Paper No.

01459

CORROSION2001

HYDRIDE FORMATION IN GRADE 2 TITANIUM EXPOSED TO SEA WATER FOR EXTENDED TIMES

Z.F. Wang, Y. Boonyongmaneerat, K.S. Kumar, C.L. Briant
Division of Engineering
Brown University
Providence, RI 02912 USA

ABSTRACT

This paper presents a study of hydride formation in titanium after exposure to NaCl solutions, synthetic sea water, and natural flowing sea water for long periods of time. We found that hydrides occurred only in samples that were galvanically coupled with an aluminum anode and tested in stagnant solutions. The results also show that –900 mV_{SCE} is probably a safe lower bound for use of titanium in a sea water environment. The paper also proposes that critical potential diagrams are a good method to summarize data of this type.

INTRODUCTION

Titanium and its alloys are finding increasing use in naval applications in which the material will come into contact with sea water. Although titanium has been reported to have excellent corrosion resistance in sea water, there is a question as to whether or not titanium hydrides can form as a result of exposure to this environment. In particular, there is concern that cathodic protection of the titanium, either by galvanic coupling or by an impressed potential, could lead to hydrogen absorption and hydride precipitation. If hydrides form in sufficient quantity, the titanium may become brittle.

In this paper we report a study of hydride formation in samples that had been exposed to NaCl solutions and synthetic sea water for periods of time of up to eight months. Both stagnant and flowing solutions were used. In addition, some samples were exposed to natural sea water at the Navy Research Laboratory Marine Corrosion Facility in Key West, Florida. The results show that, in general, the titanium was very resistant to hydride formation. We detected very small amounts of hydrides and only in samples coupled with the aluminum anode in stagnant tests.

EXPERIMENTAL

We used grade two titanium for all of the tests. Tabs that were one square centimeter in cross section were exposed to the different environments. For tests that involved galvanic coupling of titanium to another metal, we drilled a hole in the titanium tab that was 6.5mm in diameter. We then forced a slightly oversized disk of the other metal into the hole so that there was good electrical contact. The metals used for galvanic coupling were commercial purity zinc, a zinc anode, and an aluminum anode. The anodes were supplied by the US Navy.

Tests were performed in both 3.5% NaCl and synthetic sea water at room temperature. The synthetic sea water was made following ASTM standards[1]. For one set of tests the samples were placed in beakers containing stagnant solutions and examined at monthly intervals. In another set of tests, the samples were exposed to flowing NaCl solutions. Again, we examined the samples monthly to determine if hydrides had formed. Finally, one set of samples was exposed to natural flowing sea water at the Navy Research Laboratory Marine Corrosion Facility in Key West, Florida. The purpose of these tests was to determine if calcareous deposits that build up in natural sea water affected the results. The flow rate was such that the tank was refreshed approximately 10 times each day. These tests were performed at the natural surface temperature of sea water.

In another set of tests we determined the critical potential for hydride formation. These potentials were based on twenty-four hour exposures of titanium to a 3.5% NaCl solution. To perform the test the sample was held at a potential under potentiostatic control for twenty-four hours and examined by X-ray diffraction to determine if a hydride had formed. If no hydrides were detected, then the potential was made more cathodic by 100 mV. If hydrides were detected, the potential was made more noble by 100 mV. Thus we determined the potential to the nearest 100 mV.

As mentioned above, we used X-ray diffraction to determine if hydrides were present in the material. The samples were removed from solution and washed to remove any debris. A narrow range of angular values were scanned that were known to include peaks for both the γ and δ-hydride. If hydride peaks were found, we also examined the sample by scanning electron micrsocopy to determine the density of hydrides.

RESULTS

Critical Potential for Hydride Formation in Titanium

Figure 1 summarizes the results for the determination of the critical potential for hydride formation in the twenty-four hour tests. We have plotted the critical potential as a function of temperature for different pH values. For a given line on the plot we can assume that for conditions that would lie above the line hydrides would not form, whereas for conditions below the line hydrides would be expected to form. It is clear that the critical potential for hydride formation becomes more cathodic as the pH of the solution increases. The change between the values of pH=1 and pH=4 is especially significant. An increase in temperature causes the critical potential for hydride formation to become more noble.

