NASA/TP-2007-213733

Johnson Space Center Material Laboratory Reproduction and Failure Analysis of Cracked Orbiter Reaction Control System Niobium Thruster Injectors

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March 2007

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Acknowledgments

This paper is a result of considerable effort from a number of dedicated NASA civil servants and support contractors. The authors would like to thank the JSC materials laboratory support personnel for their dedicated testing and analysis support throughout this investigation. Additionally, the authors wish to acknowledge the Orbiter Materials & Processes Problem Resolution Team (M&P PRT) participation and support, in particular, the failure analysis team at Boeing Huntington Beach (Larry Korb, Michael Tarkanian, Don Sueme), and the systems support provided by the White Sands Test Facility (Terrence Kelly). Finally, the authors wish to acknowledge the rigorous technical support provided to this test program by the NASA Engineering Safety Center Materials Super Problem Resolution Team (SPRT), representing active participation from NASA Glenn Research Center (Becky A. MacKay), NASA Langley Research Center (Stephen W. Smith, Robert S. Piascik), and Marshall Space Flight Center (Sandeep R. Shah, Gregory A. Jerman, Binayak Panda).

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CONTENTS

ACRONYMS

CAR	Corrective Action Record
DMA	Dynamic Mechanical Analyzer
EDS	energy-dispersive spectrometer
HF	hydrofluoric
JSC	Johnson Space Center
KSC	Kennedy Space Center
M&P	Materials and Processes
PFPE	perfluoropolyether
PRT	Problem Resolution Team
RCS	Reaction Control System
SEM	scanning electron microscope
SPRT	Super Problem Resolution Team
SSRCS	Space Shuttle Reaction Control System
TIM	technical interchange meeting
WSTF	White Sands Test Facility
XPS	X-Ray Photoelectron Spectroscopy

1.0 SUMMARY

In April 2004, the Space Shuttle Orbiter Reaction Control System (RCS) thruster serial number (S/N) 120's injector was found to be cracked while undergoing a nozzle retrofit at the White Sands Test Facility (WSTF). The RCS is composed of safety-critical propulsion hardware elements used to control the attitude of the space shuttle orbiter during virtually all operational mission phases. Since a failure resulting from an RCS thruster burn-through (initiated from a crack) could be catastrophic, an official flight constraint was issued until flight safety could be adequately demonstrated.

One recommendation was to reproduce the cracking in the laboratory to understand fully the driving environments. The goals of this effort were to:

1. Reproduce the cracking
2. Vary the conditions required to produce the cracking
3. Bound the conditions for cracking

The Johnson Space Center (JSC) Materials & Processes (M&P) Branch initiated an effort starting in January 2005 to reproduce the cracking in the niobium injector. The results were successful. The specific conditions necessary to cause cracking were explicitly established and bounded. Each of the following conditions is necessary in combination:

1. A mechanically disturbed/cold-worked free surface (plastic deformation from machining, handling, fastener installation, etc.)
2. An externally applied sustained tensile stress near yield strength
3. Presence of fluorine-containing fluids on exposed tensile/cold-worked free surfaces
4. Sustained exposure to temperatures *greater than* 400°F

Since nominal RCS injector temperatures do not exceed 400°F, the results of this work suggest that even in the presence of the first three conditions, existing cracks in the thrusters will not grow in service (thrusters only see temperatures greater than 400°F during a 600°F insulation bake-out during the manufacturing cycle). This conclusion was included in flight rationale, which justified the continued safe flight of the RCS thruster system on as-installed orbiter hardware. No additional inspection for cracking on existing hardware was necessary.

For the RCS thruster application, it is not programmatically necessary to know which fluid caused the cracks or to understand fully the specific cracking mechanism at work, but rather that fluorine needs to be kept away from the niobium during processing. Thus, any and all fluorine-containing fluids (hydrofluoric acid, Krytox, etc.) must be controlled/eliminated from future refurbishment processing of the thrusters.

2.0 INTRODUCTION

2.1 General Background

In 1979, a space shuttle orbiter RCS thruster still in the manufacturing cycle was found to be leaking through a crack in the injector. The injector is made from the niobium alloy C103.

Both the Marquardt Corporation (thruster manufacturer) and the Rockwell International Space Division (space shuttle orbiter prime contractor) (Ref. 1) performed an extensive failure analysis in 1979. The 100-percent intergranular nature of the cracks strongly indicated a stress corrosion or hydrogen embrittlement mechanism as the cause of cracking. They tested all of the aggressive fluids used in manufacturing of the thrusters with stress corrosion and hydrogen embrittlement type specimens, none of which reproduced the cracking. Since fluorine was found on the fracture surface, they placed particular attention on the fluorine-containing fluids used in the processing of the injector. The fluorine-containing fluids included hydrofluoric (HF) acid etchants and a fluorine-containing synthetic oil called Krytox. Testing of C103 specimens in these fluids also did not reproduce the cracking.

Three years later, in 1982, several additional thrusters were found with identical cracking. Again, fluorine was found on the fracture surfaces. Additional stress corrosion testing at the time reproduced the cracking with the HF-containing etchants. The reproduction of the cracks was mentioned in a 1982 Marquardt Corrective Action Record (CAR) (Ref. 2) and in a 1983 Rockwell Engineering Design Change Proposal (Ref. 3). No lab reports describing these tests or their fractographic and metallographic analyses have been found.

In April 2004, RCS thruster S/N 120 was found to be cracked while performing a nozzle retrofit at WSTF. Much of the cracking was located in the same place on the injector as the cracking that occurred in 1979 and 1982. A failure analysis of S/N 120 performed by Boeing, Huntington Beach (Ref. 4) concluded that the cracks were similar in nature (brittle/intergranular) to the prior cracks. The failure analysis report recommended reproducing the cracking as in 1982.

At an M&P technical interchange meeting (TIM) in December 2004, a direct approach to understanding the RCS thruster cracking problem was outlined and consisted of:

- Reproducing the cracking
- Varying the conditions required to produce the cracking
- Bounding the conditions for cracking

In January 2005, JSC M&P began trying to reproduce the cracking. Others had been trying to reproduce the cracking for a number of months with little success.

JSC efforts to reproduce the thruster cracking involved the testing of the HF acid-containing etchants used in manufacturing the thrusters. Guidance on conducting the HF testing came from statements in the 1982 CAR cited above. Subsequent to the HF tests, JSC re-tested the Krytox that was used in the manufacturing of the thrusters. In this report, the HF tests will be addressed first followed by the Krytox tests, both of which produced cracking.

M&P also investigated another fluid called Oakite during this same period. During retrofit with the new nozzle at WSTF, the S/N 120 injector was immersed in an Oakite cleaning solution at 175°F for about 20 minutes. Oakite is an alkaline cleaning solution containing sodium hydroxide. In general, it is used to deoxidize surfaces and, in this case, the injector weld surface prior to welding on the new nozzle. Although this exposure was not considered to have produced the cracks in S/N 120, it did have the potential for embrittling the metal ahead of an existing crack tip (i.e., the remaining ligament). When S/N 120 cracks were opened up for failure analysis, the fractography of the freshly exposed fracture faces beyond the crack tips showed a significant amount of cleavage (brittle) fracture. M&P conducted a series of tests at JSC in which C103 test specimens were exposed to the Oakite to determine if they could cause embrittlement of niobium. Since this Oakite exposure did not cause or contribute to the cracks in S/N 120, the tests conducted as part of the JSC Oakite investigation and the test results will not be presented in this report.

2.2 Thruster Design and Crack Locations

The RCS thruster consists of three major components: the valve module, the injector, and the nozzle (the injector and nozzle are shown in Figure 1). A cross section of the thruster is shown in Figure 2, and an enlarged cross section of the injector and the crack locations are shown in Figure 3. The cracks that occurred in 1979 and 1982 were in the relief radius only. The cracks found in S/N 120 in April 2004 were in both the relief radius and the counter bores.

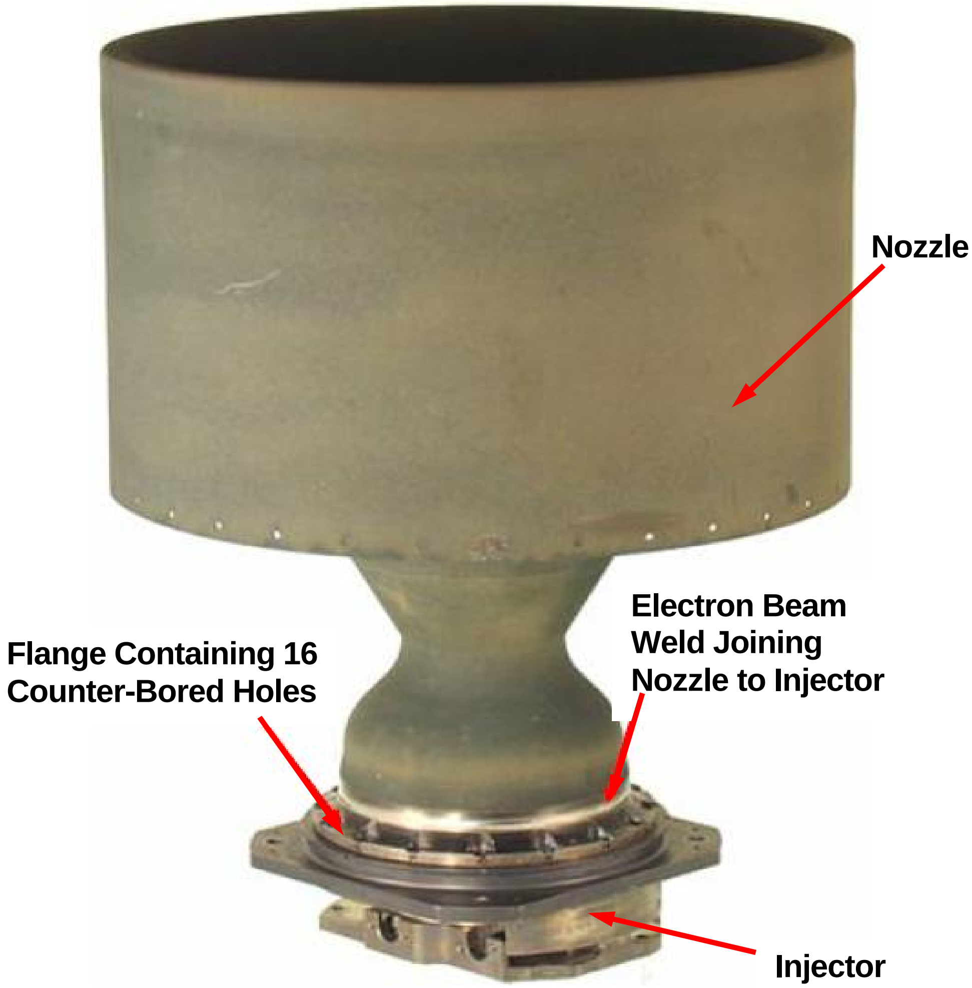


Figure 1 – RCS thruster, showing major components: injector and nozzle.

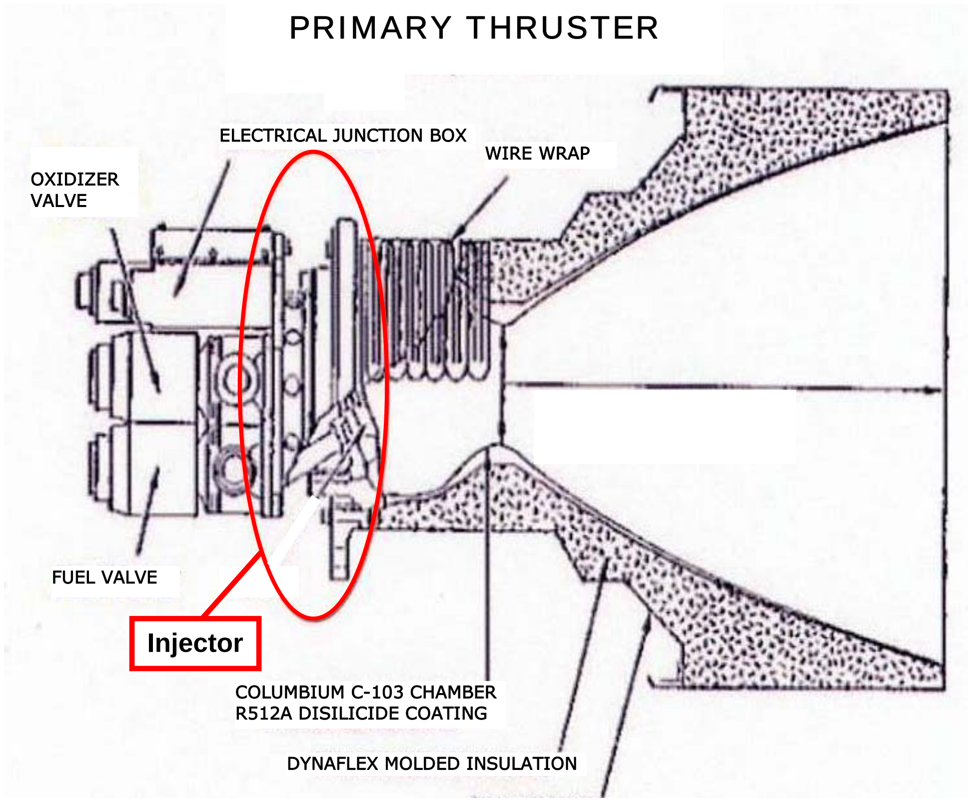


Figure 2 – RCS thruster cutaway showing major components: valve module, injector, and nozzle. Enlarged view of circled portion shown in Figure 3.

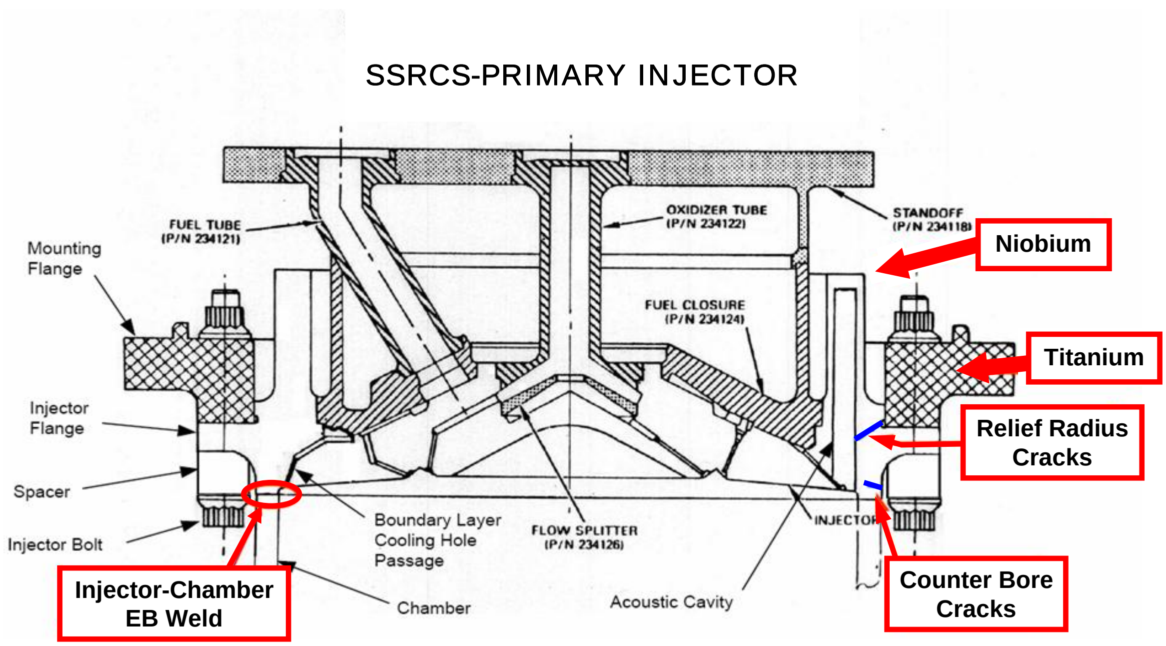


Figure 3 – Cross section of injector showing location of cracks found in S/N 120. (Note: Figure is rotated 90 degrees from Figure 2.)

The cracks in the relief radius were in all cases far more numerous and far more extensive than the counter bore cracks. In some cases, the relief radius cracks extended nearly all the way around the injector. The surface appearance of the cracks is shown in Figure 4 and Figure 5.

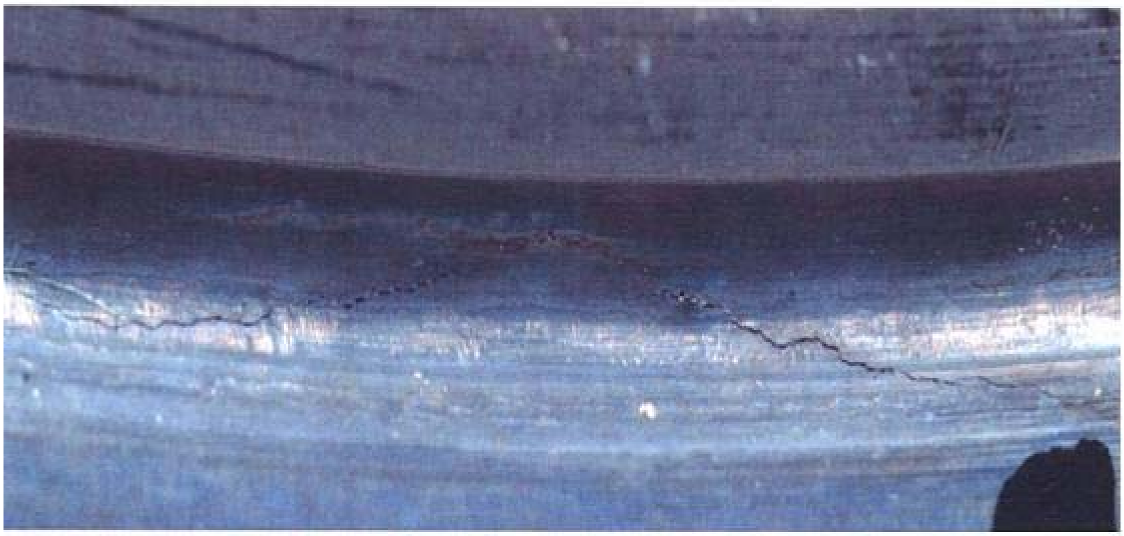


Figure 4 – Cracked relief radius from S/N 120 holes J to K.

