

THE BEHAVIOR OF TICODE 12 IN BRINE UNDER GAMMA RADIATION*

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ABSTRACT

Hydrogen absorption by Ti-CODE 12 alloy is being investigated. Data for immersions to six months in brine solution at 25°C and 108°C, both with and without gamma radiation, show that the alloy under radiation exhibit less hydrogen take-up. This is attributed to the more protective oxide layer formed under radiation than in its absence.

INTRODUCTION

Ti-CODE 12 alloy is a primary candidate overpack material for high-level nuclear waste storage in salt beds because of its superior corrosion resistance (1). Its corrosion properties have been studied since bedded salt can provide a corrosive environment if water is introduced (2). Numerous screening tests for corrosion properties of overpack materials have shown that Ti-CODE 12 is strongly resistant to stress corrosion cracking and pitting corrosion, and also to uniform corrosion at temperatures up to 250°C (3,4,5). Studies of the effect of internal hydrogen on mechanical properties by gas phase charging showed that the yield strength does not change with increasing hydrogen concentration up to 130 wt. ppm (6). In addition, hydrogen embrittlement is not caused by 130 wt. ppm of hydrogen.

Potentially important degradation phenomena have been observed, such as galvanic corrosion due to an intermetallic compound, Ti_2Ni , formed during the heat treatment (7), and also crevice corrosion in brine solution at 150°C (8). Furthermore, it has also been found (10) that hydrogen in Ti-CODE 12 at more than 671 wt. ppm causes pit-like corrosion. Studies (9,10) of the effect of surface condition on the open-circuit potential and on the kinetics of anodic film growth in brine solution have suggested that strong corrosion resistance of Ti-CODE 12 alloy is attributable to its oxide film and that the oxide film thickens during free corrosion.

The purpose of the present, ongoing study is to investigate hydrogen absorption by Ti-CODE 12 during free corrosion immersion in brine for 16 months, both under gamma-radiation and in its absence.

In this progress report, three types of preliminary results are reported: hydrogen take-up, anodic polarization and open-circuit potential behavior, and x-ray diffraction on the metal oxide.

EXPERIMENTAL APPROACH

Specimen Preparation

Ti-CODE 12 (ASTM 12) with the chemical composition given in Table-1 was supplied by the Sandia

National Laboratory. The material was in the form of 0.8 mm sheet, and specimens of 5 mm x 5 mm were cut from it. Some specimens were annealed by heating in vacuum (3.5×10^{-5} Torr) at 800°C for four hours followed by furnace cooling. This was intended to provoke the structural changes that may be produced by a welding process. Prior to immersion in the test solution, all specimens were cleaned with ultrasonic cleaning solution, acetone, isopropyl alcohol and deionized water jet. Following the immersion period, specimens were treated by the procedure shown in Table 2. For the open-circuit and anodic polarization measurements, nickel wires welded to the specimens. The wires were encapsulated in Pyrex tubing and sealed with polyester embedding material. The crevice between the specimen and the embedding material was coated with a thin film of microshield lacquer to avoid crevice corrosion.

Electrolytes

The chemical composition of the brine solution used is shown in Table 3. The pH of this solution was not adjusted. Deaerated 0.5 M Na_2SO_4 , pH 6.5, was used for the studies of anodic polarization for some of the measurements of open-circuit potential. These studies were done upon specimens that had been immersed in brine solution, some at 25°C or at 108°C, some for three months or six months, with and without gamma-radiation at about 10^9 rad/hr. The Na_2SO_4 solution was deaerated for at least three hours by purging argon gas before immersion of specimens, and then was continuously deaerated during the experiments.

Hydrogen Hot Vacuum Extraction

Preparation of specimens for the hydrogen determination by hot vacuum extraction is shown in Table 2. After weighing to the nearest 10^{-4} g, and loading the specimens on the sample tree, as shown in Fig. 1, the system was pumped down and maintained at pressure $2-5 \times 10^{-5}$ Torr for 14 hours for removal of adsorbed water vapor from the specimen and system surfaces. In this technique, the pressure over the specimen being analyzed is lowered to 10^{-5} to 10^{-6} Torr by the mercury diffusion pump. The specimen is then heated at 950°C for about ten minutes. The hydrogen evolved is pumped into a known volume and the absolute pressure in that volume is measured with a McLeod gauge. A simple

TABLE I

Nominal Chemical Composition of TiCode-12

element	C	N	O	H	Fe	Ni	Mo	Ti
wt%	0.08M	0.03M	0.25M	0.015M	0.3M	0.6 - 0.9	0.2 - 0.4	Bal.

