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Summary

In order to qualify corrosion resistant materials for high level waste (HLW) packagings acting as a long-term barrier in a rock salt repository, the corrosion behaviour of preselected materials is being investigated in laboratory-scale and in-situ experiments. This work reports about in-situ corrosion experiments on unalloyed steels, Ti 99,8-Pd, Hastelloy C4, and iron-base alloys, as modular cast iron, Ni-Resist D4 and Si-cast iron, under simulated disposal conditions. The experiments were carried out in the frame of the German/US Brine Migration Test in heated tubed boreholes in the Asse salt mine at T = 150°C to 210°C, both in the absence and in the presence of a γ-radiation field of $3 \cdot 10^2$ Gy/h (Co-60 source). In addition, the material used to protect the tubing from corrosion (Inconel 600) as well as the backfill material for the annular gap (Al_2O_3 spheres) were investigated for possible corrosion attack.

The results of the investigations can be summarised as follows:

- All materials investigated exhibited high resistance to corrosion under the conditions prevailing in the Brine Migration Test. All material specimens corroded at much lower rates than determined in the previous laboratory-scale tests. The reason for the lower corrosion attack of the materials stored under in-situ conditions is the very small amount of corrosion medium (migrated brine) involved.

- All materials and above all the materials with passivating oxide layers such as Ti 99.8-Pd and Hastelloy C4 which may corrode selectively already in the presence of minor amounts of brine had been resistant with respect to any type of local corrosion attack.

- The γ-radiation of $3 \cdot 10^2$ Gy/h did not exert an influence on the corrosion behaviour of the materials.

- No corrosion attacks were observed on the Al_2O_3 spheres. In the case of Inconel 600 traces of sulphur were detected probably resulting from the reaction of Ni with H_2S to NiS. Measurable general and local corrosion, however, have not been observed.

In situ-Korrosionsuntersuchungen an ausgewählten HAW-Verpackungsmaterialien unter simulierten Endlagerbedingungen in Steinsalzformationen

Zusammenfassung

Zur Qualifizierung eines korrosionsbeständigen Materials für die Realisierung einer langzeitbeständigen Verpackung für HAW-Kokillen als Barriere in einem Endlager in einer Steinsalzformation, wird das Korrosionsverhalten ausgewählter Materialien mittels Labor- und in situ-Experimenten untersucht. In der vorliegenden Arbeit wird über in situ-Korrosionsexperimente an unlegierten Stählen, Ti 99,8-Pd, Hastelloy C4 und Eisenbasislegierungen (Sphäroguß, Ni-Resist D4 und Si-Guß) unter simulierten Endlagerbedingungen berichtet. Die Experimente erfolgten in beheizten, verrohrten Bohrlöchern im Salzbergwerk Asse im Rahmen des deutsch/amerikanischen Brine Migration Tests bei T = 150°C-210°C ohne bzw. mit einem γ-Strahlenfeld von $3 \cdot 10^2$ Gy/h (Co 60-Quelle). Zusätzlich wurden das Korrosionsschutzmaterial für die Verrohrung (Inconel 600) und das Ringspalt-Verfüllmaterial (Al_2O_3-Kugeln) auf Korrosionsangriffe untersucht.

Die in situ-Korrosionsergebnisse lassen sich wie folgt zusammenfassen:

- Alle untersuchten Werkstoffe zeigten unter den Bedingungen des Brine Migration Tests eine hohe Korrosionsbeständigkeit. Alle Werkstoffproben korrodierten mit wesentlich niedrigeren Abtragsraten als bei den bisherigen Laborversuchen. Ursache für den geringeren Korrosionsangriff der Werkstoffe unter den in situ-Bedingungen gegenüber den Laborversuchen ist die sehr kleine Menge an Korrosionsmedium (migrierte Lauge).

- Alle Materialien und insbesondere die Werkstoffe mit passivierenden Oxidschichten wie Ti 99,8-Pd und Hastelloy C4, die bereits durch geringe Laugenmengen selektiv korrodiert werden können, waren beständig gegenüber lokalen Korrosionsangriffen jeglicher Art.