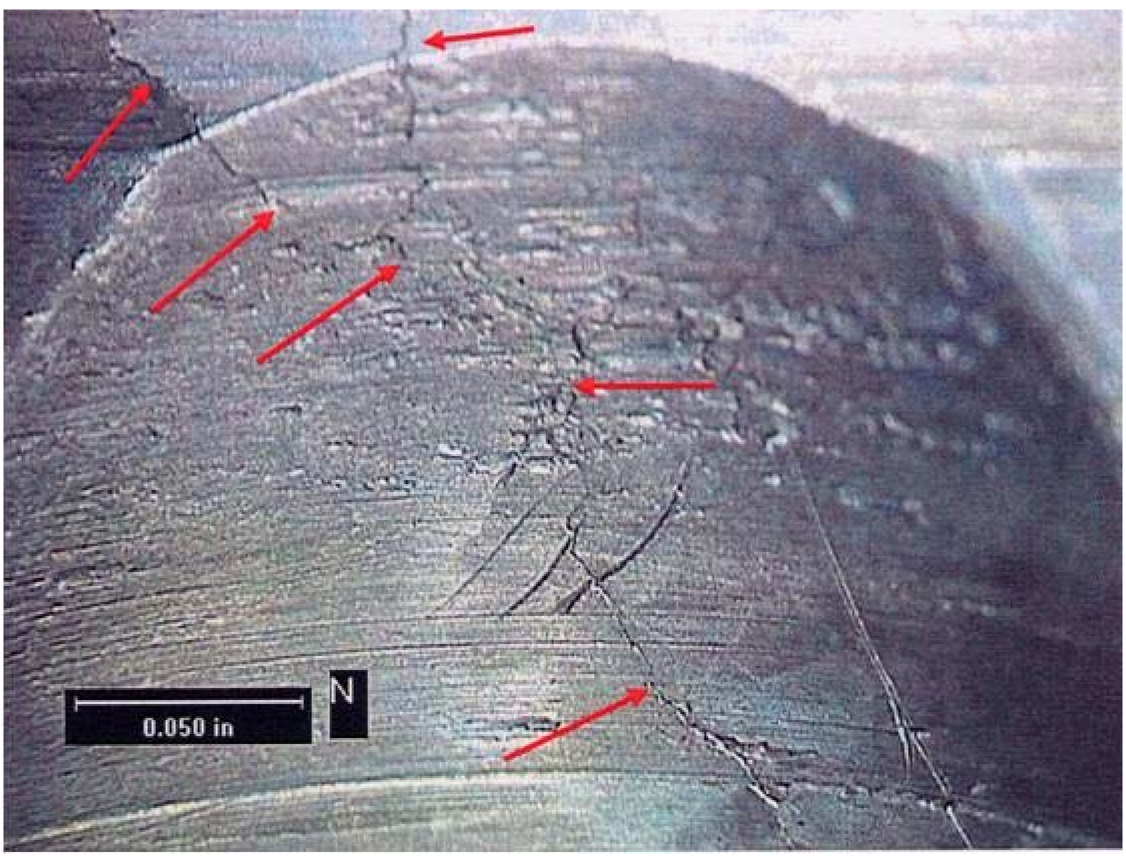


Figure 5 – Cracked counter bore from S/N 120 hole N.

The rough-machined surfaces adjacent to the cracks will be the subject of additional discussion later in this report. The cracks in the relief radius initiated in the radius and propagated at approximately 45 degrees towards the acoustic cavities and the combustion chamber. In some cases (in 1979 and 1982), the cracks actually reached the acoustic cavities, which resulted in a leak path from the combustion chamber to the exterior of the injector. A metallurgical cross section through a typical relief radius crack is shown in Figure 6.

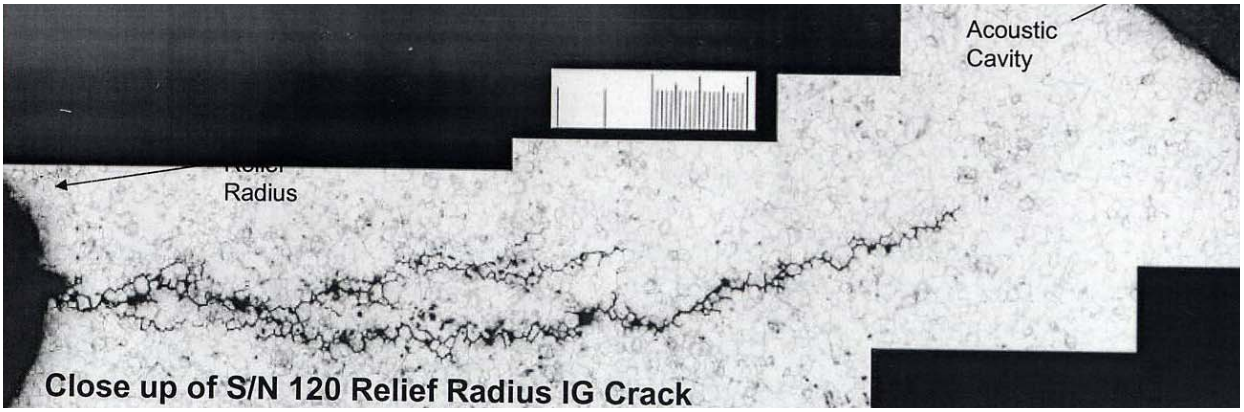


Figure 6 – Shows intergranular nature of S/N 120 relief radius crack.

The counter bore cracks are less of a concern than the relief radius cracks due to differences in the expected outcome from a potential burn-through. Burn-through of a through-crack in a counter bore location will result in an exterior leak path that directs the hot combustion gases onto a wire wrap (reference Figure 2 and Figure 3), which results in a system shutdown (the wire wrap was a thruster modification that was added to protect against a burn-through of the combustion chamber). The resulting flow path from burn-through of a relief radius through-crack could result in combustion gas impingement upon surrounding structure and could potentially result in a loss of vehicle.

3.0 TESTING PART 1: HF ACID ETCHANT EXPOSURE TESTS

Two benefits are derived from reproducing the cracks in the laboratory. First, the mechanism and/or offending species is identified so that corrective actions can be taken. Second, a set of conditions is established that is known to cause cracking. With this set of conditions as a basis, a parametric study can be performed to set boundaries on the cracking process. For example, temperature of the exposure can be varied to see if there is a threshold below which cracking does not occur. Likewise, varying the applied stress or the etchant makeup or concentration might establish other conditional thresholds. Bounding the conditions that cause the cracking allows comparisons to be made to the thruster service conditions and to whether service conditions exist that can cause cracks or can propagate existing cracks. To this end, it was important to reproduce the thruster cracking.

Insight as to the conditions necessary to reproduce the cracking and how to conduct the HF tests, came from a statement in the CAR that was written in 1982. The actual statement from the CAR is repeated here in its entirety.

> Both [The Marquardt Company] and [Rockwell International] have reproduced intergranular cracks in columbium (C103) by applying the etch to the C103, letting it dry, covering with titanium, stressing the C103 in tension to 25 KSI - 30 KSI and heating at 600°F for 48 hours.
>
> Note: Niobium was formerly named columbium.

This statement was the starting point for the tests conducted in the JSC Materials Laboratory; i.e., the conditions cited were duplicated with only minor changes. The changes included a higher stress, 40 KSI vs. 30 KSI, and placing the titanium in contact with the C103 before applying the etch. The increased stress level was for the purpose of accelerating any cracking. The application of the titanium before the etchant dried was for the purpose of ensuring that the niobium/titanium interface was wetted with the etchant so that any potential galvanic action between the two metals could occur.

The potential for reproducing the cracking was significantly enhanced when Boeing found one of the original 1982 test specimens in which the cracking had been reproduced. In conversations with Curt Brownfield, the Rockwell M&P engineer who conducted the tests, he indicated where specimens might be found. This Brownfield specimen contained multiple cracks of which none had been opened up for analysis. Boeing in December 2004 opened one of the cracks and found the fracture surface to have the same fracture features as the actual cracks in the injectors. This find validated the statement in the 1982 CAR that the cracking had in fact been reproduced.

The C103 material for the JSC tests was another fortunate find. JSC M&P came across three C103 coupons that had been sent to JSC in 1982 by Marquardt. These coupons were found with a note identifying the coupons as niobium C103. A semi-quantitative energy-dispersive spectrometer (EDS) analysis in the scanning electron microscope (SEM) confirmed the coupons were C103, consisting of 1 percent titanium, 10 percent hafnium, and the balance niobium.

3.1 HF Exposure Test Preparation

The three recovered coupons were 3.0 inches long by 1.0 inch wide by 0.043 inch in thickness. The coupons were slit crosswise into 0.2 inch wide by 1.0 inch long specimens, enabling each coupon to produce about 12 specimens. Such a small test specimen could be loaded as a cantilever beam in a Dynamic Mechanical Analyzer (DMA) test apparatus (TA Instruments DMA 2980). The DMA was used in all cantilever testing and is shown in Figure 7. The dual cantilever fixture was used in the single cantilever arrangement. Although the DMA is designed for measuring viscoelastic properties of nonmetals, it was ideal for testing these small metal specimens. The DMA apparatus had a maximum load limit of 4 lbs., but the narrow width and thin cross section of the test specimens allowed the desired stress level in the specimens to be obtained without exceeding the DMA load limit. Since these tests were constant load tests, any crack propagation increased the potential for additional cracking (the stress intensity increases substantially as a function of crack growth). This was considered to be an extremely conservative approach considering that the RCS thruster niobium materials experience constant displacement, not constant stress. The DMA thermal chamber allowed for uniform heating of the loaded specimens in place. The DMA also provided continuous recording of time, temperature, deflection, and load.

The C103 test specimens were prepared on a standard metallurgical cut-off machine with a dry diamond wheel. After cutting, the edges were lightly deburred by sanding and the specimens were water rinsed. The two HF-containing etchants used in the manufacturing of the thrusters were prepared for the exposure tests. These two etchants and their compositions were:

- The niobium weld etch: 1 part HF, 1 part HNO_3, and 3 parts H_2O
- The titanium weld etch: 1 part HF, 9 parts HNO_3, and 15 parts H_2O

The niobium etch was used in most of the etchant exposure tests. Rockwell B hardness indentations were placed in the specimen test surface at the location of maximum bending stress. This was done to simulate the heavily smeared/machined surface of the injector material (to be discussed later).

The titanium cover was prepared from a Ti-6Al-4V test specimen from another test program. Preparation consisted of cutting to size to fit in the DMA fixture and sanding all surfaces to a 600-grit finish followed by water rinsing. A niobium cover was also prepared in the same manner as the titanium cover.

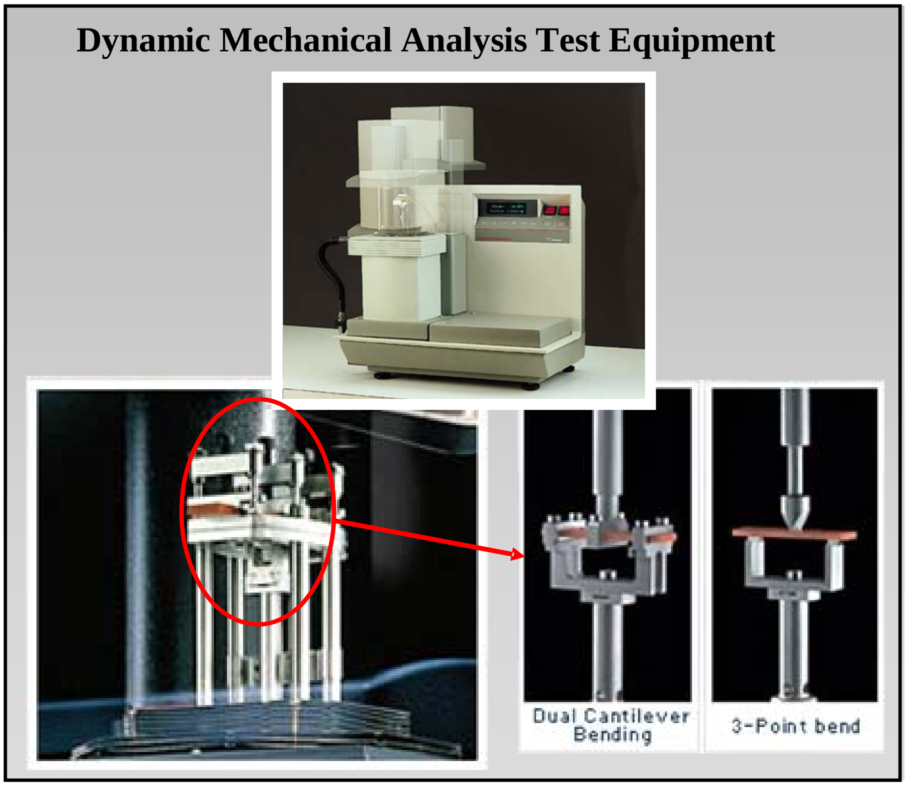


Figure 7 – Shows the DMA loading fixture used for constant load testing (the dual cantilever fixture was used in the single cantilever arrangement).

3.2 HF Exposure Test Procedures

The HF etchant exposure tests involved clamping the niobium specimen between the DMA loading fixture platens with either a titanium or niobium cover between the top platen and the top of the test specimen. A sketch of the typical loading arrangement is shown in Figure 8. After clamping, the specimen was loaded to 40 KSI and the etchant was applied at the niobium/titanium interface with a micropipette such that a drop of etchant bridged the interface. Capillary action forced the etchant into the crevice between the niobium and the titanium so that the highest stressed area of the niobium was wetted with the etchant. Several times during the day as the etchant dried, the interface was re-wetted with another drop of etchant (three to four times). The etchant was allowed to dry overnight, and the temperature exposure began the next day. Some variations to the above procedure were explored (described later), but for the most part this was typical.

The tests duplicated the same exposure temperature and time at temperature as the thrusters experienced during the manufacturing insulation bake-out operation, 600°F for 48 hours. A maximum stress of 40 KSI was selected to accelerate cracking yet stay below the approximate yield strength of 45 KSI for C103. The use of a titanium cover was implemented for two reasons: (1) This configuration duplicates the electrochemical couple present in the flight hardware (this simulated the thruster assembly where titanium is in contact with the niobium injector at the relief radius), and (2) a statement in the original orbiter CAR indicated that cracking in the niobium was reproduced originally using a titanium cover. It was speculated in the CAR that the etchant was being trapped in the relief radius between the titanium and the niobium and was not being adequately rinsed away during the subsequent water rinses. It was also observed that niobium would be cathodic to titanium and the combination of the two metals in contact with the etchant could be a source of hydrogen embrittlement for niobium.

An additional benefit of using the titanium cover was that it kept the aggressive etchant away from the DMA loading fixture and any potential dissolution of the stainless-steel fixture from entering the reaction. As can be seen in Figure 8, the etchant was applied directly at the titanium and niobium interface such that for the most part the etchant was only in the crevice and not in contact with the fixture.

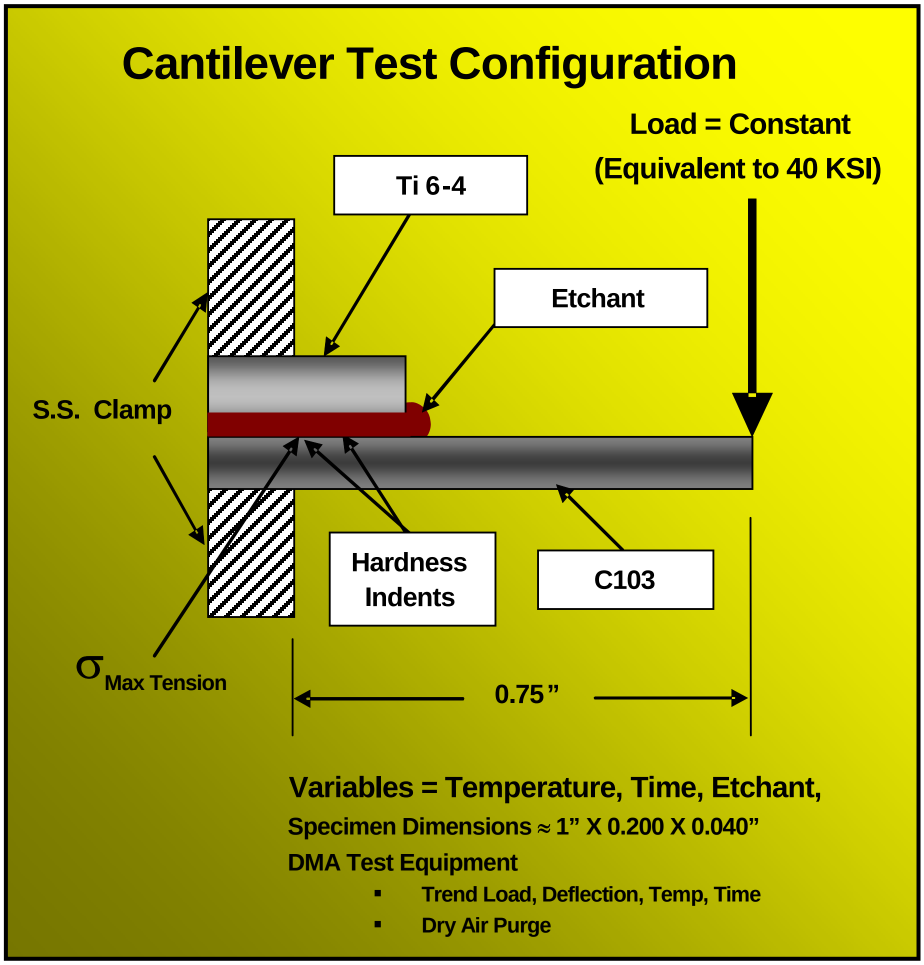


Figure 8 – DMA cantilever beam loading arrangement for HF etchant and Krytox exposure tests.

3.3 HF Exposure Test Sequence

The conditions and the application sequence for the HF exposure tests are listed in Table 1. As can be seen in Table 1, the application sequence of the test conditions varied somewhat with the first few specimens, but from Specimen 3 onward, the sequence remained constant and only the test conditions of temperature and time at temperature were varied. The “Vise” and “Vise/Hard” entries in Column 2 of Table 1 require some explanation. When an end piece was cut from the first coupon, it was clamped in the jaws of a vise. The serrations on the jaw faces of the vise indented the relatively soft niobium. As this coupon was subsequently slit into test specimens, each specimen wound up with a random pattern of surface indentations. Although unintentional, these indentations were critical to reproducing the cracks in the niobium. By Specimen 5, intentional hardness indentations were being placed in the test specimen surfaces. The “Vise” entry refers to indentations from the jaws of the vise and “Vise/Hard” refers to indentations from both the vise and a hardness tester. Subsequent test materials (Specimens 13 and on) were not clamped in a vise, and specimens cut from them only had the intentional hardness indentations. Note that Specimen 14 was tested in air at 600°F and represented a baseline 600°F air exposure.

