

CORROSION OF PROPOSED CANISTER MATERIALS
IN SALT REPOSITORIES*

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ABSTRACT

Research at Sandia is focussing on TiCode-12 (Ti-0.3Mo-0.8Ni) as a corrosion resistant alloy for fabricating canister overpacks, and possibly the canisters themselves. Tests involving the straining of this alloy at applied anodic overpotentials in brine showed that it does not stress corrode. If hydrogen is introduced, either by cathodic polarization in brine or by electrochemically charging prior to testing, embrittlement can occur. Results from gas-charged specimens indicate that noticeable embrittlement occurs at hydrogen concentration above about 400 wppm. Pitting was not observed after experiments involving exposure of coupons for several weeks to neutral brine at temperatures up to 200°C. It did occur during two tests involving brine previously acidified to pH 2, and then only under adherent salt deposits that developed during the tests. These conditions of low pH and adherent salt layer represent an overtest, and pitting is not anticipated in a salt repository. The effects of Ni and Mo alloy additions on the electrochemistry of corrosion of TiCode-12 were characterized. The uniform corrosion rates of Ni, Fe, and Ti-based alloys that are being considered as alternate, or backup materials to TiCode-12, were measured in brine. No localized corrosion occurred, and the rates of uniform attack of the Ni and other Ti-base alloys were sufficiently low to qualify them as alternate alloys to TiCode-12. The corrosion rate of cast iron in deaerated brine was 0.13 mm/yr, indicating that cast iron is a corrosion allowance material for potential use in canisters.

INTRODUCTION

Sandia's waste canister corrosion program has focused primarily on Grade-12 titanium, or TiCode-12 (Ti-0.3Mo-0.8Ni) as the optimum alloy for use either as a canister overpack, or as the material of construction for the canister itself. This approach is based on the concept of using a corrosion resistant alloy, i.e., one which corrodes at an extremely low rate during its design lifetime. It is different than one based on corrosion allowance material, which involves using an alloy that corrodes at a relatively much higher rate, and then designing canisters that will survive for the desired time period based on this higher corrosion rate.

TiCode-12 was developed for use in desalination equipment; it exhibits excellent resistance to crevice and uniform corrosion in acidic chloride-containing solutions, even at elevated temperatures (1-3). However, as with many alloys that resist uniform attack well, under severe exposure conditions TiCode-12 is susceptible to localized forms of corrosion such as pitting. Also, because of the affinity of titanium for hydrogen and hydride formation, hydrogen embrittlement (HE) is another failure mode of concern. Prior research (4) has indicated that the uniform rate of corrosion of TiCode-12 in solutions thought to simulate those to be encountered in salt repositories is acceptably low, about 10^{-3} mm/yr. Consequently, current research is addressing the following corrosion related issues: a) environmental cracking; b) localized corrosion, including pitting and crevice attack; c) effects of the alloying additions Mo and Ni on conferring corrosion resistance; and d) corrosion behavior of alternate alloys. The study of γ irradiation effects was only recently begun at Sandia, and no data are yet available for reporting.

ENVIRONMENTAL CRACKING

The susceptibility of TiCode-12 to stress corrosion cracking (SCC) and HE was determined by slow strain rate testing of smooth and notched tensile samples. Previous investigations (5; 6) had indicated that two distinct types of morphologies develop on the fracture surfaces of specimens strained to failure at the open circuit corrosion potential, E_{oc} , in WIPP Brine A; it was suspected that this two-feature morphology was caused by HE. No results were obtained at potentials other than E_{oc} .

To assess the degree of susceptibility to HE, hydrogen was introduced into samples either during, or prior to testing. Notched samples were pre-charged to levels as high as ~1000 wppm and then tested in air and brine. Also, smooth tensile bars were polarized cathodically (galvanostatically or potentiostatically) to introduce H while straining. Susceptibility to SCC was evaluated by potentiostatically polarizing smooth specimens in Brine A at potentials anodic to E_{oc} , and then pulling the specimens to failure at strain rates ranging from 10^{-7} to 10^{-4} sec $^{-1}$.

