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GEOTHERMAL MATERIALS STUDIES

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GEOHERMAL MATERIALS STUDIES

By

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with Contributions from

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1. INTRODUCTION

Since its inception in 1974, the LLL Geothermal Program has evolved into two basic activities:

- - To provide advanced technologies for hydrothermal systems with emphasis on the Total Flow Process.
- - A recently initiated Industrial Support Program to provide technical assistance to joint ERDA/industry projects.

The Metallurgy Division is carrying out a materials effort in support of both activities.

In the Total Flow Process, the total flow of the wellhead is expanded through converging-diverging nozzles to convert the enthalpy contained in the fluid into kinetic energy in the form of low temperature, high velocity streams of two-phase fluids to drive impulse turbines. This process is expected to be as much as 60% more efficient than either the flashed-steam or binary-cycle process. In the latter two processes, a large fraction of the enthalpy is lost in the relatively high temperature brine that is rejected. The goal for the Total Flow Process Program is to solve the brine chemistry and materials problems in order to be able to test this process using the high temperature/high salinity brines located in the Salton Sea Geothermal Field. This particular resource was chosen because it represents the greatest technical challenge and economic potential.

The short-range goal of the geothermal materials group is to select structural materials and fabrication processes for a 100-kW, brine tolerant turbine scheduled to be field tested by the end of FY 1977. The materials

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selected must be corrosion resistant to the high salinity acid brines and exhibit resistance to erosion-assisted corrosion that may arise from impingement by the high velocity brine droplets and entrained particulates. The turbine material must also be capable of supporting high sustained stresses due to centrifugal forces without being subjected to delayed failure by stress corrosion cracking or corrosion fatigue. Candidate materials will be evaluated through an integrated program of laboratory activity and field testing.

In the Industrial Support Program, we will monitor corrosion during operation of the San Diego Gas and Electric Company's (SDG&E) Geothermal Test Loop Facility. We will also test other candidate plant materials for their corrosion resistance to provide a basis for substitution should present materials prove to be inadequate.

2. TOTAL FLOW PROCESS

2.1. Nozzle-and-Turbine Materials Erosion Studies

a) Introduction

A number of metallic materials (e.g., Ti-, Ta-, Co-, Ni-, and Fe-base alloys) are available which will not exhibit significant corrosion rates -- even in acid brine environments under static situations. However, the severe environment present in the high velocity nozzle exhaust might be expected to destroy the protective films that are responsible for the corrosion resistance of such materials and, thereby, result in high wear rates from the erosion-assisted corrosion. It is highly unlikely that a material will be obtained that will show adequate resistance to both erosion-assisted corrosion and stress corrosion and, therefore, some type of composite approach will have to be used. Alternatives that we are considering to provide the required structural strength and resistance to erosion-assisted corrosion are surface hardening by chemical diffusion, the use of coatings, and the use of inserts both for the turbine blades and nozzles.

Currently, the chemical diffusion studies are limited to Ti-base alloys, and in particular, Ti and Ti-6Al-4V. Coatings are being applied by several techniques on a number of Ti-, Fe-, Ni-, and Co-base alloys. Inserts consist of ceramic materials which, because of their lack of toughness, cannot be considered for the present turbine design, except as blade inserts. We are also

examining some of the noble metals and their alloys (Au, Pt, Rh) as either substrates or coatings. Because of the unusually wide range of passivity of its oxide (Pourbaix diagram) Ta and some of its alloys are also being considered. All these materials, in the form of wedge-shaped wear plates (or coatings on such plates), will be exposed to high velocity fluids. The wear plates have an overall dimension of 12.70 by 44.45 by 66.68 mm (0.5 by 1.75 x 2.63 in.). The wedge edge is tapered to an included angle of 20° and a tip radius of 250 μ m (0.010 in.). It is exposed to the fluids exiting the nozzle as shown in Fig. 1. One of the three bent-beam, stress corrosion cracking specimens that are supported in the wear plate holder can also be seen in this view. To date, four wear plate samples have been tested in the fresh water LLL facility. Reference to these is made below. A number of samples have been prepared, or are in the process of being prepared, for exposure. Pending the startup of the chemistry geothermal field test unit, additional samples will be exposed in the LLL facility to provide some interim data. We are interacting with industry in developing techniques for producing the erosion/corrosion resistant hard surfaces.

