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INTERIM REPORT

CORROSION OF TiCode-12 IN A SIMULATED WASTE ISOLATION PILOT PROJECT (WIPP) BRINE*

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ABSTRACT

The corrosion behavior of TiCode-12 (Ti-0.3 Mo-0.8 Ni) high level nuclear waste container alloy has been studied for a simulated WIPP brine at a temperature of 150°C or below. Crevice corrosion was identified as a potentially important failure mode for this material. Within a mechanical crevice, a thick oxide film was found and shown to be the rutile form of TiO_2, with a trace of lower oxide also present. Acidic conditions were found to cause a breakdown of the passive oxide layer. Solution aeration and increased acidity accelerate the corrosion rate. In hydrogen embrittlement studies, it was found that hydrogen causes a significant decrease in the apparent stress intensity level in fracture mechanics samples. Hydride formation is thought to be responsible for crack initiation. Stress corrosion cracking under static loads was not observed. Attention has also been given to methods for extrapolating short term uniform corrosion rate data to extended times.

INTRODUCTION

Currently in the U.S.A. there is an effort to develop titanium alloy TiCode-12 (Ti-0.3 Mo-0.8 Ni) as a prime corrosion resistant material for high level nuclear waste containers which will be emplaced in mined geologic repositories [1-7]. Preliminary data indicate that although uniform corrosion is unlikely to present a problem with respect to failure of the container, little information is available on possible localized corrosion failure mechanisms. The assessment of localized corrosion mechanisms is, therefore, essential for the prediction of the life time of the containers. This paper outlines initial results on the possible major localized failure modes of TiCode-12 in simulated rock salt brine solutions. Emphasis was on the study of crevice corrosion and hydrogen embrittlement. Crevice-type environments are expected to form between the TiCode-12 container and surrounding backfill materials or metallic emplacement sleeves. Hydrogen embrittlement is also possible since this material typically contains 30 ppm of hydrogen as a residual element. Furthermore, radiolysis of the groundwater may cause an increase in the hydrogen level. Preliminary results on stress corrosion cracking (SCC) are presented. Attention has also been given to methods for extrapolating short term uniform corrosion rate data to extended times, in order to predict container performance.

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MATERIALS AND ENVIRONMENT

TiCode-12 is a two-phase material composed of alpha and minor beta phases. Plate and sheet materials were obtained from three different sources: RML, Timet, and Crucible. The nominal compositions are shown in Table I. Differences in the compositions were found by BNL in the analysis of Ni, Mo, and Fe in the various heats of TiCode-12. The maximum variation was a factor two larger than values specified by the vendors.

TABLE I
Nominal compositions of TiCode-12 (weight percent)

Ni	Mo	Fe	C	H	N	O	Ti
0.80	0.30	0.3M[a)]	0.1M	0.015M	0.03M	0.25M	Balance

[a)] M denotes the maximum.

Brine solutions selected for this study were based on those used by Sandia National Laboratories [1] which are considered to simulate salt repository conditions at the Waste Isolation Pilot Plant site. The concentrations of the major ions in the two solutions used are shown in Table II. The majority of the work was performed on Brine A. The reference text temperature was 150°C. Lower temperatures were sometimes used to develop an understanding of the mechanisms of failure.

TABLE II
Compositions of brine solutions (ppm) [1]

Brine	Na^+	K^+	Mg^{+2}	Ca^{+2}	Sr^{+2}	Cl^-	SO_4^{-2}	I^-	HCO_3^-	Br^-	BO_3^-
A	42000	30000	35000	500	5	190000	3500	10	700	400	12000
B	11500	15	10	900	15	175000	35000	10	10	400	10

EXPERIMENTAL PROCEDURES

Three different sizes of coupon were used (1 x 2, 2 x 2, and 2 x 4 cm) for the tests on crevice corrosion. After mirror polishing of the coupons, a crevice was simulated by joining metal/metal or metal/Teflon couples with titanium bolts. The immersion studies were performed in quartz tubes or in static autoclaves for two to four week periods at 150°C. The solution acidity and oxygen concentration of the solutions were varied. The degree of corrosion was examined optically and the corrosion products were analyzed by SEM and TEM.

Hydrogen embrittlement was evaluated at room temperature using thermally hydrogenated single-edged-notched (SEN) tensile samples [8] (cross head speed 0.005 cm/min) to determine the susceptibility of TiCode-12 to hydrogen embrittlement and to ascertain the probable mechanisms involved. The hydrogen concentration was determined after the tests by the vacuum extraction method and the fracture surface was examined by SEM. Hydrogen uptake experiments were performend in Brine B during immersion tests on single and creviced coupons at 150°C in an autoclave with a hydrogen overpressure at a room temperature of 1.5 MPa (220 psi).