SCC did not occur at any of the applied anodic potentials in the range investigated. As shown in Figure 1, the time to failure, t_f , and percent reductions in area, %RA, remained essentially unchanged at potentials anodic to E_{oc} . No indication of SCC was evident on the fracture surfaces, which showed only ductile failure; no dependence of morphology on anodic potential applied during the test was observed.

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LOCALIZED CORROSION

Pitting of TiCode-12 has not been observed at Sandia after exposure of flat coupons in Brine A at temperatures to 200°C. This absence of pitting reflects the excellent stability of the passive film on this alloy and its resistance to electrochemical breakdown by chloride ion. However, TiCode-12 did experience severe pitting under overtest conditions. These overtest conditions consisted of pre-acidification of the brine to pH 2 by addition of HCl, formation of an adherent salt layer on the coupon surfaces, presence of atmospheric oxygen, and temperatures in the range of 150 to 200°C. Some pits even perforated a 1.6 mm thick sheet of TiCode-12 during a two week exposure period, as shown in Figure 5. The pitting presumably occurred because of localized breakdown of the passive TiO₂ film in the crevice formed between the TiCode-12 and a very adherent salt layer; this early form of crevice attack was stabilized by the presence of oxygen in the brine, which permitted oxygen concentration cells to develop. The pitting observed in these tests is not thought to represent a threat to the future use of TiCode-12 in a salt repository because overtest conditions, including acidification and the relatively high brine temperature of 200°C should not exist.

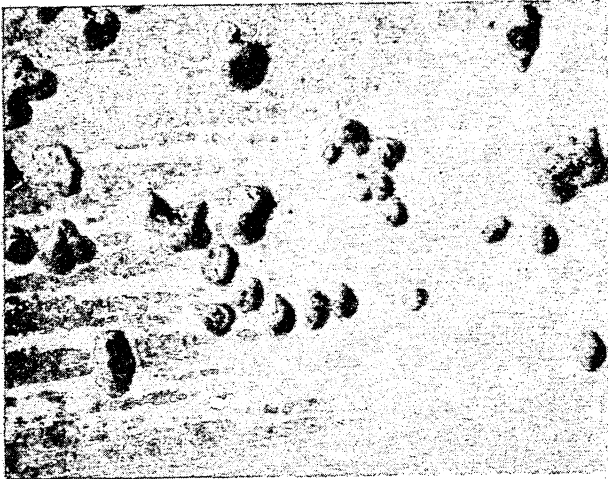


Fig. 5. Pits on TiCode-12 sheet exposed for two weeks in non-deaerated Brine A over the temperature range from 150 to 200°C. Pits developed under an adherent salt deposit, which was removed prior to photographing.

Another conceivable cause of pitting of TiCode-12 is iron smeared onto the surface of waste canisters as a result of contact with ferrous alloy components during fabrication and shipping. Surface contamination by iron prevents titanium from forming a highly protective passive film, such that upon exposure to corrosive electrolytes the surface may develop pits. In addition, cathodically generated hydrogen may enter the alloy at contaminated areas and produce subsurface hydrides and localized HE. Currently, Sandia is investigating the effects of iron contamination on localized corrosion of TiCode-12. Surfaces have been contaminated by drilling and threading specimens with steel tools, and they are now being

exposed in a synthetic seawater solution for several weeks at 150°C. Visual inspection after four weeks of exposure did not reveal any localized attack; these experiments are continuing.