*M represents maximum

TABLE II

Schematic of Experimental Procedure

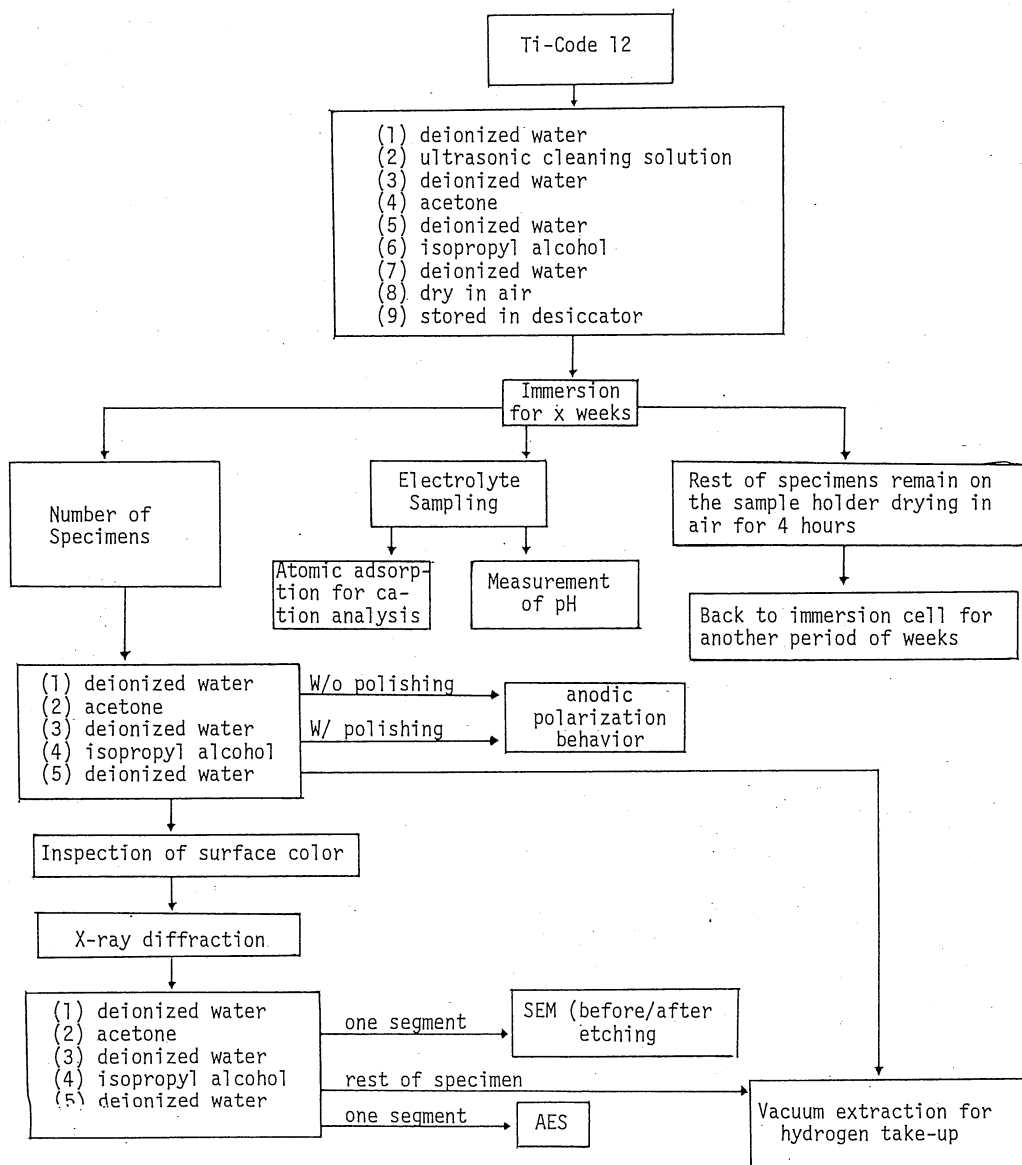


TABLE III

Chemical Composition of Brine Solution (pH 6.5)

200.2g/2ℓ NaCl	+	5mℓ of 5g/ℓ FeCl ₃ ·6H ₂ O
12.4g/2ℓ Na ₂ SO ₄		5mℓ of 0.52g/ℓ CsCl
3.9g/2ℓ Na ₂ B ₄ O ₇ ·10H ₂ O		50.0g/ℓ LiCl
1.92g/2ℓ NaHCO ₃		10.87g/ℓ RbCl
1.04g/2ℓ NaBr		6.00g/ℓ SrCl ₂ ·6H ₂ O
114.4g/2ℓ KCl		5.20g/ℓ KI
584.2g/2ℓ MgCl ₂ ·6H ₂ O		
4.40g/2ℓ CaCl ₂ ·2H ₂ O		

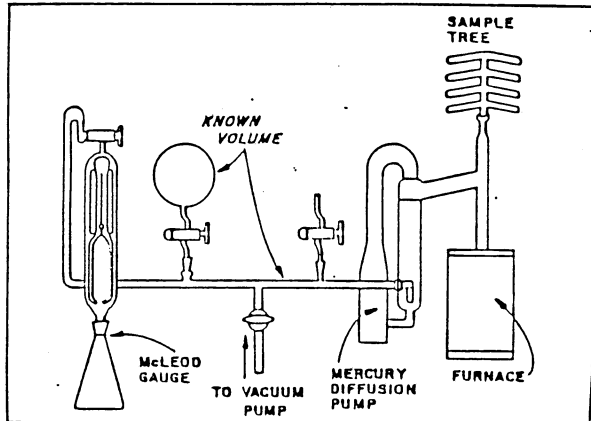


FIGURE 1: HYDROGEN HOT VACUUM EXTRACTION APPARATUS.

calibration factor then gives the hydrogen concentration in the pre-weighed specimen.