- Die γ-Strahlung von $3 \cdot 10^2$ Gy/h hatte keinen Einfluß auf das Korrosionsverhalten der Materialien.

- An den Al_2O_3-Kugeln wurde keine Korrosion beobachtet. An Inconel 600 wurden Spuren von Schwefel nachgewiesen, die vermutlich aus der Reaktion von Ni mit H_2S zu NiS stammen. Eine meßbare Flächen- oder Lokalkorrosion war allerdings nicht festzustellen.

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1. Introduction

Radioactive waste disposal in deep rock salt formations relies on the concept of isolating the radionuclides from the biosphere through a combination of geological and engineered barriers. According to this multi-barrier concept [1] investigations are going on at KfK into the development of a long-term resistant packaging for high-level waste canisters to serve as a barrier in the repository during the high-temperature phase (> 100°C). The investigations include:

- Laboratory-scale and in-situ corrosion experiments on the qualification of a packaging material with sufficient long-term corrosion resistance in salt brines as may occur as a result of thermal migration of brine inclusions in rock salt or in hypothetical accidents in a repository.

- Work on the development of a suitable packaging concept, inclusive of closing techniques.

This paper reports about in-situ corrosion tests on selected packaging materials under simulated disposal conditions. The materials investigated were Ti 99.8-Pd, Hastelloy C4, fine-grained steel, cast steel, spheroidal cast iron, Ni-Resist D4, and Si-cast iron. The experiments were carried out in heated tubed boreholes in the Asse salt mine in the framework of the German/US Brine Migration Test [2,3].

The investigations focussed on the unalloyed steels (fine-grained steel, cast steel), Ti 99.8 Pd and Hastelloy C4 because they proved to be the most promising packaging materials in the previous comprehensive laboratory-scale experiments /e.g. 4,5,6/. The investigations into spheroidal cast iron, Ni-Resist D4 and Si-cast iron served to supplement the laboratory results available so far. A long-term barrier function cannot be expected from the said materials because in previous laboratory-scale experiments they exhibited a high susceptibility to local corrosion.

Besides the packaging materials mentioned above the Inconel 600 corrosion protection material to be used for the tubing and the Al_2O_3 annular gap backfill material were examined for possible corrosion attacks in order to obtain additional information about their corrosion behaviour under in-situ conditions.

2. Corrosion studies on selected HLW packaging materials

2.1 Materials investigated

The chemical compositions of the materials investigated, Ti 99.8 Pd, Hastelloy C4, fine-grained steel, cast steel, spheroidal cast iron, Si-cast iron and Ni-Resist D4, have been entered in Table 1. The materials Ti 99.8-Pd and Hastelloy C4 were investigated as delivered (hot-rolled sheet metals, annealed, descaled) without any subsequent surface treatment. Ti 99.8-Pd, as a result of the manufacturing process, exhibited an approx. 200 to 400 µm thick deformation layer which was covered by a uniform oxide layer (50 to 100 nm thickness). Before the corrosion experiments the specimens made of fine-grained steel (hot-rolled and annealed sheet metal), cast steel and spheroidal cast iron were freed from the adhering oxide layer and cast skin, respectively, by milling. The material specimens made of Ni-Resist D4 and Si-cast iron were investigated in the as-delivered condition, i.e., with a surface ground allround.

2.2 Specimen form and specimen treatment

All materials were investigated for their resistance to general corrosion (weight change) and local corrosion under in-situ conditions. Plane specimens with the following dimensions were used: Ti 99.8-Pd, Hastelloy C4 and fine-grained steel 40mmx20mmx3-4mm; Si-cast iron 36mmx18mmx5mm; and the rest of cast materials 40mmx10mmx10mm.