Table 1 - HF Exposure Tests
Sequence of Application of Test Conditions

Specimen #	C103 Cantilever Beam Tests (Constant Load)	X = Cracks
1	Vise + Nb etch + Ti cover + dry + 40KSI + 600°F + 48hrs	
2	Vise + Nb etch + dry + Ti cover + 40KSI + 600°F + 48hrs	
3	Vise + Ti cover + 40KSI + Nb etch + dry + 600°F + 48hrs	**X**
4	Vise + Nb cover + 40KSI + Ti etch + dry + 600°F + 48hrs	
5	Vise/Hard + Ti cover + 40KSI + Nb etch + dry + 600°F + 48hrs	**X**
6	Vise/Hard + Ti cover + 40KSI + Nb etch + dry + 400°F + 48hrs	
8	Vise/Hard + Ti cover + 40KSI + Nb etch + dry + 500°F + 48hrs	**X (minor)**
9	Vise/Hard + Ti cover + 40KSI + Nb etch + dry + 600°F + 3hrs	**X**
10	Vise/Hard + Ti cover + 40KSI + Nb etch + dry + 600°F + 48hrs + 70°F + H2O (3X/day) + 260hrs	**X**
11	Vise/Hard + Ti cover + 40KSI + Nb etch + dry + 600°F + 168hrs	**X**
12	Vise/Hard + Nb cover + 40KSI + Nb etch + dry + 600°F + 48hrs	**X**
13	See Table 2	
14	Hard + Ti cover + 40KSI + air + + 600°F + 48hrs	

3.4 HF Exposure Test Results & Discussion

Application of a drop of the HF etchant to the niobium surface produced a visible and vigorous bubbling action that only lasted for a matter of seconds. After the etchant dried and the 600°F temperature exposure was completed, a relatively thick reaction product was observed on the test surface, which completely covered and obscured the niobium surface. In order to determine if cracking was present, this product had to be removed in a manner that minimized alteration of the niobium surface. This product strongly adhered to the surface of the niobium and could not be removed with water rinsing, ultrasonic cleaning, or vigorous brushing. The best technique found for removal was by immersion in the etchant for a short period of time (10–30 seconds). Etchant removal of the reaction product was not always complete but was generally sufficient to observe the metal surface.

A typical surface appearance and the reaction product after exposure to the HF etch and 600°F for 48 hours is shown in Figure 9.

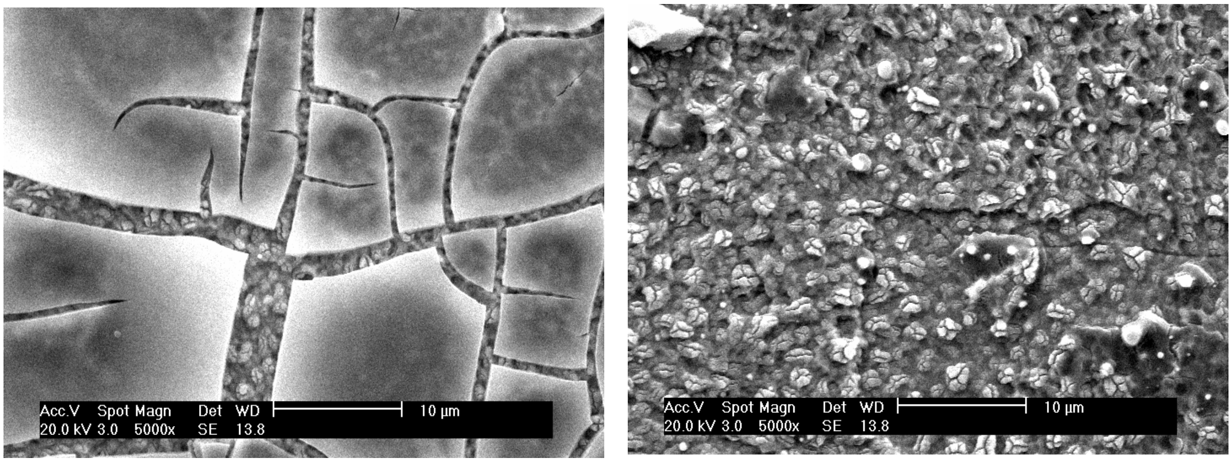


Figure 9 – Typical appearance of the oxide film formed as a result of exposure of a flat niobium surface with one drop of the niobium etch covered with titanium and heated to 600°F for 48 hours. The left SEM image reveals a semi-translucent brittle oxide crust (titanium oxide), with eruptions in the niobium oxide film underneath. These eruptions have been referred to as "popcorn," as shown on the right image. This oxide film was subsequently cleaned off for surface evaluation. Magnification – 5000x.

Note the very obvious eruptions in the oxide film. These eruptions were referred to as "popcorn" (for obvious reasons) during the 1979 and 1982 investigations of the thruster cracking. Back then and until recently, the popcorn was thought to be unique to this cracking problem. It was, however, pointed out at the December TIM (Ref. 5) that popcorn appears as a result of eruptions in the oxide film when niobium is exposed to an oxidizing environment at elevated temperature. The occurrence of and the density of the popcorn features on the fracture surface were the focus of considerable effort and analyses by others during this investigation of S/N 120 and will be documented in their reports. EDS analysis of the elemental makeup of this surface oxide product shows a high oxygen and fluorine content indicative of a complex of niobium oxides, fluorides, and oxy-fluorides as could be expected. The analysis is shown in Figure 10. No attempt was made to determine the actual composition of the reaction products. Work by others (Refs. 6, 7, and 10) has indicated a major component of the product is the niobium oxide Nb_2O_5.

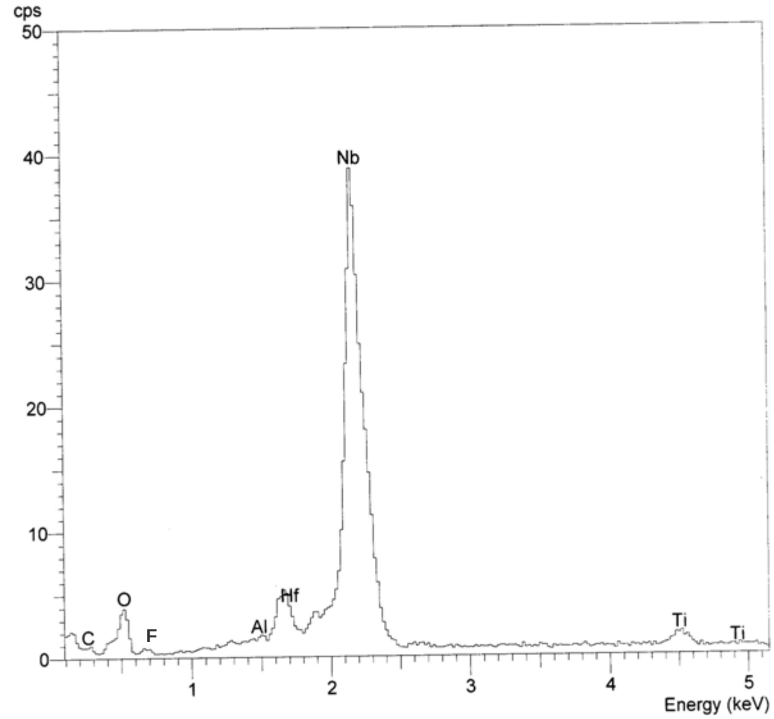


Figure 10 – EDS analysis of surface deposits on niobium surface after one drop of HF etch + titanium cover + 600°F + 48 hours. These oxide film eruptions were referred to as "popcorn" in the original Marquardt failure analysis. Significant oxygen content was observed, but fluorine was barely detected.

During post-exposure evaluation, difficulties arose in positively identifying surface cracks on all test specimens. This was due to a number of factors:

- The surfaces of the specimens were masked by the HF reaction products (heavy oxidation from etchant/elevated temperature exposure)
- Subsequent acid cleaning (≈15 seconds) resulted in a lightly etched surface
- The nature of the intergranular cracking mechanism produced very "tight" cracking, easily disguised by the surrounding surface morphology

Thus, the presence or absence of surface cracking could not be definitively determined by simple microscopic examination of the undeformed surface. In all cases, each specimen was mechanically bent to open up any residual intergranular cracking on the tensile surface. It is noted that in all of the test specimens, numerous short/shallow cracks were observed after bending, even in areas that had not been exposed to the etchant.

Specimen 3 was the first test specimen in which cracking was successfully produced. The test conditions for Specimen 3 consisted of clamping the titanium and niobium together in the DMA test fixture as in Figure 8, loading the specimen to 40 KSI, and applying a drop of the niobium etch to the titanium/ niobium interface and allowing the etch to air dry. The etch was reapplied several times during the day and was allowed to air dry overnight. The following day, the DMA heating apparatus was put in place and the specimen was heated to 600°F for 48 hours. After completing the 48-hour temperature exposure, the specimen was examined in a stereomicroscope and in the SEM. No obvious cracking was noted, but the actual metal surface was completely hidden by the oxide film that was present. After cleaning by a short immersion in the etchant, a patch of intergranular attack was observed on the high stress HF exposed surface. It appeared to be intergranular corrosion rather than a crack. This condition is shown in Figure 11.

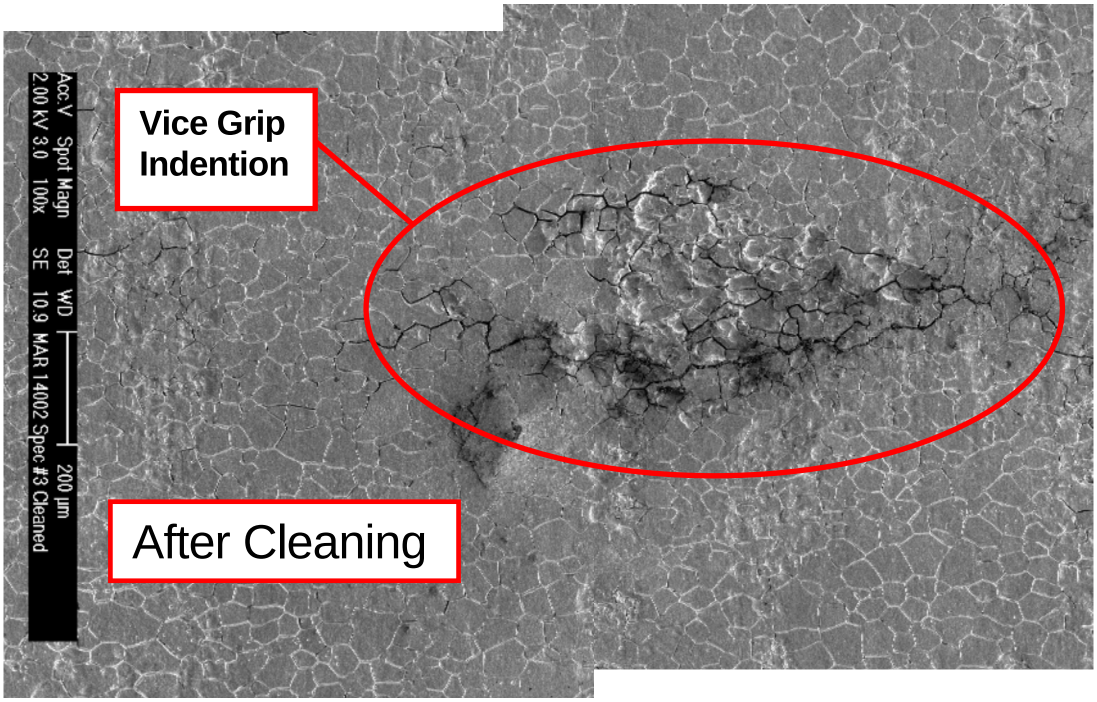


Figure 11 – Specimen 3 showing intergranular attack (after cleaning), 100x Magnification. Note that cracking is commensurate with the location of a vice grip indentation.

To determine if the attack had any significant depth, the specimen was mildly deformed by bending in a vise by hand. The result is shown in Figure 12.

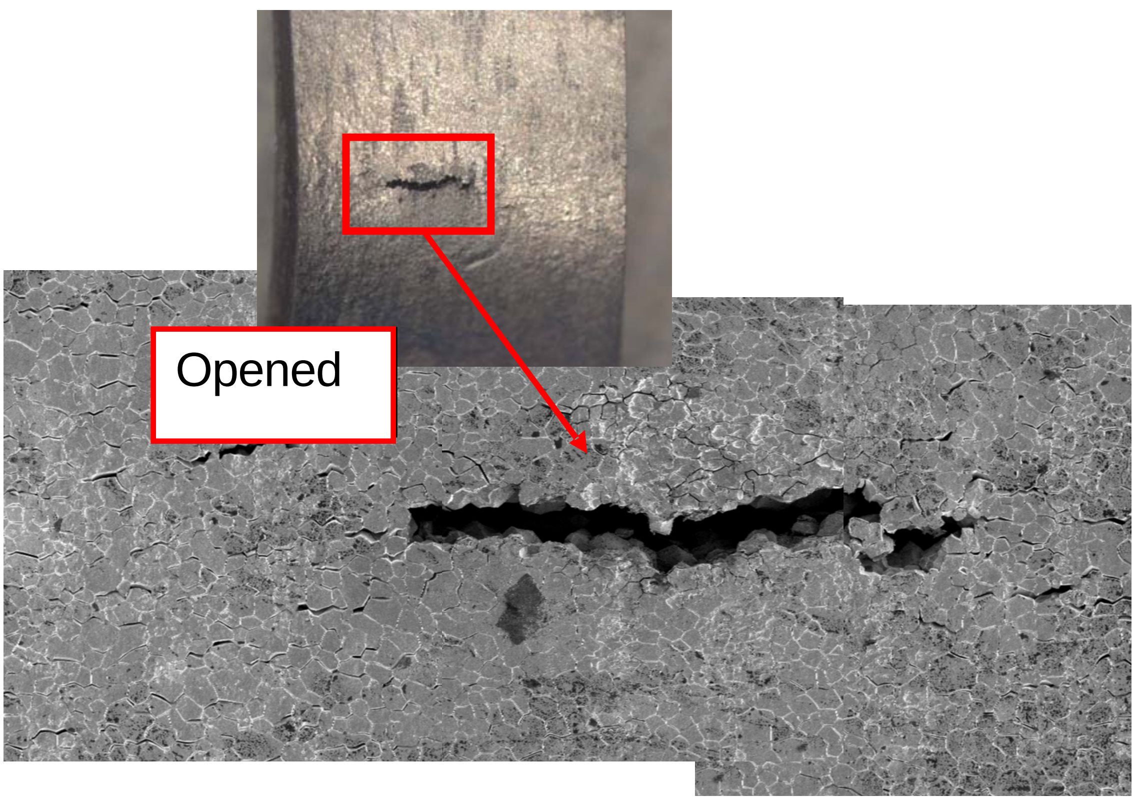


Figure 12 – Specimen 3 after bending.

A crack of significant depth approximately halfway through the thickness of the specimen was opened up. Examination of the fracture surface showed the crack was 100-percent intergranular in nature and had a very distinct blue/purple appearance. These fracture surface features are shown in Figure 13 and Figure 14 and were very similar to the cracks in the thrusters and the Brownfield specimen.

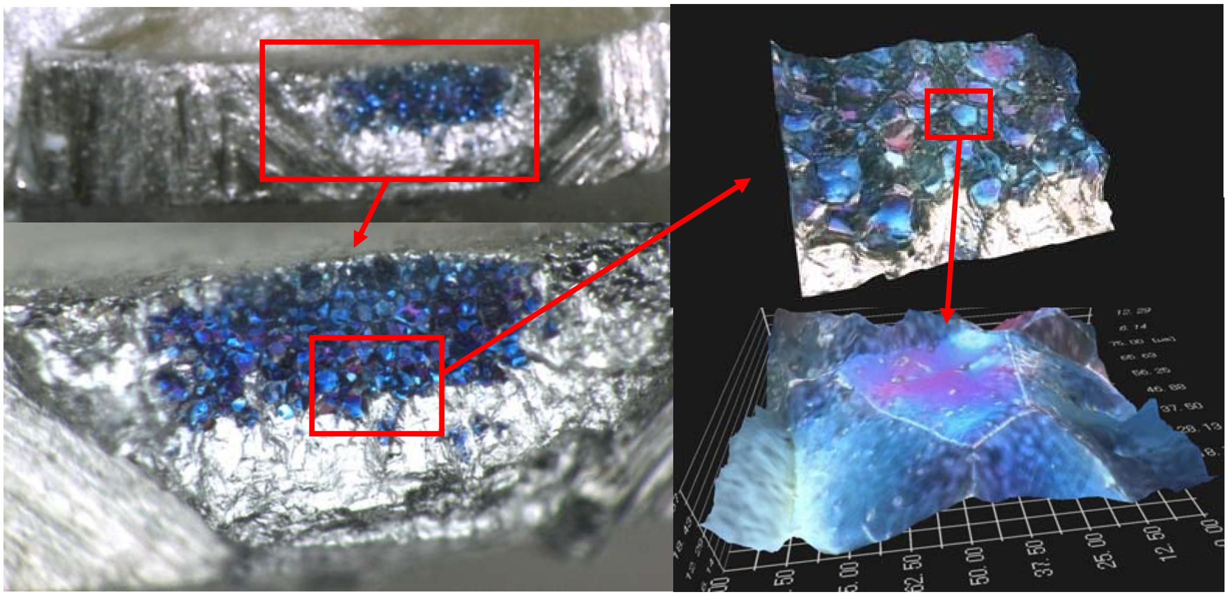


Figure 13 – Specimen 3 Microscopy: Upper (~20x) and Lower (~40x) Left Images – Optical stereomicroscope images of fracture showing intergranular nature/"rock candy" appearance of crack morphology. Upper (~150x) and Lower (~1500x) Right Images – High magnification close-ups via Keyence digital microscope. All images display the vivid blue discoloration of fracture surface (result of oxidation).