Anodic Polarization and Open-Circuit Potential

After immersion in brine solution, nickel wires were welded to some specimens. Some of these specimens were polished with 0.05 μm Al₂O₃ on a wet wheel, and the rest were used without polishing. Directly upon the introduction of a specimen into the Na₂SO₄ electrolyte, potential scanning at 0.1 mV/sec in the anodic direction was started.

In situ measurements of open-circuit potential of specimens immersed in brine solution were performed at 108°C without gamma-radiation. Some of these specimens had been under γ-radiation in the brine for six months, and others had been immersed in brine without radiation. Other specimens, after brine immersion for six months at 25°C or at 108°C, with and without gamma radiation were removed and cleaned according to Table 2, but without any surface treatment. These specimens were used for measuring the open-circuit potential in 0.5M Na₂SO₄ solution. Depth profiles of the oxide layers by AES and analyses of the oxide phase by x-ray diffraction were carried out.

RESULTS AND DISCUSSION

The amounts of hydrogen take-up by as-received and by annealed Ti-CODE 12 after free corrosion in brine at 25°C and 108°C, both under gamma radiation and without, are given in Table 4. Each entry in Table 4 is an average of four or five specimens. Figures 2 and 3 show the hydrogen take-up versus immersion time. We see that the hydrogen take-up by Ti-CODE 12 under gamma radiation is less than that in the absence of the radiation in all cases.

TABLE IV
Measurements of Hydrogen Take-up by TiCode-12 in Brine

Specimen	Temp.	[H] wt. ppm						
		0 day	14 days	1 Month	3 Months	6 Months		
As-received TiCode-12	R. T.	w/o	Y	20.2	X	37.3	45.7	51.4
		w/	Y			33.0	36.4	40.7
	b. T.	w/o	Y	20.2	30.8	41.3	51.7	58.3
		w/	Y		20.2	30.2	38.6	45.1
Annealed- furnace cooled TiCode-12	R. T.	w/o	Y	1.3	X	14.4	25.9	34.4
		w/	Y			11.2	17.4	27.0
	b. T.	w/o	Y	1.3	X	30.5	37.9	43.7
		w/	Y			22.2	26.6	33.2

X represents no data available

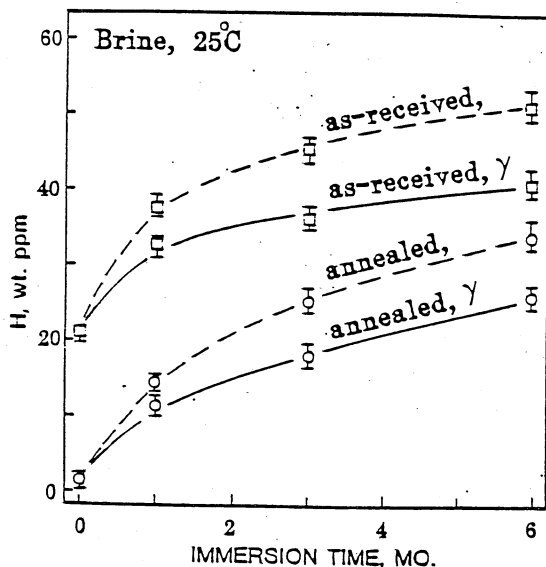


Figure 2: HYDROGEN CONTENT VERSUS IMMERSION TIME, MONTHS. DASHED LINES: WITHOUT GAMMA RADIATION. SOLID LINES: UNDER GAMMA RADIATION (γ : UNDER γ -RADIATION).

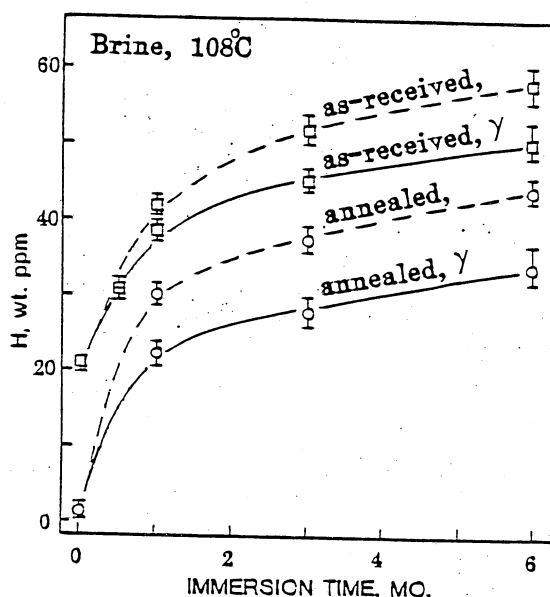


Figure 3: HYDROGEN CONTENT VERSUS IMMERSION TIME, MONTHS. DASHED LINES: WITHOUT RADIATION. SOLID LINES: UNDER RADIATION (γ : UNDER γ -RADIATION).

