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Technical Progress Report

**Corrosion Studies of a Stainless Steel Structure for the
ITER Aqueous Lithium Salt Blanket Concept**

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ABSTRACT

The aqueous lithium salt blanket (ALSB) employs water, with a dissolved lithium compound, as both the coolant and tritium breeding medium. The ALSB concept is one of three blanket options currently being examined for breeding tritium in the International Thermonuclear Experimental Reactor (ITER). To provide data and recommendations for materials and chemistry selection relevant to application of the ALSB in ITER, corrosion studies have been initiated, focusing on type 316 stainless steel in lithium hydroxide and lithium nitrate solutions. This report presents the preliminary results of these corrosion studies.

The results to date, while preliminary, suggest that even at 90 C, a blanket utilizing 10% LiOH (the current lithium salt of choice for ITER ALSB applications) will not cause catastrophic failure of 316 stainless steel by either stress corrosion cracking or localized corrosion; that the general corrosion rate will not exceed about 40 $\mu\text{m}/\text{yr}$ and transport of material will certainly be much less than this value since most of the corrosion product will be included in the strong adherent surface film; and that, although hydrogen may be evolved due to electrolysis, the maximum amount of hydrogen is small compared to that expected to be produced by radiolysis. These observations are predicated on the assumption that

the blanket will be completely deaerated, and that the corrosion potential of the alloy will be similar to that observed in the laboratory.

1. INTRODUCTION

The aqueous lithium salt blanket (ALSB) employs water, with a dissolved lithium compound, as both the coolant and tritium breeding medium. The ALSB concept is one of three blanket options currently being examined for breeding tritium in the International Thermonuclear Experimental Reactor (ITER). In order to provide data and recommendations for materials and chemistry selection relevant to application of the ALSB in ITER, Rensselaer Polytechnic Institute has initiated a program of corrosion studies. The scope of this effort includes investigation of the corrosion of thermo-mechanical treatments of stainless steel alloys (the structural material designated for ITER [1]) in environments relevant to the ALSB design proposed for ITER [2]. Specifically, this study focuses on type 316 stainless steel in lithium hydroxide and lithium nitrate solutions. The type and concentrations of lithium salts and solution temperatures studied are those under consideration by the U.S. ITER design team. [1,2]

The approach to this task is primarily experimental, involving electrochemical studies, metallographic investigations, and environment-mechanical property interactions. Electrochemical experimentation is being performed as a function of temperature, solution concentration, time in solution, and thermo-mechanical

treatment of the alloys of interest. Metallographic studies are being utilized to examine microstructural corrosion damage resulting from exposure to the proposed environments. Susceptibility to stress corrosion cracking (SCC) is being determined by both constant load and slow strain testing. The effects of electrolysis and radiolysis on the corrosion of the materials are also being examined.

This report presents the results of the work performed at Rensselaer during the period 1 July 1988 to 30 June 1989. The results presented should be interpreted cautiously since they are by no means complete and need to be verified by additional experimentation. This report is organized into sections describing the material being studied, the method of experimentation, results of the study to date, and finally, preliminary conclusions about the material selection and solution chemistry.

2. MATERIAL STUDIED

Most of the material utilized in these studies was obtained from the fusion materials inventory at Oak Ridge National Laboratory. The material is a type 316 stainless steel containing 16.6% Chromium, 11.8% Nickel, 2.4% Molybdenum, 1.7% Manganese, 0.7% Silicon, 0.06% Carbon, 0.02% Sulfur, and the remainder Fe (percentages

throughout this report are weight percent unless otherwise noted). The material was received in a 50% cold worked condition, having been rolled from 0.38 cm (.15") to 0.19 cm (.075") after being annealed for one hour at 1050 C.

Four different heat treatments are currently being studied: (1) as received (50% cold worked); (2) sensitized (2 hours at 650 C) after cold work; (3) solution annealed (30 minutes at 1300 C); and (4) sensitized after annealing. The heat treatment of choice for the ITER ALSB option is currently the solution annealed condition.