b) Chemical Diffusion Coatings (Contributed by J. M. Johnson)

A review of the literature on the effects of coatings of various materials, 50 to 100 μ m (0.002 to 0.004 in.) thick, on the wear resistance and mechanical properties of titanium reveals that very little data is available. There is evidence, however, that failure caused by particulates impacting on a metal coating appears to result from initial fracture of the coating followed by spalling of small fractured areas which lack adequate adhesion to the titanium substrate. Adequate adhesion between the coating and the titanium depends on such factors as physical or chemical bonding, diffusion across the interfacial region, the metallurgical nature of the interfacial structure, and the thickness and brittleness of the coating.

The optimum interface, to maximize adhesion, is one in which stresses in the interfacial region are dispersed over an appreciable volume without generating a brittle or low-strength region. This is best accomplished by grading the composition of the interface from that of the bulk alloy to that of the coating. This gradation can be achieved through diffusion and chemical reaction in the surface region of the part to be coated.

Because of their availability, commercially pure titanium (C.P.Ti) and Ti-6Al-4V were used in a preliminary study to determine the feasibility of case-hardening these materials by nitriding and/or carbo-nitriding. The initial studies were done on nominal 6.35 mm (0.25 in.) bar stock. It was anticipated that we would be able to produce specimens with a graded hardness profile from bulk to surface varying from ≈ 300 to 600 DPH.

Figures 2a and 2b show the microstructures of a Ti-6Al-4V sample after being exposed for four hours at 1000°C in an $\text{H}_2\text{-N}_2\text{-CH}_4$ atmosphere and furnace cooled. Note the continuous, hardened surface layer and the "fingers" of hardened material extending into the main body of the specimen. Figure 3 shows the hardness profile ranging from 584 DPH at the edge to 362 DPH toward the center of the specimen. Further examination of Fig. 2b reveals the presence of a very thin surface layer. We believe that this is a layer of TiN, which is very hard (1200 DPH), but too thin to be reflected in the hardness profile values. This would be consistent with the slightly gold appearance of the specimen following nitriding.

Figures 4a and 4b show the microstructure of a sample of Ti-6Al-4V following six hours at 1000°C in an $\text{H}_2\text{-N}_2\text{-CH}_4$ atmosphere. Note that the additional two hours of exposure caused further penetration of the hardened case and fingers. Furthermore, the hardness was increased from a maximum reading of 585 to 725 DPH. The hardness profile for the six-hour exposure is shown in Fig. 5. The thin outer TiN layer appears to be more continuous following the six-hour exposure than that following the four-hour exposure; compare Fig. 2b with 4b.

Figures 6a and 6b show the microstructure of C.P.Ti nitrided during the same furnace run as used for the specimen shown in Figs. 2a and 2b. Note the discrete layering of the coating and the areas of poor adhesion of the coating to the substrate. Fractures emanating from the hardness indentations in Fig. 6b indicates that the coating is very brittle. Poor adhesion is also indicated.

Next, a series of wear plates were nitrided varying the time and temperature in an attempt to optimize the coating. It was planned that after taking metallographic specimens, selected wear plates would be run in the test facility.

Preliminary metallography has been completed. Figures 7, 8, and 9 show some of the microstructures resulting from various treatments of Ti-6Al-4V. Note in all cases, we have achieved a layer of TiN on the surface with a graded

hardness underneath. Figure 10 is a view of a surface-hardened C.P.Ti exposed to a different treatment than that shown for Fig. 6. Again, the use of a C.P.Ti substrate has resulted in an inferior surface coating as indicated by the discrete layering, the lack of a graded hardness, and the presence of a slightly porous nitride surface layer.