The materials cast steel, spheroidal cast iron, Ni-Resist D4 and Si-cast iron were investigated exclusively in the as-delivered condition. For the most promising HLW packaging materials fine-grained steel, Ti 99.8-Pd and Hastelloy C4 the influence of welding on their corrosion behaviour was also studied with a view to container welding in later application. For this purpose, specimens were examined with a TIG weld bead applied. In order to test the suitability of Hastelloy C4 as a container material for direct filling of HLW glass some of the specimens were subjected to thermal treatment either before or after welding. This simulated the loading of the bottom and lid welds in practical application. The thermal treatment of the specimens was described in an earlier publication [4].

All material specimens were cleaned in alcohol in an ultrasonic bath before they were stored. After storage the specimens were freed from the adhering salts and corrosion products using suitable pickling solutions and then their corrosion attack were investigated.

The weight change of the specimens after corrosion was determined by gravimetry. The depth of any local corrosion attacks was determined with an electronic depth gauge as well as from surface profiles and metallographic transverse sections.

2.3 Testing conditions

The material specimens to be investigated were stored in four boreholes, two of them accommodating Co-60 sources. A detailed description of the test set-up is given in [7]. The longitudinal section of one of these boreholes as well as the corrosion conditions to which the specimens were exposed have been represented in Fig. 1. It can be noticed that under the selected conditions the brine migrating into the boreholes evaporated so that the specimens were exposed to a steam atmosphere with salt constituents. Besides, gases emanating from the rock salt participated in the corrosion process in addition to gaseous products generated during corrosion of the materials and radiolysis of the brine. The measured values in Fig. 1 of the volume and composition of the brine and gas as well as the temperature profile and the pressure building up are maximum and minimum values applicable to all four boreholes. They were determined by the Institut für Tieflagerung, Brunswick. Detailed information about the development versus time of the measured values is given in [7] which includes also information about the distribution of the specimens in the boreholes. The materials were tested at temperatures between 120°C and 210°C. The testing temperatures for the individual materials are given in

Table 2. The maximum γ dose rate was $3 \cdot 10^2$ Gy/h and the calculated maximum rock pressure was 28 MPa. The maximum testing period for the materials was about 900 days.

2.4 Results

The materials tested corroded at extremely low rates under the in-situ testing conditions, both in the presence and in the absence of γ radiation. No noticeable influence has been observed of TIG welding or thermal treatment (only for Hastelloy C4) on the corrosion behaviour of the materials.

The weight losses of the materials determined by gravimetry and the linear corrosion rates calculated from them have been entered in Table 2. Some specimens did not lend themselves to gravimetric evaluation because they were damaged mechanically in the course of retrieval. These specimens were used for local corrosion examinations. It is apparent from Table 2 that the corrosion rates of all materials not exposed to irradiation, are < 2 µm/a and that, except for fine-grained steel, γ radiation of $3 \cdot 10^2$ Gy/h has not resulted in an increase of these values.

The low corrosion rates of the materials can be explained by the fact that only 140 ml brine at the maximum had flown into the boreholes by migration which spread over the large surface of the inserts (tubing, etc.) of about 71 m². For corrosion of the material specimens of a maximum surface of 250 cm² only a very low amount of brine was available.

The higher corrosion rate determined for fine-grained steel exposed to irradiation (about 14 µm/a) is not attributed to the effect of radiation. This assumption relies on the finding that for the similar material, cast steel, there was no difference in the corrosion rates with and without γ radiation. The increase in the corrosion rate is probably attributable to the fact that after the heater had been shut down because of plugging of a tube it was not possible to condense more than about half of approx. 1600 ml of inflowing brine. Thus, these specimens suffered corrosion attack by non-condensed brine for an additional period of approx. 12 months (i.e., the time interval between shut-down of the heater and specimen retrieval) at a mean temperature of about 70°C.

The metallographic examination of the specimens has shown that, with the exception of fine-grained steel, all the other materials undergo uniform corrosion under the in-situ conditions if they are exposed to irradiation. Figures 2 and 3 show by way of example micrographs of Ti 99.8-Pd, Hastelloy C4 and fine-grained steel before and after storage. Corrosion attack under shallow pit formation of fine-graind steel with a maximum depth of about 60 μm is attributed to corrosion through non-condensed brine as already discussed.