3. EXPERIMENTS PERFORMED

3.1 IMMERSION

Immersion or exposure testing has been conducted utilizing a two-point bend technique. The two-point bend exposure testing allows a screening of the alloy's susceptibility to general and localized corrosion under stressed and unstressed conditions. Additionally, the technique allows a preliminary screening of stress corrosion cracking susceptibility. The tests were performed by mounting 1 cm (w) by 7 cm (l) by 0.1 cm (t) bars of the stainless steel in a two-point bend apparatus and immersing the entire rig into the environment of interest. A schematic diagram of the apparatus used in

these tests is shown in Figure 1. Tests have been performed in aqueous solutions of 10% LiOH, saturated LiOH, 16% LiNO₃, acidified 16% LiNO₃ (pH 1), and mixed 5% LiOH/8% LiNO₃ at temperatures of 25 C and 90 C.

3.2 ELECTROCHEMISTRY

Electrochemical polarization experiments have been performed as a function of solution chemistry, temperature and pH. A typical (schematic) electrochemical polarization curve is shown in Figure 2. Using electrochemical polarization techniques, general corrosion rates as well as susceptibility to localized corrosion and stress corrosion cracking can be predicted and correlated with corrosion potentials of an alloy in a given environment. For example, zone 1 (Figure 2) is the region near the naturally occurring corrosion potential of the alloy. In this region general dissolution of the alloy surface is predicted. If the electrochemical potential of the alloy surface is shifted in the positive direction, the rate of general dissolution increases (as measured by an increase in current density). However, for larger increases in the potential the alloy may enter zone 2 which is a transition between general dissolution and passivity. For many alloy systems this zone is associated with susceptibility to stress corrosion

cracking. At still higher potentials the alloy may enter zone 3 where localized corrosion may be observed.

These shifts in potential can be induced by either electrical or chemical perturbations in the aqueous environments. For example, in ITER these perturbations may result from solute concentration changes, dissolved oxygen, electrolysis or radiolysis.

Tests have been performed at concentrations of 5% and 10% LiOH and 16% LiNO₃ and at temperatures of 25, 60/70 and 90 C. Tests in these solutions have been conducted at a variety of electrochemical potential scan rates and for durations of up to 1 week in solution. The effect of pH on the corrosion in lithium nitrate solutions has also been examined.

3.3 RADIOLYSIS

In addition to conventional corrosion experiments, the effects of radiolysis products on the corrosion of the stainless steel are being evaluated utilizing the Rensselaer linear electron accelerator (LINAC). The source for these studies is a beam of 17 MeV electrons with currents of up to 800 μ A. This yields energy depositions in the aqueous solution of up to 11 kW. The samples being tested are suspended in the aqueous salt environment of interest in stainless steel or platinum cradles. The temperature of the solution is maintained

during testing by the use of auxiliary heating and cooling. The linear energy transfer (LET) of the electron beam energy to the aqueous solution varies from 2 MeV/cm at the surface of the reaction vessel to about 21 MeV/cm at a position about 6 cm into the solution. Because primary radiolysis product yields vary with LET, the containment vessel was designed to allow for sample positioning. By varying the position of the samples relative to the beam's path in the aqueous solution, the effects of local LET and dose can be studied. For initial experiments, the primary position chosen is one centered in the beam path and 6 cm from the beam's entrance point. This provides a local LET on the order of 20 MeV/cm and a dose of about 80% of the inlet dose. Experiments have been performed in 16% LiNO_3 and 5% LiOH , both at 90 C.

3.4 STRESS CORROSION CRACKING

Constant load stress corrosion cracking experiments were performed on cold-worked and sensitized 316L stainless steel wire samples in 10% and saturated aqueous LiOH solutions at 25 C and 90 C. The 316L material differs from the 316 material described in Section 2 in that it contains less than 0.02% Carbon (compared with 0.06% Carbon) and is less susceptible to sensitization. Initially 316L stainless steel wire is being used because

of its availability; wire drawn from the stock described in Section 2 will also be tested and compared with the 316L. The yield strength of these wires was determined from standard tensile tests to be 232 MPa, and loads of 10% and 110% above the yield strength (37 and 71 ksi respectively) were applied during the testing.

4. EXPERIMENTAL RESULTS

4.1 IMMERSION

The duration of each of the exposure tests was 200 hours. In all of the two-point bend tests there has been no indication of stress corrosion cracking in any of the test solutions at any temperature. Samples exposed to lithium hydroxide environments exhibit some general corrosion and slight intergranular attack as shown in Figure 3. Of the 27 samples tested in 16% LiNO_3 , 8 specimens exhibited shallow pitting over much of the surface with a concentration of pits near the most highly stressed areas; the remaining 19 specimens showed evidence of crevice corrosion at the edge of the material where it was in contact with the mounting material (See Figure 1). In the samples exposed to the mixed LiOH/LiNO_3 environments (Figure 4), pits were observed which were deeper and of greater number than in lithium nitrate alone.

