Investigation of Environmentally Assisted Fracture of Metallic Nuclear Waste Package Barrier Materials in Simulated Basalt Repository Environments

S. G. Pitman

November 1982

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INVESTIGATION OF ENVIRONMENTALLY ASSISTED
FRACTURE OF METALLIC NUCLEAR WASTE
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SUMMARY AND CONCLUSIONS

Statically loaded corrosion tests, slow strain rate (SSR) tests, and fatigue crack growth rate (FCGR) tests have been conducted by Pacific Northwest Laboratory (PNL) to evaluate the relative susceptibility of two titanium-base nuclear waste package candidate structural barrier materials--Ti-grade 2 and Ti-grade 12--to environmentally enhanced cracking in a simulated repository environment. Statically loaded corrosion tests were done in oxic basalt ground water^(a) at 250°C; SSR tests were done in oxic basalt ground water at 150°C, 250°C, and 300°C and in air at 20°C and 250°C; and FCGR tests were done in basalt ground water, fluoride-ion-enhanced basalt ground water, high-purity water, and air at 90°C. This document summarizes results of previous tests and presents data from recent tests. From the results obtained to date, the following conclusions can be drawn:

- The general corrosion rate of statically loaded corrosion coupons was very low in a 3-mo test, and no pitting or cracking of the specimens was observed.
- Ti-grade 2 and Ti-grade 12 exhibited strain rate dependent ductility diminution in SSR tests.
- The ductility diminution was most severe in Ti-grade 2 at 300°C and in Ti-grade 12 at 250°C.
- The ductility diminution of Ti-grade 12 was found to be highly orientation dependent. (Only one orientation of Ti-grade 2 was tested.)
- The ductility diminution was also found in tests conducted in air as well as in those conducted in the basalt ground water environment; however, the extent of the degradation was less in air.

(a) The term "basalt ground water" describes a simulated ground water representative of the Columbia Plateau Basalt Region (Rockwell Hanford Operations 1980). The term "oxic" indicates that the ground water has a dissolved oxygen concentration equivalent to that expected if the ground water were in equilibrium with the air.

- The ductility diminution cannot be attributed to stress corrosion cracking (SCC) because the fracture mode was microvoid coalescence in all tests.
- Evidence obtained in the current study and correlation of the present results with results obtained by other researchers indicate that dynamic strain aging is responsible for the loss of ductility. It is suggested that environmental effects are caused by breakdown of the passivating film and subsequent diffusion of interstitials into the metal, causing the degree of dynamic strain aging to increase with decreasing strain rate.
- The FCGR of Ti-grade 2 and Ti-grade 12 was not affected by any of the environmental conditions used in this study, which indicates that no environmental cracking mechanism is operative under the conditions tested (90°C, oxic ground water, and frequencies from 0.01 to 5 Hz).

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INTRODUCTION

An effort to select and characterize materials for licensable engineered barrier systems for long-term containment of nuclear wastes has been under way at Pacific Northwest Laboratory (PNL)^(a) since January 1979. The effort is currently funded by the Office of Nuclear Waste Isolation (ONWI) as the Structural Barrier Development Task of the PNL Waste Package Program. The objective of the task is to characterize and recommend materials suitable for use as structural barriers (for example, canisters, overpacks, or hole sleeves) in a waste package capable of maintaining radioisotope release rates at near-zero values for ~1000 yr.

Past work in related PNL programs has involved corrosion and material property screening tests of ~20 metals, ~15 ceramic materials, and ~30 polymeric materials (Westerman 1980). These studies included corrosion testing of metals and ceramics, thermal- and radiation-degradation testing of polymers, mechanical and fracture toughness testing of titanium, and preliminary environmental-mechanical testing of titanium. Subsequent work has focused on the most promising materials from the screening studies: Ti-grade 2, Ti-grade 12, ductile cast iron, and low-alloy cast steels.

Current work in the Structural Barrier Development Task involves long-term general corrosion testing, irradiation-corrosion testing, and environmentally assisted fracture testing.^(b) Initial results obtained for the first two areas (general corrosion and irradiation-corrosion tests) have been published (Westerman, Pitman, and Nelson 1982).

