specimens regarding local corrosion was carried out by surface profilometry and metallography. To obtain information on the corrosion mechanisms, XPS-analyses of the oxide-film formed on the specimens surface are in progress.

The corrosion results obtained in the $MgCl_2$-rich Q-brine at 150°C are given in Table I and can be summarized as follows:

- The general corrosion of Ti99.8-Pd in Q-brine at 150°C is negligible low (< 1 μm/a). The imposition of a 10 Gy/h radiation field on the 150°C brine environment does not increase the corrosion rate of the material.

- Surface profiles and metallographic examinations (see micrographs Figures 5 and 6) show that the alloy Ti99.8-Pd is resistant to pitting corrosion both with and without irradiation. Under the test conditions, a completely uniform corrosion was observed.

C.1.2 Electrochemical and radiochemical studies (FU Berlin) (B.1.2)

Combined electrochemical and radiochemical studies are performed on Ti99.8-Pd in salt brines in order to get detail insight into corrosion kinetics and especially into the potential influence of the radiolytic product H_2O_2 on corrosion. Both unwelded and welded specimens are examined. The studies are performed in Q-brine, an $MgCl_2$-rich salt solution, and in an NaCl-rich solution, at temperatures between 25°C and 80°C at Free Corrosion Potential (E_{Corr}) and at various applied potentials between 0 V and 1 V. The method applied is the Radioisotope Method (RIM) which combines classical electrochemical procedures (potentiostatic and potentiodynamic measurements, impedance and photocurrent measurements) with radiochemical ones, especially neutron activation analysis. In addition, microscopic examinations are carried out in order to decide whether pit corrosion or general corrosion has taken place.

In the period under review, the influence of the radiolytic product H_2O_2 on corrosion of Ti99.8-Pd was investigated in saturated NaCl brine at 25°C. Experiments were performed both at rest potential and at various anodic potentials of 0 V, 0.5 V and 1 V (passive range). The dissolved titanium was measured continuously by mean of γ-spectroscopy. The experiments were performed under conservative conditions, namely at very high H_2O_2 concentrations in the brine between $6x10^{-4}$ and $1.7x10^{-1}$ mol/l. Under realistic disposal conditions, an H_2O_2 concentration in the brine of only 10^{-6} - 10^{-7} mol/l is expected, if a gamma dose rate of 1 Gy/h on the surface of the thick-walled container is taken into account.

Corrosion investigations at rest potential

The mass loss of the material was measured continuously for 200 - 250 hours. Figure 7 shows the time-dependence of the mass loss of Ti99.8-Pd at 25°C in the saturated NaCl solution containing different concentrations of peroxide ($6x10^{-4}$ mol/l, $6x10^{-3}$ mol/l and $3x10^{-2}$ mol/l). From the slope of the straight line, the linear corrosion rate can be determined. From Figure 7 two corrosion ranges can be seen. Within the first 50 hours, the corrosion of Ti99.8-Pd is relative high and depends on the H_2O_2 content in the solution. In the second range starting at 60 - 65 hours, the corrosion is very low and independent from the H_2O_2 content. This behaviour can be explained as follows:

In the first range, the titanium dissolves in accordance with the following equations:

$$Ti + 2\,H_2O \rightarrow TiO_2 + 4\,H^+ + 4\,e^- \qquad (1)$$

$$TiO_2 + H_2O_2 + 2\,H^+ \rightarrow TiO_2 + 2\,H_2O \qquad (2)$$

In addition, H_2O_2 decays into water and oxygen corresponding to the equation:

$$2\,H_2O_2 \rightarrow 2\,H_20 + O_2 \qquad (3)$$

Because of equations 2 and 3, the peroxide concentration of the solution decreases with time. After 60 - 65 hours there is not any H_2O_2 in the brine any more and the corrosion is definitely lower. By means of UV-Vis-spectroscopy, H_2O_2 could not be detected in these solutions, only TiO_2^{2+} was present.

In the second range, the corrosion rate of Ti99.8-Pd corresponds to the corrosion rate in H_2O_2-free NaCl solution (< 0.5 µm/a).

Figure 8 shows the dependence of the rest potential from the H_2O_2 concentration of the solution. The rest potentials are not constant, because the H_2O_2 is used up in time (see equations 2 and 3). But all rest potentials are in passive range between 350 mV and 450 mV and they increase with growing concentration from 6×10^{-3} to 1.7×10^{-1} mol/l. For an interpretation of this behaviour, more measurements are urgently needed.

The influence of H_2O_2 on the corrosion of Ti99.8-Pd can be seen from Table II. For comparison, the corrosion rates for a peroxide free solution obtained in previous experiments [6] are given. In the first range (60 - 65 h), the corrosion rates are directly proportional to the H_2O_2 concentration of the solution. But it can bee seen, that H_2O_2 concentrations smaller than 10^{-4} mol/l have no influence on the corrosion of Ti99.8-Pd at all. In other words, under practical conditions with H_2O_2 concentrations from 10^{-4} to 10^{-7} mol/l, the corrosion behaviour of Ti99.8-Pd will not have any influence al all.

Corrosion investigations at various potentials

Potentiostatic measurements were carried out on Ti99.8-Pd within the potential range from 0V to +1 V (passive range) at 25°C and a high H_2O_2 concentration in the NaCl brine of 6×10^{-2} mol/l. The dissolved titanium was measured continuously for 20 - 24 hours by means of γ-spectroscopy. The corrosion rates obtained at the various potentials are given in Table III. For comparison, the values determined in H_2O_2-free brine are also given. In the H_2O_2 containing brine, the corrosion rates amount 6 - 16 µm/a and are therefore clearly higher than the value determined in the H_2O_2-free brine (1 µm/a).