It is to be expected that the characteristics of the oxidic corrosion products that accumulate on the surface of an alloy control the amount of hydrogen absorbed by the alloy (11,12). The porosity, the electronic conductivity, or the permeability of the oxide for protons or for neutral hydrogen will control how much hydrogen from the corrosion reaction gets into the metal. That γ -radiation can cause marked changes in the nature of the oxide produced has been shown by several investigators. Our result, that the amount of hydrogen absorbed by the TiCode-12 under γ -radiation is less than when without radiation might therefore be attributable to a change in the character of the oxide

produced by the radiation. Indeed, our x-ray diffraction data (Figs. 4 and 5) give clear evidence that the oxide structure develops differently under γ -radiation than without radiation. Whereas both the anatase and the rutile forms of TiO_2 are found in both oxides, it is clear that the anatase form is enhanced by radiation in our experiments. Since under radiation less hydrogen is taken up by the alloy, one must conclude that the anatase is in some way associated with providing a greater protectivity to the alloy. This contrasts interestingly with the situation for titanium in dry air or oxygen, where the thermodynamically more stable form, rutile, forms a continuous film (13,14). However, in titanium-electrolyte systems anatase forms the continuous barrier layer with rutile forming a porous outer layer (15-17).

The inference that the oxide that forms under radiation is more protective is corroborated by our anodic polarization curves from specimens taken out of the brine after three months and six months immersion at 25°C and 108°C, some under gamma radiation and some without it (Figs. 6 and 7). The passive current in Na_2SO_4 solution of the specimens that had been under radiation is less than that of those that had not been under radiation. In addition, the anodic polarization behavior in Na_2SO_4 solution of specimens withdrawn from the brine and after removal of the oxide layer is identical, whether or not radiation had been employed (Fig. 8). This suggests that the properties of only the oxide layers were affected by radiation, not those of the metal.

To obtain more information on the effect of γ -radiation on corrosion properties, open-circuit potential measurements were carried out, both in the brine without withdrawing the specimens that had been in brine with and without radiation, and also in Na_2SO_4 solution after withdrawing other specimens from the brine. Figures 9-11 show that in all cases the potential of the specimens that had been under radiation in brine is more noble than that of specimens that had not been radiated. Again, we have indication that radiation produces a more protective oxide on the TiCode-12.

Figures 12 and 13 display AES depth profiles of the oxide films on brine-immersed, radiated and non-radiated specimens. The former has thicker oxide layers. We see therefore that γ -radiation produces thicker, anatase-rich oxide layers that exhibit lower passive currents, more noble open-circuit potentials, and permit less hydrogen take-up by the metal.

It is known that the radiolytic process produces hydrogen and hydrogen ions, as well as peroxides (18) and other oxidizing species. One can think that the radiolytic environment is responsible in some way for kinetically repressing the dissolution of the anatase, thereby producing a thicker oxide richer in anatase. In turn, the hydrogen absorption by the metal is impeded more by the anatase-rich oxide than by the oxide formed without γ -radiation. However, one can only conjecture about the responsible mechanisms at the present time.

ACKNOWLEDGMENT

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REFERENCES

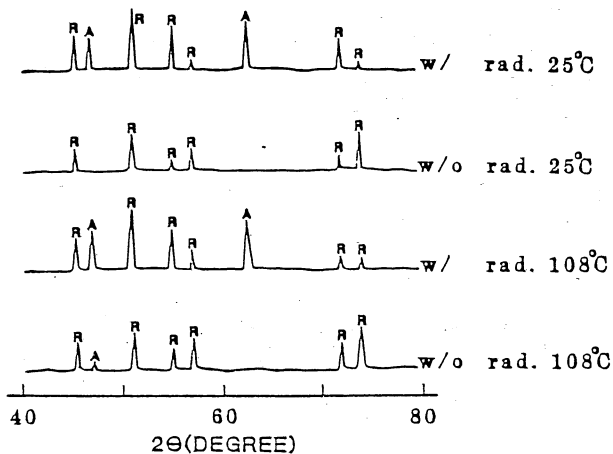
1. L. Abrego and H. J. Rack, Presented at NACE, Corrosion/81 Meeting Sheraton Center, Toronto,

Ontario, Canada, April 6-10, 1981.