This report discusses the environmentally assisted fracture testing of Ti-grade 2 and Ti-grade 12, primarily by slow strain rate (SSR) tests and fatigue crack growth rate (FCGR) tests. Background information pertinent to

(a) Operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute.

(b) The term "environmentally assisted fracture" collectively describes degradation mechanisms such as stress corrosion cracking (SCC), hydrogen embrittlement, hydriding, and various forms of metallurgical embrittlement that may be related to the presence of stress and an aggressive environment.

the environmentally assisted fracture of these materials is presented, and the materials studied and the experimental methods used are described. Results of recent tests and summaries of earlier tests are presented and discussed, with emphasis on results that could affect material selection and design.

BACKGROUND

The environmentally enhanced propagation of cracks from pre-existing defects or flaws is one of the potentially most damaging failure modes for waste package structural barrier materials. In susceptible materials, failure from crack propagation can occur in the absence of general corrosion at stresses well below the general yield strength. This failure mode is also the most difficult to quantify because of the normally long initiation times, the difficulty in detecting minor amounts of crack growth, and its generally unpredictable nature. The approach taken in this investigation uses statically loaded corrosion tests with U-bends and wedge-opening load (WOL) specimens, SSR tests, and environmental FCGR tests.

In the statically loaded corrosion tests, a static load (or, equivalently, a fixed strain) is applied to the specimens prior to their exposure in the test medium. After the test, the weight change of the U-bend specimens is measured, and the U-bend and WOL specimens are examined for pitting and cracking.

In the SSR tests, a tensile specimen is strained to failure at a constant strain rate in the presence of the service environment or an environment representative of the service environment. The deformation of the specimen and the imposed load are continually measured and recorded. Environmentally enhanced fracture is often found to be influenced by strain rate. At high strain rates, the influence of the environment is limited by the time of exposure. At very low strain rates, the oxide film is able to reform during straining so that environment-base metal interaction is again limited. The lowest ductility is often found in tests conducted at intermediate loading rates where interaction between the metal and the environment occurs as the passivating film is broken.

In SSR testing, susceptibility of metals to environmentally enhanced fracture is indicated if one or more of the following phenomena are observed:

- Ductility is lower in the service environment than in an innocuous environment.
- Ductility is influenced by strain rate.

- Fractographic evidence of an environmentally enhanced fracture mode(s) exists; for example, an anomalous cleavage fracture.

When sensitivity of ductility to environment or strain rate is observed, the mode of failure is determined by examining the fracture surfaces. If the mode of failure is not influenced by the presence of the environment, the ductility diminution cannot be attributed to a specific mechanism of environmentally enhanced fracture (Payer, Berry, and Boyd 1976).

The effects of an aggressive environment on FCGRs are determined from methods analogous to those used in SSR tests: If a frequency dependence or an accelerated crack growth rate relative to an innocuous environment is observed, environmentally enhanced fracture is suspected. The mechanism of crack growth rate acceleration must be determined by examining the fracture surface.

SSR and FCGR tests are considered conservative tests for determining relative susceptibility to environmentally enhanced fracture. These tests use an actively loaded specimen, where the surface corrosion film is broken and fresh metallic material is continually exposed to the environment. The FCGR test is particularly severe because of the combination of a pre-existing sharp crack, continual plastic straining at the crack tip, and the presence of high triaxial stresses (in thick specimens). The loading conditions imposed on specimens are not intended to simulate loading conditions expected in repositories but to provide severe tests of susceptibility to environmentally enhanced fracture.

EXPERIMENTAL METHODS AND MATERIALS

The experimental methods and materials used for environmentally assisted fracture testing are essentially the same as those reported previously; for detailed descriptions of methods, materials, and preliminary environmental-mechanical test results, see Westerman (1980) and Pitman (1981). The statically loaded corrosion, SSR, and FCGR test procedures are briefly described in this section of the report.

STATICALLY LOADED CORROSION TESTS

Two types of corrosion tests were used for initial evaluations of susceptibility to environmentally enhanced fracture: U-bend tests and WOL tests. In the U-bend tests, material was used that contained a simulated weld bead that was made by melting the material using a tungsten-inert gas (TIG) welding torch. The 3/4 x 4-1/2-in. samples were bent into U-bends using the two-stage stressing method described in ASTM G30-72. The samples were insulated from the stressing bolts by alumina washers.