It can be stated from the results available on in-situ corrosion that the corrosion rates of the iron-base alloys investigated have been much lower than those obtained in laboratory-scale experiments [6] involving salt brines and rock salt/salt brines. For Ti 99.8-Pd and Hastelloy C4 no significant differences between laboratory and in-situ results of the corrosion rates have been found. The very pronounced local corrosion attacks on spheroidal cast iron, Ni-Resist D4, Si-cast iron and Hastelloy C4 (only at 200°C and under irradiation at 1000 Gy/h), respectively) observed in the laboratory-scale experiments have not appeared under the in-situ conditions. The lower corrosion attack of the materials under in-situ conditions, compared with the laboratory-scale tests, is attributed to the very low amounts of corrosion medium present.

3. Supplementing corrosion tests on Inconel 600 and Al_2O_3 spheres

This study aimed at finding out whether the plating material of the Inconel 600 tubing (material No. 2.4816) and the Al_2O_3 spheres uses as backfill of the annular gap participated in the corrosion process.

Metallographic and scanning electron microscopic examinations of selected material specimens taken from the four tubings have not indicated any corrosion attack. Semi-quantitative examinations using EDAX (Energy Dispersed X-Ray Analysis) have not made evident a change in the Fe, Cr and Ni contents compared with the initial material. Looking at these results and the minor weight losses suffered by the corroded specimens (Ti 99.8-

Pd, Hastelloy C4, iron base alloys) the maximum H_2 concentrations of 2.2 vol.% measured in the boreholes cannot be explained by corrosion attack. However, it should be taken into account that these methods of investigations do not allow to measure corrosion layers of < 1 µm thickness. As for a tubing surface of about 3 m² minor general corrosion of several tenths micrometers would already lead to significant amounts of H_2, surface examinations based on more sophisticated methods are required to clarify a potential contribution by Inconel to H_2 formation.

These methods are:

- Auger Electron Spectroscopy (AES)
- Electron Spectroscopy for Chemical Analysis (ESCA),
- X-ray Photoelectron Spectroscopy (XPS).

Hydrogen, which is present in low amounts in rock salt [8], has not been detected in the gas analyses conducted in the boreholes 1 to 4. Two indications of the supposed reaction taking place between nickel from Inconel 600 and hydrogen sulphide to give NiS have been found with the help of EDAX:

- Contrary to the starting material, sulphur has been detected in the transverse sections of the Inconel specimens.
- Sulphur has likewise been identified to be present on the surface of an Inconel specimen taken from borehole 4.

Micrographs of Al_2O_3 spheres from all boreholes have not exhibited noticeable modifications compared with the initial state. No attack of the grain boundaries of Al_2O_3 spheres by penetrating constituents of the migrating brine (e.g., Na, Cl) similar to that found in the laboratory-scale experiments [9] conducted on the Al_2O_3 material in Q-brine has been detected in the examinations relying on EDAX.

4. Literature

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TABLE 1 CHEMICAL COMPOSITION OF THE MATERIALS USED IN THE IN SITU-CORROSION EXPERIMENT

MATERIAL	COMPOSITION (wt.%)												
	Cr	Ni	Mo	Ti	Pd	C	Si	Mn	Nb	O_2	N_2	H_2	Fe
Ti 99.8-Pd (DIN No.3.7025.10)	-	-	-	BAL	0.17	0.01	-	-	-	0.04	0.01	0.001	0.05
HASTELLOY C4 DIN No. 2.4610)	16.8	BAL	15.9	0.33	-	0.006	0.05	0.09	-	-	-	-	0.05
FINE-GRAINED STEEL (DIN No. 1.0566)	-	-	-	-	-	0.17	0.44	1.49	-	-	-	-	BAL
CAST STEEL (DIN No. 1.1131)	-	-	-	-	-	0.16	0.61	1.51	-	-	-	-	BAL
SPHEROIDAL CAST IRON (DIN No. 0.7043)	-	-	-	-	-	3.7	1.83	0.21	-	-	-	-	BAL
Ni-RESIST D 4 (DIN No. 0.7680)	5.5	30.9	-	-	-	2.6	4.25	0.5	-	-	-	-	BAL
Si-CAST IRON	-	-	-	-	-	0.72	15.0	0.62	-	-	-	-	BAL