C.1.3 Stress corrosion cracking studies in salt and granitic environments (ENRESA/INASMET) (B.1.3 + B.2)

The resistance of three candidate container materials to stress corrosion cracking (SCC) is investigated in NaCl brine (25.9 wt.% NaCl) and in bentonite buffered granitic groundwater at 170°C and 90°C, respectively, by means of the slow strain rate technique (SSRT).

The materials to be studied have the following compositions (wt.%):

Carbon steel TStE355: 0.16 C; 0.41 Si; 1.5 Mn; 0.017 P; 0.002 S; 0.036 Al; 0.006 Ni; bal. Fe

Stainless steel AISI 316L: 0.021 C; 0.31 Si; 1.3 Mn; 0.029 P; 0.002 S; 17.4 Cr; 11.5 Ni; 2.2 Mo; bal. Fe

Ti99.8-Pd (TiGr-7): 0.008 N; 0.040 C; 0.003 H; 0.04 Fe; 0.12 0; 0.15 Pd; bal. Ti

Besides the parent metals, welded joints simulating potential container closure techniques are also considered. These are:

- EBW (Electron Beam Welding) for the three candidate container materials.
- FCAW (Flux Cored Arc Welding) for the carbon steel.
- PAW (Plasma Arc Welding) for the titanium alloy.

- GTAW (Gas Tungsten Arc Welding) for the stainless steel.

Following test conditions are applied:

SALT BRINE 170°C:

- TStE355 steel: Strain rates ranging from 10^{-4} to $10^{-7}s^{-1}$.
- Ti99.8-Pd alloy (TiGr-7): Strain rates of 10^{-6} and $10^{-7}s^{-1}$.

GRANITIC GROUND WATER 90°C:

- TStE355 steel: Strain rates ranging from 10^{-4} to $10^{-7}s^{-1}$.
- AISI 316L steel: Strain rates ranging from 10^{-4} to $10^{-7}s^{-1}$.

In addition, comparative tests are performed in argon as an inert reference medium.

During the reporting time, the chemical, mechanical and metallographic characterization of the materials has been performed, and slow strain rate (SSR) tests have been conducted in NaCl brine (5M NaCl) at 170°C.

Material characterization

Metallographic studies show a ferritic microstructure with perlite bands for the hot-rolled and annealed TStE355 carbon steel. AISI 316L stainless steel shows an austenitic structure with numerous maculas due to the annealing process. The alloy Ti99.8-Pd presents an equiaxic alfa structure. To characterize the weldments, metallographic specimens transversal to the welded joint have been studied. Microhardness tests (Vickers) have been performed along the welded joints. In general, a slight increase of the hardness in the welded joint occurred compared to the base material.

Slow strain rate tests

In the case of the TStE355 carbon steel, round specimens of 6mm diameter and 30mm gauge length were used. The test specimens of the titanium alloy had a diameter of 3.5mm and a gauge length of 25mm.

The experiment equipment used is described in a previous work [5]. Shortly, the specimens were located in Hastelloy C-276 autoclaves with one end being attached to fixed frame and the other to the pull rod. Then, the autoclaves were filled either with brine or argon, closed, pressured and heated. Once the testing temperature (170°C) and pressure (13 MPa) were reached, the specimens pulled until fracture at the selected actuator displacement speed.

Load, position, time and temperature data were continuously logged by the microprocessor that controls the testing machine. After each test, the elongation (E), reduction of area (R.A.), energy, yield strength (Y.S.), maximum load, and true stress at fracture were determined. To evaluate the resistance of the materials to SCC, metallographic and scanning electron microscopic (SEM) examinations of specimens were performed, in addition to the tensile experiments.

RESULTS

TStE355 steel

The results of the SSR tests on unwelded and FCA welded steel specimens show that the elongation, reduction of area, energy, and true stress at fracture are clearly lower in the brine than in argon. The values of the yield strength and maximum load in the brine, however, are very close to those obtained in argon. Figure 9 shows the elongation and reduction of area versus the strain rate in both media at 170°C. Figures 10 and 11 show for comparison macrographs of FCA welded specimens before testing and after testing in argon and in NaCl brine at 170°C and a strain rate of $10^{-7}s^{-1}$. In the metallographic examinations, shallow secondary cracks (less than 12 μm) were observed both for unwelded and welded specimens after testing in the brine at the slowest strain rate of $10^{-7}s^{-1}$. This indicates a slight sensitivity of the steel to SCC under the severe conditions of the SSR tests. Scanning electron microscopic (SEM) examinations show a change from fully ductile fracture surface (dimples) for specimens tested in argon, to a more brittle one when tests are performed in the brine.

Ti99.8-Pd (TiGr 7 alloy)

The results of the SSR tests on Ti99.8-Pd do not show any loss of ductility for unwelded and EB and PA welded specimens under the applied test conditions in brine and in argon (Table IV). Furthermore, no secondary cracks were observed in the metallographic studies. The fracture surface is fully ductile both in brine and in argon, which indicates the resistance of this Ti-alloy to SCC in the test brine. Figures 12 and 13 show SEM micrographs of the fracture surface of a EB welded Ti99.8-Pd specimen tested in brine at 170°C and a strain rate of $10^{-7}s^{-1}$.