WOL tests were conducted on precracked 1/2-in. thick specimens. The specimens were stressed in a screw-driven testing machine to a high stress intensity ($\sim 50 \text{ ksi}\sqrt{\text{in.}}$), and wedges were inserted to maintain the stress intensity when the specimens were removed from the machine. In this type of specimen, the opening at the crack mouth is maintained at a constant value during the test; thus, the stress intensity remains constant unless crack extension occurs.

The U-bend and WOL specimens were exposed to basalt ground water at 250°C. Inlet ground water at ~ 6 -ppm dissolved oxygen flowed through crushed basalt at about 30 ml/h before reaching the specimens. The test duration was 89 days for the WOL specimens and 270 days for the U-bend specimens. The composition of the inlet solution is given in Table 1.

SLOW STRAIN RATE TESTS

SSR tests were conducted using tensile specimens fabricated from sheet material. Gage marks inscribed at 1.00-in. intervals on the specimens were

TABLE 1. Composition of Basalt Ground Water(a)

Chemical Species	Concentration, mg/l	
	Statically Loaded Corrosion Tests	FCGR and SSR Tests
Na ⁺	139	250
K ⁺	13	1.9
Ca ⁺²	1.6	1.3
Mg ⁺²	0.5	0.4
CO ₃ ⁻²		27
HCO ₃ ⁻	167 ^(b)	70
OH ⁻	32	1.4
H ₃ SiO ₄ ⁻	36	103
Cl ⁻	52	148
SO ₄ ⁻²	0.8	108
F ⁻	8	37

(a) Target makeup composition; actual compositions varied slightly.

(b) Total CO₃.

used to determine the elongation of the specimens. A gear-driven loading device applied constant extension rates to the specimens. The load was measured using a load cell that was external to the autoclave (see Figure 1). Extension was measured on a linear variable differential transformer (LVDT) between the autoclave and the loading rod.

Reduction of area was determined by measuring the dimensions of the specimen before the test and by measuring the fracture surface area after the test. The fracture surfaces were examined using optical and scanning electron microscopy to determine the mode(s) of failure.

The environment used in the SSR tests was the same as that used in corrosion tests. Inlet ground water flowed through crushed basalt in the bottom of the autoclave at about 40 ml/h. Tests were also conducted in air at 250°C using the same test machine.

FIGURE 1. Slow Strain Rate Testing System

FATIGUE CRACK GROWTH RATE TESTS

FCGR tests were performed in basalt ground water, fluoride-ion-enhanced basalt ground water, and high-purity water. The tests were done at 90°C, using the environmental chamber shown in Figure 2. The flow rate was maintained at ~100 ml/h using an in-line metering device. The inlet water chemistry was the same as that given in Table 1, except for the fluoride-ion-enhanced ground water, which contained ~220-ppm F⁻.

FCGR tests were done at cyclic frequencies of 5.0, 1.0, 0.1, and 0.01 Hz so that effects of cyclic loading frequency on crack growth rate could be determined. A sinusoidal waveform with a loading ratio of $R = 0.1^{(a)}$ was used for all tests.

The simulated ground water solution used in the FCGR tests was exposed to air before and during the tests. This exposure technically violates the "reference Hanford basalt ground water" storage condition (Rockwell Hanford Operations 1980) because oxygen fugacity was not controlled and CO₂ was absorbed in the solution. However, the purpose of these preliminary FCGR tests was to investigate possible adverse effects of ground waters on titanium in a scoping sense and not necessarily to accurately simulate repository conditions.

MATERIALS

The materials used in this study (Ti-grade 2 and Ti-grade 12) are commercially available ASTM grades. Grade 2 is one of the commercial purity grades, specified by maximum allowable impurity content. Grade 12, which contains nominally 0.8% Ni and 0.3% Mo, was developed for resistance to crevice corrosion and pitting in elevated temperature, high-chloride environments (Covington and Palmer 1974). The Ti-grade 2 sheet was 1.27 mm (0.050 in.) thick, and the Ti-grade 12 sheet was 0.79 mm (0.031 in.) thick. Compositions and room temperature mechanical properties are listed in Tables 2 and 3, respectively.