It is useful to compare these results to reports in the literature where titanium has been exposed to sea water environments for long periods of time and the material has been examined to determine whether hydrides are present or not. Figure 2 replots the data in Figure 1 but now each curve is on a separate plot. The regions where hydrides would be expected to form and those where no hydrides should form are indicated. Data points taken from the literature are also on the plot. These measurements were primarily drawn from long term exposures of titanium to sea water, and in all of them hydrides were reported to form. In general, we see that all of these points lie below the lines on the plots and thus agree with our determinations of the critical potential for hydride formation. However, in neutral solutions there are some points that lie slightly above the line. This information suggests that hydrides may form over long periods of time at potentials above the critical potentials determined by the twenty-four hour tests. Therefore, it is important to test samples for long periods of time to determine whether or not hydrides would be expected to form.

Long Term Tests in Stagnant Solutions

We now consider the results of the long term tests. First we will consider those samples in which the titanium was placed in a stagnant solution.

Figure 3 shows the corrosion potential of uncoupled grade 2 titanium measured in both NaCl and synthetic sea water plotted as a function of time. We see from these results that in both cases the corrosion potential is significantly more noble than the critical potential for hydride formation for neutral pH at room temperature. The value of this critical potential is shown by the horizontal line on the plot. We also held the titanium at a controlled potential of $-0.869\ V_{SCE}$ for seven months and found no evidence of hydride formation. This latter test suggests that titanium can be safely used at more electropositive values than $-0.869\ V_{SCE}$ in sea water.

We next consider samples that were galvanically coupled with either commercial purity zinc or a zinc anode. Figure 4 shows the couple potential plotted as a function of time for the sample coupled with commercial purity zinc immersed in both NaCl and synthetic sea water. The horizontal line on the figure represents the critical potential for hydride formation at this pH and temperature. The potentials are much more electronegative than those for the non-coupled sample (Figure 3) and are clearly very close to the critical potential. X-ray analysis showed that after eight months of exposure, no hydrides formed in the samples coupled with commercial purity zinc. We examined samples coupled with the zinc anode that had been exposed to the NaCl solution for six months. Again no hydrides had formed in the sample.

The final set of samples that we examined were those that were coupled to an aluminum anode. Figure 5 shows the couple potential for these samples plotted as a function of time. Even though the average potential was slightly more noble than that for the samples coupled with the zinc, we found that after an exposure of six months to 3.5% NaCl and seven months to synthetic sea water, hydrides were observed. These were first detected by X-ray diffraction, but they could also be observed in the scanning electron microscope. An example is shown in Figure 6. Thus it appears that the presence of the aluminum corrosion products must enhance the formation of hydrides. It would seem most reasonable that the ions formed as a result of the corrosion enhance the kinetics of hydrogen absorption by the titanium. This result would also suggest that it may be necessary to adjust the critical potential diagrams for various galvanic couples.

Long Term Tests in Flowing Solutions

Two types of tests were run in which the titanium was exposed to flowing solutions. One set was done in a laboratory system in which flowing NaCl solution was slowly passed through a beaker containing a set of samples in a re-circulating system. The samples were titanium galvanically coupled either to commercial purity zinc or an aluminum anode. The tests lasted for six months and no evidence of hydride formation was observed.

Another set of samples was exposed to natural flowing sea water. Four types of samples were exposed. These included uncoupled grade 2 titanium, titanium coupled with commercial purity zinc, titanium coupled with a zinc anode, and titanium coupled with an aluminum anode. To date, the exposures have lasted up to three months. No hydrides have been detected in the samples. However, calcareous deposits formed rapidly on the surface. An example is shown in Figure 7 from a samples that was tested for three months.

DISCUSSION

In this discussion we wish to consider two points. One is the usefulness of the critical potential diagrams. The second is the role of other ions on the uptake of hydrogen.

The critical potential diagrams shown in Figure 2 are designed to be a guide for use of titanium in sea water environments. Since they are based on short term tests, it is possible that the values for the critical potential for hydride formation are more noble than would be the case for long term exposures. However, the comparison between observations of hydrides in commercial situations and long term tests reported in this paper and in Figure 2 suggests that the diagrams do provide a useful guide.