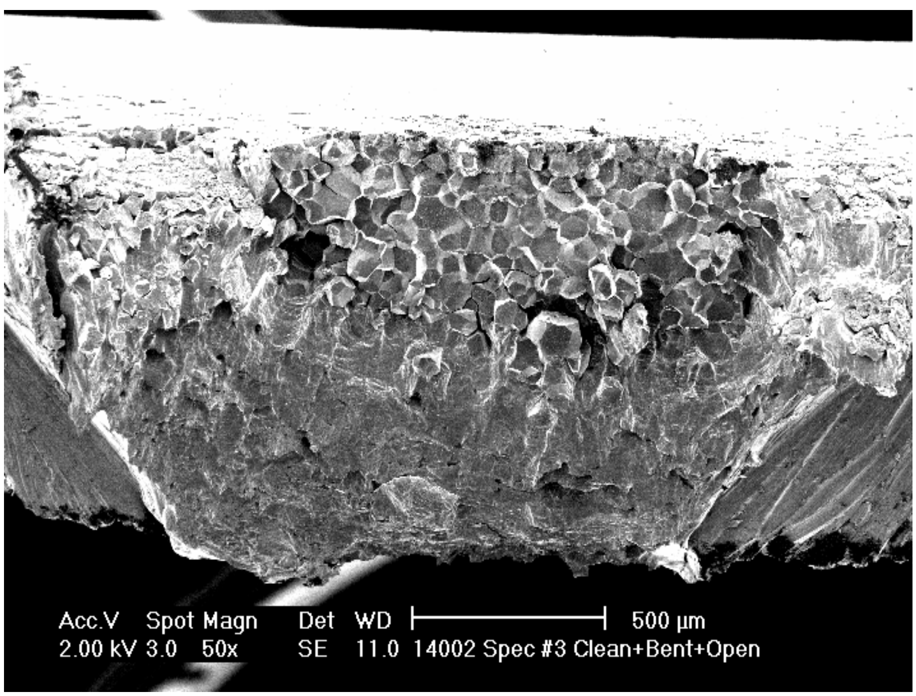


Figure 14 – Specimen 3 fracture surface showing intergranular nature of crack. Magnification: 50x.

At higher magnification in the SEM, the characteristic popcorn features were evident on the intergranular facets as shown in Figure 15.

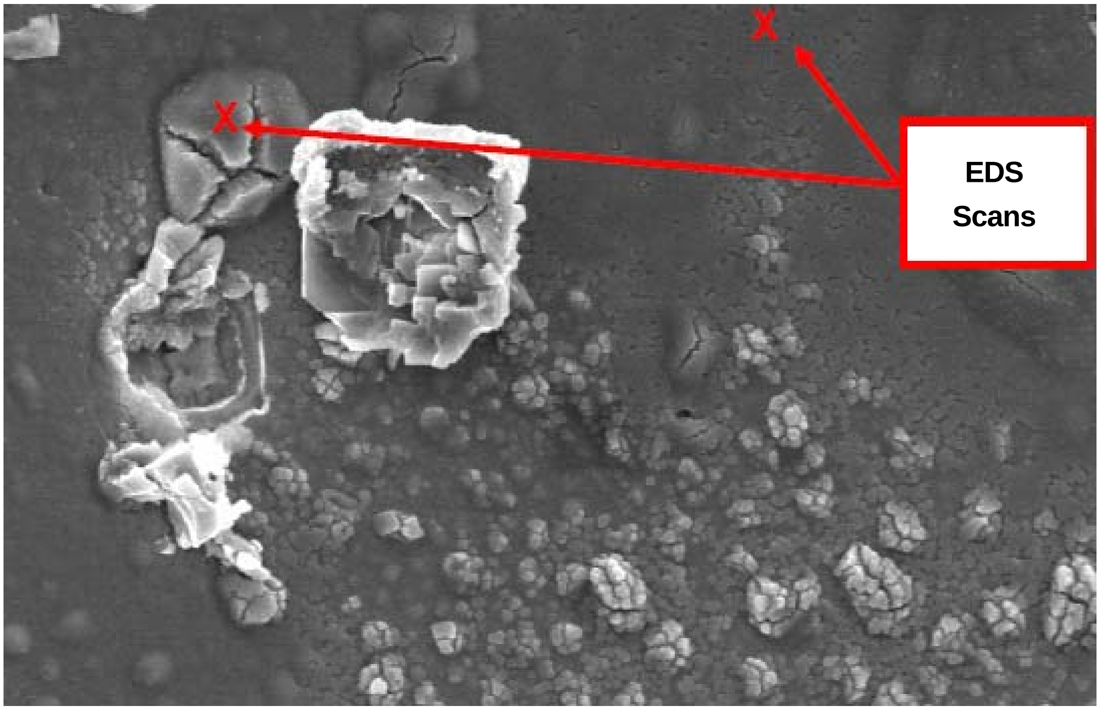


Figure 15 – Specimen 3 fracture surface eruptions in the oxide film referred to as "popcorn." EDS analyses were performed on the areas noted and are presented in Figure 16 and Figure 17. Magnification: 5000x.

EDS analysis of a popcorn feature and the adjacent surface showed high oxygen and fluorine with the popcorn feature having a significantly higher fluorine content. These analyses are shown in Figure 16 and Figure 17. The similarities between the crack in this specimen and the thruster cracks indicated that a very good reproduction of the thruster cracking had occurred. These similarities included the 100-percent intergranular crack propagation, the blue discoloration, the presence of oxygen and fluorine, and the presence of the popcorn features.

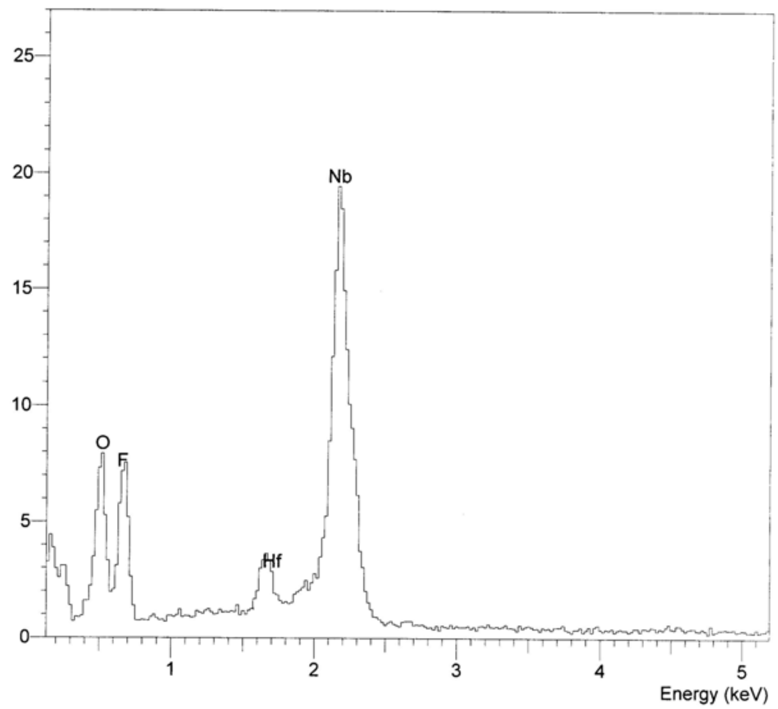


Figure 16 – EDS analysis of popcorn feature in Figure 15. Note high fluorine content and compare to analysis in area adjacent to popcorn feature.

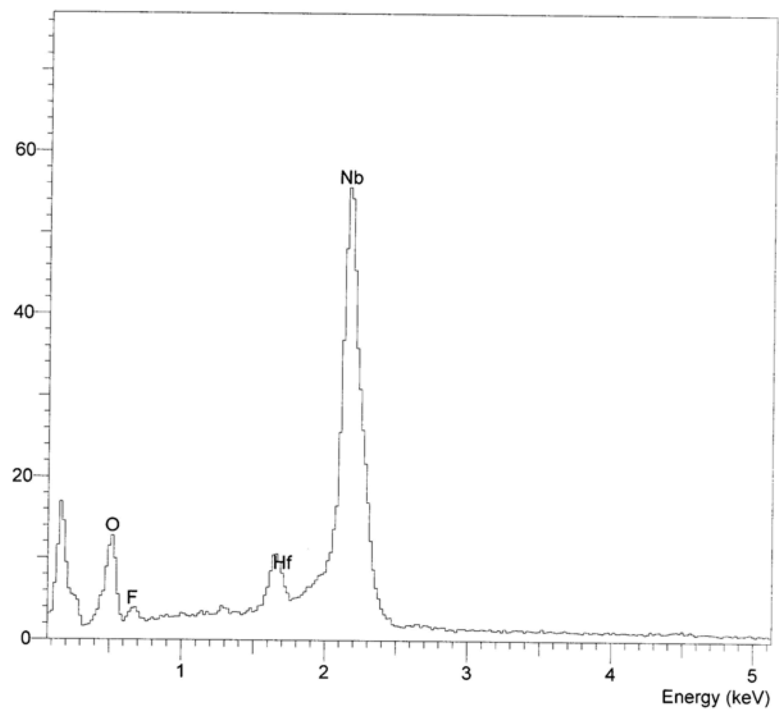


Figure 17 – EDS analysis of area adjacent to popcorn feature showing a much reduced fluorine content.

An unusual surface feature that was noted in this specimen and in most of the other specimens was cracks or separations in the oxide film on the grain boundary surfaces. A typical oxide film separation is shown in Figure 18. This feature was only observed at or near the tips of the cracks. It was also noted in the original failure analysis of S/N 128 (Ref. 1) and was referred to as "broken grains." These separations in the oxide film attest to the very brittle nature of the oxide film and results from the plastic strain the underlying ductile niobium undergoes at the crack tip when the cracks are opened for examination. This condition was another fracture surface feature that was reproduced during these tests.

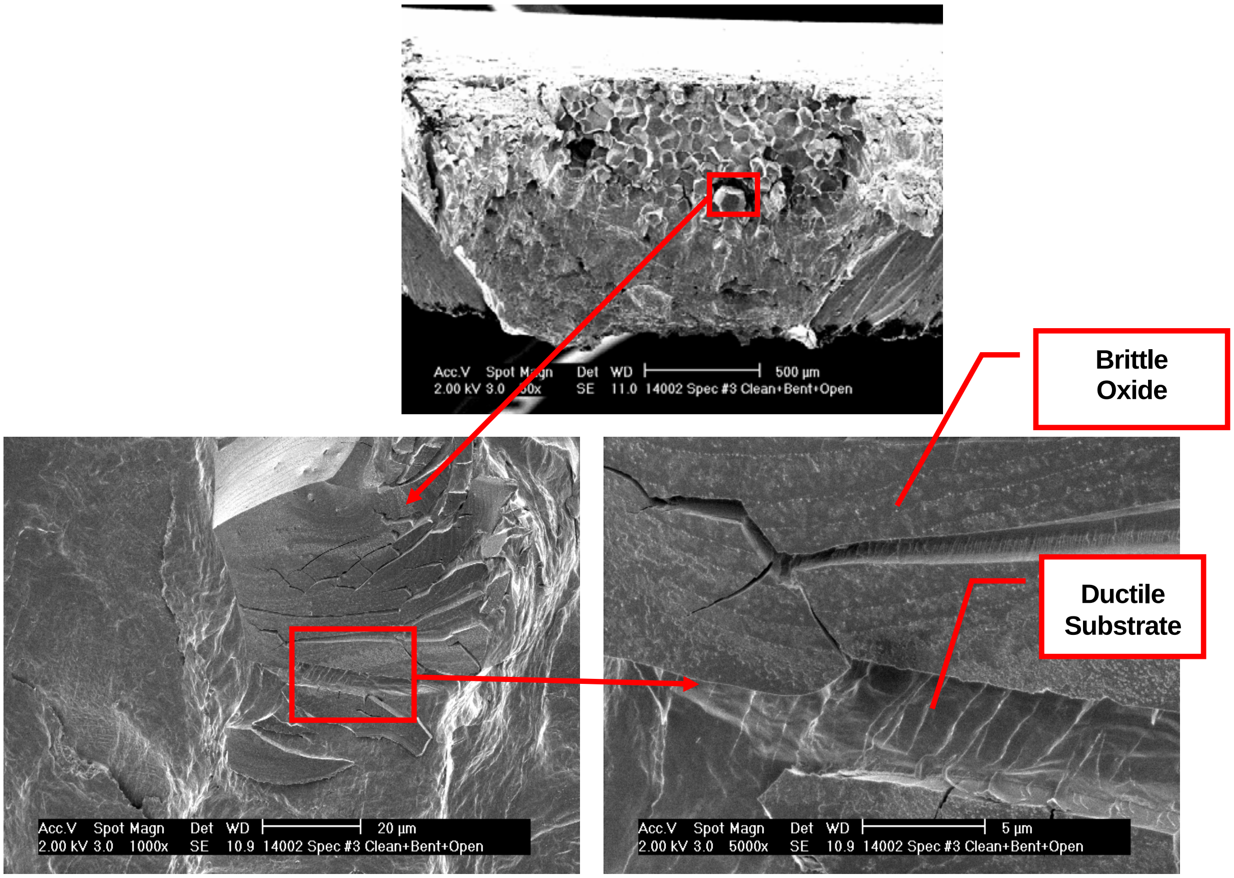


Figure 18 – Cracking of the brittle intergranular oxide near the intergranular crack tip (as a result of sample overloading to separate fracture surfaces).

Although it is not obvious in Figure 11, all of the intergranular attack is contained within a surface indentation that was created by the aforementioned clamping in a vise. This observation was critical to being able to consistently reproduce the cracking. Since all of the intergranular attack and its associated crack were in the indentation, it was apparent that another condition was required to produce the cracking. This added condition was mechanical deformation of the test surface and the residual stresses that accompany such deformation. How this deformation is involved is not fully understood, but it certainly appeared to be a necessary condition at this point in the test program. Instead of relying on the random location and depth of penetration of the vise indentations, it was decided to put controlled and repeatable indentations in the test surface with a hardness tester (Rockwell B). Specimen 5 was the first specimen to have the hardness indentations as did all of the subsequent specimens.

Specimen 5 was a repeat of the test conditions of Specimen 3 to be sure that the cracking could be repeated. The only difference was the addition of the hardness indents. After completing the 600°F temperature exposure and cleaning with the etchant, cracking was evident but obscured by remnants of the oxide film. After bending, the extent of the cracking was very evident as shown in Figure 19.

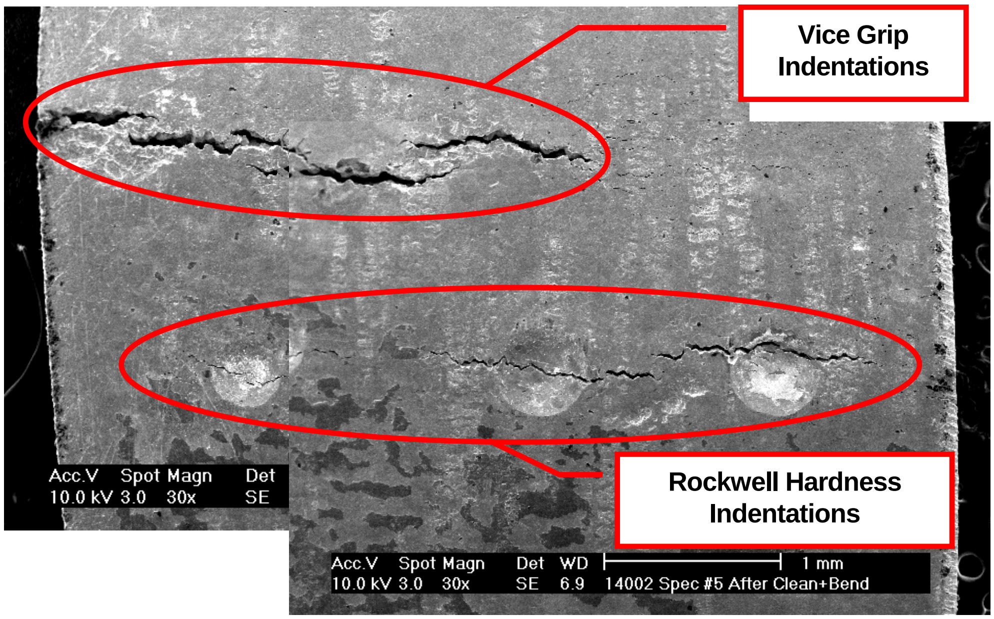
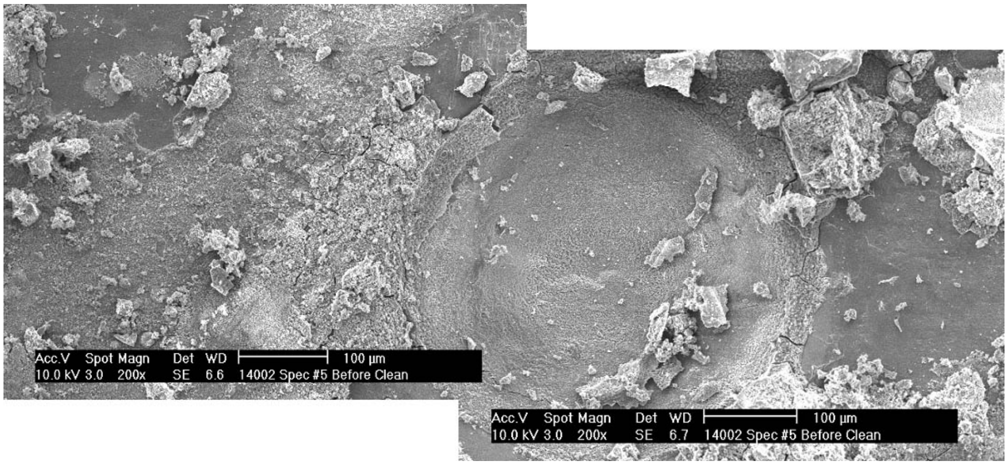
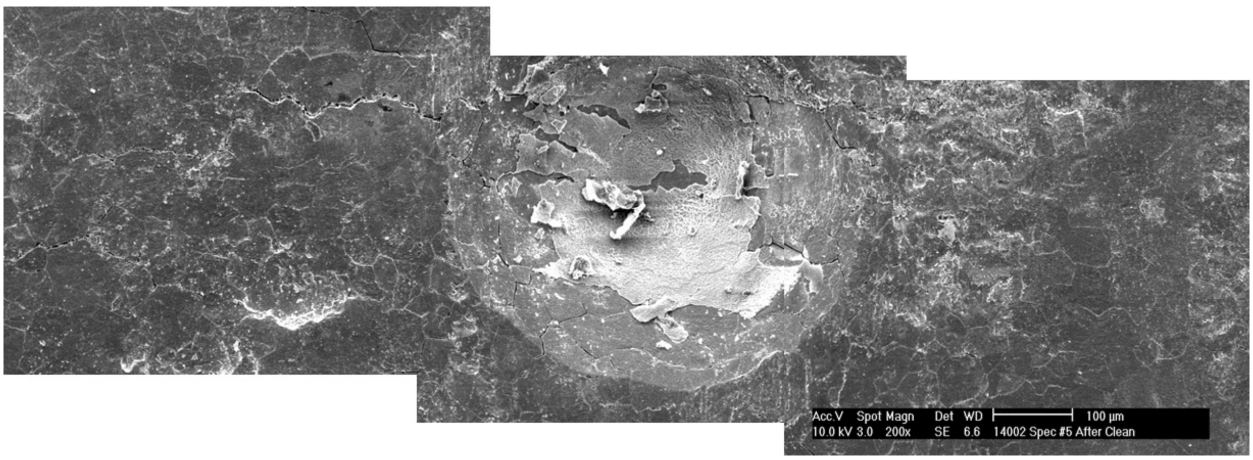


Figure 19 – Specimen 5 shows cracks extending out of each hardness indent as well as several vise indents. Magnification: 30x.