EFFECTS OF Ni AND Mo ALLOY ADDITIONS

Both Ni and Mo improve the resistance of titanium to uniform and localized corrosion in hot acidic chloride solutions (7-10). One beneficial effect of Ni may derive from the fact that it forms an intermetallic phase, Ti₂Ni, at annealing temperatures in the range from about 600 to 770°C. This phase precipitates within the β phase, and at α-β interfaces, in TiCode-12. Ti₂Ni is more effective than α titanium in supporting the hydrogen evolution reaction, as shown in Figure 6(9). This fact is evident because the E_{oc} for Ti₂Ni is about 460 mV more positive than the E_{oc} of the titanium. Because the E_{oc} of Ti₂Ni lies in the passive potential range of α-titanium, when Ti₂Ni is galvanically coupled to titanium the intermetallic is polarized cathodically and the titanium is polarized anodically. If the area ratio of Ti₂Ni to titanium is sufficiently large, then the titanium is polarized from the region of active corrosion into the passive region, resulting in passivation of the titanium. Precipitation of Ti₂Ni in the TiCode-12 matrix can form such a galvanic couple between this intermetallic phase and the remaining metal matrix and it has been proposed that this second phase can induce passivation of TiCode-12 in acidic electrolytes (9).

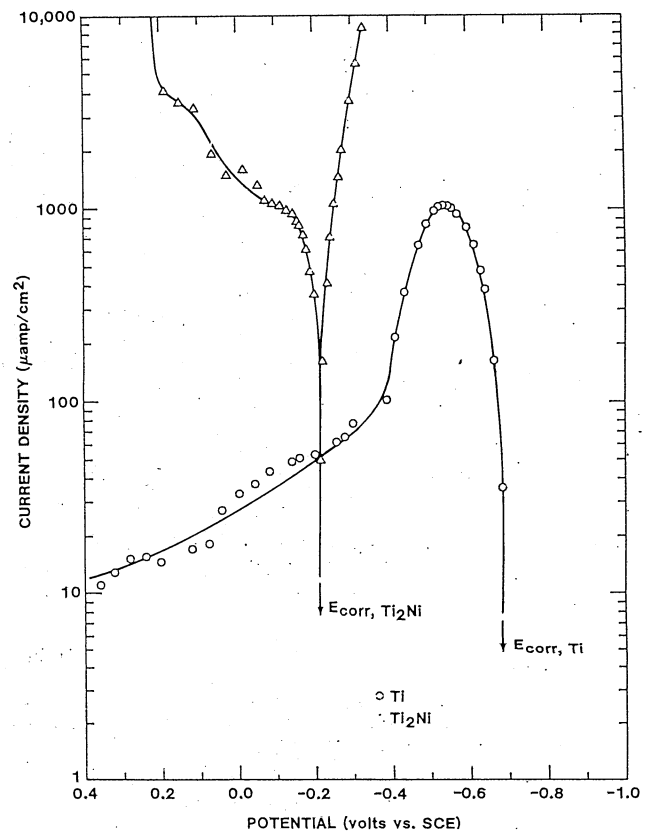


Fig. 6. Polarization behavior of Ti and Ti₂Ni in boiling 1.0N HCl (Ref. 9).

When present as an alloying addition, molybdenum decreases the intensity of active dissolution of titanium. Recent research at Sandia has shown that Mo reduces the corrosion of titanium even when it is present in the electrolyte as molybdate ion (10). Figure 7 shows the effect of adding molybdate ion to boiling 1N H₂SO₄ in which titanium is actively corroding. Upon addition of 4 mM Mo⁺⁶ the electrode immediately passivated, as shown by the shift of E_{OC} from the characteristic active state value of about -830 mV(SCE) to a passive value of 200 mV(SCE). Additions of more molybdate ion produced smaller positive shifts in the corrosion potential, but the major change occurred after the first addition. Although the E_{OC} for titanium in molybdate solution is controlled predominantly by redox processes, a protective salt film containing Mo is formed on the electrode surface. This film replaces the native TiO₂ film. Following passivation in a molybdate solution, if the titanium electrode is removed and transferred to a molybdate-free solution the protective salt film remains intact and titanium remains passive. These results suggest that the resistance of TiCode-12 to crevice corrosion may be due, in part, to the accumulation of Mo⁺⁶ ions in the occluded region of the crevice during the pre-initiation stage of attack, followed by the formation of a protective salt film which prevents subsequent initiation of crevice corrosion. Also possible, and likely, is that Mo accumulates in the passive oxide film via a direct solid-state reaction.