A wear plate of Ti-6Al-4V with a microstructure of the type shown in Fig. 9 was exposed in the erosion testing system in the LLL Geothermal Test Facility. No measurable wear was observed after a three-hour test period. Following a thorough examination of the leading edge of the wear plate specimen, we plan to accumulate another nine hours of testing on the specimen to generate an erosion-wear data profile.

Work planned for the next quarter includes carburization and boronization of C.P.Ti and Ti-6Al-4V, accumulation of optimized specimens and, time permitting, preliminary screening of specimens in the LLL Geothermal Test Facility.

c) Coatings (Contributed by R. E. Garrison)

Three spray processes are being examined: (1) the ceramic-rod, oxyacetylene, flame-spray technique, (2) the tungsten-cathode, plasma spray technique, and (3) the detonation-gun spray technique. With these three methods, a wide variety of materials may be applied, including metals, alloys, ceramics, and cermets. Heavy buildups, in excess of 0.65 mm (25 mils) are possible. The ceramic-rod and tungsten-cathode spray techniques yield a spray temperature of 16,700°C, melting the powder to a plastic state and accelerating it to approximately $335 \text{ m}\cdot\text{s}^{-1}$ ($1100 \text{ ft}\cdot\text{s}^{-1}$). Coatings can be made with any material that will not sublime and is available in powder form. However, due to the relatively low impact force, excessive interconnecting porosity may be present.

The detonation gun technique produces high-particle velocities of up to $915 \text{ m}\cdot\text{s}^{-1}$ ($3,000 \text{ ft}\cdot\text{s}^{-1}$), as well as high-melt temperatures resulting in higher density and hardness values than those obtained by the former two processes. For example, hardness values of 1300, 1100, and 625 DPH are obtained for 91WC-9Co, 99Al₂O₃, and 70Cr₃C₂-30NiC₂, respectively.

Union Carbide, Linde Division, will be producing coatings for use. We plan on testing 60Al₂O₃-40TiO₂ and Co-25Cr-10Ni-7W on Ti-6Al-4V and type 304 stainless steel substrates which they will prepare for us. We will also examine Ta sprayed

on TZM wear plates. The Ultramet Company is presently preparing to produce chemically vapor-deposited coatings of WC, TiC, W-22Re, and Re on Mo wear plates.

d) Ceramics (Contributed by R. E. Garrison)

We have contacted a number of laboratories and commercial companies who have expertise in the fabrication and testing of ceramics. Haselden Company, of San Jose, California, is hot pressing six materials into wear plates for testing at the geothermal test unit in the Imperial Valley. These materials are TiB_2 , Si_3N_4 , SiC, B_4C , AlN and on Al_2O_3 -TiC mixture. We are examining the possibility of other materials such as 502-1100 grade AREMCOLOX machineable ceramic.

e) Inventory of Wear Plates (Contributed by R. E. Garrison)

Wear plates made of the following materials are ready for testing in the field or at LLL: C.P.Ti, Ti-6Al-4V, Ni, Fe-26Cr-1Mo, Fe-26Cr-1Mo-Cr-plated, Fe-26Cr-1Mo-Ni-plated, Mo, TZM carburized, Hastelloy G, Hastelloy 276, Inconel 833, Inconel 862, and Ti and Ti-6Al-4V case hardened as described above in Item 2.