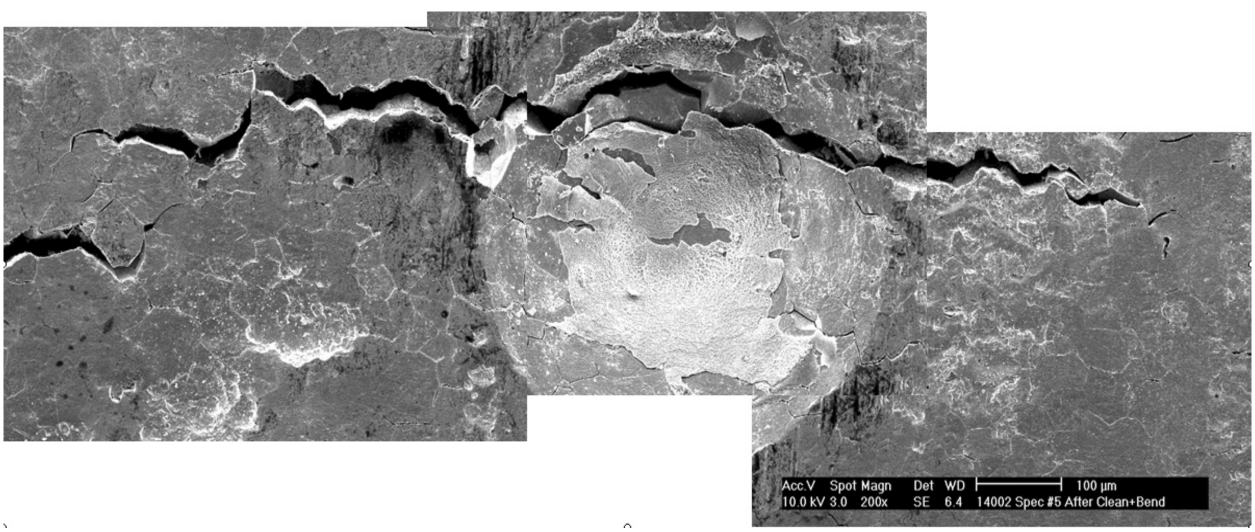
Cracks initiated in and grew out of each of the hardness indents as well as several of the vise indents. The difficulty of seeing the cracks is illustrated in Figure 20 where the same hardness indent is shown in the as-tested, as-cleaned, and as-bent conditions. Because of crack tightness, each specimen had to be bent through the expected crack location to be sure whether cracking had occurred. It is obvious in the as-bent photograph that the cracks had propagated in an intergranular manner.



<u>As-Tested</u>



<u>As-Cleaned</u>



<u>As-Bent</u>

Figure 20 – Specimen 5 comparing the as-tested, as-cleaned, and as-bent surfaces. The need to clean and bend the specimen to verify the presence of cracks is evident. Magnification: 200x.

The crack faces were exposed by bending back and forth until separation occurred. The crack surface is shown in Figure 21. Again, the cracks were 100-percent intergranular and had a blue discoloration. At higher magnifications in the SEM, the popcorn features were again present as shown in Figure 22.

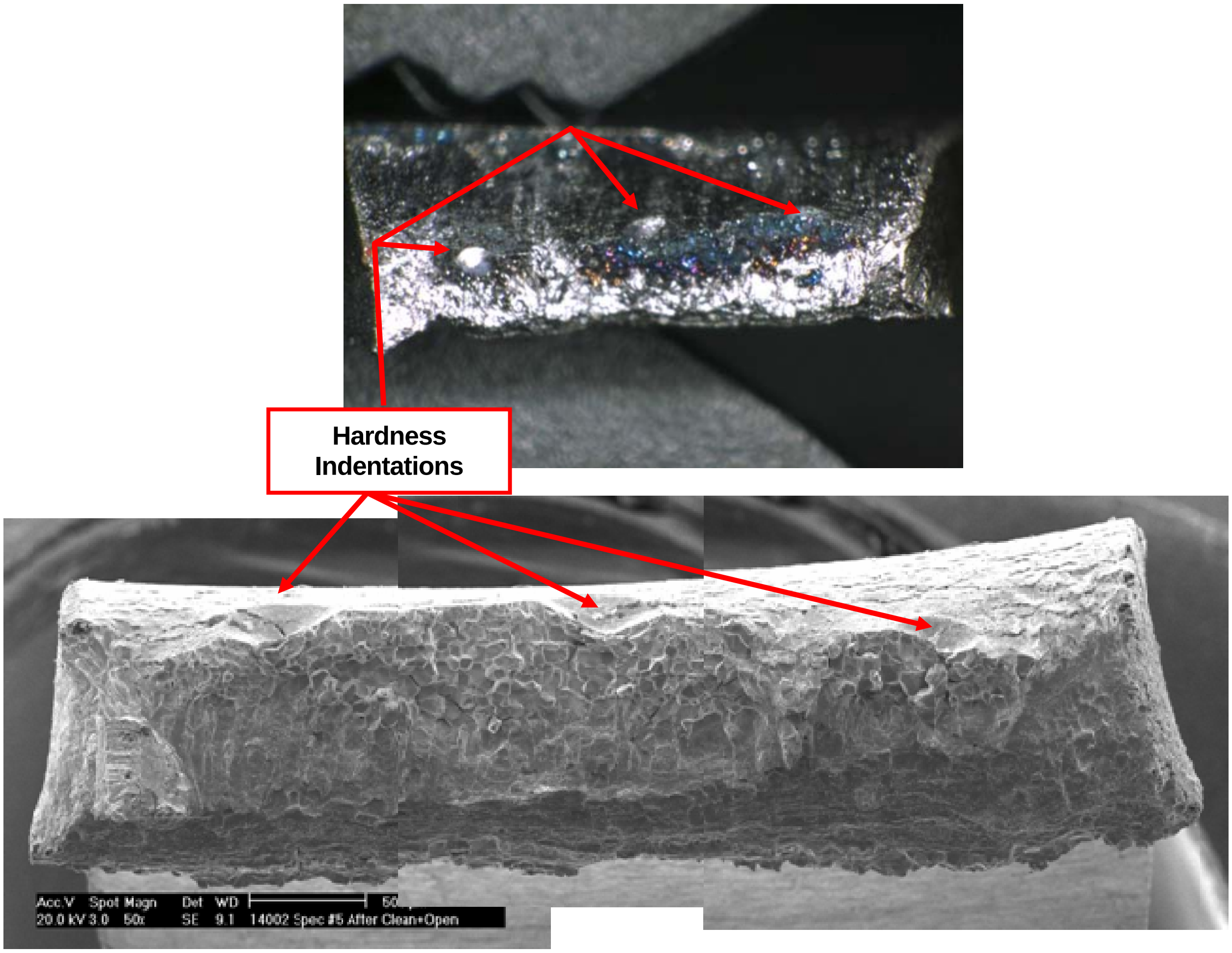


Figure 21 – Specimen 5 showing the intergranular nature of the crack surface. Cracking extends about halfway through the thickness. Hardness indents are visible at the specimen surface. Magnification: 50x (lower image).

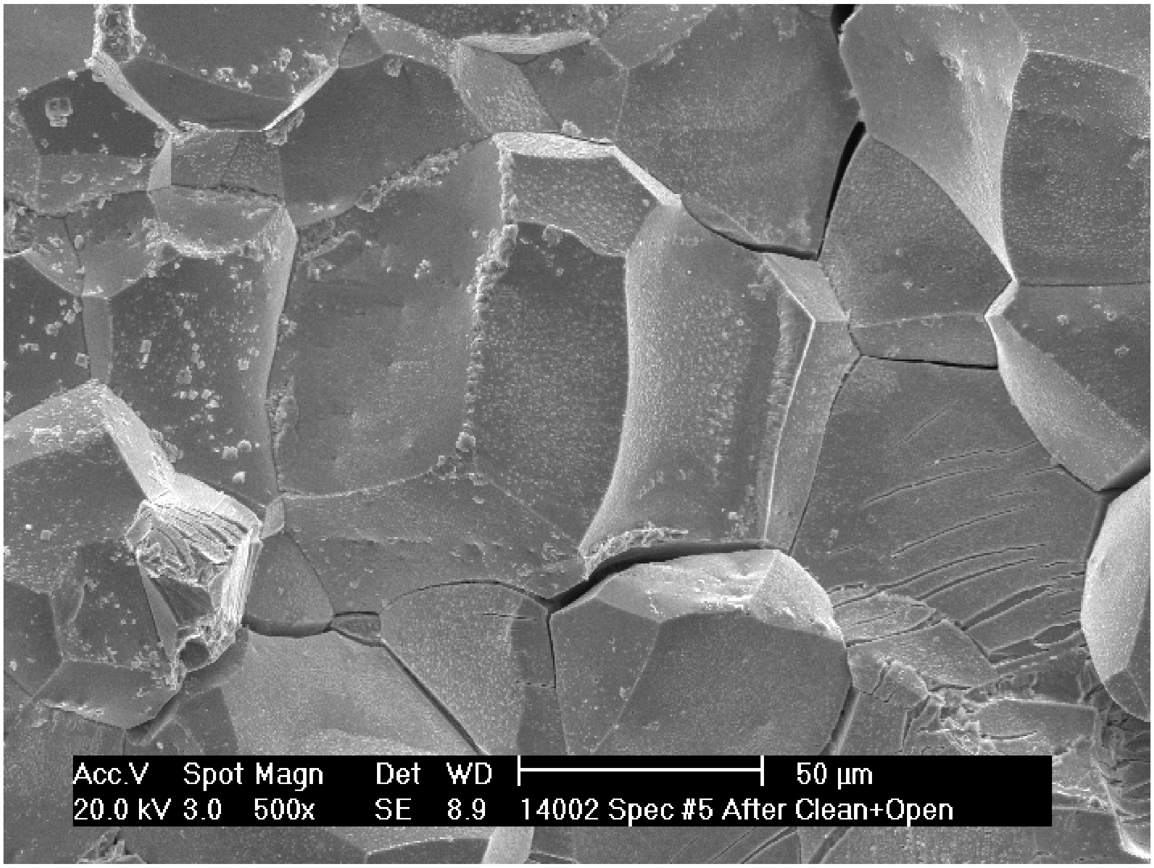


Figure 22 – Specimen 5 showing intergranular facets near crack tip. Popcorn-like features are present on most of the facets. Cracking of the oxide is visible. Magnification: 500x.

The results of Specimens 3 and 5 confirmed that stressed and mechanically deformed C103 could be cracked by exposure to an HF containing acid with subsequent heating to 600°F. The cracks produced had the same characteristics as the actual cracks in the thrusters (i.e., the thruster cracking had been reproduced). These two specimens also showed that the laboratory cracking was repeatable.

Given the test conditions that caused cracking, the one condition that could most easily be related to the thruster service conditions was temperature. Measurements of injector temperatures during qualification testing and during flights provide a large database of temperatures with which to compare the test results. These data suggest that injector material temperatures do not exceed 400°F during nominal operation.

Specimen 6 was tested exactly as Specimen 5 except the exposure temperature was lowered to 400°F. After 48 hours at 400°F and after cleaning and bending, no evidence of cracking was found.

Specimen 8 was tested at 500°F. After exposure, only minor cracking could be found, as shown in Figure 23. Based upon evaluation of the surface via SEM and comparison with other test coupons, it was determined that these cracks were shallow (no attempt was made to open them). The surface appearance indicates that the cracks were intergranular.

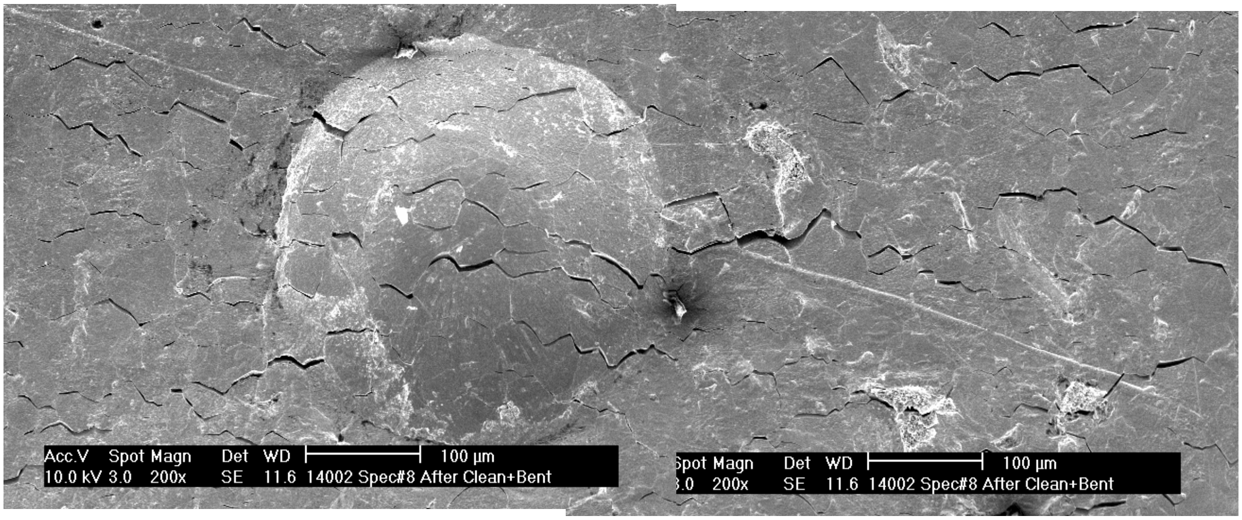


Figure 23 – Specimen 8 showing intergranular cracks after 500°F exposure. Magnification: 200x.

A clear temperature threshold of 400°F was apparent in these tests. No cracking occurred at 400°F and only minor cracking occurred at 500°F. The actual temperature threshold for cracking appears to be somewhere between these two temperatures.

Time of exposure was also a test condition that could be easily related to thruster service condition. Several tests were conducted at 600°F for different exposure times, both shorter and longer than the 48-hour tests.

<u>Specimens 9 and 11</u> were tested at 3 hours and 168 hours, respectively. Both specimens had about the same degree of cracking as shown in Figure 24 (Specimen 9) and Figure 25 (Specimen 11). These results indicate that the cracking process begins early in the exposure. The cracking process under these conditions appears to be self-limiting in some way since the test is a constant load test and the cracking should accelerate as the crack grows. Apparently, the reactive species are used up or depleted early in the temperature exposure cycle, and the cracking is subsequently arrested. If the cracking species were in abundant supply or regenerative in nature, the constant loading of the test would necessarily have grown the cracks to failure (certainly in the 168-hour test).

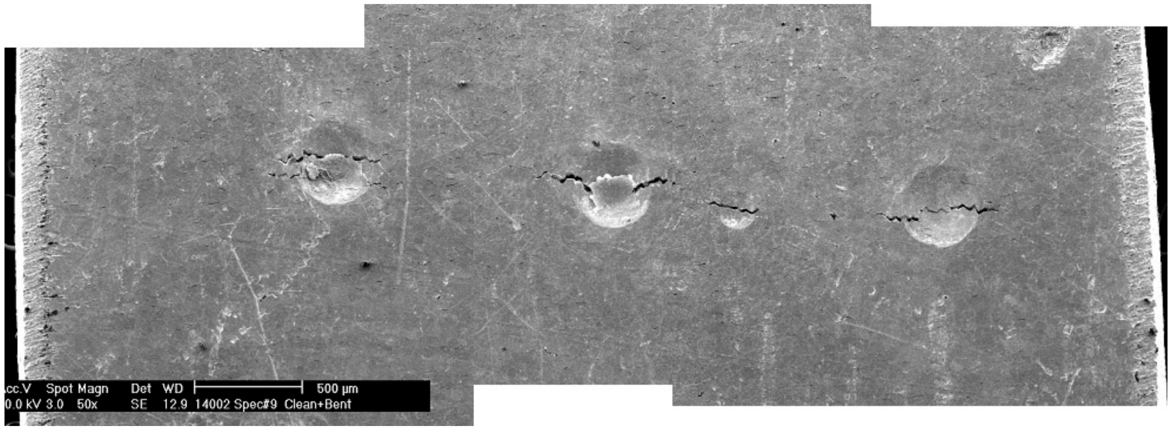


Figure 24 – Specimen 9 showing degree of cracking after 3 hours of exposure to HF at 600°F. Magnification: 50x.

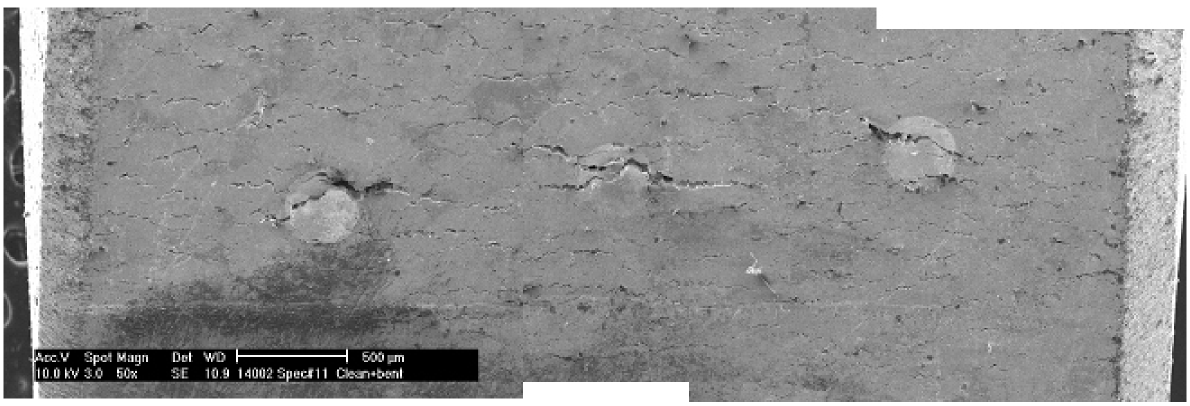


Figure 25 – Specimen 11 showing degree of cracking after 168 hours of exposure to HF at 600°F. Magnification: 50x.