The results reported in this paper show that titanium that is not galvanically coupled to another metal will never approach the potential at which hydrides would start to form. However, galvanic coupling to zinc or aluminum lowers the potential significantly so that the potential is very close to the critical potential for hydride formation. Our results show that in stagnant solutions hydrides formed in the sample coupled with the aluminum anode. Several important points should be noted about this result. The first is that the amount of hydride formed in these samples is very small. It is much less than we obtained when we charged a sample in an acidic solution. We also note that the hydrides formed in the acidic solution were not sufficient to alter mechanical properties significantly, so it is unlikely that the small amount formed here would affect mechanical properties either. The second point is that it would appear that the detailed chemistry of the solution near the surface of the sample may affect either the local hydrogen concentration available to enter the titanium or the kinetics of hydrogen absorption. At this time we cannot determine which of these possibilities is more likely. However, the fact that the titanium-aluminum anode couple formed hydrides in a stagnant solution and the titanium-zinc couple, which had a slightly higher couple potential, did not suggests that the detailed chemistry of the solution affects whether or not hydrides will form.

Finally, we note that it has been recommended that titanium not be used in sea water when the potential goes below –700 mV_{SCE} [13]. This result may be somewhat conservative, in that we did not observed hydrides in samples polarized to –869 mV_{SCE}. The results for the aluminum anode – titanium couple suggest that –900 mV_{SCE} may be a safe cut-off potential.

CONCLUSIONS

The conclusions of this study are the following:

1. Critical potential diagrams can be used as a guide to determine whether or not hydrides will form when titanium is exposed to sea water.
2. When commercial purity titanium is exposed to sea water, it will not achieve a corrosion potential at which hydrides are likely to form.
3. Galvanic coupling of titanium with an aluminum anode can lead to hydride formation. In our experiments hydrides were found when the titanium – aluminum anode sample was exposed to stagnant NaCl solution or synthetic sea water for six and seven months, respectively.

ACKNOWLDEGMENTS

The research at Brown University was sponsored by the Office of Naval Research, Contract N00014-96-0272. The authors would especially like to thank Mr. Keith Lucas of the Navy Research Laboratory Marine Corrosion Center in Key West, Florida, for performing the tests in natural flowing sea water.

REFERENCES

1. ASTM Spec. D1141 –98.
2. L.Lunde, R. Nyborg, and H. Kooyman, Institutt for Energiteknikk, Report IFE/Kr/F-88/150.
3. L.C. Covington, Corrosion, vol. 35, p. 378 (1979).
4. J.-I. Lee, J.C. Lin, and J.C. Oung, MRL Bull. Res. Dev., vol. 2, p. 51 (1988).
5. S. Sato, K. Nagata, Y. Watanabe, T. Nakamura, and T. Hamada, Boshoku Gijutsu – Corrosion Engineering, vol 25, p. 311 (1976).
6. S. Sato, K. Nagata, and S. Yamauchi, Titanium Science and Technology, vol 2. Munich, Sept. 1984, p. 397.
7. L. Lunde, R. Nybort, and W. Wilhelmsen, in Titanium 92, F.H. Froes and I. Caplan, eds., TMS, Warrendale (1993) p. 2087
8. H. Satoh, T. Fukuzuka, K. Shimogori, and H. Tanabe, in Second International Congress on Hydrogen in Metals, paper 6A1, Paris, 1977.
9. T. Fukuzuka, K. Shimogori, H. Satoh, F. Kamikubo, International Congress on Desalination and Water Re-Use, Nice, France, (1979), p. 389.
10. H. Togano, Metal Finishing Society of Japan, col. 30, p. 116 (1979).
11. I. Azkarate and A. Pelayo, INASMET, 20009, San Sebastian.
12. R. W. Schutz and J.S. Grauman, Corrosion 89, Paper 110.
13. H. Satoh, T. Fukuzuka, K. Shimogori, and H. Tanabe, in Proceedings of the Second International Congress on Hydrogen in Metals, Oxford, Pergamon Press, 1977.
14. S. Sato, K. Nagata, and S. Yamauchi, Titanium Science and Technology, vol 2. Munich, Sept. 1984, p. 397.
15. JRB Gilbert, Titanium Science and Technology, vol 2. Munich, Sept. 1984, p. 1105