C.2 Corrosion studies in clay/bentonite environments (SCK.CEN)

In addition to previous in-situ corrosion experiments [7], electrochemical corrosion studies are performed on candidate container materials aimed at investigating the influence of important environmental parameters on localized corrosion. Such parameters are: the temperature (16°C - 90°C) and the content of O_2, Cl^- and $S_2O_3^{2-}$ of the corrosion medium. The corrosion medium is oxidizing synthetic interstitial clay water having the following composition in wt.%;

> 1.01 Mg^{2+}; 10.2 SO_4^{2-}; < 15 K^+; 49.7 Cl^-; 413 Na^+; 1.62 F^-; 832 HCO_3^-/CO_3^{2-}; 5.86 Ca^{2+}.

The materials under investigation are compiled in Table V. The emphasis is laid on the study of carbon steel and stainless steels as these materials are the most important in the current disposal concept. Nevertheless, the nickel base alloy Hastelloy C4 and the titanium alloy Ti99.8-Pd (Ti/0.2Pd, Ti-grade 7) are investigated too, albeit to a less extent.

The electrochemical experiments are performed in a corrosion cell containing a working electrode, a saturated calomel reference electrode with lugging capillary, and two graphite counter electrodes. Before mounting the specimens, they were ground and polished to a 600 grit paper finish, degreased with acetone and rinsed with demineralized water. Prior to testing, the electrolyte was purged with nitrogen to remove the oxygen from the solution.

In the electrochemical investigation of pitting corrosion, the simultaneous occurrence of crevice corrosion is a major obstacle. Therefore, several methods of preparing the work electrode were examined, none of them, however, being completely successful in eliminating crevice corrosion. Besides of presenting an experimental problem and complicating the straightforward interpretation of the cyclic voltammograms, the abundant occurrence of crevice corrosion raises the question if crevice corrosion can be neglected in the practice of final disposal of nuclear waste. At SCK.CEN, an electrode is now being developed, which should allow to perform pitting corrosion tests free from crevice corrosion.

The electrochemical corrosion behaviour of the materials is examined by plotting polarization curves (determination of the characteristic pitting potentials), and post-examination of the corroded specimens by optical microscopy.

In the period under review, first qualitative results were obtained into the influence of temperature and Cl^- concentration in clay water on the corrosion of the materials. The test temperatures were 16°C (initial temperature of Boom clay) and 30°C (reference temperature). The Cl^- concentrations of the clay water investigated were 16 ppm (measured natural concentration), 1000 ppm and 10000 ppm. Qualitative results obtained by optical microscopic examination of specimens after potentiodynamic testing in deacerated clay water are given in Table VI. The results can be summarized as follows:

- At all test temperatures and Cl^- concentrations, the high alloyed stainless steels (UHB 904L, Cronifer 1925hMo), the nickel alloy Hastelloy C4 and the titanium alloy Ti99.8-Pd are resistant to general, pitting and crevice corrosion.
- The stainless steel AISI 316L is also resistant to general and local corrosion at all test temperatures and a Cl^- concentration of 16 ppm. However, at higher Cl^- concentrations (1000 and 10000 ppm) the steel exhibits crevice and/or pitting corrosion. For this steel, the breakdown potential decreases with increasing Cl^- content which indicates an enhanced susceptibility to local corrosion.
- The carbon steel TStE355 undergoes significant general corrosion, mainly at the higher temperatures (30°C) and the higher Cl^- concentrations in clay water.

From the results obtained so far it seems that the breakdown potentials are statistically distributed rather then obeying a deterministic law. Although the experimental conditions were strictly controlled in order to obtain a maximum reproducibility, variations of up to 200 mV of the breakdown potential for a determined set of experimental parameters were observed. Due to the stochastic nature of the pitting process, more experiments are needed to be able to draw quantitative conclusions. Such investigations are in progress.

D. CONCLUSIONS

In the disposal relevant $MgCl_2$-rich Q-brine (T = 150°C) the alloy Ti99.8-Pd is resistant to pitting corrosion, and its general corrosion is, as expected from previous work, very low (< 1 µm/a). The imposition of the 10 Gy/h radiation field on the 150°C brine environment does not influence the corrosion behaviour of the material.

H_2O concentrations in NaCl brine (T = 25°C) smaller than 10^{-4} mol/l do not influence the corrosion behaviour of Ti99.8-Pd. Furthermore, slow strain rate tests performed at 170°C in this brine indicate that the Ti-alloy is resistant to stress corrosion cracking at strain rates up to $10^{-7}s^{-1}$.

In case of the TStE355 carbon steel, pH values of the test brine ($MgCl_2$-rich, T=170°C) between 3 and 7 do not enhance the corrosion rate. At the very slow strain rate of $10^{-7}s^{-1}$ and 170°C, the steel shows a very slight sensitivity to stress corrosion cracking in NaCl-brine.

The results obtained in oxidizing clay water (T=16°C and 30°C) show that high alloyed stainless steels, Hastelloy C4 and Ti99.8-Pd are highly resistant to corrosion. However, the stainless steel AISI 316L is susceptible to pitting and crevice corrosion at high Cl^- concentrations (1000 ppm and 10000 ppm Cl^-) in clay water , and the carbon steel undergoes significant general corrosion.

Further investigations on steels, Hastelloy C4 and Ti99.8-Pd in rock salt, clay and granite environments are in progress (see session E).