In the SCC study, both notched and un-notched C-rings were designed following ASTM standards [9] and these were loaded and sealed in quartz tubes containing acidified brines (pH = 1.1) to simulate crevice conditions. The test was performed at 150°C for an exposure time of three months. The acidified brine was also used in an attempt to understand the passivation behavior of TiCode-12. The open circuit corrosion potential was measured at 80°C for this purpose.

Immersion tests on single coupons (1 x 2 cm) were performed at 150°C. The weight gain was measured after varying exposure time to obtain uniform corrosion kinetics.

RESULTS AND DISCUSSIONS

During the initial stage of the crevice corrosion in Brine A (first few days immersion) a very thin multicolored corrosion product was observed (Fig. 1). This film was found to be the anatase form of TiO_2. For exposures of over two weeks the largest samples (2 x 4 cm) with the smallest crevice gap showed a thicker black corrosion product (Fig. 2). This was composed of the rutile form of TiO_2 with traces of lower oxides such as Ti_3O_5. Higher O_2 concentrations promote rutile formation. In general, lower pH, larger sample sizes, and smaller crevice gaps gave higher crevice corrosion rates. In order to understand the crevice corrosion mechanism, measurements of the open-circuit corrosion potentials were made at 80°C. These showed a breakdown of the passive film occurs as the pH of the brine falls below 1.0. Since a pH drop is expected to occur in the crevice, loss of passivation and crevice attack are also anticipated. These results are similar to the crevice corrosion of pure titanium in NaCl solution [10,11]. However, the crevice corrosion rates are much slower in TiCode-12. Mass transport calculations for oxygen inside the crevice showed a significant oxygen depletion in this region. The results imply that the compact and passive anatase form of TiO_2 [12] is no longer stable as the macroscopic concentration cell is developed. Consequently, the more porous rutile form of TiO_2 and lower oxides are probably formed in the crevice.

In the hydrogen embrittlement tests for SEN samples, the apparent stress intensity (K_Q) [13] values and hydrogen concentrations were determined and are given in Table III. At the 100 ppm hydrogen concentration level, the sample was very ductile (Fig. 3) with a slanted fracture surface and it had a high K_Q value. The K_Q values for 6560 and 10900 ppm of hydrogen were decreased by a factor of about 10 compared to the 100 ppm hydrogen sample. Fractographs show both alpha phase brittle fracture and alpha-beta interface cracking (Fig. 4). These features are similar to those observed in other near-alpha titanium alloys [14,15], and implies that the formation of hydride is responsible for crack initiation [16,17].

In the hydrogen uptake tests, single coupons, as well as creviced samples, were used to check the enhanced hydrogen uptake rate caused by the breakdown of the passive film inside the crevice. As shown in Table IV, the hydrogen uptake rate in the crevice sample was significantly higher than that for the single coupons. The breakdown of the passive film inside the crevice is probably responsible for the enhanced attack. Also, the reducing environment may have slowed down oxide scale growth which in turn inhibits hydrogen penetration.

C-ring tests did not show cracking for either elastically or plastically deformed samples. However, there is a possibility that dynamic tests, or the presence of radiation-induced oxidants such as ClO_3^- or H_2O_2, may

Fig. 1. The initial stage of the crevice corrosion of TiCode-12.