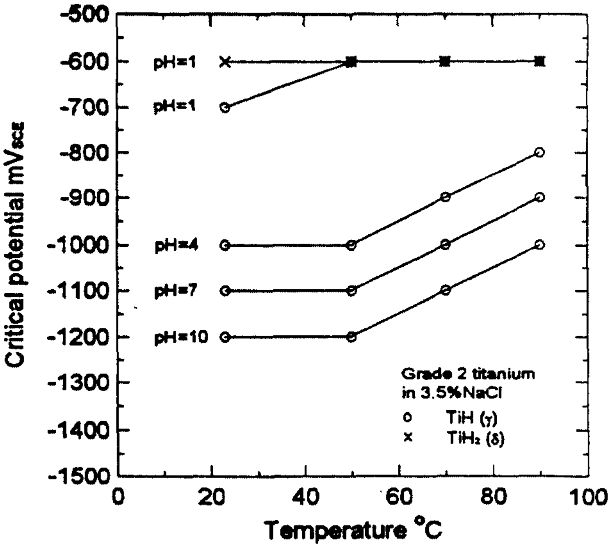

Figure 1 – The critical potential for hydride formation in 3.5% NaCl. The potential is plotted as a function of temperature. Different lines on the plot correspond to constant pH values.

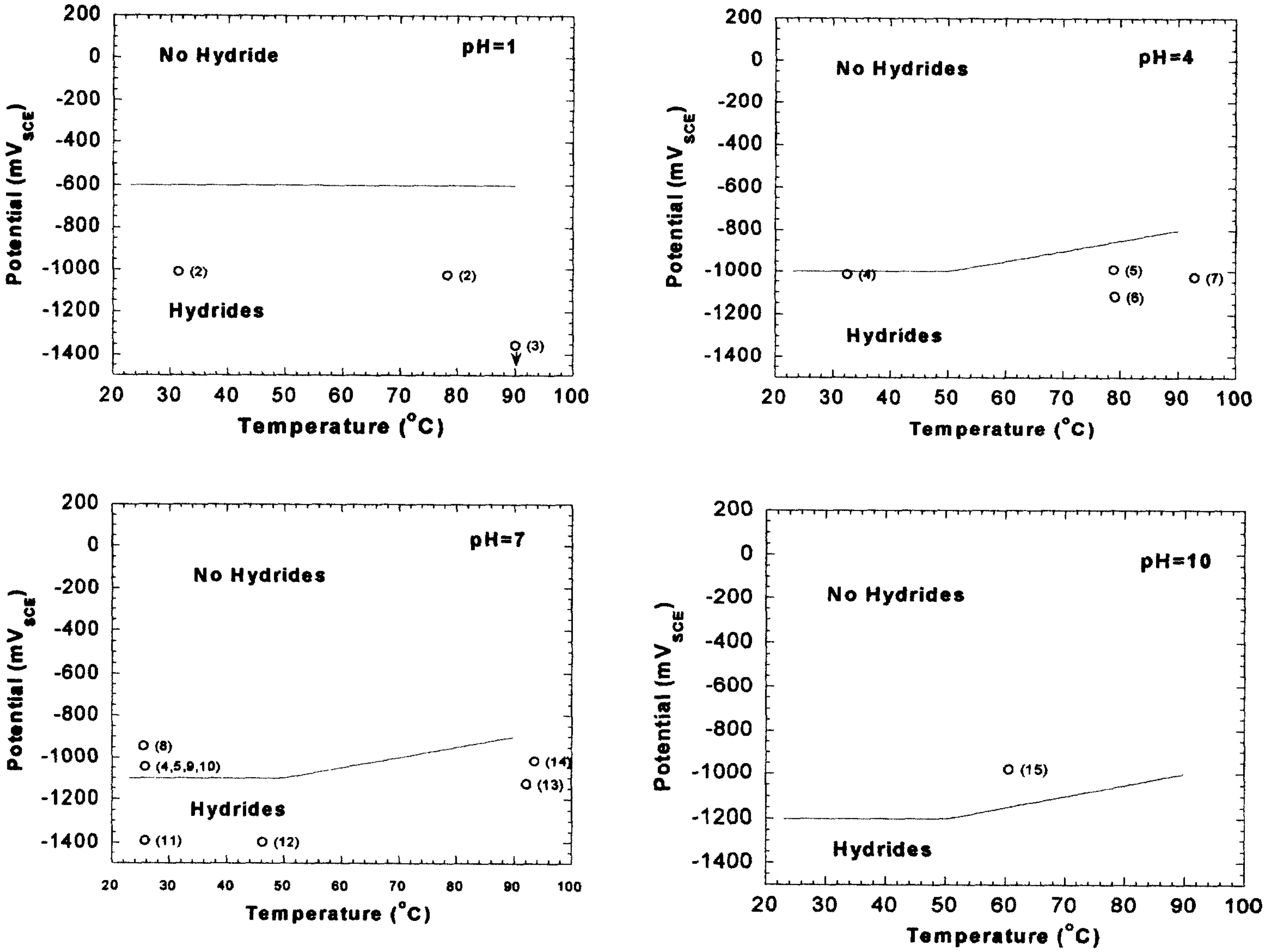

Figure 2 – The critical potential for hydride formation in 3.5% NaCl. The potential is plotted as a function of temperature and each