E. PLANNED WORK FOR THE NEXT REPORTING PERIOD

Corrosion studies in salt environments (B.1)

- Continuation of the long-term immersion tests into the influence of pH on corrosion of the TStE355 carbon steel. Investigation of the potential synergistic effect of gamma radiation and salt impurities in brines on steel corrosion.
- Electrochemical and radiochemical studies on Ti99.8-Pd in saturated NaCl brine at higher temperatures (55°C, 80°C) and various H_2O_2 concentrations. (10^{-7} - 10^{-3} mol/l). Begin of corresponding studies in the $MgCl_2$-rich Q-brine. Characterization of the protecting titanium oxide layers by independence measurements.
- Continuation of the slow strain rate tests on electron beam (EB) welded TStE355 specimens in NaCl brine at 170°C and strain rates of 10^{-4} - $10^{-7}s^{-1}$.

Stress corrosion cracking studies in granitic environments (B.2)

Beginning of slow strain rate tests on welded and unwelded TStE355 specimens in bentonite buffered granitic groundwater at 90°C and strain rates of 10^{-4} - $10^{-7}s^{-1}$.

Corrosion studies in clay/bentonite environments (B.3)

Further electrochemical corrosion studies on preselected container materials (steels, Hastelloy C4, Ti99.8-Pd) in clay environments into the influence of temperature, Cl^- and $S_2O_3^{2-}$ concentrations on corrosion.

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Table I. Corrosion of Ti99.8-Pd in Q-brine at 150°C with and without gamma radiation field

Exposure time (d)	Weight loss*) (mg)	Dose rate (Gy/h)	Corrosion rate*) (µm/a)
63	0.10 ± 0.04	0	0.09 ± 0.040
125	0.06 ± 0.06		0.02 ± 0.020
191	3.50 ± 0.02		0.73 ± 0.004
268	0.10 ± 0.04		0.02 ± 0.008
63	0.10 ± 0.10	10	0.06 ± 0.060
174	0.62 ± 0.09		0.14 ± 0.020
244	3.79 ± 0.06		0.62 ± 0.010
356	1.49 ± 0.14		0.21 ± 0.020

*) average value of three specimens

Table II. Dependence of the corrosion of Ti99.8Pd on concentration of H_2O_2 in saturated NaCl solution at rest potential (350 mV- 450 mV) at 25°C

Initial concentration of H_2O_2 $mol \cdot l^{-1}$	Corrosion rates (first range) $\mu m \cdot a^{-1}$	Corrosion rates (second range) $\mu m \cdot a^{-1}$
0	0.3 ± 0.2	---
$6 \cdot 10^{-4}$	0.5 ± 0.3	0.3 ± 0.2
$3 \cdot 10^{-3}$	1.0 ± 0.3	0.4 ± 0.2
$6 \cdot 10^{-3}$	1.8 ± 0.5	0.2 ± 0.3
$3 \cdot 10^{-2}$	9.5 ± 1.7	0.5 ± 0.4
$6 \cdot 10^{-2}$	22.1 ± 2.4	0.3 ± 0.3

Table III. Dependence of the corrosion rate of Ti99.8-Pd on the applied potential (saturated NaCl solution at 25°C. H_2O_2 concentration: $6 \cdot 10^{-2}$ $mol \cdot l^{-1}$)

Potential (SHE) V	Corrosion rates (with H_2O_2) $\mu m \cdot a^{-1}$	Corrosion rates (without H_2O_2) $\mu m \cdot a^{-1}$
0	16 ± 5	1 ± 2
0.5	12 ± 5	1 ± 2
1	6 ± 4	

Table IV. SSR test results for welded and unwelded Ti 99.8-Pd (TiGr7) specimens in argon and NaCl-brine (170°C, 10^{-7} s^{-1})

	TiGr7		TiGr7 EBW		TiGr7 PAW	
	Argon	NaCl	Argon	NaCl	Argon	NaCl
Elongation (%)	30.0	31.3	23.6	26.4	19.1	18.2
Reduction in area (%)	71.9	68.7	68.7	69.2	69.4	70.8
Yield Strength (MPa)	178	181	187	185	194	199
True Stress Fract.(MPa)	538	540	581	573	592	577
Maximum Load (MPa)	228	243	246	244	248	239
Secondary cracks	None	None	None	None	None	None
Failure mode	Dimples	Dimples	Dimples	Dimples	Dimples	Dimples

EBW=electron beam welded; PAW=plasma arc welded

Table V. Chemical composition of the container materials tested in clay environments

	Chemical composition (wt%)										
	Fe	Cr	Ni	Mn	Mo	Si	Ti	C	S	P	Others
Carbon steel											
TStE 355	bal	0.03	0.03	1.12	0.00	0.34	0.003	0.180	0.002	0.010	Nb 0.017; N_2 0.005
Stainless steels											
AISI 316L	bal	16.9	11.0	1.54	2.08	0.54	-	0.017	0.001	0.032	
AISI 316hMo	bal	17.6	12.5	1.16	2.84	0.61	-	0.015	0.001	0.030	
AISI 316Ti	bal	16.8	10.7	1.08	2.05	0.40	0.3	0.044	0.009	0.028	
Higher alloyed stainless steel											
UHB 904L	bal	19.7	25.0	1.48	4.47	0.19	-	0.019	0.001	0.019	Cu1.5;N_2 0.08
Cronifer 1925hMo	45.4	20.6	24.8	0.92	6.40	0.30	-	0.005	0.002	0.018	Cu0.86;N0.19
Nickel alloy											
Hastelloy C4	0.98	15.7	67.0	0.04	15.8	0.02	<0.01	0.003	0.003	0.004	Co:0.01
Titanium alloy											
Ti/0.2Pd	0.04	-	-	-	-	-	bal	0.010	-	-	Pd:0.16;O_2:0.1 N2<0.01; H_2:0.001