Wear plates of the following materials are now being fabricated: Ti-6Al-4V, Fe-2.5Cr-1Mo, 50Re-50Mo, Illium-98, Illium-PD, Fe-21Cr-6Mn-9Ni, Ta, Ti-8Al-1Mo-1V, Ti-1.5Ni, Ti-6Al-2Nb-1Ta-1Mo, Ti-6Al-6V-2Sn, Ti-70, Au, 60Au-40Pt, Ti-70 nitrided, Ti-6Al-4V nitrided, Mo-CVD plated with WC, Mo-CVD plated with TiC, Mo-CVD plated with W-22Re Mo-CVD plated with Re, Duriron 304 stainless with a Ni-diamonized composite and 304 stainless with a Ni-SiC composite. Other alloys which also will be used for wear plates have recently been received.

f) Inventory of Nozzles (Contributed by R. E. Garrison)

Nozzles made out of Ti-6Al-4V and Au are ready for testing. The following nozzle inserts are ready for coating experiments: Ti-6Al-4V, reactor grade graphite, 60Au-40Pt, Ni, Ni with electroplated Pt, and Ni with electroplated Rh. Bars of Haynes Alloys 25 and 6B have just been received which also will be machined into nozzles.

g) Fresh-Water, LLL Facility, Wear Plate Results (Contributed by R. E. Garrison)

Figure 11 shows the relative amount of wear for four wear plates (C.P.Ti, case hardened Ti-6Al-4V, and hot isostatically pressed, 98% theoretical density B_4C and ZrB_2) exposed to the fresh water, LLL Geothermal Test Facility for

approximately 3-1/2 hours. The results are normalized in terms of wear rate per hour. As may be seen, these preliminary results suggest that at least for short time exposures, ceramics and case-hardened Ti-6Al-4V show promise as erosion-resistant materials.

h) Plating (Contributed by H. J. Wiesner)

A UCID covering the work done last quarter on electroless nickel plating of the 7075 T-6 aluminum turbine wheel built for testing in the LLL Geothermal Test Facility is being drafted. Preliminary planning for the plating of the second turbine wheel is now underway.

Wedges for further tests aimed at improving adhesion of the electroless nickel will be available in about one month. The tentative schedule for plating of the turbine is either August or September 1976.

2.2 Stress Corrosion Cracking

a) Introduction

High static stresses due to the centrifugal forces, which are proportional to the material density, will be developed in the rotating turbine wheel. Based on the behavior of various materials in chloride containing environments and their strength-to-weight ratio, Ti-base alloys appear to be the favored materials for turbine applications in the geothermal field environment. Static stresses of the order of 350 MPa (51 ksi) are estimated for a Ti alloy turbine wheel. Superimposed will be cyclic stresses arising, in part, from the cyclic impact of the exhaust from the nozzles. Therefore, the effect of the environment on limiting the material to withstand either static or cyclic loading must be considered. In cyclic loading, the effect of a corrosive environment is to cause a continuous drop in fatigue strength relative to that obtained in an inert environment and without the appearance of a well defined fatigue limit. Under a static load, failure may occur at a stress level considerably below the yield strength of the material in an inert environment. Both of these phenomena should be similarly affected by similar environments and, since studies related to static (noncyclic) loading are more widely documented, we will address the question of static loading as an illustration of the problem. Needless to say, in the final choice of materials, both static and cyclic testing must be done; however, in the initial screening process of many materials we have elected to use the much simpler static loading techniques.

The failure (cracking) which occurs under the combined action of a static stress and corrosion is referred to as stress corrosion cracking (SCC). It does not take place if either the stress or the corrosion action act independently. It occurs predominantly in alloys and seldom in pure metals. Stresses may be due to applied loads, residual stresses, or to the wedging action of corrosive products. One of the more insidious characteristics of SCC is that frequently the alloy is virtually or almost inert to the environment in which SCC occurred. For example, trace quantities of chloride in drinking water can cause failure within several hours for most stainless steels loaded to below their yield strength. In general, the susceptibility of a given material to SCC refers to a specific environment. Frequently, it is the presence of only trace amounts of some constituent in that environment that causes the damage, i.e., different alloys or groups of alloys are susceptible to different environments and, furthermore, this susceptibility will vary with even minor changes of a given environment. The pH, temperature, and oxidizing potential are also important parameters. Thus, although it may be advisable for economical or logistic reasons that initial screening tests on various candidate materials be performed in simulated environments, it is extremely important that the final selection of materials is based on analyses made from their exposure in the actual service environment.