2. J. W. Braithwaite and M. A. Molecke, Nuclear and Chemical Management, 1, 3n (1980).
3. M. A. Molecke, D. W. Schaefer, R. S. Glass, and J. A. Ruppen, Sandia Report SAND81-1585, October, 1981.
4. M. A. Molecke, J. A. Ruppen, and R. B. Diegle, Presented at the American Nuclear Society Annual Meeting, Los Angeles, June, 1982.
5. M. A. Molecke, and L. Abrego, Presented at the 1980 NWTS/ONWI Public Information Meeting, Columbus, Ohio, December 9-11, 1980.
6. N. Moody and S. Robinson, Presented at the Electrochemical Society Meeting, Detroit, October, 1982.
7. J. A. Ruppen, R. B. Diegle, R. S. Glass and T. J. Headley, Presented at the Electrochemical Society Meeting, Detroit, October, 1982.
8. T. M. Ahn, H. Jain and P. Soo, Presented at the Electrochemical Society Meeting. Washington, D.C. October, 1983.
9. Y. J. Kim, Y. K. Hong and R. A. Oriani, Paper Number 79, the Extended Abstracts of Electrochemical Society Meeting, p. 122 ECS, May, 1983.
10. Y. J. Kim, M. S. Thesis, University of Minnesota (1983).
11. M. Kurkela and R. M. Latanision, Scripta Metallurgica, 13, 927 (1979).
12. F. H. Heubbaum and B. J. Berkowitz, Scripta Metallurgica, 16, 659 (1982).
13. T. Nakayama and T. Koizumi, Report of the Casting Res. Lab., Waseda University, No. 17, 11 (1966).
14. R. O. Shannon and T. A. Pask, Bull. Am. Ceram. Soc., 48, 391 (1965).
15. L. L. Shreir, Corrosion 1, 5-34, Newnes, London (1963).
16. N. D. Tomashov, G. P. Chernova, Yu S. Ruscol and G. A. Ayuyan, Electrochimica Acta. 19, 159 (1974).
17. T. Koizumi and T. Nakajama, Corrosion Science, 8, 195 (1968).
18. R. S. Glass, "Effects of Radiation on the Chemical Environment Surrounding Waste Canisters in Proposed Repository Sites and Possible Effects on the Corrosion Process," Sandia Report, SAD81-1677, December (1981).

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A: ANNEALED TI-CODE 12



B: ANNEALED TI-CODE 12

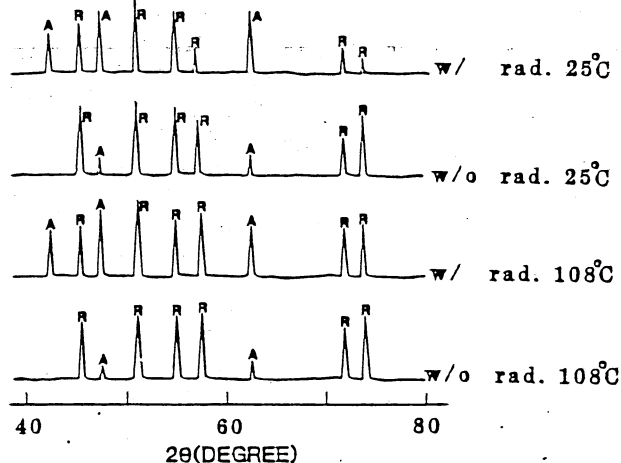
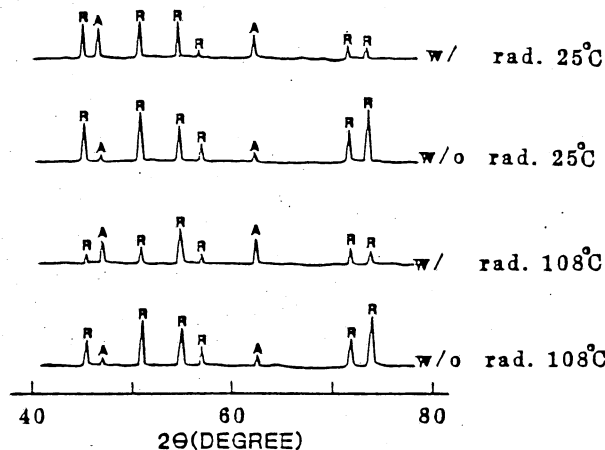


FIGURE 4: X-RAY DIFFRACTION SPECTRA OF OXIDE FILM OF AS-RECEIVED TI-CODE 12 FORMED IN BRINE SOLUTION (R: RUTILE, A: ANATASE) IMMERSED FOR (A) 3 MONTHS AND (B) 6 MONTHS.