Table VI. Corrosion results obtained for various container materials in oxidizing synthetic interstitial clay water (anaerobic conditions)

Temperature	16°C			30°C		
[Cl-] (ppm)	16	1000	10000	16	1000	10000
Material						
TStE 355	G	G	G	G	G	G
AISI 316L	N	C	-	N	C,P	C,P
AISI316hMo	-	-	-	-	-	-
AISI 316Ti	-	-	-	-	-	-
UHB 904L	N	N	N	N	N	-
Cronifer	N	N	N	N	N	N
Hastelloy	N	N	N	N	N	N
Ti/0.2Pd	N	N	N	N	N	N

G=General corrosion; C=Crevice corrosion; P=Pitting corrosion;
N=no corrosion; - =not tested

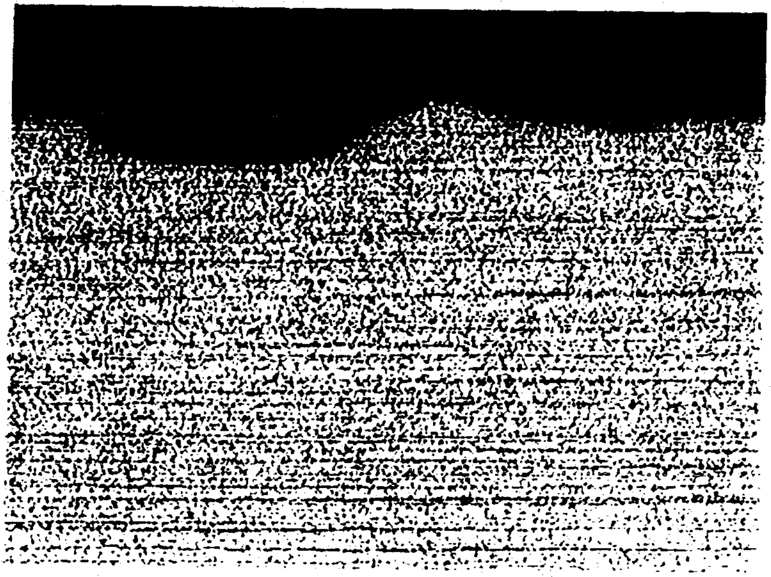


Figure 1. pH3 x50

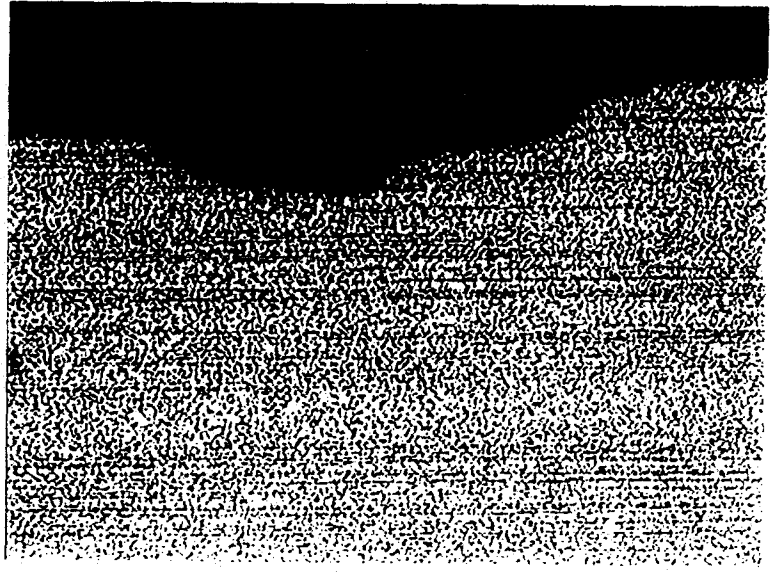


Figure 2. pH7 x50

Figures 1-2. Optical micrographs of TStE 355 steel after 1 year exposure to Q-brine at 170°C and various pH values

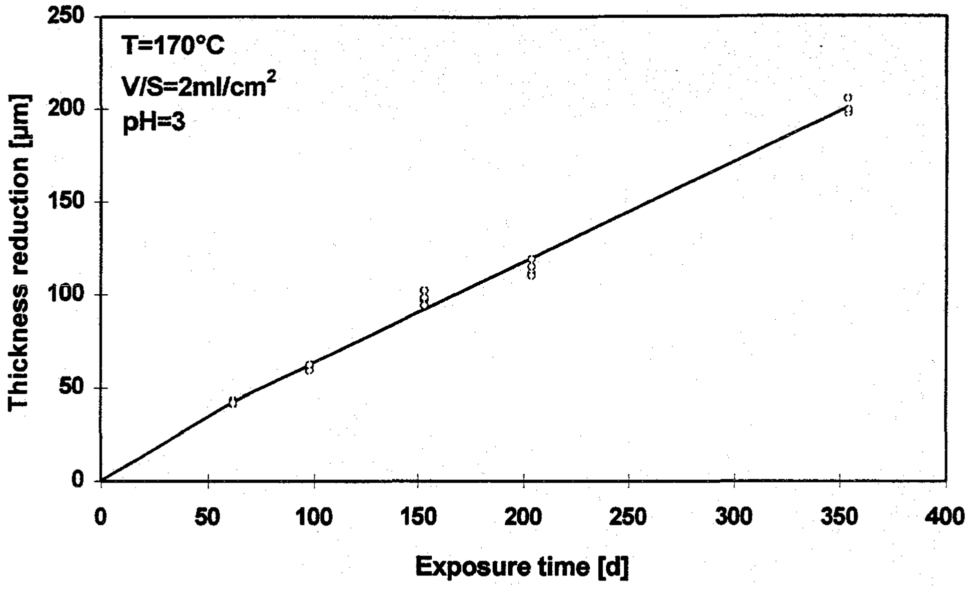


Figure 3. Time-dependence of the thickness reduction of TStE 355 steel in Q-brine at 170°C and pH=3