4.2 ELECTROCHEMISTRY

Electrochemical polarization experiments have been performed as a function of solution chemistry, solution concentration, and temperature. Table I summarizes the general corrosion results based on the performed electrochemical studies of 316 stainless steel in the solutions of interest. These corrosion rates include both material being utilized in forming the passive surface film, as well as, material entering solution as soluble and insoluble species. The reported corrosion rates are expected to be higher than will be observed in service because in most instances corrosion rates decrease with time as the corrosion product films become more stable. Table I lists the salt and concentration and reports corrosion rates for both deaerated (oxygen is removed by bubbling argon through the solution prior to and during the experiment) and non-deaerated (oxygen at solubility point) cases as a function of temperature.

The polarization experiments have shown susceptibility to localized corrosion in lithium nitrate solutions. The critical pitting potential for the stainless steel in 16% LiNO_3 at 90 C is between 100 and 200 mV relative to the standard hydrogen electrode (SHE). No susceptibility to localized corrosion is indicated in any concentration of lithium hydroxide at any temperature

or in basic (pH 12) solutions of lithium nitrate, although pitting was observed in immersion tests.

Characteristic electrochemical polarization curves are shown in Figures 5 to 7. The data in Figure 5 indicate that the electrochemical response of the stainless steel in lithium nitrate is sensitive to the time of exposure. Increasing exposure times decreases the resistance to localized corrosion, as indicated by the more active breakdown potential at 96 hours versus no apparent breakdown potential initially and at 24 hours. Figure 6 shows that the susceptibility to corrosion of stainless steel in lithium hydroxide is in general reduced by reducing the test temperature (the current density decreases with decreasing temperature). The effect of lithium nitrate solution pH is illustrated by the data in Figure 7 which indicates that a small addition of lithium hydroxide decreases the general corrosion rate of the stainless steel and reduces the susceptibility to localized corrosion as indicated by the lack of a breakdown potential in the solution with the lithium hydroxide addition.

4.3 RADIOLYSIS

Radiolysis experiments have been conducted in 16% LiNO_3 and in 5% LiOH solutions. A shift of the corrosion potential, as well as formation of a thick oxygen

containing surface film, have been noted in the lithium hydroxide experiments. A shift in potential is also noted in the nitrate solution, however, with no measurable effect on the corrosion behavior. It should be emphasized that these results are preliminary and are yet to be interpreted. Further experiments are currently in progress.

4.4 STRESS CORROSION CRACKING

Susceptibility to stress corrosion cracking has not been observed under any of the conditions studied. Most of the experiments were terminated after 200 hours, however, a sensitized specimen in saturated LiOH solution at 90 C under a load 210% (71 ksi) of the yield strength had not failed after 1000 hours.

4.5 ELECTROLYSIS

Electrolysis occurs when potential differences on metallic surfaces are generated as a result of an electrolyte flowing in a magnetic field. This phenomenon was demonstrated by E J. Kelly at Oak Ridge National Laboratory [3] for titanium in sulfuric acid. Although the effects of electrolysis on the corrosion behavior of 316 stainless steel are yet to be demonstrated in the ITER ALSB design, several comments can be made related to the potential effects of this phenomenon. Based on calculations made at the University of Wisconsin, the

maximum electrolysis voltage generated in the ALSB design would be about 800 mV [4]. According to Kelly [3] this voltage would be uniformly divided between anodic areas and cathodic areas (± 400 mV), as shown in Figure 8. The corrosion rate for the anodic areas, in a well deaerated solution, is expected to be unchanged in 10% LiOH at 90 C and will be of the order reported in Table I. For cathodic areas on the alloy, hydrogen will be evolved at a rate equivalent to approximately 1.0 mA/cm^2 . This current density will support the evolution of approximately $5 \times 10^{-5} \text{ mole H}_2 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, or $1.5 \text{ ml} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at 90 C. This rate of hydrogen production is small compared with that expected due to radiolysis [4]. It is emphasized that these predictions are based on the corrosion potentials and currents measured at Rensselaer on cathodically reduced samples in well deaerated solutions. The specific amounts of corrosion and hydrogen evolution will depend sensitively on the free corrosion potential of the alloy under actual service conditions; and the free corrosion potential will be a function of pre-exposure of the alloy, flow rates, and probably surface preparation considerations.