plot corresponds to a different pH value. The individual data points are taken from the literature, and the number beside them gives the reference.

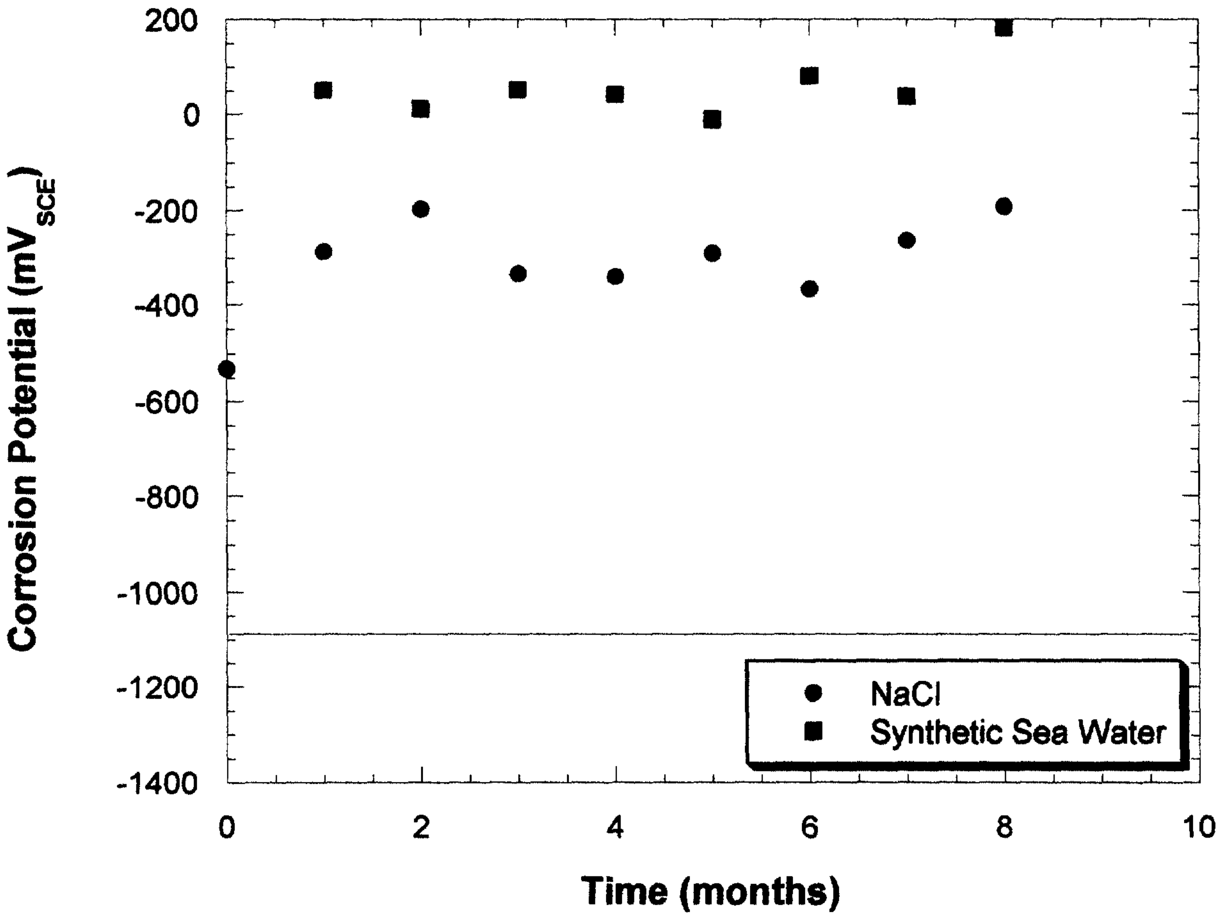

Figure 3 – The corrosion potential plotted as a function of time for titanium in neutral NaCl and synthetic sea water. The horizontal line is the critical potential for hydride formation at this temperature and pH.