- = NOT EXISTING OR NEGLIGIBLE

Table 2 Weight Loss and Corrosion Rate of the Materials used in the in situ-corrosion Experiment with and without Gamma - Irradiation

Material	Test Temperature (°C)	without Gamma - Irradiation (Exposure Time: 900 d)		with Gamma - Irradiation $3 \cdot 10^2$ Gy/h (Exposure Time: 700 d)	
		Weight Loss (g/m^2)	Corrosion Rate (µm/a)	Weight Loss (g/m^2)	Corrosion Rate (µm/a)
Ti 99,8 - Pd	210	+	+	1,4	0,16
Hastelloy C4	210	+	+	19,19	1,18
Fine-Grained Steel	150	17,79	0,95	200,06	13,68
Cast Steel	150	22,72	1,18	9,49	0,63
Ni-Resist D4	150	5,43	0,29	3,23	0,22
Spheroidal Cast Iron	120	+	+	13,26	1,01
Si-Cast Iron	120	29,31	1,72	+	+

\+ Specimens not retrievable or mechanically damaged

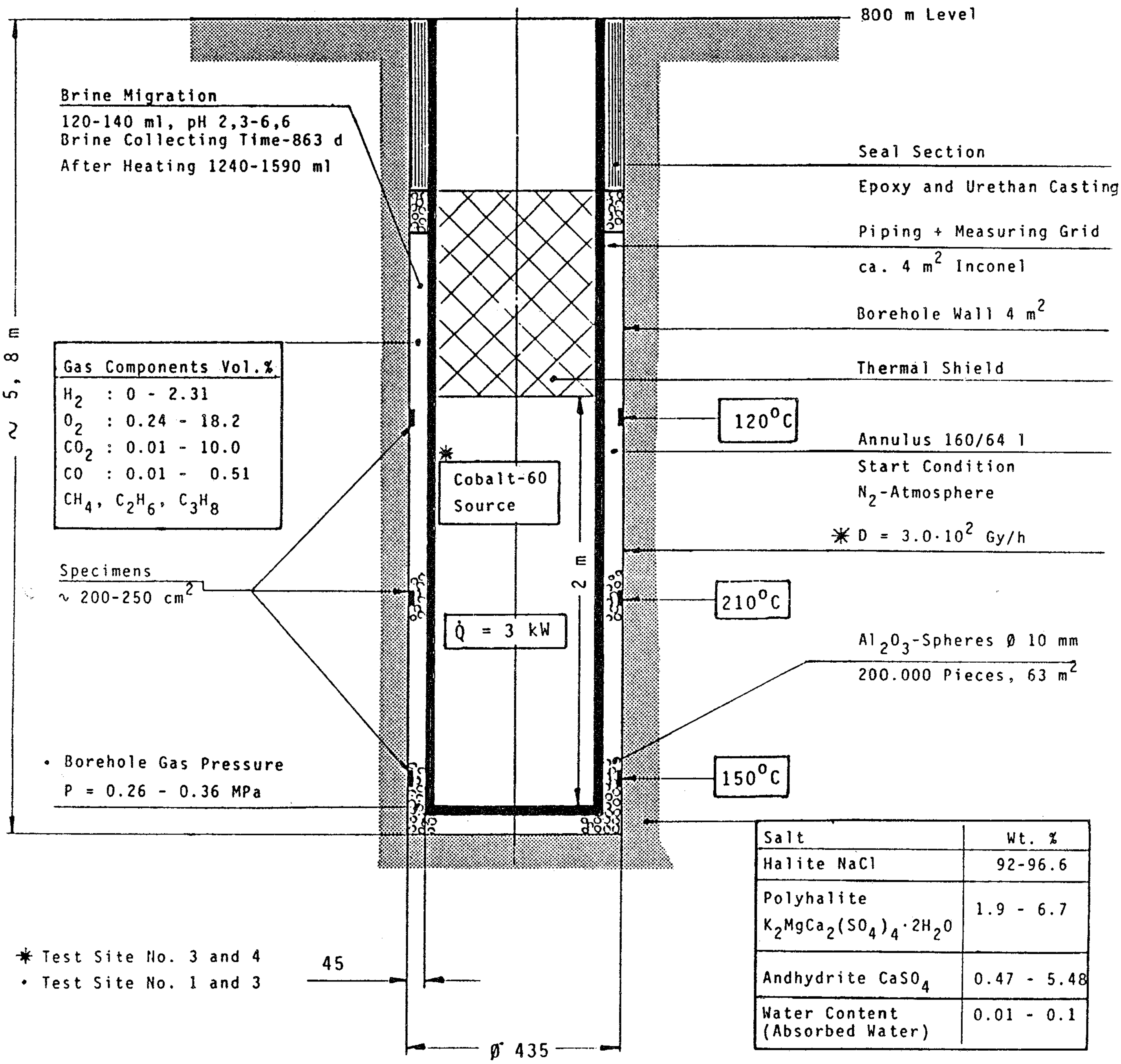
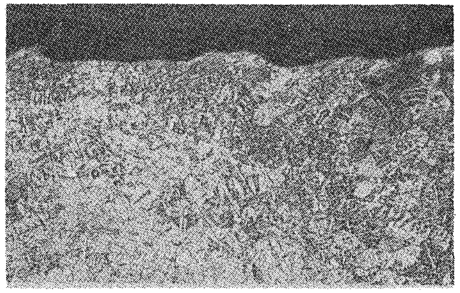
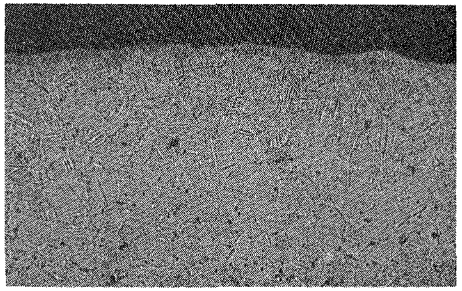
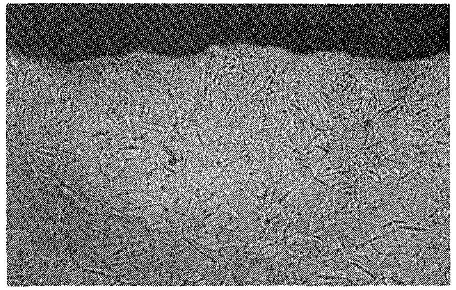
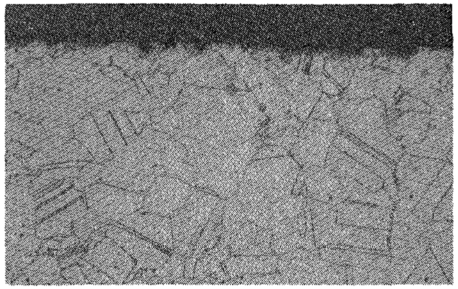
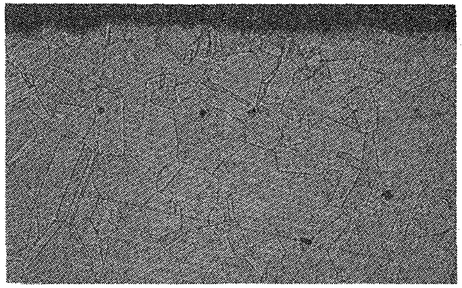
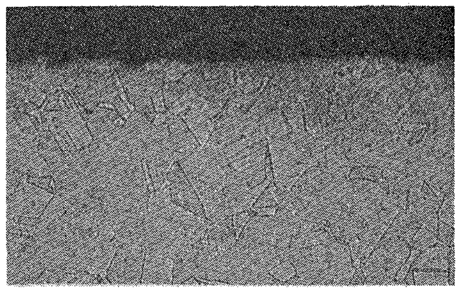