The literature is prolific with examples of industrial failures, laboratory test results, and mechanistic interpretations related to SCC. Such information may have to be used as a first-round guide in the selection of candidate materials for service in what may appear to be a similar environment. One cannot state apriori that the final choice will be among these materials, for testing must be performed in the actual environment. This is especially true for geothermal brines. Information available on chlorides is related largely to sea water compositions, boiling MgCl_2 solution, and to a lesser extent various other (noncontaminated) chlorides. Neither the pH nor the oxidizing potential is usually controlled or specified. Other constituents such as H_2S and CO_2 that are present in the brines are most likely absent.

Very little information is available on SCC in geothermal brines -- and different brines may be expected to behave differently -- and since chloride-containing solutions are one of the most aggressive environments causing SCC, the need for extensive preliminary screening of materials is obvious. Using

the information available in the literature and consulting with experts in industry and other laboratories, we have selected a number of Ti-, Fe-, Ni-, and Co-base alloys as possible candidate materials for SCC experiments in our laboratory and in the field. Most of the materials have now been received.

b) Laboratory SCC Experiments (Contributed by Shroyer and Goldberg)

This past quarter, we have been concerned with standardizing our techniques for SCC in order to obtain reproducible, meaningful results. For SCC to occur, some type of notch effect must be present. In most structural materials, such as in Fe- and Ni-base alloys, pitting will occur, and eventually this will provide a source for the initiation of a stress corrosion crack. For such materials, smooth, notch-free, U-bend (constant strain) specimens may be used as a first-round screening technique for SCC susceptibility. If, however, the material is not susceptible to pitting, then a smooth, notch-free, U-bend specimen should not exhibit SCC within a reasonable length of test time, although in the presence of a notch this material may undergo SCC. Many Ti-base alloys fall in this latter category; therefore, such alloys, if tested under constant strain conditions, must be prenotched. In addition, if the notch is not sufficiently sharp, the oxide coating formed prior to insertion into the environment, and even after insertion, may impede the action of SCC. Thus, the sharpness and reproducibility of the notch and the tendency to form protective oxide coatings are important factors in considering the effectiveness of any given test.

Bent-beam, notched specimens, supported in a restraining jig (constant strain) and measuring 13.0 mm wide by 100 mm long (0.51 by 3.94 in.) and of various thicknesses, will be used for the Ti-base alloys. These specimens will be notched with a diamond scribe on an end mill to a depth of 125 μ m (0.005 in.). To assure that fresh surface is exposed to the corroding solution, the notch is again lightly scribed, by hand, after inserting the stressed sample and holder in the solution. The sample holders are made of C.P.Ti. Duplicate samples will be loaded to a fixed percentage of the yield strength (e.g., 90% of yield) and to above yield.

For most of the other alloys, U-bend samples will be used measuring 13.0 mm wide by 150 mm long (0.51 by 5.91 in.). These will be bent in a jig to a 12.5 mm (1 in.) radius and restrained with a bolt. A teflon sleeve will be used to

insulate the bolt from the specimen. Both notched and smooth U-bend specimens will be examined, although the materials tested in a U-bend configuration will be those that are expected to be susceptible to pitting. Both bent-beam and U-bend samples will be surface finished with 320 mesh emery paper and, finally, cleaned in MEK.

Eight test cells measuring 152.4 mm diameter by 177.8 mm high (6 by 7 in.) were constructed. These are heated with quartz immersion heaters. Pass-throughs are provided in the lid for purging, steam condensation, and instrumentation. Magnetic stirrers provide uniformity in temperature. The test solution currently used is made up of 16.4 NaCl-3KCl-8.1CaCl-bal H₂O in W/O. It is maintained at a pH of 3 and heated to 105°C. Depending on requirements, the system can be purged with argon or aerated. Redox potentials are periodically taken. Each cell is capable of containing at least four samples.