In 16% LiNO₃ solutions, electrolysis equivalent to a shift in potential of ± 400 mV can be expected to polarize anodic areas of the alloy well into the potential region where pitting occurs, as illustrated by Figure 9. Thus,

severe localized attack of the alloy can be anticipated for this system. On the other hand, hydrogen production would be expected to be at least one and perhaps even two orders of magnitude less than in the case of lithium hydroxide for a similar potential shift.

5. PRELIMINARY CONCLUSIONS

Caution should be exercised in over-interpreting the data presented here since they are by no means complete and need to be verified by additional experimentation. Moreover, it is noted that the results should be viewed as conservative since the reported corrosion rates are expected to be higher than will be observed in service; in most instances corrosion rates decrease with time as the corrosion product films become more stable. The present results, while preliminary, suggest that even at 90 C, a blanket utilizing 10% LiOH will not cause catastrophic failure of 316 stainless steel by either stress corrosion cracking or localized corrosion; that the general corrosion rate will not exceed about 40 $\mu\text{m}/\text{yr}$ and transport of material will certainly be much less than this value since most of the corrosion product will be included in the strong adherent surface film; and that, although hydrogen may be evolved due to electrolysis, the maximum amount of hydrogen is small compared to that expected to be produced by radiolysis.

These observations are predicated on the assumption that the blanket will be completely deaerated, and that the corrosion potential of the alloy will be similar to that observed in the laboratory. Finally, it should be understood that the results presented in this report represent work in progress. Future results will be reported as they become available.

REFERENCES

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- [3] Eugene J. Kelly, Magnetic Field Effects on Electrochemical Reactions Occurring at Metal/Flowing Electrolyte Interfaces, J. Electrochem. Soc., 124, 987 (1977).
- [4] Private communications with M. Sawan, University of Wisconsin, Madison, April 1989.

Table I: Summary of Corrosion Rates from
Electrochemical Experiments (averages of all data taken
for reported condition)

Solution	Corrosion Rate [$\mu\text{m}/\text{yr}$]			Comments
	25 C	60 C	90 C	
16% LiNO_3 occurs				Pitting
Ar Deaerated	5	----	8	after 72 hr.
After 24 hr.			2	
Non-deaerated	5	----	8	
10% LiOH				
Ar Deaerated	8	20	42	
Non-deaerated	40	210	420	

LIST OF FIGURES

1. Schematic diagram of Two-Point Bend Apparatus used for immersion and stress corrosion cracking tests.
2. Schematic of Typical Electrochemical Polarization Curve. The potential zones shown correspond to (1) the onset of general dissolution; (2) the onset of stress corrosion cracking; and (3) the onset of localized corrosion.
3. Intergranular Attack of Cold-Worked SS-316 after 200 hours in 10% LiOH at 90 C. (400x)
4. Pitting of Cold-Worked SS-316 after 200 hours in 8% LiNO₃/5% LiOH at 90 C. (8x)
5. Effect of time in solution on the polarization behavior of 316 stainless steel in 16% LiNO₃ at 90 C
6. Effect of solution temperature on the polarization behavior of 316 stainless steel in 10% LiOH at 90 C
7. Effect of pH on the polarization behavior of 316 stainless steel in 16% LiNO₃ at 90 C
8. Anticipated effect of electrolysis on the corrosion behavior of stainless steel in deaerated 10% LiOH at 90 C
9. Anticipated effect of electrolysis on the corrosion of stainless steel in deaerated 16% LiNO₃ at 90 C

Corrosion Studies ... Lithium Salt Blanket Option
Figure: 1

Corrosion studies ... Lithium Salt Blanket Option
Figure: 2

Corrosion Studies ... Lithium Salt Blanket Option
Figure: 3

Corrosion Studies ... Lithium Salt Blanket Option
Figure: 4

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Figure: 5

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Figure: 7

Corrosion Studies ... Lithium Salt Blanket Option
Figure: 8

Corrosion Studies ... Lithium Salt Blanket Option
Figure: 9

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