Fig. 1 Schematic Vertical Section of the Test Assembly with Indication of the Corrosion Conditions

MATERIAL	Before Exposure	After Exposure without Gamma-Irradiation $T = 210^{o}C$, $t = 900$ d	After Exposure with Gamma-Irradiation $T=210^{o}C$, $t=700$ d, $\dot{D}$ ca. $3\cdot10^{2}$ Gy/h
Ti 99.8-Pd			
Hastelloy C4			

0.1 mm 0.1 mm 0.1 mm

Fig. 2 Optical Micrograph of in situ - Corrosion Specimens

MATERIAL : FINE - GRAINED STEEL

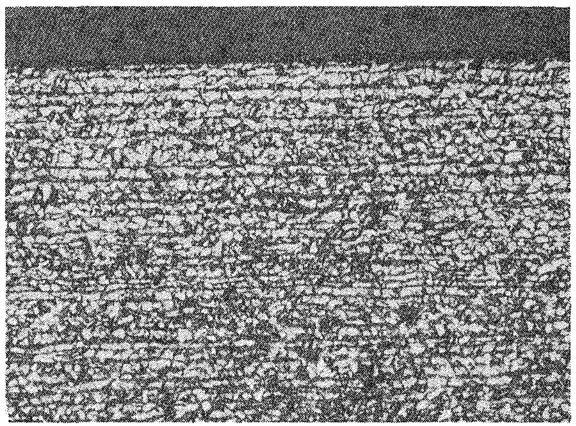
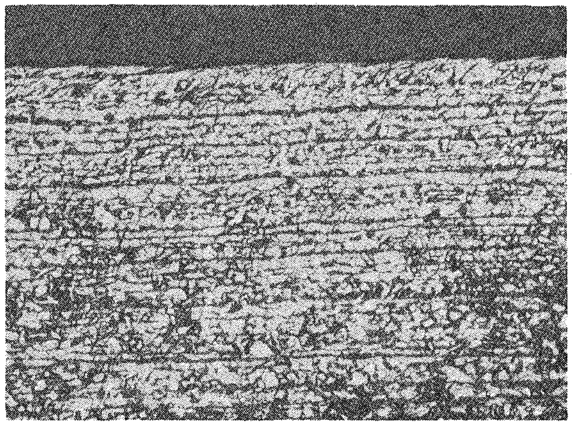
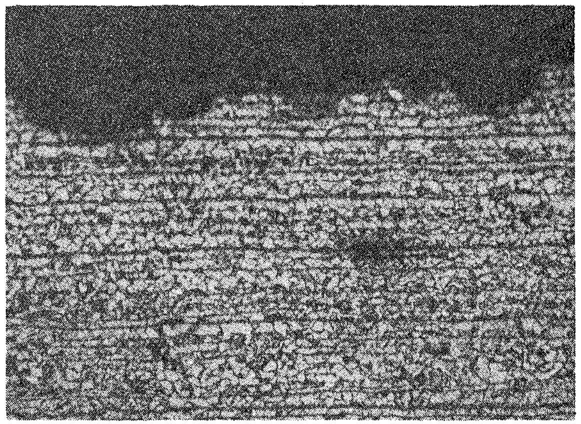
Before Exposure	After Exposure without Gamma-Irradiation $T = 150^{o}C$, $t = 900$ d	After Exposure with Gamma-Irradiation $T=150^{o}C$, $t=700$ d, $\dot{D}$ ca. $3\cdot10^{2}$ Gy/h
		
0.1 mm	0.1 mm	0.1 mm

Fig. 3 Optical Micrograph of in situ - Corrosion Specimens

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