For Ti-base alloys the SCC occurs preferentially along the basal plane of the α phase; this plane is preferentially aligned in a plane containing the rolling and thickness directions. Insoluble impurities or residual segregation will also be aligned parallel to the rolling direction. Therefore, to examine the most susceptible orientation, samples will be sheared from the sheet material so that the long axis of a specimen (tensile stress direction) is perpendicular to the rolling direction. When notched, the notch is, therefore, parallel to the rolling direction. Specimens cut in the transverse direction will also be examined. To eliminate the cold-worked sheared edge, samples are sheared oversize and milled with fine cuts to the final dimensions.

Sheet materials, which we have received to date and either have been or are in the process of being made into SCC samples, follow:

Ti-base alloys: Ti-50, Ti-75, Ti-6Al-4V, Ti-6Al-4V ELI, Ti-1.5Ni, Ti-0.15Pd, Ti-6Al-6V-2Sn, Ti-8Al-1Mo-1V, Ti-6Al-2Sn-2Zr-2Mo-0.25Si, Ti-5Al-5Sn-2Zr-2Mo-0.25Si, Ti-3Al-8V-6Cr-4Mo-4Zr, Ti-0.3Mo-0.8Ni, Ti-4Al-3Mo-1V, Ti-8Mo-8V-2Fe-3Al.

Fe-base alloys: Fe-29Cr-4Mo, Fe-26Cr-1Mo-0.38Ti, Fe-26Cr-1Mo, Fe-18Cr-2Mo, Fe-26Cr-24Ni-6.5Mo, Fe-20Cr-7Ni-8Mn-2.5Mo, Fe-29Cr-4Mo-2Ni, Fe-18Cr-14Mn-3Ni, Types 304, 316 and 316L stainless.

Ni-base alloys: Hastelloys C-276 and G, Inconel 625.

Co-base alloys: Haynes 25.

To date, we have examined two Ti-base alloys, Ti-8Al-1Mo-1V, and Ti-6Al-4V; both are α - β alloys with the Ti-8-1-1 being known for its susceptibility to SCC. With this latter alloy, we observed that the tendency for cracking varied considerably from sample to sample. As yet, we have not been able to initiate cracking in the Ti-6-4 alloy. With the Ti-8-1-1 alloy cracking frequently did not occur at the notch but rather at some defect at the surface or edge, and it is largely due to the variable results obtained with the Ti-8-1-1 that led to standardizing our procedure as described in the above. We tried using machined notches, fatigue cracks, and scribed notches on both U-bend and bent-beam samples.

We will now initiate our SCC studies in the laboratory in a systematic, controlled fashion on materials in the metallurgical as-received conditions, which will represent the conditions usually supplied by the manufacturer. We plan at an early date to initiate studies on the effect of heat treatment. This would be especially important for Ti-base alloys where the susceptibility to SCC is greatly affected by the nature and mode of distribution of the α and β phases.

c) Field SCC Tests

A number of Ti-base specimens are now available for field testing in the geothermal brine. These will be mounted in wear plate jigs as shown in Fig. 1. Each jig will contain 3 SCC specimens. One side will have a single specimen; the other side will have two overlapping samples to provide additional information on crevice corrosion. Specimens of other alloy bases are presently being machined in preparation for SCC testing in the field.

d) Fatigue Testing

Although the mechanistic details for corrosion fatigue may differ from those for SCC, it is to be expected that the environment causing SCC will also cause corrosion fatigue. The presence of cyclic stresses in the rotating turbine was pointed out above. It is, therefore, important that we examine the corrosion fatigue behavior of the more promising candidate materials. With this in mind, a corrosion fatigue system is being designed for field studies in the actual geothermal brines.