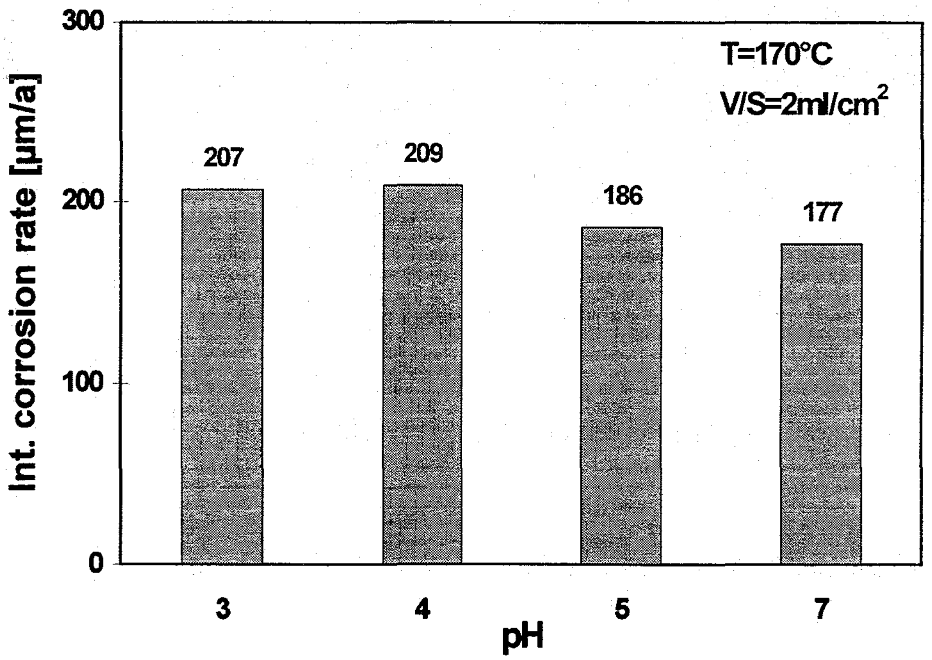


Figure 4. Corrosion rate of TStE 355 steel as a function of pH in Q-brine at 170°C

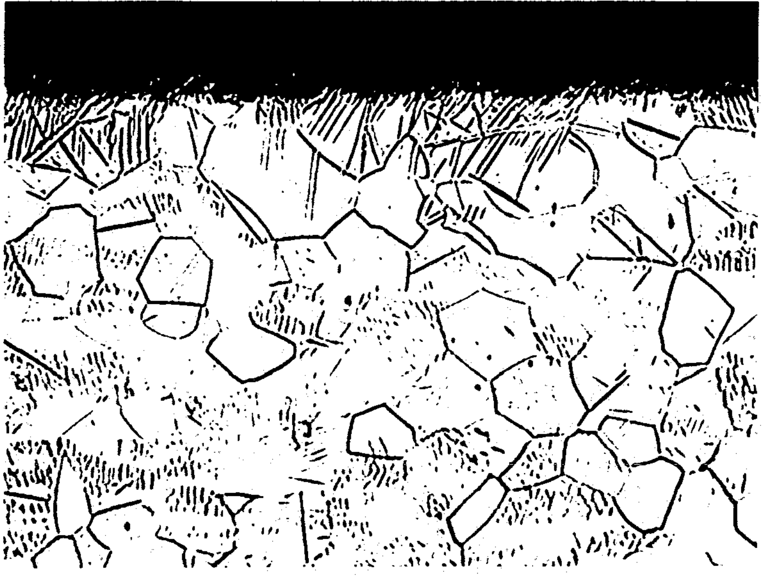


Figure 5. Q-brine/150°C/341days x200

Figure 6. Q-brine/150°C/10Gy/h/244days x200

Figures 5-6. Optical micrographs of Ti99.8-Pd after exposure to Q-brine at 150°C with and without gamma irradiation