Specimen 10 was tested at 600°F for 48 hours to produce cracking that could subsequently be exposed to water at room temperature to see if the cracks would propagate when exposed to a simulated wet/humid environment. After 48 hours at 600°F, the specimen was etchant-cleaned so that the cracks that were induced could be documented in the SEM. After the cracks were documented, the specimen was placed back in the load fixture and reloaded to 40 KSI with the titanium cover in place. Drops of water were periodically applied to the niobium/titanium interface. This re-wetting occurred several times a day to keep the cracked surface wet. This water exposure was continued for 260 hours. Before and after (water exposure) comparisons at the same magnifications showed no evidence of crack growth. These comparisons are shown in Figure 26 and Figure 27. Although this test was not a standard corrosion test, it was quite sensitive in that deflection of the test article was actively measured in the DMA during testing, and crack growth was subsequently measured in the SEM at high magnification. This look at exposure of these cracks to water shows that short-term exposure to moisture and humidity does not grow the cracks.

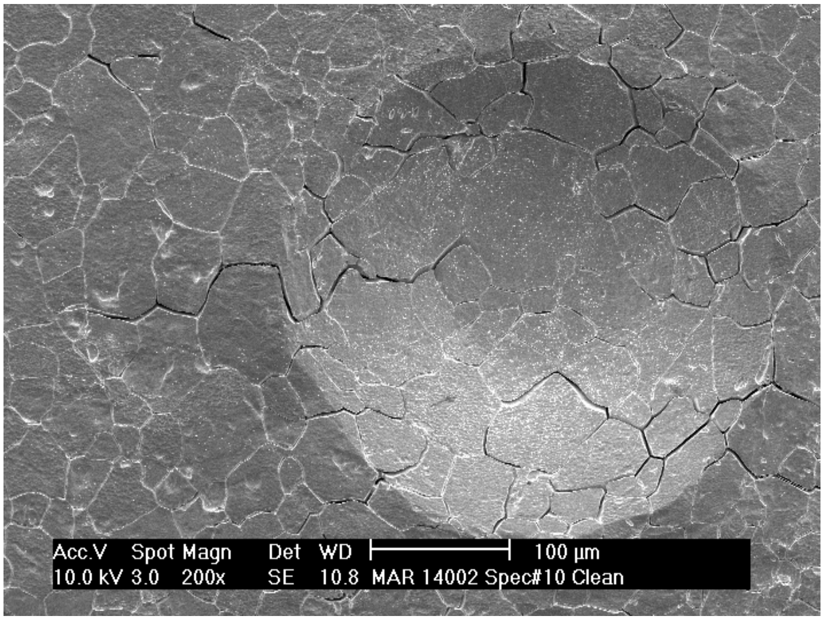


Figure 26 – Specimen 10 showing crack locations after HF, 600°F, 48 hours, and etch cleaning. Compare to Figure 27 after water exposure. Magnification: 200x.

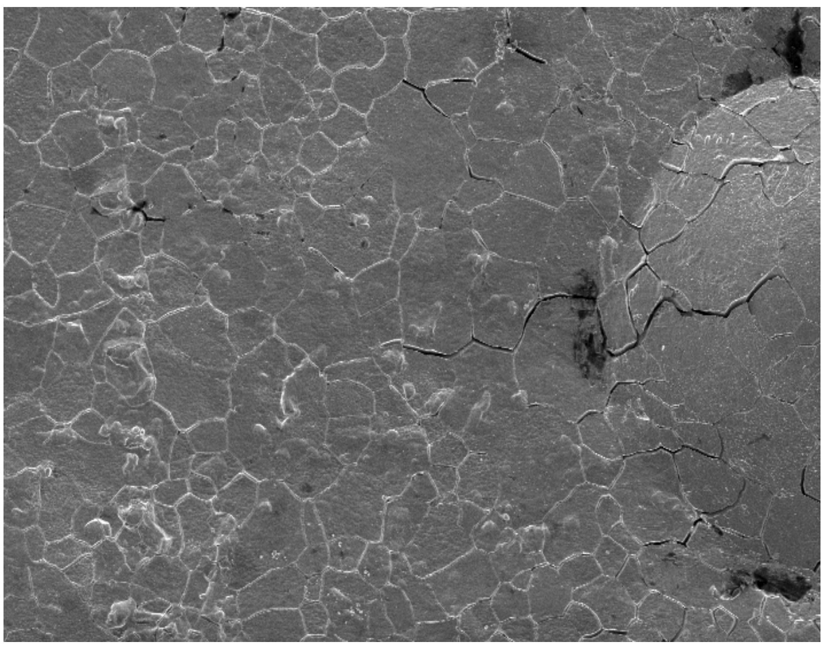


Figure 27 – Specimen 10 showing exact same area as Figure 26 after 260 hours exposure to water and 40 KSI constant stress. No change in the apparent crack locations is evident. Magnification: 200x.

Specimen 12 was tested at 600°F for 48 hours with a niobium cover instead of a titanium cover to see if the titanium/niobium couple was a necessary condition for cracking. Examination after the exposure showed a significant amount of cracking was present, which indicated that titanium is not a factor or a necessary condition in the cracking process.

Specimens 1, 2 and 4 did not show any cracks even though the same conditions were present during their exposures as were present in all of the specimens that did crack. Although not completely understood, several possible explanations are offered here for the lack of cracking in these three specimens. The sequence of application of the test conditions differed for Specimens 1 and 2 where the stress was not applied until just before the heating cycle began; i.e., the specimens were unstressed when the surfaces were wet with the etch. In addition, since these three specimens did not have the intentional hardness indents, the random locations and depths of the vise indents may have been located out of the stressed area or the associated level of residual stress may not have been sufficient to initiate cracks. This is substantiated by testing later in the matrix, which consistently reproduced cracking in high-stress locations where hardness indentations were intentionally placed.

Specimen 14 was a test conducted in air at 600°F for 48 hours to establish a baseline for comparison with the other test specimens. After the 600°F air exposure, this specimen was mildly bent and numerous short shallow cracks were opened up as shown in Figure 28. Apparently, a minor amount of grain boundary oxidation occurs in this alloy when it is exposed to air at 600°F for 48 hours. Upon bending, the oxidized brittle grain boundaries crack.

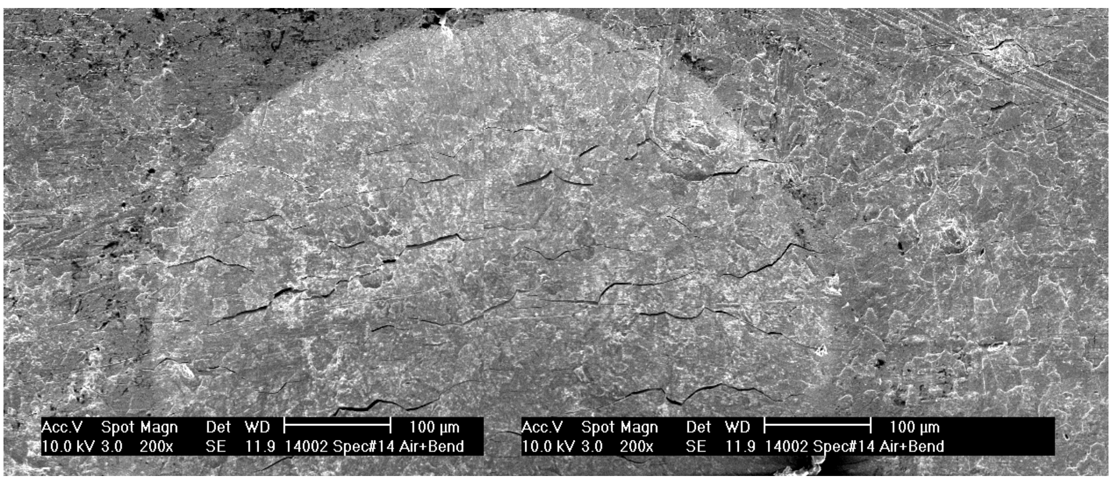


Figure 28 – Specimen 14 baseline 600°F, 48 hours test in air. Shallow intergranular cracks evident in indent after bending. Only short straight cracks in oxide film evident between indents. Magnification: 200x.

4.0 TESTING PART II: KRYTOX EXPOSURE TESTS

Although the HF tests reproduced the injector cracking, Krytox was re-examined in the JSC tests because:

- Krytox contains fluorine
- The original Marquardt examination of Krytox included testing only at 1100°F and not at 600°F
- The X-Ray Photoelectron Spectroscopy (XPS) analysis completed by Marshall Space Flight Center, reported at the December TIM (Ref. 8), indicated the presence of a fluorine-containing synthetic oil residue on the fracture surface of S/N 120

Krytox oil is a perfluoropolyether (PFPE) polymer, a fluorinated synthetic oil that is composed of carbon, oxygen, and fluorine. It was used a number of times during both the original thruster manufacturing operations at Marquardt and during subsequent rework at WSTF. One of its uses was to lubricate the mounting bolts used to assemble the injector to the titanium mounting flange. Subsequent exposures to elevated temperatures (both during manufacturing and in service), would have allowed for migration of Krytox to both of the sites where the injector cracking occurred (the relief radius and the counter bore surfaces).

Upon examination of the Krytox test results, Brayco 815Z, another common aerospace PFPE-based oil, was also tested.

4.1 Krytox/Brayco Exposure Test Procedures

The Krytox cantilever beam exposure tests in the DMA apparatus were conducted in essentially the same manner as the HF tests. The niobium specimen was clamped in the DMA loading apparatus with a titanium cover. The specimen was loaded to 40 KSI and a drop of Krytox was applied to the titanium/ niobium interface. Since Krytox does not evaporate at atmospheric pressure, no replenishment of the oil was needed and the specimen was immediately heated to the test temperature for the specified time. As in the HF tests, hardness indentations were included in the Krytox tests. The test specimens for the Krytox tests came from the second C103 coupon, so no vise indents were present in these specimens (only intentional hardness indentations). Although probably not needed, the titanium cover was retained in these Krytox cantilever beam tests in order to change as few variables as possible from the HF tests.

A three-point bend fixture was fabricated for testing the small C103 specimens and was used for several of the Krytox and Brayco exposure tests. A schematic and photograph of the fixture are shown in Figure 29. For each of the PFPE exposure tests, the specimens were loaded slightly above yield in the three-point bend fixture. Loading was accomplished by deflecting the specimen until a slight permanent set was observed, then continuing the deflection slightly beyond that. Since this was accomplished manually, the stress was only known qualitatively; i.e., “just above yield.” For the three-point bend tests, a drop of Krytox or Brayco oil was placed in the center of the specimen covering the hardness indentations. By keeping the fixture in the upside-down position, the drop remained centered on the specimen tension surface in the gravity-down position (see Figure 29). No titanium cover was used in these three-point bend tests.

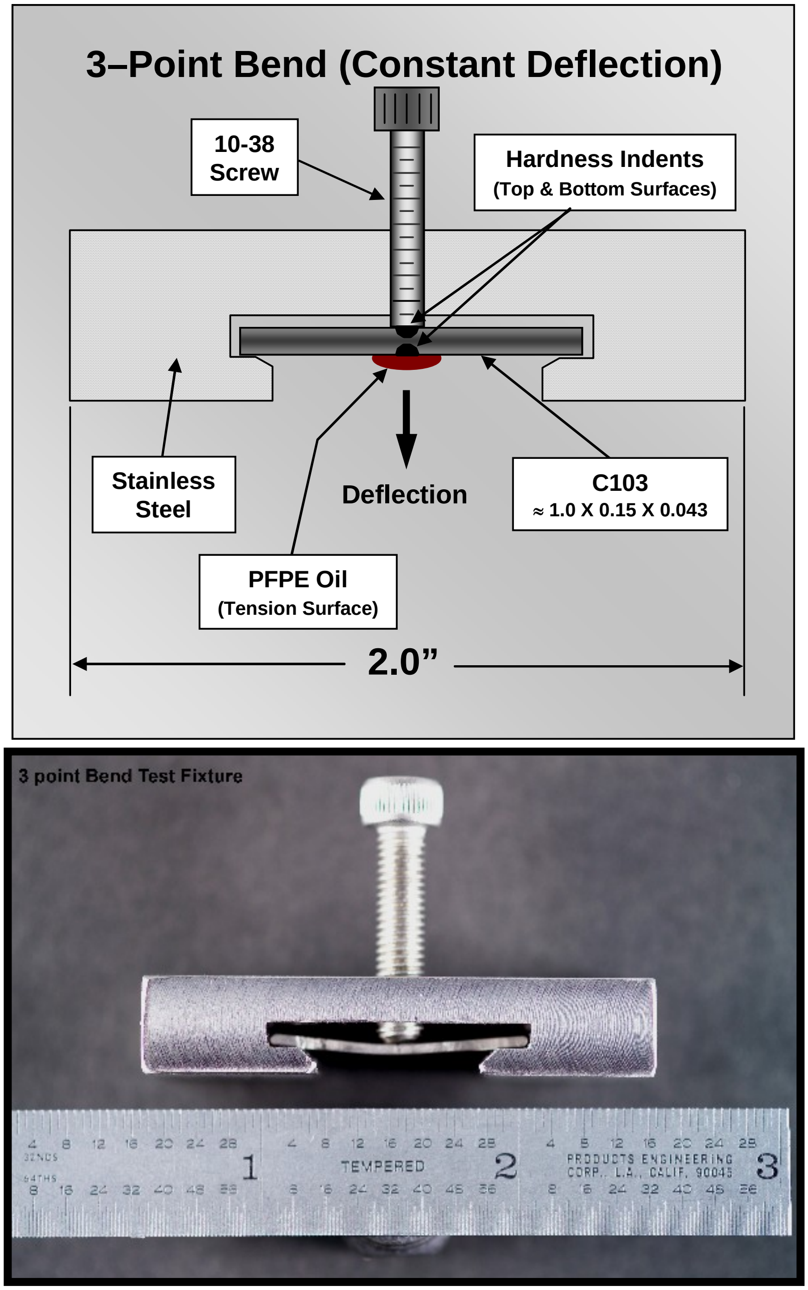


Figure 29 – Three-point bend fixture for Krytox/Brayco tests.

The test conditions and the application sequence for Krytox and Brayco testing are shown in Table 2. The second column refers to the intentional hardness indents that were placed in the specimens. Note that Specimen 30 did not have hardness indentations.

Table 2 – PFPE Exposure Tests
Sequence of Application of Test Conditions

Specimen #	C-103 Cantilever Beam Tests (Constant Load)						X = Cracks
13	Hardness	+ Ti cover	+ 40KSI	+ Krytox	+ 600°F	+ 48hrs	**X**
14	*See Table I*						
15	Hardness	+ Ti cover	+ 40KSI	+ Krytox	+ 400°F	+ 48hrs	
16	Hardness	+ Ti cover	+ 40KSI	+ Krytox	+ 500°F	+ 48hrs	X (minor)
17	Hardness	+ Ti cover	+ 40KSI	+ Krytox	+ 600°F	+ 96hrs	**X**
18	Hardness	+ Ti cover	+ 40KSI	+ Krytox	+ 600°F	+ 3hrs	**X**
Specimen #	**C-103 Three-Point-Bend Tests (Constant Deflection)**						
29	Hardness	+ no Ti	+ >45KSI	+ Krytox	+ 600°F	+ 1hrs	**X**
30	No indent	+ no Ti	+ >45KSI	+ Krytox	+ 600°F	+ 1hrs	
31	Hardness	+ no Ti	+ >45KSI	+ Brayco	+ 600°F	+ 1hrs	
Specimen #	**Cb752 Three-Point-Bend Tests (Constant Deflection)**						
32	Hardness	+ no Ti	+ >45KSI	+ Brayco	+ 600°F	+ 23 hrs	**X**

4.2 Krytox/Brayco Exposure Test Results and Discussion

Specimen 13 was clamped in the DMA test fixture with a titanium cover and loaded to 40 KSI. After a drop of Krytox was applied to the titanium/niobium interface, the specimen was heated to 600°F for 48 hours. After completing the exposure, the specimen was examined in the SEM. Cracks were present in all of the hardness indents as shown in Figure 30.

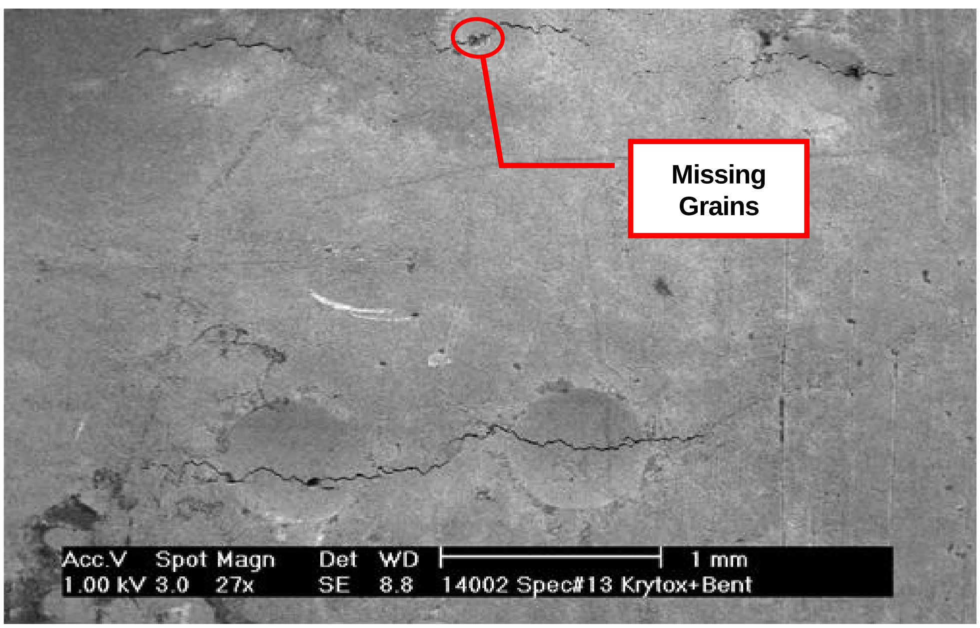


Figure 30 – Specimen 13 showing cracks in each of the hardness indents. Test conditions were 40 KSI + Ti cover + Krytox + 600°F + 48 hours. Magnification: 27x.

Crack propagation was obviously intergranular in nature as some grains were missing from the crack edges before the crack was even opened. The missing grains are shown in Figure 31. The popcorn features were present on the exterior surface as well as the grain faces as shown in Figure 32.