A: AS-RECEIVED TI-CODE 12



B: AS-RECEIVED TI-CODE 12

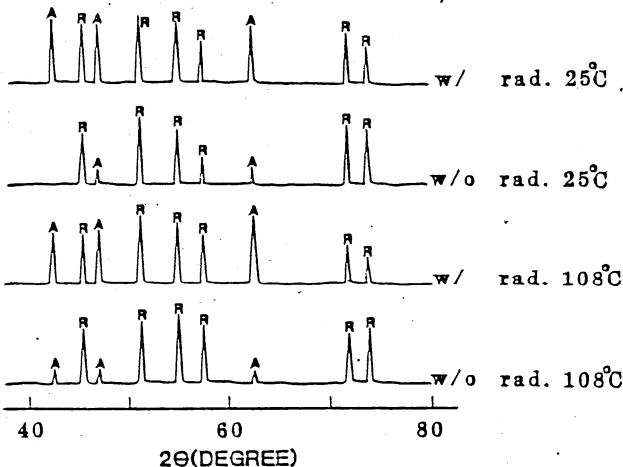


FIGURE 5: X-RAY DIFFRACTION SPECTRA OF OXIDE FILM OF ANNEALED TI-CODE 12 FORMED IN BRINE SOLUTION (R: RUTILE, A: ANATASE) IMMERSED FOR (A) 3 MONTHS AND (B) 6 MONTHS.

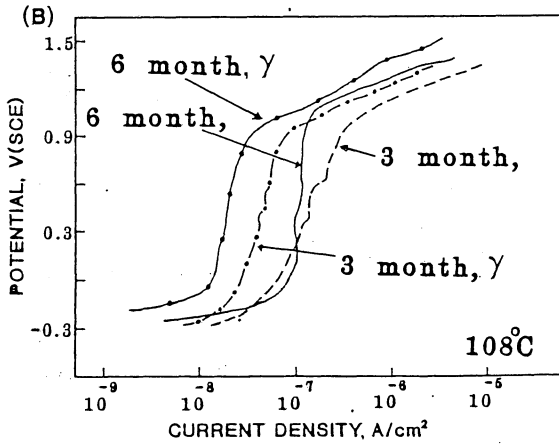
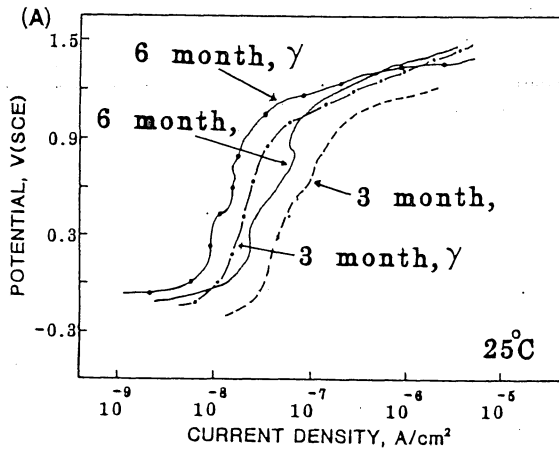


FIGURE 6: ANODIC POLARIZATION BEHAVIOR IN 0.5M Na₂SO₄ (pH 6.5) AT 25°C, OF AS-RECEIVED TI-CODE 12 AFTER 3 AND 6 MONTHS IMMERSION IN BRINE SOLUTIONS AT (A) 25°C AND (B) 108°C.

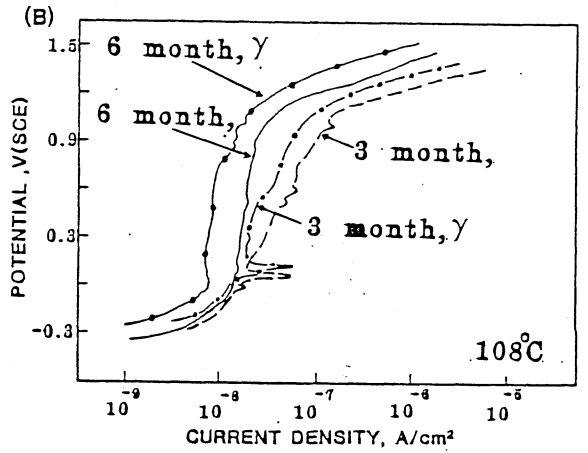
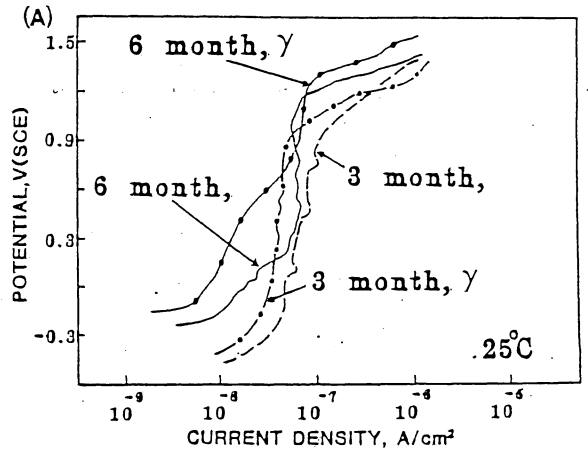


FIGURE 7: ANODIC POLARIZATION BEHAVIOR IN 0.5M Na₂SO₄ (pH 6.5) AT 25°C, OF ANNEALED TI-CODE 12 AFTER 3 AND 6 MONTHS IMMERSION IN BRINE SOLUTION (A) AT 25°C (B) 108°C.