3. INDUSTRIAL SUPPORT PROGRAM

a) Introduction

During this past quarter, we have been concerned with (1) examining pitting corrosion of the Sinclair No. 4 wellhead casing and surface piping, (2) considering designs of corrosion spools for exposure of corrosion specimens and electrochemical measurements in the flowing brines, and (3) evaluation of potential materials problems at the Niland Test Site.

b) Pitting Corrosion of Carbon Steel Pipe Materials

Figure 12 shows a cross section of a pitted surface pipe that was exposed to a varied history which included flowing brine, flushing with ditch water, and shutdowns. Shown in the figure is part of the pit that penetrated through the pipe wall and the adjacent continuous corroded layer which contains many small pits. Pits were always either relatively small or they had completely penetrated the wall of the pipe. The corrosion product frequently appears as fingers or wedges protruding into the steel, suggesting the possibility of stress corrosion cracking induced by the wedging action of the corrosion products. Figure 13 shows a typical example of corrosion fingers or wedges protruding into the steel at a pit/steel interface. A similar structure may be seen in Fig. 14 of a sample taken from a corroded wellhead casing. This casing was recently shut down for some ten months and presumably suffered ingestion of air (O_2) as the brine level dropped. The casing had previously been in service for about three months. Figure 15, taken of the same sample, shows that these protrusions or wedges can be unusually fine.

It is difficult to see how such protrusions into the steel can occur by other than a wedging stress corrosion phenomenon. Examination of etched microstructures indicated that there was a tendency for preferential attack of the pearlite constituents. A typical analysis of the corrosion product based on microprobe measurements is: 3.0Si, 0.3Mn, 0.4Cu, 0.03S, and 48Fe in W/O. Of particular interest is the low Si/Fe weight ratio of about 0.06; by contrast, the Si/Fe ratio in the deposited scale is closer to about 0.5. The corrosion product is due to interaction of the metal with the brine; the scale is due to precipitation from the brine. We (Staehle and Goldberg) are presently preparing a technical note on metallographic observations of the pitted steels.

c) Design for Corrosion Spools

We have given some thought to design of corrosion spools for exposure of samples and electrochemical measurements in the geothermal brines. Since multiphase flow with stratification of the different phases is likely to be present, we are designing the corrosion spools so that three layers of samples can be exposed. The samples will measure 25.4 mm wide by 50.8 mm high (1 by 2 in.). The lower portion of the sample will be modified to obtain crevice corrosion information. It is planned that these samples will be installed in a series of T-shaped corrosion spools in a by-pass line. In addition, it is proposed that we install corrosion spools of various readily available steel pipe materials directly into the flow line, between the wellhead and the SDG&E Test Facility. These tests will provide a basis for materials substitution in case present materials prove to be unsatisfactory. Pipe sections, 273 mm diameter (10.75 in.), of N80, L80, and K55-grade B are being obtained for this purpose. We are also attempting to purchase Soo-90, which is thought to have better resistance to H_2S SCC than do the other pipe materials.

We are designing a system which will allow us to perform polarization studies in the flowing brine without being affected by the scaling of electrodes prior to the initiation of the test. Several alternatives are being considered both for the Chemistry Geothermal Field Test Unit and for a by-pass line between the wellhead and the SDG&E Test Facility.

d) 316L Stainless Steel Cladding Problem

Two steam separator drums at the Niland, San Diego Gas and Electric Company Geothermal Test Facility consist of 316L clad on ASTM A-53 grade B carbon steel. We are concerned about SCC of the clad due to the possibility of ingestion of even trace quantities of oxygen, especially during shutdown. We have prepared a first draft of a UCID addressing this problem. In the UCID, we point out the history of SCC failures of austenitic stainless steels, including 316L, in chloride/oxygen environments. We propose several alternative solutions to this cladding problem. The failure of the cladding in itself is not too serious. What may be serious is the possible rapid accelerated corrosion of the carbon steel vessel in the immediate vicinity of the cracks in the cladding which will result in leakage. The cladding will expose a large cathodic area to a relatively small anodic carbon

steel area; it will also provide regions for crevice corrosion. One of the alternatives is close surveillance of the redox potential and the oxygen content with provisions for isolating the drum from the system if danger of failure is indicated.