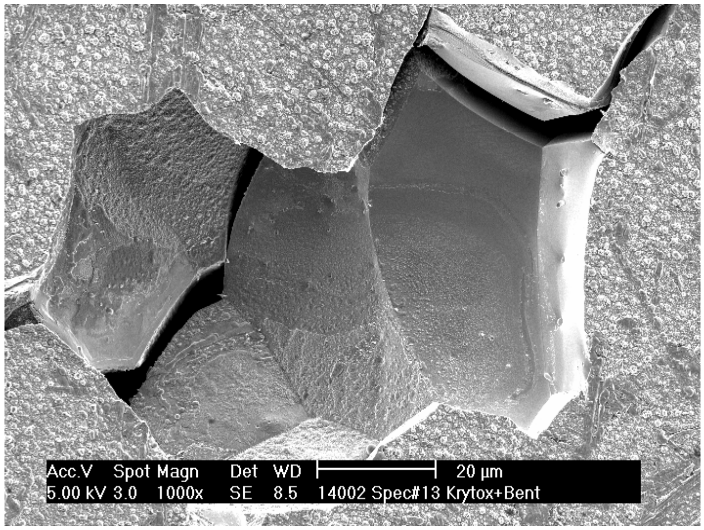


Figure 31 – Specimen 13 after Krytox exposure showing missing grains. The intergranular nature of the crack is emphasized. This area is macroscopically visible in the upper center indent in Figure 30. Note the thickness of the oxide film in upper right. Magnification: 1000x.

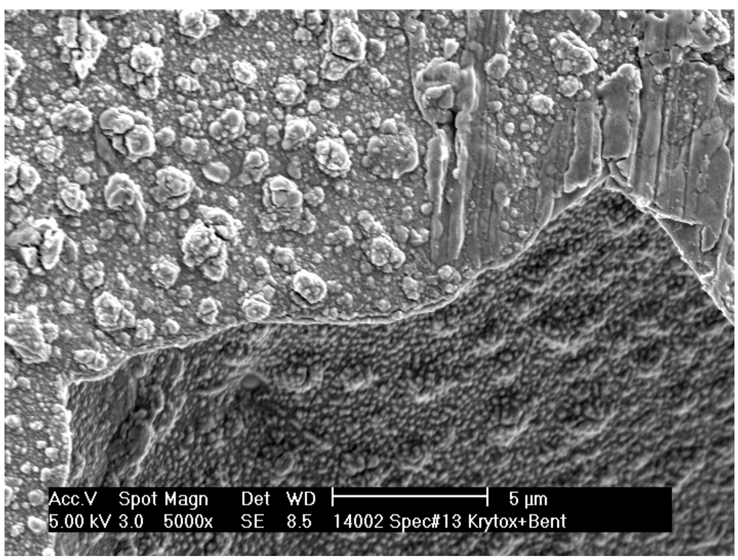


Figure 32 – Specimen 30 showing the missing grain area at higher magnification to resolve popcorn eruptions on exterior surface as well as on the grain boundary faces. Magnification: 5000x.

After opening the cracks, the 100-percent intergranular nature of the crack propagation was confirmed. The crack surface was dark gray to dark blue in appearance. An EDS analysis of a typical grain facet showed high oxygen and carbon peaks with a minor fluorine peak. The area analyzed is shown in Figure 33 and the analysis is shown in Figure 34.

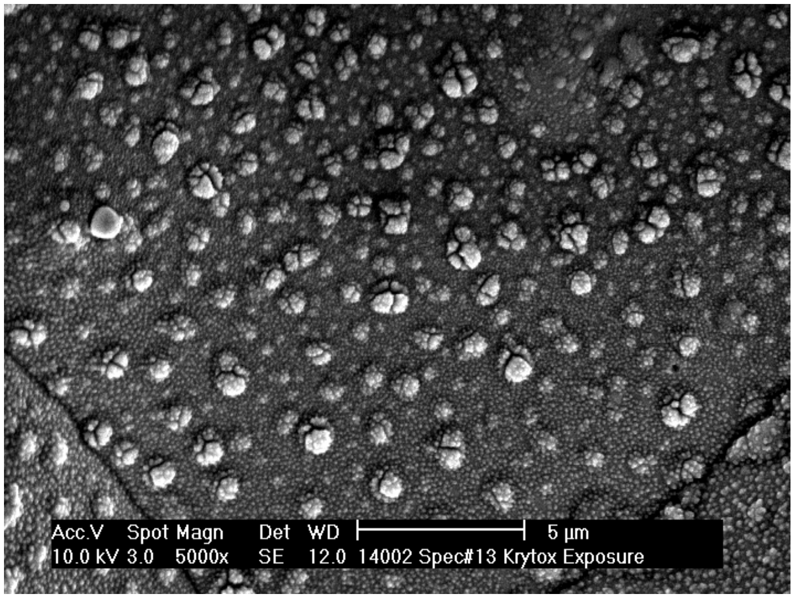


Figure 33 – Specimen 13 intergranular facet near crack origin showing popcorn-like features in the oxide film. The EDS analysis of this surface is shown in Figure 34. Magnification: 5000x.

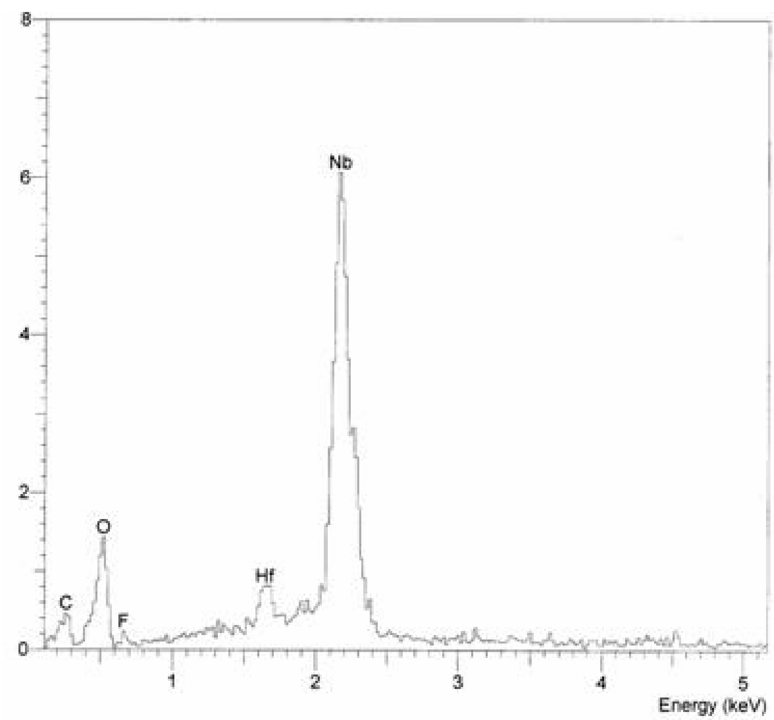


Figure 34 – Specimen 13 EDS analysis of popcorn features and surrounding area shown in Figure 33. Oxygen and carbon peaks are significant, but the fluorine peak is barely discernible.

The popcorn features on this fracture surface were very prominent. All of the same fracture characteristics were produced in this test as in the HF tests. This Krytox exposure also resulted in carbon showing up on the fracture surfaces, as was noted in the actual injector cracks. The occasion of carbon on the injector crack surfaces was neither accounted for nor explained in the earlier failure analyses. Krytox exposure as the cause of the cracking or post-cracking exposure to Krytox would certainly account for the presence of the carbon found on the injector crack surfaces.

Specimens 15 and 16 were tested at lower temperatures, Specimen 15 at 400°F for 48 hours and Specimen 16 at 500°F for 48 hours. The results were the same as occurred in the HF tests at lower temperatures. No cracking was found in the 400°F test specimen and only minor cracking was found in the 500°F test specimen. The appearance of the surface of the 400°F specimen is shown in Figure 35 and the EDS analysis of the test surface is shown in Figure 36.

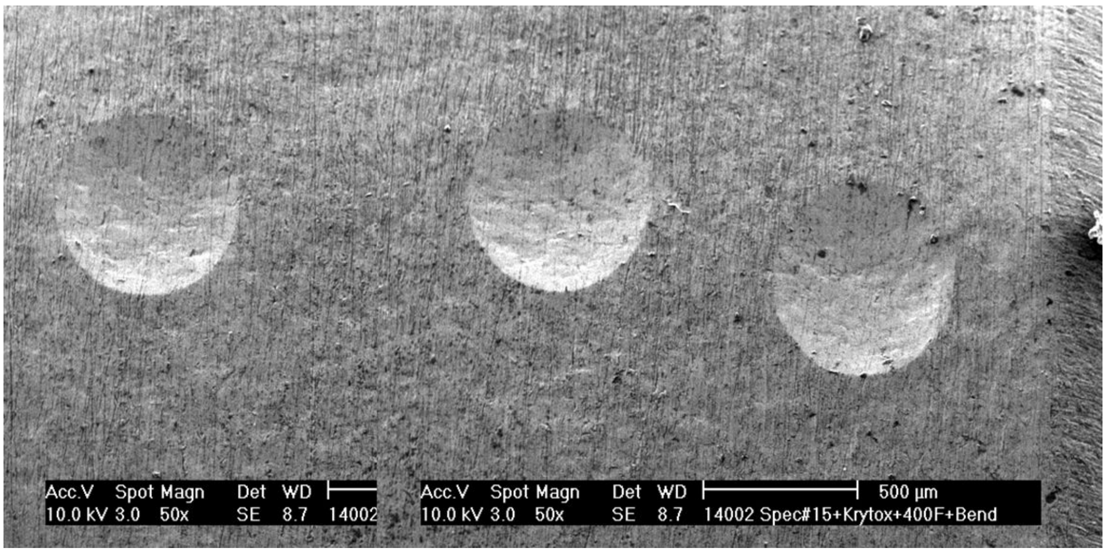


Figure 35 – Specimen 15 exposed to Krytox at 400°F for 48 hours showing no cracks are evident after bending. Magnification: 50x.

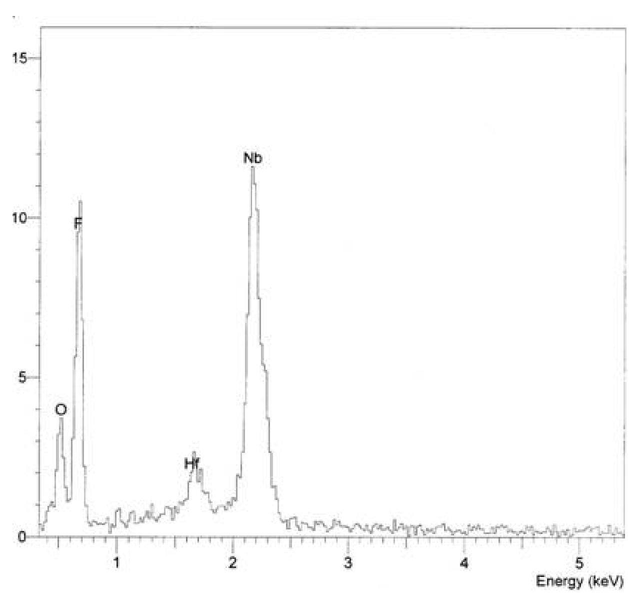


Figure 36 – EDS analysis of Specimen 15 between indents. The fluorine is very high after the 400°F exposure but decreases dramatically after the 600°F exposure as shown in Figure 34. Apparently, the fluorine is reacting and volatilizing in some manner.

It is interesting to note the very high carbon, oxygen, and fluorine content of the Krytox residue on the 400°F specimen surface. This composition probably compares to the composition of the Krytox before it decomposes or reacts with niobium at higher exposure temperatures. At higher temperatures, the fluorine in the surface films is always significantly reduced and in some cases barely detectable. This is illustrated by comparing the analyses in Figure 34 and Figure 36.

The minor cracking in Specimen 16 is shown in Figure 37. These two tests indicate a threshold temperature for cracking in Krytox somewhere between 400°F and 500°F. This is directly consistent with the results from the HF exposure tests, suggesting a common temperature threshold for cracking. Additionally, strong similarities in fracture morphology and surface chemistry between the HF and Krytox tests strongly suggest the same cracking mechanism is operating in the two fluids.

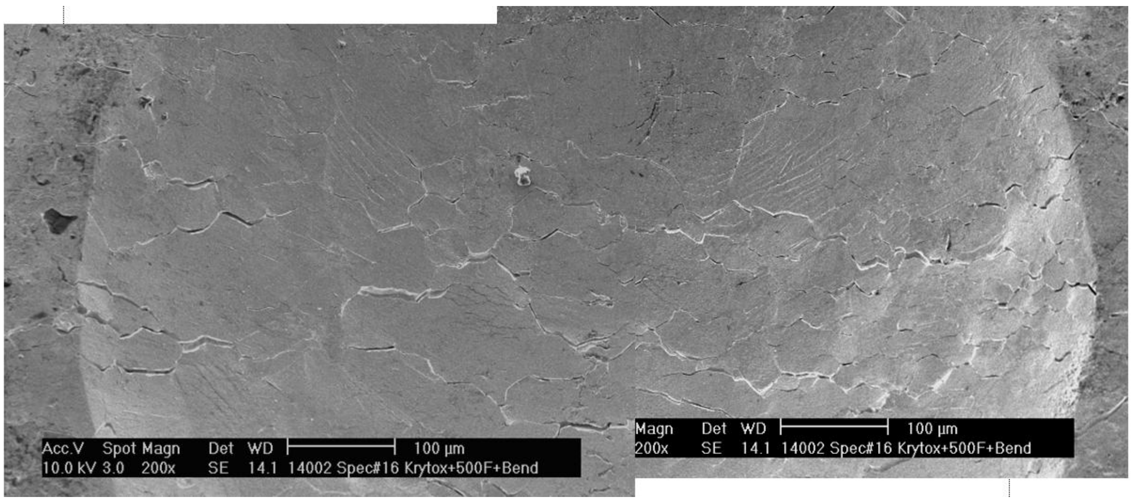


Figure 37 – Specimen 16 showing minor intergranular cracks in the hardness indent after the 500°F exposure and bending to open the cracks. Magnification: 200x.

Specimens 17 and 18 were tested at 600°F at different exposure times. Specimen 17 was exposed for 96 hours and Specimen 18 for 3 hours. Both specimens had significant cracking, but the 96-hour specimen had the most extensive cracking of any specimen tested to this point. The extent of cracking in these two specimens is compared in Figure 38 and Figure 39. Obviously, the cracking process begins early in the exposure as was also observed in the HF tests.

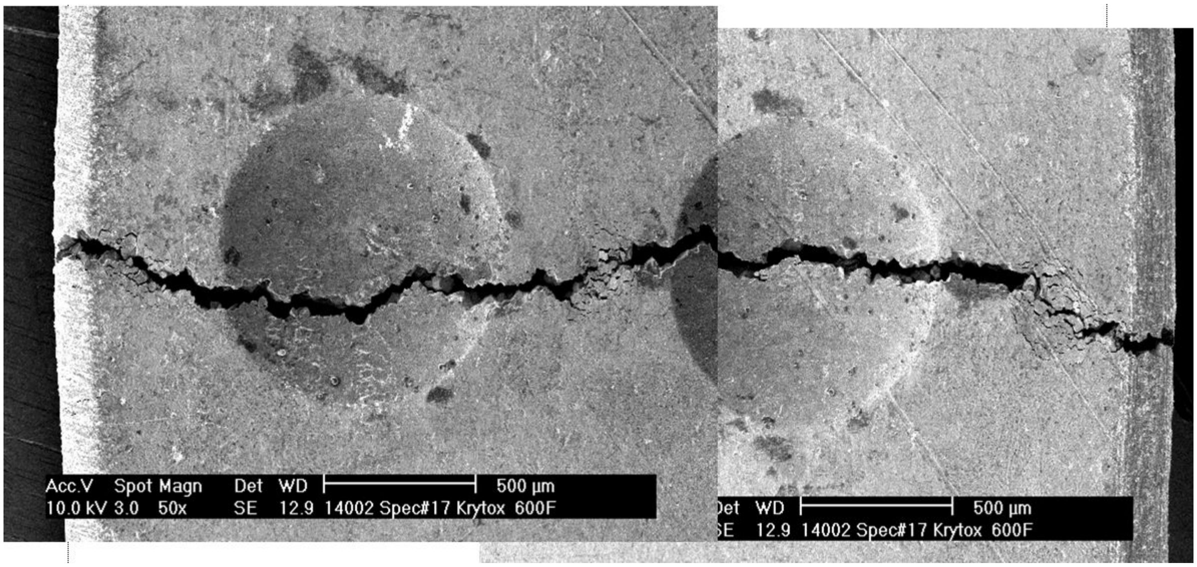


Figure 38 – Specimen 17 showing extensive cracking after 96-hour exposure. Note surface dimpling where crack tips intersected. The crack propagated through the entire thickness in an intergranular manner. Magnification: 50x.

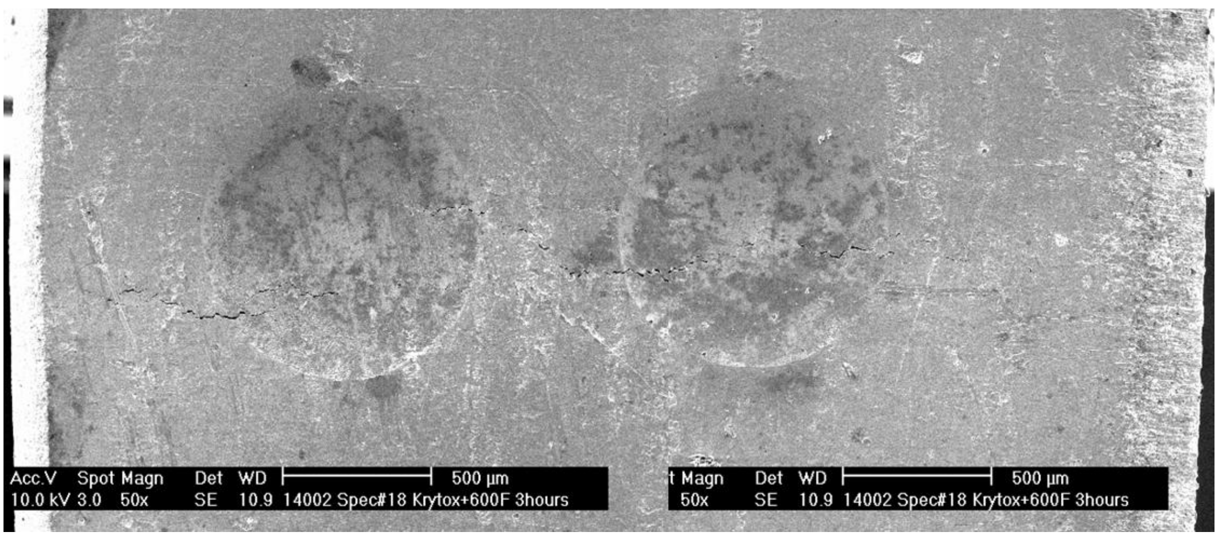


Figure 39 – Specimen 18 showing cracks after exposure to Krytox at 600°F for 3 hours. This illustrates that cracking began early in the exposure. Magnification: 50x.