(a) The loading ratio is the ratio of minimum to maximum applied load.

FIGURE 2. Fatigue Crack Growth Rate Testing System

TABLE 2. Composition of Ti-Grade 2 and Ti-Grade 12 Used in This Study and ASTM Nominal Compositions

ASTM Grade per B-265-78	Element, wt%						
	N	C	H	O	Fe	Mo	Ni
Grade 2 Actual	0.009	0.011	0.005	0.12	0.12		
Grade 2 ASTM Nominal (a)	0.030	0.100	0.015	0.250	0.300		
Grade 12 Actual	0.008	0.021	0.005	0.13	0.12	0.30	0.67
Grade 12 ASTM Nominal (a)	0.03	0.08	0.015	0.250	0.300	0.2 to 0.4	0.6 to 0.9

(a) Maximum elemental levels except as noted, per ASTM B-265-78.

TABLE 3. Room Temperature Mechanical Properties of Ti-Grade 2 and Ti-Grade 12

Titanium Grade and Orientation	Yield Strength,	Tensile Strength,	Elongation, %
	MPa (ksi)	MPa (ksi)	
Grade 2 L ^(a)	351 (51)	497 (74)	29
Grade 2 T ^(b)	393 (57)	517 (72)	28
Grade-12 L	427 (62)	600 (87)	22
Grade 12 T	600 (87)	696 (101)	18

(a) L = longitudinal; loading stress is parallel to the rolling direction of the material.

(b) T = transverse; loading stress is perpendicular to the rolling direction of the material.

RESULTS

Statically loaded corrosion tests, SSR tests, and FCGR tests have been performed to determine the relative susceptibility of Ti-grade 2 and Ti-grade 12 to environmentally assisted fracture. The results presented in this section represent a summary of the work completed to date.

STATICALLY LOADED CORROSION TESTS

Statically loaded U-bend and WOL corrosion specimens were used for scoping tests to evaluate the susceptibility of titanium to environmentally enhanced fracture. The titanium U-bend specimens exhibited no signs of pitting or cracking at 250°C, and the weight change after cleaning was very low ($<2 \text{ mg/dm}^2$). Analysis of the water at the autoclave inlet and outlet indicated that dissolved oxygen was readily consumed by basalt at 250°C. (An inlet oxygen concentration of ~6 ppm decreased to ~0.3 ppm at the outlet in an autoclave containing basalt chips but no metallic specimens.)

WOL specimens were exposed to oxic basalt ground water at 250°C for 3 mo. The stress intensity in the specimens ($\sim 50 \text{ ksi}\sqrt{\text{in.}}$) was high enough to initiate tunneling^(a) fracture in the Ti-grade 12 specimens; this stable crack growth occurred as the specimens were loaded and before they were exposed to ground water. The compliance and wedge load were measured before and after the exposure. There was no indication that crack growth occurred as a result of the exposure, even at this relatively high stress intensity.

SLOW STRAIN RATE TESTS

SSR tests of Ti-grade 2 and Ti-grade 12 were conducted in basalt ground water at 150°C, 250°C, and 300°C and in air at 20°C and 250°C. Ti-grade 2 was tested in the LT^(a) orientation, and Ti-grade 12 was tested in both the LT

(a) Tunneling is a type of crack growth common in low-strength titanium, where interior crack growth exceeds surface crack growth. In this case, crack growth occurred inside the specimen during loading in air but could not be observed at the surface. The WOL specimens were fatigue precracked to provide the most favorable conditions for crack extension.

and TL orientations. The grain texture of the two materials is similar although the mechanical properties of Ti-grade 12 have been found to be more anisotropic.

In tests of Ti-grade 2 and Ti-grade 12 at 150°C and 300°C, only the end points (highest and lowest strain rates) were evaluated. This test design was chosen as the most effective way of determining strain rate effects from a limited number of specimens, based on earlier observations that the maximum ductility decrease occurred at the lowest strain rates. The effects of temperature on ductility of Ti-grade 2 can best be seen by comparing results from the 150°C and 300°C tests (see Figure 3). The reduction of area is enhanced by testing at a higher temperature at the higher strain rates, but the opposite effect is found at the lower strain rate. Elongation is lower at 300°C than at 150°C, especially in tests conducted at a low strain rate.