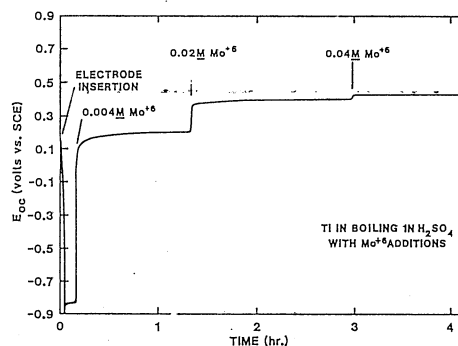


Fig. 7. E_{OC}-time behavior following addition of successively greater concentrations of Mo⁺⁶ to a deaerated, boiling 1N H₂SO₄ solution in which Ti was actively corroding. No Mo⁺⁶ was initially present in solution.

ALTERNATE ALLOYS

The uniform and localized corrosion behavior of several alloys that are being considered as alternates to TiCode-12 were tested in Brine A at 200°C. Results of weight change measurements are presented in Table 1. All of these alloys exhibited sufficiently low corrosion rates to be considered as alternates to TiCode-12; in addition, they did not suffer pitting or crevice corrosion. The corrosion rate of ductile cast iron also was measured during a year long test in deaerated Brine A at 150°C. The corrosion rate was constant during this test, with a value of 0.13 mm/yr. No pitting occurred. This corrosion rate indicates that a wall thickness in excess of 13 cm would be required to prevent perforation of a cast iron canister during a 1000 year design lifetime,

TABLE I

Weight Change Data From Long Term Exposure Tests of Alternate Alloys in Deaerated Brine A at 200°C

Alloy	Weight Change (gm/cm ²)		
	47 Days	182 Days	253 Days
TiCode-12	3.9 x 10 ⁻⁵	8.8 x 10 ⁻⁵	3.2 x 10 ⁻⁵
C.P. Ti	2.8 x 10 ⁻⁵	5.7 x 10 ⁻⁵	0.8 x 10 ⁻⁵
Ti-0.2 Pd	-1.3 x 10 ^{-5a}	5.0 x 10 ⁻⁵	NA ^b
	41 Days	183 Days	254 Days
Hastelloy C-4	1.3 x 10 ⁻⁵	NA ^b	8.0 x 10 ⁻⁵
Hastelloy C-276	1.8 x 10 ⁻⁵	5.5 x 10 ⁻⁵	6.5 x 10 ⁻⁵
Inconel 625	1.2 x 10 ⁻⁵	4.9 x 10 ⁻⁵	-1.4 x 10 ^{-5a}
Incoloy 825	-1.3 x 10 ^{-5a}	4.7 x 10 ⁻⁵	NA ^b

^a Negative changes indicate weight gains, which are the result of oxygen pickup caused by thickening of corrosion films.

^b Data are not available.

under the given test conditions. However, the absence of oxygen represents an undertest, while the high temperature and simulated brine inundation represent an overtest of actual anticipated exposure in salt repositories.

CONCLUSIONS

All tests performed to date involving the corrosion behavior of TiCode-12 indicate that this alloy is a suitable choice for the containment of nuclear wastes. No stress corrosion cracking of TiCode-12 occurred; HE was observed, as well as pitting, but only under conditions that represent severe overtesting. Such overtest conditions are not expected in any repository. A better understanding of the mechanisms involved in the corrosion behavior of TiCode-12 has been gained through work with Ti-Mo and Ti-Ni alloy systems. All alternate alloys tested, including cast iron, exhibit acceptable corrosion behavior relative to their role as backup canister materials. In the case of cast iron, the material provides for a corrosion allowance design in contrast to the corrosion resistant design offered by Ti alloys.

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