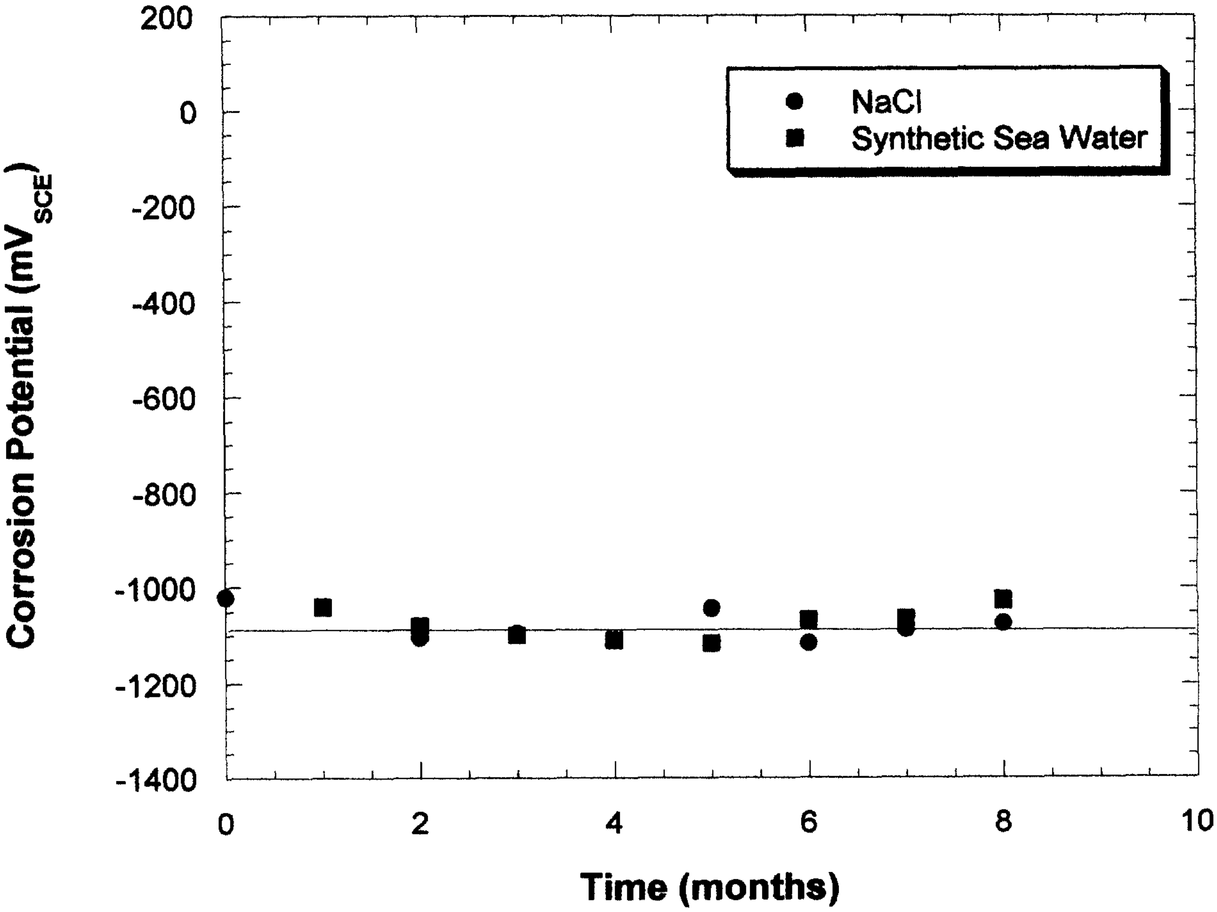

Figure 4 - The couple potential plotted as a function of time for titanium galvanically coupled with commercial purity zinc in neutral NaCl and synthetic sea water. The horizontal line is the critical potential for hydride formation at this temperature and pH.