Results of the SSR tests of Ti-grade 2 in basalt ground water and in air at 250°C are presented in Figure 4. In each case, ductility decreased with decreasing strain rate. The extent of the ductility decrease is about the same in each environment.

SSR test results of Ti-grade 2 are summarized in Figure 5. At the higher strain rate, elongation increased at higher temperatures; at the lower strain rate, elongation decreased at higher temperatures. Reduction of area decreased with increasing temperature at both strain rates.

Ti-grade 12 (LT orientation) is less sensitive to strain rate and temperature effects (see Figure 6). Elongation is somewhat diminished by testing at 300°C; however, reduction of area is unaffected. At 250°C, both elongation and reduction of area decrease with decreasing strain rate (see Figure 7). The magnitude of the decrease is about the same in basalt ground water as it is in air. A comparison of tests done at 20°C, 150°C, 250°C, and 300°C at 10^{-4} /s and 2×10^{-7} /s in air and basalt ground water is given in Figure 8. Reduction of

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- (a) "LT" indicates that the specimen is loaded in the longitudinal (rolling) direction and the crack propagates in the transverse direction (perpendicular to the rolling direction). "TL" indicates that the specimen is loaded in the transverse direction and the crack propagates in the longitudinal direction.

FIGURE 3. Reduction of Area and Elongation of Ti-Grade 2 (LT orientation) in Basalt Ground Water at 150°C and 300°C

FIGURE 4. Reduction of Area and Elongation of Ti-Grade 2 (LT orientation) in Basalt Ground Water and Air at 250°C

FIGURE 5. Reduction of Area and Elongation of Ti-Grade 2 (LT orientation) as a Function of Temperature

FIGURE 6. Reduction of Area and Elongation of Ti-Grade 12 (LT orientation) in Basalt Ground Water at 150°C and 300°C

FIGURE 7. Reduction of Area and Elongation of Ti-Grade 12 (LT orientation) in Basalt Ground Water and Air at 250°C

FIGURE 8. Reduction of Area and Elongation of Ti-Grade 12 (LT orientation) as a Function of Temperature

area is sensitive to strain rate. At the higher strain rate, reduction of area increased with increasing temperature; but at the lower strain rate, reduction of area was lower at 250°C than at 150 or 300°C. In other words, reduction of area reached an apparent minima at ~250°C.

The results of SSR testing of Ti-grade 12 (TL orientation) are similar to those of Ti-grade 12 (LT orientation). At 150°C, the effect of strain rate on reduction of area was small (see Figure 9); and at 300°C, reduction of area was strain rate sensitive, but elongation was only marginally affected. Elongation of Ti-grade 12 in the TL orientation was lower than in the LT orientation regardless of the environment due to the smaller effective grain size and the associated higher strength. At 250°C, Ti-grade 12 was severely affected by changes in strain rate; this effect is more pronounced in basalt ground water than in air (see Figure 10). A summary of data from the highest (10^{-4} /s) and lowest (2×10^{-7} /s) SSR tests is presented in Figure 11. The greatest susceptibility to strain rate effects was found at 250°C. The ductility of Ti-grade 12

FIGURE 9. Reduction of Area and Elongation of Ti-Grade 12 (TL orientation) in Basalt Ground Water at 150°C and 300°C

FIGURE 10. Reduction of Area and Elongation of Ti-Grade 12 (TL orientation) in Basalt Ground Water and Air at 250°C

FIGURE 11. Reduction of Area and Elongation of Ti-Grade 12 (TL orientation) as a Function of Temperature

(TL orientation) was strongly influenced by the testing environment, and elongation was severely diminished at 250°C when the tests were conducted in basalt ground water. This effect was judged to be of sufficient importance to warrant further investigation. A study of the microstructure of the material and the fracture surfaces was conducted in an attempt to determine the causes of the ductility diminution.