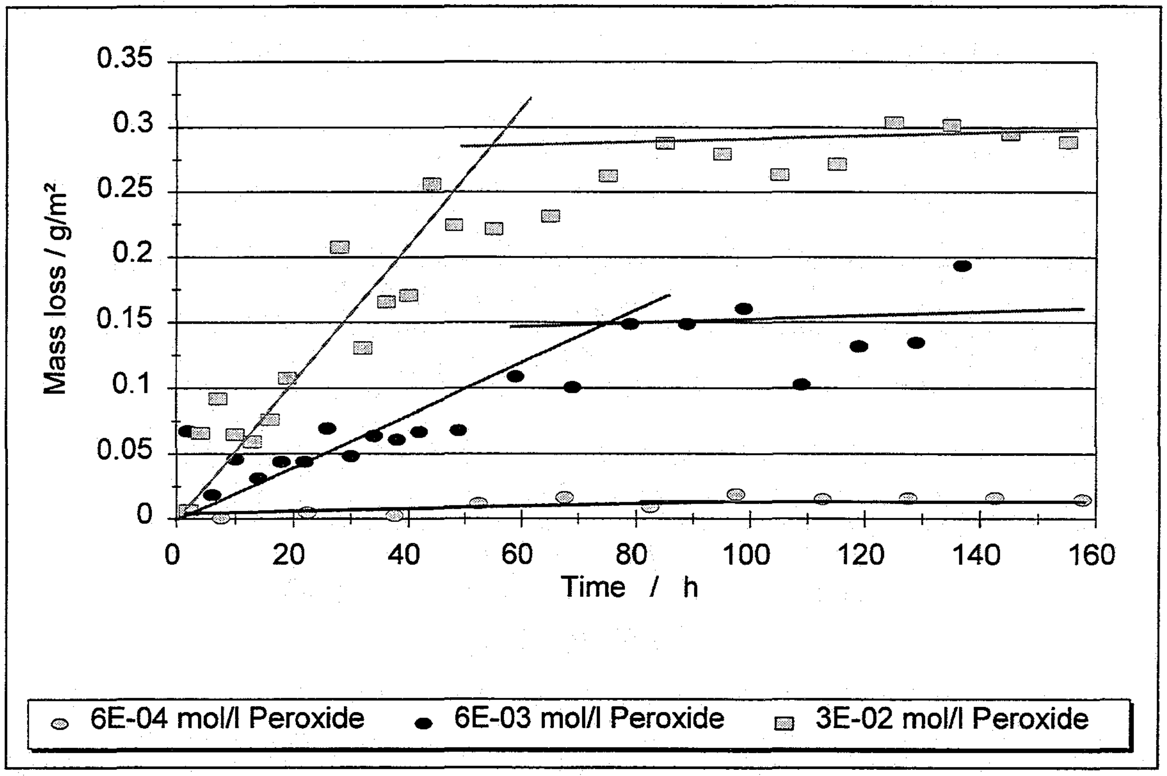


Figure 7. Time-dependence of the mass loss of Ti99.8-Pd at rest potential in saturated NaCl brine containing H_2O_2 (25°C)

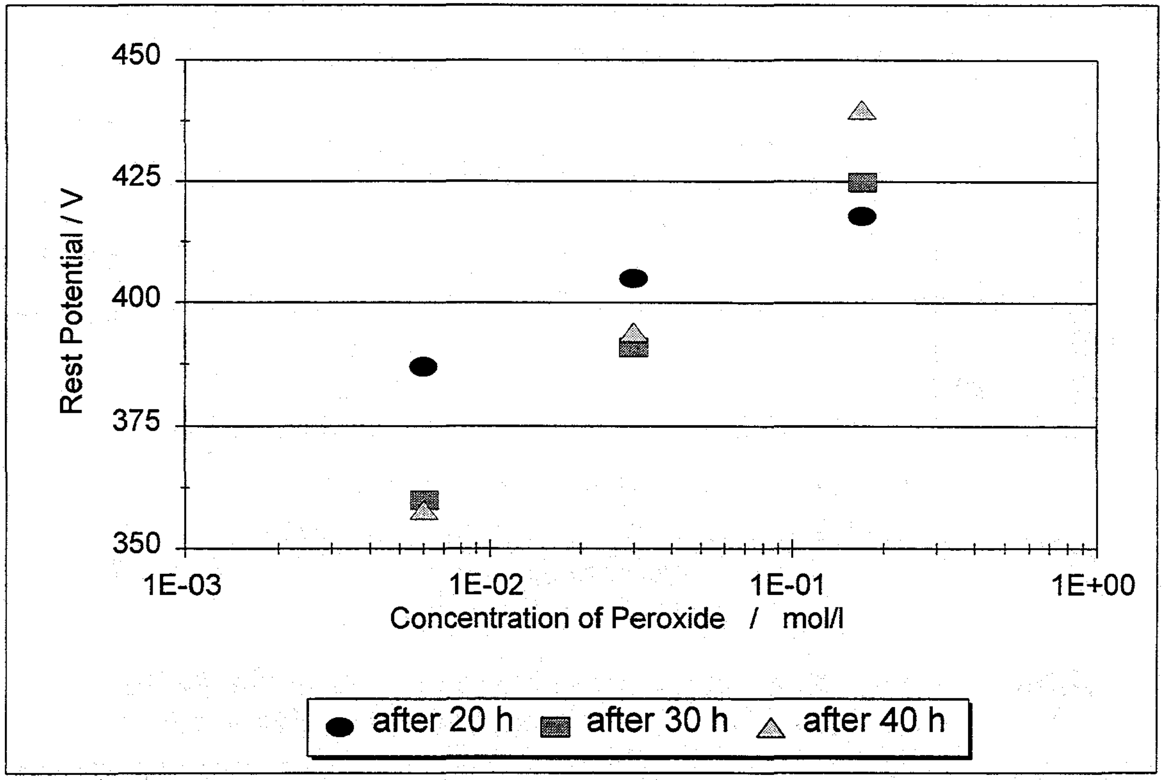


Figure 8. Dependence of the rest potential on the H_2O_2 concentration (saturated NaCl brine at 25°C)