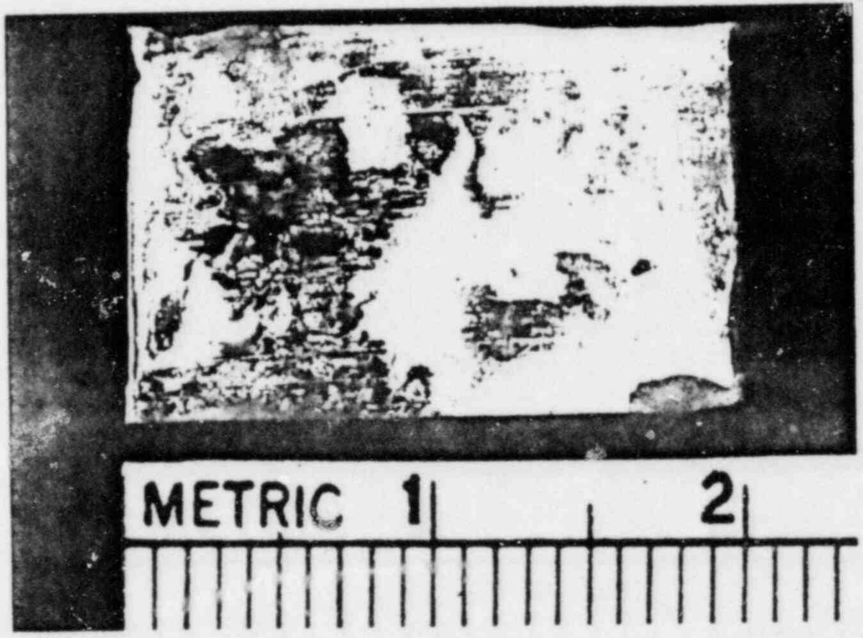

Fig. 2. Well developed crevice corrosion product on TiCode-12.

TABLE III
The apparent stress intensity factor of SEN samples at three hydrogen concentration levels

Hydrogen concentration (ppm)	100	6560	10900
Approximate K_Q ($MPa\sqrt{m}$)	43.0	6.1	5.5

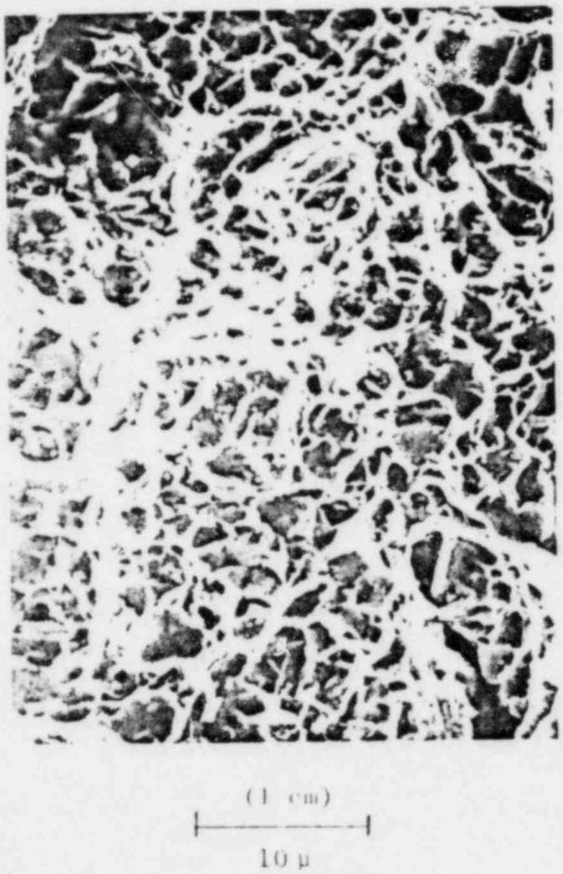

Fig. 3. Ductile fracture of TiCode-12 at 100 ppm hydrogen concentration.

Fig. 4. Brittle fracture of TiCode-12 at hydrogen concentration in access of 6560 ppm. Note the interface cracking in the center.

TABLE IV
Hydrogen uptake results (ppm) for TiCode-12 in Brine B

Run	Single coupon	Crevice samples
1	65.8	80.6 91.2
2	32.5	74.4

Note: The hydrogen concentration is 34 ppm in the as-received sample.

induce stress corrosion cracking since we observed hydrogen embrittlement and an increase in the open-circuit corrosion potential with the addition of oxidants to the brine.

Preliminary data on long term uniform corrosion rates showed that the corrosion rates decrease gradually with time. Corrosion rates are not reproducible at the present time because of the formation of precipitates (amorphous products of Mg and Si) on the samples. For the extrapolation of uniform corrosion rates to longer periods, the effect of this precipitate on the kinetics must be established.

CONCLUSIONS

The corrosion of TiCode-12 in simulated rock salt brine was investigated. The following conclusions may be drawn from this study:

- Crevice corrosion of TiCode-12 was observed at 150°C. The corrosion product was the rutile form of TiO_2 with a trace of lower oxides.
- Hydrogen caused a significant decrease in the apparent stress intensity level in fracture mechanics samples. Hydride formation is thought to be responsible for crack initiation.
- Enhanced hydrogen uptake was observed in crevice samples.
- Static C-ring tests did not show stress corrosion cracking in acidified brines.
- Extrapolating of short term uniform corrosion rate data is complicated by the presence of precipitates on the sample.

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