A specimen that had exhibited low ductility and a piece of the as-received sheet were metallographically examined to determine whether or not the loss of ductility at low strain rates was caused by formation of hydrides. The specimen and the original material were polished and anodized to reveal a hydride phase. There was no concentration of hydrides near the fracture surface, and the distribution of hydride phase appeared to be the same in the fractured specimen as it was in the as-received sheet.

Fracture surfaces of specimens with high and low ductility in SSR tests were examined to determine the mode of fracture. Fracture surfaces of Ti-grade 2 specimens (LT orientation) are shown in Figure 12. The fracture occurred by microvoid coalescence in both cases, and there is no apparent difference between the fracture surfaces although the strain rate was 500 times lower in Figure 12b than in Figure 12a. Similar results were obtained with Ti-grade 12 (not shown) where specimens of each strain rate and orientation were examined; no significant differences were found.

FATIGUE CRACK GROWTH RATE TESTS

FCGR tests were conducted to determine the relative susceptibility of Ti-grade 2 and Ti-grade 12 to environmentally enhanced fracture in an environment similar to that expected in a basalt repository. In these tests, susceptibility to environmentally enhanced fracture is indicated by increased crack growth rate relative to an inert environment or by frequency-dependent FCGR.

No acceleration of crack growth rate was found in a repository-representative environment relative to an innocuous environment as is shown in Figures 13 and 14. The crack growth rate of Ti-grade 12 (LT and TL orientations) in fluoride-ion-enhanced basalt ground water was compared with the

(a) $10^{-4}/s$ Strain Rate

(b) $2 \times 10^{-7}/s$ Strain Rate

FIGURE 12. Fracture Surfaces of Ti-Grade 2 Specimens (LT orientation)
Strained to Failure in Basalt Ground Water at 250°C

FIGURE 13. Fatigue Crack Growth Rate of Ti-Grade 12 (LT orientation) Tested at 0.1 Hz in Fluoride-Ion-Enhanced Basalt Ground Water and High-Purity Water at 90°C

FIGURE 14. Fatigue Crack Growth Rate of Ti-Grade 12 (TL orientation) Tested at 0.1 Hz in Fluoride-Ion-Enhanced Basalt Ground Water and High-Purity Water at 90°C

crack growth rate in high-purity water. The fluoride-ion-enhanced ground water was used for this comparison because it is more likely to be aggressive in causing environmentally enhanced fracture due to the ability of fluoride ions to break down the passivating film.

Results of the investigation of the potential effects of frequency and fluoride-ion additions to the simulated ground water on FCGR are illustrated in Figures 15 and 16. In Figure 15, the FCGR of Ti-grade 2 (TL orientation) was found to be unaffected by the presence of high fluoride-ion content or the frequency of cyclic loading. A similar result was found for Ti-grade 12 (LT orientation); see Figure 16. Although both the decreased frequency and the increased fluoride-ion content are considered possible accelerating factors, the FCGR did not increase.

FIGURE 15. Fatigue Crack Growth Rate of Ti-Grade 2 (TL orientation) Tested at 1 Hz in Basalt Ground Water and at 0.1 Hz in Fluoride-Ion-Enhanced Ground Water at 90°C

FIGURE 16. Fatigue Crack Growth Rate of Ti-Grade 12 (LT orientation) Tested at 1 Hz in Basalt Ground Water and at 0.1 Hz in Fluoride-Ion-Enhanced Ground Water at 90°C

DISCUSSION

In statically stressed corrosion tests, low corrosion rates of Ti-grade 2 and Ti-grade 12 were obtained and no localized corrosion was observed. These results contrast to results obtained in an oxidizing brine environment at 150°C (Slate et al. 1982), where the Ti-grade 2 was severely pitted and the weight changes were greater. The fact that Ti-grade 2 was pitted at 150°C in brine but was not pitted at 250°C in basalt ground water indicates that the basalt ground water is a less aggressive environment and that Ti-grade 2 is susceptible to pitting under certain conditions. The low oxygen fugacity of the basalt ground water in contact with the specimens and the relatively higher concentration of halide and sulfate ions in the brine may account for the difference.