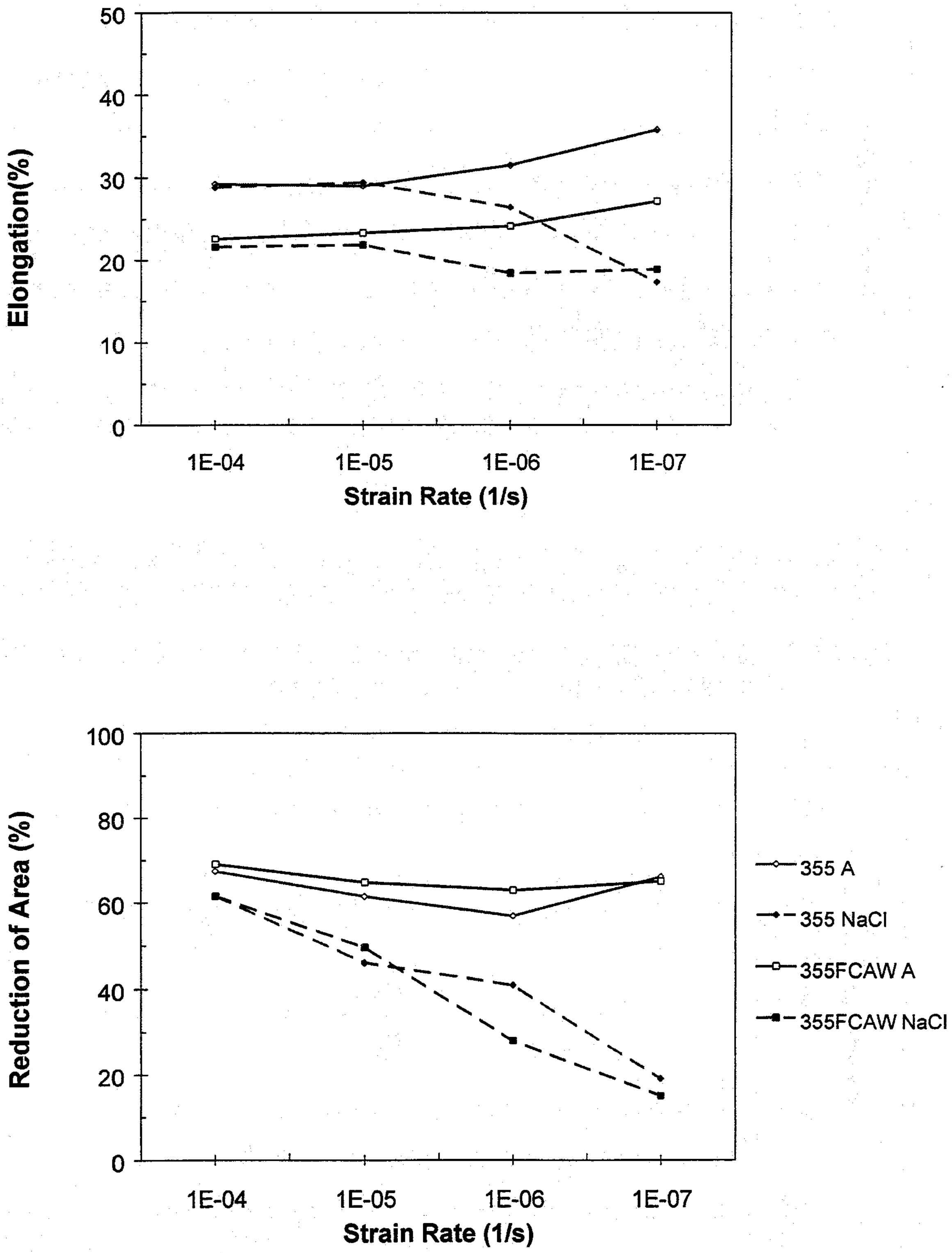
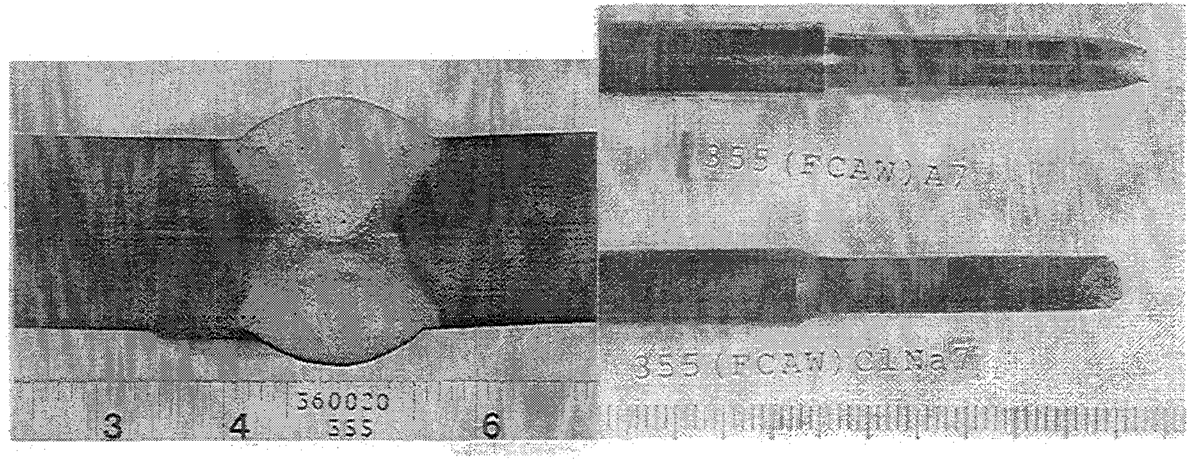


Figure 9. Elongation and reduction of area versus strain rate for the unwelded and FCA welded TStE355 steel tested at 170°C in argon (A) and NaCl brine



Figures 10-11. Macrographs of FCA welded TStE 355 steel specimens before testing (left side) and after testing in argon (right side, upper photograph) and NaCl brine (170°C, 10^{-7} s^{-1})

Figures 12-13. SEM micrographs of the fracture surface of a EB welded Ti99.8-Pd specimen tested in NaCl brine (170°C, 10^{-7} s^{-1})