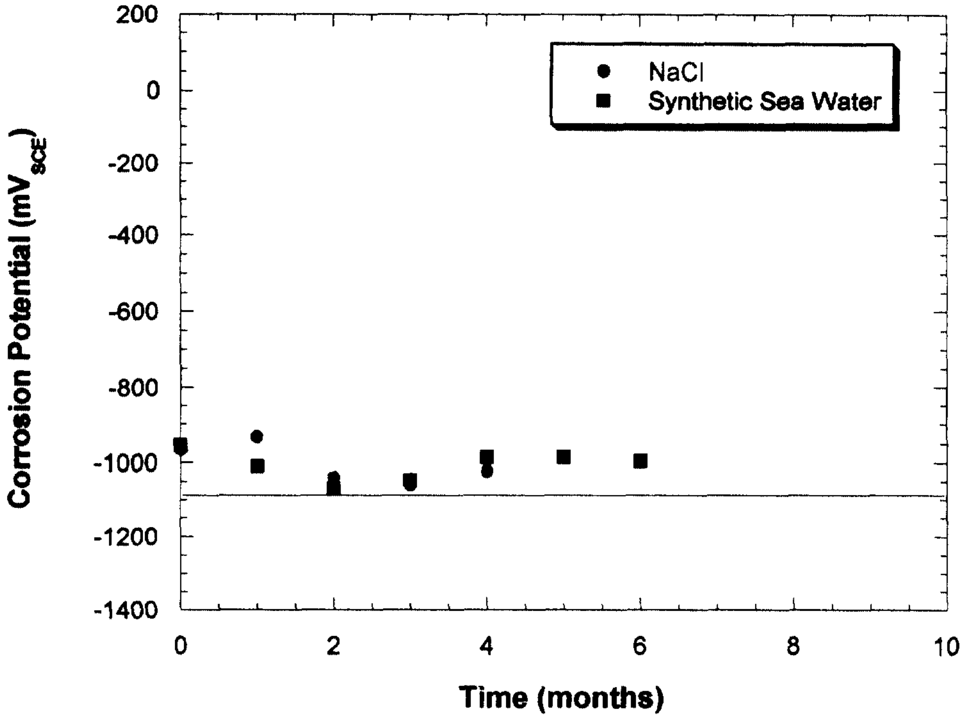

Figure 5 - The couple potential plotted as a function of time for titanium galvanically coupled to an aluminum anode in neutral NaCl and synthetic sea water. The horizontal line is the critical potential for hydride formation at this temperature and pH.

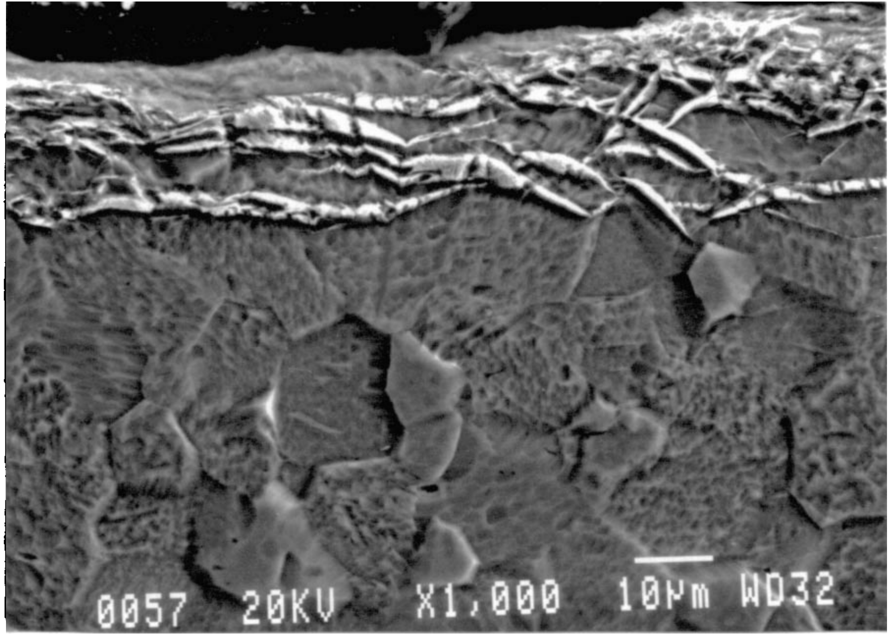

Figure 6 – A scanning electron micrograph of hydrides formed in titanium galvanically coupled with an aluminum anode.