Both Ti-grade 2 and Ti-grade 12 exhibited strain rate dependency in SSR tests at particular combinations of temperature and strain rate. This dependency was characterized by a loss of ductility at lower strain rates. Ti-grade 2 was most susceptible to strain rate effects at 300°C (over the range of temperatures studied), and Ti-grade 12 was most susceptible at 250°C.

The most severe strain rate effect—in Ti-grade 12 (TL orientation) at 250°C—was enhanced by the basalt ground water environment; however, the effect cannot be attributed entirely to the presence of the environment. Examination of specimens fractured at 10^{-4} , 10^{-5} , 10^{-6} , and 2×10^{-7} /s in basalt ground water and in air revealed no signs of any fracture mode other than microvoid coalescence. This result indicates that the mechanism of ductility diminution was not SCC because it would have caused a fracture surface with a faceted or granular appearance. The ductility diminution cannot be attributed to hydriding because there was no evidence of environmentally enhanced or strain-enhanced hydride formation.

The effects of strain rate on reduction of area and elongation are shown clearly in Figures 17 and 18, where the difference between ductility measurements at the highest and lowest strain rates is plotted as a function of temperature for Ti-grade 2 and Ti-grade 12. This difference is highest in Ti-grade 2 at 300°C and in Ti-grade 12 at 250°C. The effect is clearly less

FIGURE 17. Summary of Strain Rate Effects in Ti-Grade 2 (LT orientation)

FIGURE 18. Summary of Strain Rate Effects in Ti-Grade 12 (TL orientation)

pronounced in air, indicating that the strain rate effects are partly due to an interaction with the testing environment but that another (nonenvironmental) mechanism must be active.

Analysis of the available data suggests that the ductility decrease may be due to an internal strengthening mechanism. Research by Okazaki and Conrad (1973) indicates that the rate-controlling mechanism during the low-temperature ($T < 0.3 T_m$) plastic deformation of titanium is the overcoming of interstitial solute atoms by dislocations. Both static and dynamic strain aging have been observed in α titanium by various researchers. Static strain aging was observed in titanium after heating from 200 to 400°C at strain rates of $2.7 \times 10^{-5}/s$ to $2.7 \times 10^{-3}/s$ (Rosi and Perkins 1953). Dynamic strain aging was found to reach a maximum at ~430 to 530°C; the temperature at which the maximum was found decreased with decreasing strain rate. The maximum strain aging found in this study occurred at 300°C in Ti-grade 2 and at 250°C in Ti-grade 12. These temperatures correspond more closely with those associated with static strain aging, but the lowest strain rate used in the current study ($2 \times 10^{-7}/s$) is two orders of magnitude lower than the lowest strain rate used by Santhanam and Reed-Hill (1971).

Dynamic strain aging is normally associated with serrations in the load-displacement curve; however, in commercial-purity titanium, these serrations may be difficult to detect (Donor and Conrad 1973). In the current investigation, load was measured outside the autoclaves, and seal friction caused variations in the load-displacement curves. It was difficult to accurately measure load on the specimens, and small load variations resulting from discontinuous yielding could not be resolved.

Dynamic strain aging is associated with the interaction of interstitial solute atoms with dislocations. The exact mechanism has not yet been proven although two predominant theories exist. In one proposed mechanism, dislocations are pinned by impurities and more dislocations are generated to maintain the imposed strain rate. In another proposed mechanism, dynamic strain aging results from the drag of impurity atmospheres. In either case, diffusion of impurities, which is temperature dependent, must be sufficient to allow solute atoms to interact with dislocations at the imposed strain rate.

It appears reasonable to attribute most of the ductility decrease found in Ti-grade 2 and Ti-grade 12 to strain aging occurring during the test; however, some environmental effects were also found (see Figures 17 and 18). It is possible that these effects may be caused by impurities introduced to the metal by breakdown of the passivating film and subsequent strain-assisted diffusion.

In FCGR tests of Ti-grade 2 and Ti-grade 12, the FCGR was found to be independent of testing environment (fluoride-ion-enhanced basalt ground water or high-purity water) and frequency (from 0.1 to 5.0 Hz). This independence indicates that no mechanism of environmentally enhanced cracking is operative at 90°C.

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