<u>Specimens 29 and 30</u> were tested in the three-point bend fixture (constant displacement) at a stress level that was just above the yield strength (≈45 KSI for C103). The purpose of these tests was to see if the loading arrangements of constant load versus constant deflection affected the cracking. In addition, the need for indentations was tested with this new loading arrangement where the test surface was taken beyond yield. Since several of the load-deflection plots from the DMA tests had shown that cracking had initiated very early in the exposure, the time of these tests were shortened to 1 hour. The results were quite stunning: Specimen 29 with hardness indentations was cracked all the way through the thickness of the specimen. Upon removal from the oven, the specimen actually fell out of the fixture. Examination in the SEM showed the fracture surface had all of the same characteristics as previous cracked specimens – 100-percent intergranular crack propagation, dark discoloration of the fracture surface, lots of popcorn features, and similar surface chemistry (oxygen, fluorine, and in this case carbon). By contrast, Specimen 30 without any hardness indentations was not cracked at all. These tests showed rather dramatically that the cracking process can occur very rapidly and that indentations or mechanical deformation of the

surface is a very necessary condition for this cracking to occur. As mentioned previously, the titanium cover was probably not needed in the Krytox tests. Specimen 29 was a dramatic demonstration that titanium has no role in this cracking process. It should also be mentioned here that without the titanium cover, there is also no crevice, alleviating another concern that a crevice and possibly crevice corrosion has a role in this cracking process.

Specimen 31 with hardness indents was exposed to a different fluorinated synthetic oil called Brayco 815Z (Fomblin Z). This test was conducted exactly as was Specimen 29; i.e., loaded slightly above yield in the three-point bend fixture at 600°F for 1 hour. No cracking was observed in this specimen, raising questions as to whether or not all fluorinated fluids will cause cracking in niobium under similar environmental conditions. Fomblin Z, a straight-chain PFPE polymer, in theory should decompose at a lower temperature threshold (lower activation energy) than Krytox, a branched PFPE polymer. This suggests that Fomblin oil should be more reactive with niobium than Krytox, potentially resulting in a more readily available cracking mechanism. This test experiment was not duplicated to validate the results. Additional testing with another niobium alloy (Cb752 – Specimen 32) was completed to pursue further the effects of Fomblin Z on niobium.

Specimen 32 was prepared to further pursue the effects of Fomblin Z on niobium, although this specimen used Cb752 with a composition of 10 percent tungsten, 2.5 percent zirconium, and balance niobium instead of C103 (1 percent titanium, 10 percent hafnium, and balance niobium). This material was chosen as a substitute due to the immediate availability for testing (the C103 material on hand had been depleted). This test specimen was prepared and tested in exactly the same fashion as Specimen 31 except that the 1-hour, 600°F exposure period was extended to 23 hours. This resulted in complete cracking of the test specimen in exactly the same fashion as the previous C103 specimens, which were exposed to Krytox (i.e., Specimen 29). Testing with both Fomblin Z and Krytox materials at lower isothermal and stress thresholds should be pursued to gain additional understanding.

4.3 Other Testing

Several other Krytox exposure tests were conducted in the three-point bend fixture with Cb752. These tests produced the same result as the C103 coupons; i.e., the Cb752 specimens cracked in an intergranular manner, all the way through the thickness, upon exposure to 600°F (this occurred in 1 hour for the case of Krytox). This result strongly suggests that the cracking mechanism is related only to niobium and not to any of the major alloying elements such as the hafnium in C103.

These last several tests do not bear directly on the S/N 120 cracking, but they do raise interesting questions with regard to the larger issue of fluorine-containing fluids and their ability to crack niobium, and they generically substantiate the sensitivity of niobium alloys to fluorine exposure at elevated temperatures.

5.0 DISCUSSION OF TEST PROGRAM RESULTS

The JSC tests have reproduced the injector cracking to the extent that can be expected in a laboratory reproduction. The fracture characteristics that have been reproduced include the 100-percent intergranular mode of crack propagation, matching fracture surface chemistry, fracture surface morphology, and fracture discoloration.

Because of this laboratory test program, specific conditions necessary to cause cracking in niobium have been explicitly established and bounded. Each of the following conditions is necessary in combination:

1. A mechanically disturbed/cold-worked free surface (plastic deformation from machining, handling, fastener installation, etc.)
2. An externally applied sustained tensile stress near yield strength
3. Presence of fluorine-containing fluids on exposed tensile/cold-worked free surfaces
4. Sustained exposure to temperatures *greater than* 400°F

5.1 Mechanically Disturbed Surface/Sustained Tensile Stress

A significant finding of the JSC tests was that a mechanically disturbed surface was needed for cracking to occur. When other investigators resorted to indenting their test specimens, they also reproduced the cracking (Refs. 9 and 10). Externally applied stresses, either by constant load cantilever bending just below yield or by constant deflection three-point bending just above yield, were not sufficient to cause significant cracking by itself. Adding hardness indentations to either of these load cases promoted cracking. The residual stresses from the hardness indentation in combination with the externally applied stresses results in stresses considerably beyond the yield strength of the C103 material.

The relationship of the test specimens' mechanically disturbed surfaces to the injector cracking is observed by the rough-machined appearance of S/N 120 relief radius and counter bore surfaces. A stereoscopic examination revealed galling and smearing of the metal that was extreme along the entire relief radius and particularly at the top of the counter bore surfaces where the counter bore cracks seemed to originate. Examples of the rough machined surfaces were shown in Figure 4 (relief radius) and Figure 5 (counter bore). Although not proof, the rough appearance suggests that these surfaces were heavily disturbed by machining processes and therefore were much like the hardness-indented test specimens (i.e., susceptible to cracking). Some evidence of the surface deformation due to machining was presented in the Boeing failure analysis report (Ref. 11), where a metallurgical cross section showed a compressed microstructure along the edges of the relief radius and the acoustic cavities. The extent to which thrusters in the field have such rough-machined surfaces is not well characterized.

All testing in this evaluation was completed slightly below or above the tensile yield strength of the material (the allowable yield strength of C103 = 35 KSI, actual ≈ 45 KSI). This stress level was initially established as a conservative baseline, with the intention to complete follow-on testing at lower stress levels once the cracking mechanism had been reproduced. There was significant debate about how much stress could be generated at either or both the relief radius and counter bore locations. Upon demonstrating that both sustained tensile stresses near yield and mechanical surface damage were required to produce cracking, stresses from flange assembly were further investigated by detailed stress analysis (Aerojet Corporation). It was subsequently determined that the slight out-of-flatness condition of the niobium flange interface was sufficient to generate this significant level of stress during assembly/bolt-up with the titanium flange.

5.2 Exposure to Fluorine-Containing Fluids

These tests have conclusively shown that three different fluorine-containing fluids can cause niobium cracking at elevated temperatures (HF, Krytox, and Brayco 815Z). Both HF and Krytox were used in the manufacture of the RCS thruster hardware. It should be emphasized here that the similarities between cracks produced from HF etchant and from Krytox exposure (particularly that both fluids show the same temperature threshold) suggest that the same basic cracking mechanism is operating in both fluids. The obvious commonality between the three fluids is their high fluorine content.

5.3 Sustained Exposure to Elevated Temperatures

These tests have also shown that even though contact with fluorine poses a threat to the niobium injector, a temperature threshold must also be exceeded for cracking to occur. The temperature threshold established by the JSC tests is greater than 400°F (most likely ≥ 450°F), although temperatures approaching 600°F are required to produce cracking of significant depth. This temperature threshold is significantly higher than nominal injector operation temperatures. Injector temperatures higher than the threshold would be very unusual and of short duration (off-nominal). In other words, it is very unlikely that this cracking mechanism could affect thrusters in service since they would rarely, if ever, experience temperatures above 400°F.

5.4 Other Test Results

The constant load coupon test method is considered a very severe test compared to the expected constant deflection load that the thruster cracks experience from the fit-up mismatch of the mounting flanges. In a constant load test, the stress intensity increases as the crack front propagates, providing an increasing driving force for additional cracking. This is extremely conservative as compared to the constant displacement experienced by the RCS thruster niobium materials in service, which experience a decrease in stress intensity as the crack propagates (tending to crack arrest).

The results from the constant load testing show that the cracking mechanism is limited by the availability of the cracking species. These test results indicate that cracking began early, yet the cracks in most cases did not go to failure as would be expected with increasing stress intensity. Since cracking was observed to have initiated in the first hour of the high-temperature exposure, 48 hours would have been enough time for the cracking to go to completion, resulting in complete separation of the specimen. The likely explanation for the crack arrest is that the offending species were depleted in the cracking process (during exposure to elevated temperatures). This finding is supportive of the Boeing failure analysis conclusion that the thruster cracking is a one-time event that occurred during the insulation bake-out. Since no additional crack growth was found beyond that which occurred in the bake-out, it was likely because the cracking species were consumed or used up, as was demonstrated in these tests.

When cracks generated from HF etchant were exposed to a water drip environment at room temperature under constant load, no evidence of additional crack growth was evident. This indicates that the KSC high-humidity environment will not cause cracks to propagate in the flight thrusters during ground processing. The humidity-controlled thruster environment at KSC further reduces the threat of any possible crack growth from moisture.

Statements in the original Marquardt CAR implied that an interaction between niobium and titanium (e.g., the galvanic couple and/or a crevice condition) was a necessary condition of the cracking process (this was established in their original crack reproduction test program). The JSC tests show that this was not the case. When a C103 niobium cover was substituted for the titanium cover in the HF exposure test, cracking still occurred. When the titanium cover was eliminated altogether in the three-point bend Krytox tests, cracking also occurred. Eliminating the titanium altogether in the Krytox tests also eliminated the crevice. The JSC tests show that the cracking process proceeds without galvanic action or crevice corrosion processes.

6.0 DISCUSSION OF ROOT CAUSE AND CRACKING MECHANISMS

From a programmatic viewpoint, it is sufficient to know that the root cause of the thruster cracking was the combined exposure of RCS thruster hardware to fluorine-containing fluids at elevated temperatures (temperatures beyond those expected in service).

From a scientific viewpoint, a more fundamental understanding of the cracking process is desirable. For future NASA programs that use niobium and for the technical community in general, it is important to understand the niobium-fluorine cracking problem to a reasonable extent and to determine if this cracking mechanism affects other niobium alloys or metal systems. This test program stopped short of establishing a specific root cause cracking mechanism, but did establish the engineering boundaries and operational guidelines required to continue successful and safe use of the RCS thrusters.

The subject of environmentally assisted cracking is extremely complex. This work will not attempt to summarize the many cracking mechanisms that have been proposed over the years. No brief review here in a few short paragraphs could do justice to or encompass the enormous amount of work and research that has been completed in this field. For example, for stress corrosion cracking, a recent review (Ref. 12) categorizes the crack propagation mechanisms into two classifications: dissolution models and mechanical fracture models. The dissolution classification is further divided into the widely accepted film-rupture model and, to a lesser extent, the active-path intergranular stress corrosion cracking model. The mechanical fracture classification is also further divided into ductile and brittle fracture models. The ductile models include the corrosion tunnel and the tarnish rupture models while the brittle models include the film-induced cleavage and the adsorption-induced brittle fracture models.

The stress corrosion cracking mechanisms alone are complex, not to mention all of the other brittle cracking mechanisms such as hydrogen embrittlement, oxygen embrittlement, dynamic embrittlement, etc., and their many models. None of these mechanisms has been proven in this case, although hydrogen embrittlement is considered the most probable candidate. Hydrogen availability is assured in the case of the HF etchant, but is not straightforward in the case of either Krytox or Brayco (there is no hydrogen in the PFPE base oil molecule). One theory suggests that Lewis Acid catalyzed decomposition of Fomblin/ Krytox oil (Ref. 13) may produce free hydrogen with the addition of water. However, discussions with PFPE experts at DuPont Corporation revealed that nominal water concentrations in Krytox oil at room temperature are less than 10 ppm (Ref. 14). Thus, the presence of sufficient water at temperatures above 400°F is not likely. During this investigation, considerable effort by others has been invested in attempting to reproduce the injector cracks directly by exposing niobium materials to classic hydrogen embrittlement methods. The niobium was embrittled (by electrochemical methods) via hydrogen uptake in many of the tests, but the injector fracture characteristics were never duplicated (transgranular cleavage was produced vs. intergranular fracture).

The JSC tests did not provide specificity for any particular cracking mechanism, and none can be suggested here (any of the above mechanisms could be operating). Conjectures, opinions, declarations, etc. have been put forward during the S/N 120 investigation, but no proof has been forthcoming regarding any of the potential cracking mechanisms. Considerable additional work will be required to prove exactly which mechanism is operational. A significant test and analysis effort remains to identify conclusively the specific mechanism responsible for the thruster cracking.

In the end, the test results substantiate the fact that the observed thruster cracking in C103 occurs only under the influence of the four conditions outlined above. For the RCS thruster application, it is not necessary to know which fluid caused the cracks or to understand fully the specific cracking mechanism at work, but rather that fluorine needs to be kept away from the niobium during processing and that existing cracks will not grow appreciably in service due to environmentally assisted cracking mechanisms. An action to eliminate the root cause of the thruster cracking was taken 23 years ago when the HF etchants were removed from all thruster-manufacturing processes. Based upon knowledge at the time, Krytox was not eliminated; thus, the root cause effect remained through the end of the thruster manufacturing cycle. The use of Krytox has continued through to the current thruster refurbishment processing cycle. Obviously, any and all fluorine-containing fluids (HF, Krytox, Brayco, etc.) must be eliminated from future refurbishment processing of thruster materials at WSTF and the Kennedy Space Center (KSC).

7.0 CONCLUSIONS

The JSC tests have been instrumental in providing the basis for a number of important conclusions regarding the injector cracking and the associated space shuttle orbiter flight rationale.

7.1 Flight Rationale Conclusions Derived from the JSC Tests

- The test program successfully reproduced the thruster cracks in the laboratory.
- The test program explicitly established and bounded the conditions necessary to cause cracking in C103. Each of the following conditions is necessary in combination:
    1. A mechanically disturbed/cold-worked free surface (plastic deformation from machining, handling, fastener installation, etc.)
    2. An externally applied sustained tensile stress near yield strength
    3. Presence of fluorine-containing fluids on exposed tensile/cold-worked free surfaces

4. Sustained exposure to temperatures *greater than* 400°F

- The thruster cracking occurred during ground processing due to exposure of the flight hardware to the combined environments listed above. In this case, the four listed conditions only occur in combination together during ground processing. (Here, the fluorine-containing fluids were HF/Krytox acting either independently or collectively.)
- Since nominal RCS injector temperatures do not exceed 400°F, the tendency for existing cracks in the thrusters to grow in service is very small (even during sustained exposure to conditions 1–3)

These conclusions were included in flight rationale, which justified the continued safe flight of the RCS thruster system on as-installed orbiter hardware. No additional inspection for cracking on existing hardware was deemed necessary.

7.2 Other Important Conclusions Derived from the JSC Tests

- Cracks will arrest when the cracking species are depleted or consumed in the reaction products.
- Exposure to moisture at room temperature does not propagate the cracks.
- The titanium-niobium galvanic couple is not a factor in the injector cracking.
- Crevice corrosion conditions are not necessary to produce injector cracking.
- Results strongly suggest that the same cracking mechanism is operating in the HF etchant, Krytox, and Brayco 815Z.
- WSTF and KSC need to control/eliminate the use of any fluorine-containing fluids that are being used during processing.
- The test program did not specifically identify the actual cracking mechanism.

8.0 FOLLOW-ON WORK

The JSC tests have raised many questions with regard to cracking of niobium in the presence of fluorine-containing fluids and elevated temperatures. The next-generation spacecraft will use the shuttle experience in developing new thrusters and will continue with niobium injectors. With this in mind, it would be beneficial and essential to develop a better understanding of this cracking problem. The wider technical community and other users of niobium would also benefit from a more fundamental understanding of this problem. Some of the questions that these tests have raised as areas needing further work are listed below.

1. Are all niobium alloys susceptible?
2. Are similar metals in the periodic table susceptible such as tantalum?
3. What are the exact stress and temperature thresholds?
4. Does cracking occur in inert gas or vacuum?
5. What embrittling species are released from HF, Krytox, and Brayco?
6. Can the specific crack-driving mechanism be explicitly established and substantiated?

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.			
1. AGENCY USE ONLY *(Leave Blank)*	2. REPORT DATE March 2007	3. REPORT TYPE AND DATES COVERED NASA Technical Paper	
4. TITLE AND SUBTITLE JSC Material Laboratory Reproductin and Failure Analysis of Cracked Orbiter Reaction Control System			5. FUNDING NUMBERS
6. AUTHOR(S) Jeremy B. Jacobs, William L. Castner			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Lyndon B. Johnson Space Center			8. PERFORMING ORGANIZATION REPORT NUMBERS S-991
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) 1National Aeronautics and Space Administration Washington, DC 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER TP-2007-213733
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified/Unlimited Available from the NASA Center for AeroSpace Information (CASI) 7115 Standard Hanover, MD 21076-1320 Category: 18			12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

In April 2004, the Space Shuttle Orbiter Reaction Control System (RCS) thruster serial number (S/N) 120's injector was found to be cracked while undergoing a nozzle retrofit at the White Sands Test Facility (WSTF). The RCS is composed of safety-critical propulsion hardware elements used to control the attitude of the space shuttle orbiter during virtually all operational mission phases. Since a failure resulting from an RCS thruster burn-through (initiated from a crack) could be catastrophic, an official flight constraint was issued until flight safety could be adequately demonstrated.

One recommendation was to reproduce the cracking in the laboratory to understand fully the driving environments.

The Johnson Space Center (JSC) Materials & Processes (M&P) Branch initiated an effort starting in January 2005 to reproduce the cracking in the niobium injector. The results were successful. The specific conditions necessary to cause cracking were explicitly established and bounded. Each of the following conditions is necessary in combination:

1. A mechanically disturbed/cold-worked free surface (plastic deformation from machining, handling, fastener installation, etc.)
2. An externally applied sustained tensile stress near yield strength
3. Presence of fluorine-containing fluids on exposed tensile/cold-worked free surfaces
4. Sustained exposure to temperatures greater than 400°F

14. SUBJECT TERMS	15. NUMBER OF PAGES	16. PRICE CODE
Materials, fractures, tests, reaction control	48	

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unlimited	Unlimited

Standard Form 298 (Rev Feb 89) (MS Word Mar 97) NSN 7540-01-280-5500
Prescribed by ANSI Std. 239-18
298-102