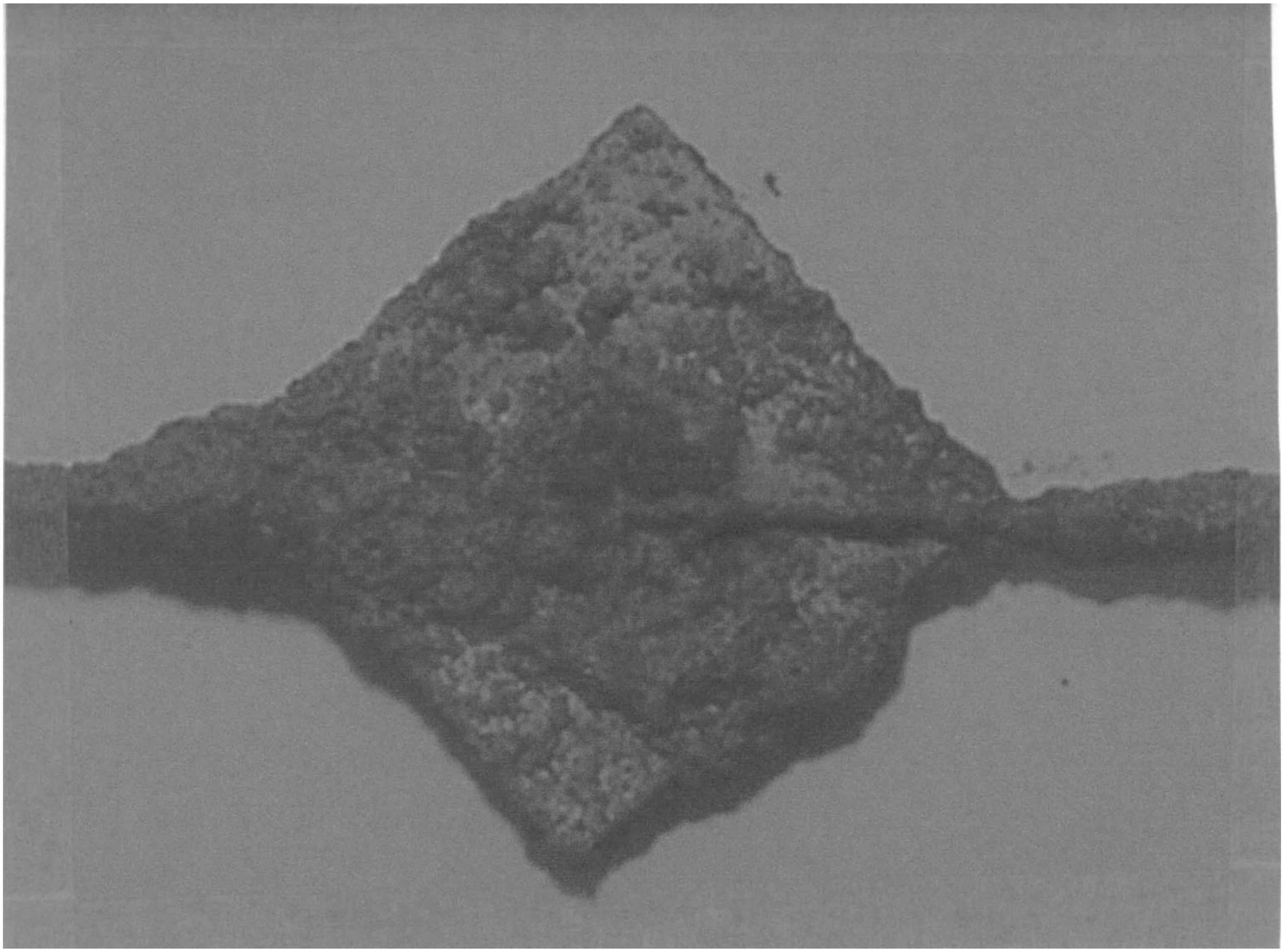

Figure 7 – Calcareous deposits for a sample exposed to natural flowing sea water