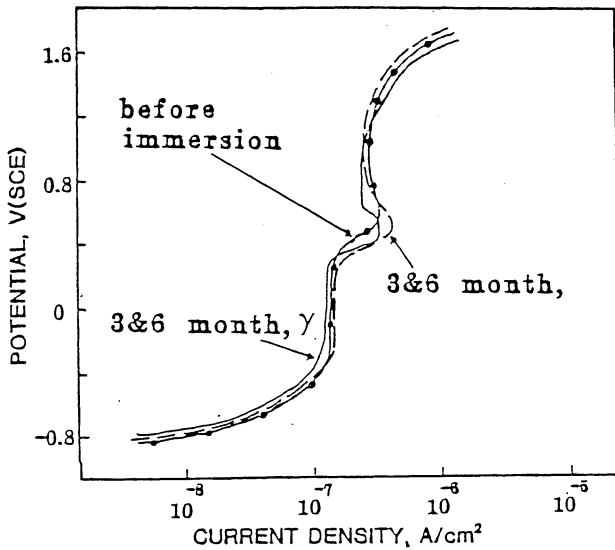


FIGURE 8: ANODIC POTENTIODYNAMIC POLARIZATION CURVES OF ANNEALED, POST-IMMERSION SPECIMENS OF TI-CODE 12 AFTER REMOVAL OF OXIDE.

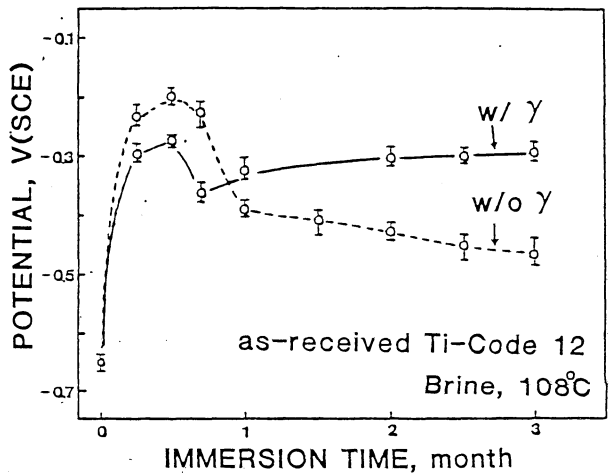


FIGURE 9: CHANGE OF OPEN-CIRCUIT POTENTIAL OF AS-RECEIVED TI-CODE 12 IN BRINE SOLUTION AT 108°C MEASURED IN-SITU.

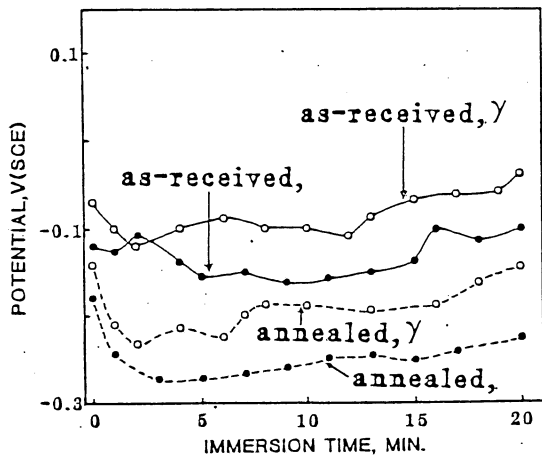


FIGURE 10: OPEN-CIRCUIT POTENTIAL CHANGE IN 0.5M Na_2SO_4 (pH 6.5) AT 25°C, OF IMMERSED TI-CODE 12 IN BRINE SOLUTION FOR 6 MONTHS AT 25°C.

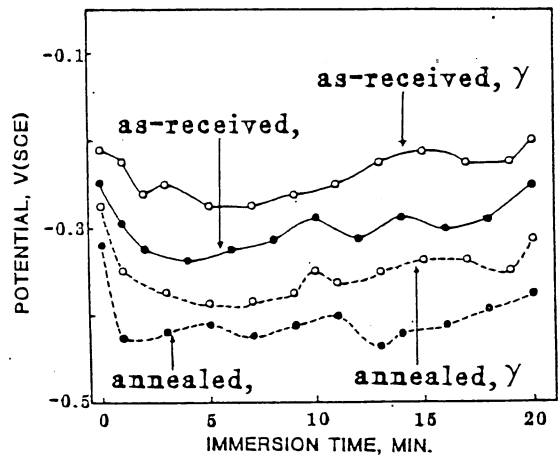


FIGURE 11: CHANGE OF OPEN-CIRCUIT POTENTIAL IN 0.5M Na_2SO_4 (pH 6.5) AT 25°C, OF IMMERSED TI-CODE 12 IN BRINE SOLUTION FOR 6 MONTHS AT 108°C.