In addition to addressing the potential failure problem of the cladding, we describe some new developments in stainless steels and discuss the merits of these new steels relative to the more conventional ones. The new class of stainless steels include ferritic, duplex ferritic/austenitic, and austenitic structures and they appear to be more resistant to chloride SCC than do the conventional stainless steels. It should be pointed out, that historically where a problem of chloride SCC was expected ferritic stainless steels were specified in preference to the austenitic grades. Other problems, however, existed with the conventional ferritic steels (e.g., poor welded ductility) which are largely overcome in the new stainless steels.

Fig. 1. Experimental test jig and specimens for exposure of nozzle, wearplate and SCC specimens to high velocity flow both at the fresh water LLL facility and at the geothermal field LLL test unit in the Salton Sea area. Assembly shown here was exposed to the fresh water facility for 3 h.

(a)

100X

(b)

400X

Fig. 2. Ti-6Al-4V exposed 4 h. at 1000°C in $H_2-N_2-CH_4$ atmosphere.

(a)

100X

(b)

400X

Fig. 4. Ti-6Al-4V exposed 6 h at 1000°C in $H_2-N_2-CH_4$ atmosphere.

Fig. 5 Hardness traverse of Ti-6Al-4V exposed 6h at 1000°C in $H_2-N_2-CH_4$ atmosphere.

(a)

100X

(b)

400X

Fig. 6 Commercially pure Ti exposed 4h at 1000°C in $\text{H}_2\text{-N}_2\text{-CH}_4$ atmosphere.

Fig. 7 - Ti-6Al-4V exposed
6h at 1000 to 1015°C
 $H_2-N_2-CH_4$ atmosphere
200X magnification.

Fig. 8 - Ti-6Al-4V exposed
6h at 1000 to 1015°C plus
4h at 1050 to 1075°C both
in $H_2-N_2-CH_4$ atmosphere
200X magnification.

Fig. 9 - Ti-6Al-4V exposed
16h at 950°C in $H_2-N_2-CH_4$
atmosphere
200X magnification.

200X

Fig. 10 Commercially pure Ti exposed 16h at 950°C
in $H_2-N_2-CH_4$ atmosphere.

Materials

Commercial purity
titanium

Ti-6Al-4V nitrided
at 1000°C-6h in
 $N_2-H_2-CH_4$ atmosphere

B_4C pressed to 98%
theoretical
density

ZrC_2 pressed to 98%
theoretical
density

LLL Geothermal
Fresh Water Facility
Test Data

No measurable erosion

No measurable erosion

No measurable erosion

Test Conditions

Boiler temperature: 275°C

Boiler pressure: 7.9 MPa (1150 psi)

Nozzle inlet pressure: 2.8 MPa (400 psi)

Fluid velocity at nozzle: $488 \text{ m}\cdot\text{s}^{-1}$ ($1600 \text{ ft}\cdot\text{s}^{-1}$)

0 5 10 15 20 25
Wear rate, $\mu\text{m}\cdot\text{h}^{-1}$

Fig. 11 Average wear rates for four wear plates exposed for 3.5 hours to the LLL Geothermal Fresh Water Facility.

15X

Fig. 12 View showing portion of large pit which penetrated the pipe wall and general corrosion along rest of surface showing frequent small pits. Sample from surface pipe, Sinclair No. 4.

250X

Fig. 13 Typical appearance of small pit showing wedge, or finger-like protrusions into the steel. Sample from surface pipe, Sinclair No. 4

Fig. 14 Typical appearance of scaled and corroded surface of a sample taken from the wellhead casing, Sinclair No. 4. Note many corrosion product protrusions into steel.

Fig. 15 Examples showing the relatively fine protrusions suggesting the phenomena of wedge-assisted SCC.