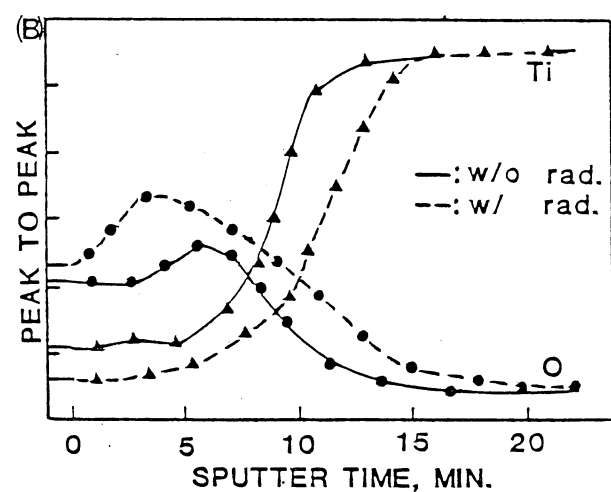
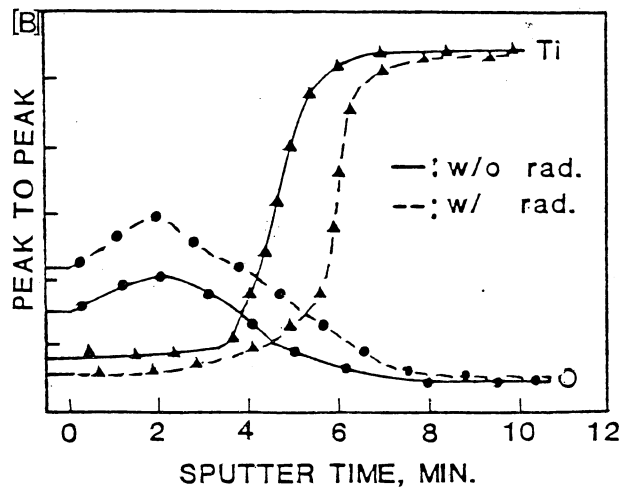
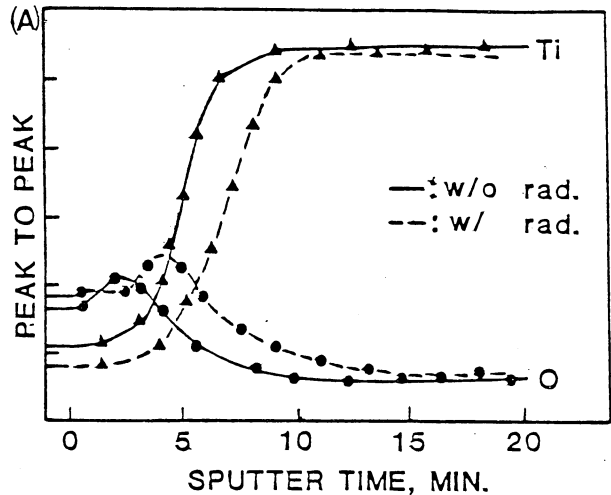
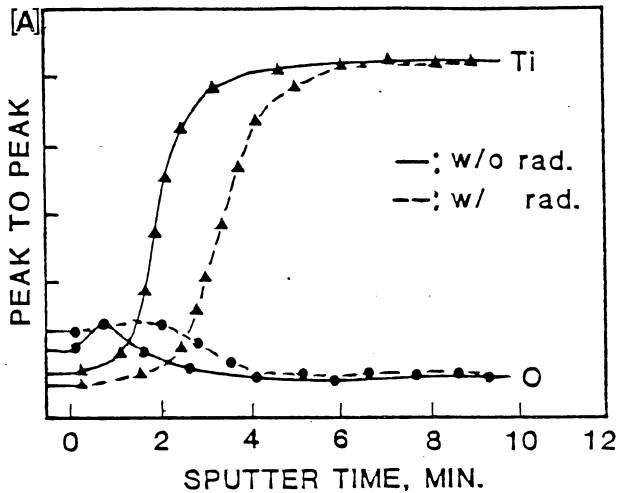


FIGURE 12: AES DEPTH PROFILE OF THE OXIDE ON AS-RECEIVED TI-CODE 12 AFTER IMMERSION IN BRINE SOLUTION AT 108°C FOR (A) 3 MONTHS AND (B) 6 MONTHS.

FIGURE 13: AES DEPTH PROFILE OF THE OXIDE ON ANNEALED TI-CODE 12 AFTER IMMERSION IN BRINE SOLUTION AT 25°C FOR (A) 3 MONTHS AND (B) 6 MONTHS.