Report No. 5005.0005 **August 15, 2014**

EXAMINATION OF A 0.75-INCH DIAMETER STAINLESS STEEL TUBE COMPRESSION JOINT INVOLVED IN THE TESORO MARTINEZ ACID SPILL THAT BURNED TWO WORKERS ON FEBRUARY 12, 2014

Customer Authorization: Requisition Number CSB-1I25-14-0020

Report To: U. S. Chemical Safety Board
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1.0 INTRODUCTION

The 0.75-inch diameter stainless steel tube assembly that was involved in the Tesoro Golden Eagle Refinery acid spill that burned two workers on February 12, 2014 was submitted by Cal OSHA, the CSB, and the Tesoro Refining and Marketing Company for laboratory examination. It was reported that the assembly was part of a sulfuric acid sampling station that was being pressurized at the time of the incident. Representatives from each party were present on April 9, 2014 for the majority of the work reported here. Sample sectioning, scanning electron microscopy, and dimensional measurements were performed at a later date. The objective of this evaluation was to determine the likely immediate physical cause of the acid spill.

The sample was evaluated by the following laboratory procedures:

1) Visual and macroscopic examination
2) Scanning electron microscopy and energy dispersive X-ray spectroscopy

Based on the results of this evaluation, the immediate physical cause of the acid spill was insufficient clamping force between the tube and a compression union. Semi-quantitative chemical analysis indicated the tube, ferrule, union, and compression nut were made of Type 316 stainless steel.

2.0 EVALUATION

2.1 Visual Examination

The subject is shown as-received in Figure 1 and Figure 2. The assembly consisted of several sections of 0.75-inch diameter tube joined by compression fittings, an NPT tee with NPT to compression fittings, and a ball valve joined to one side of the tee. White colored friable deposits were present on the subject, with the greatest accumulation on the tee. It was reported that the spill occurred at the compression union indicated by the boxed area in Figure 1, referred to in this report as the subject joint, and all of the following descriptions and observations relate to the subject joint. Photographs of the subject joint in the as-received condition are shown in Figure 2. The end of the subject tube that had been connected by the union was relatively free of white deposits, and there was no evidence of fracture on the tube end, or parts of the subject tube remaining in the union. Consequently, the subject tube had pulled out of the union.

Wrenches were used to disconnect the subject union from the remainder of the assembly opposite the subject tube, and the compression nut was found to be tight. Surfaces of the opposite union and ferrule were bright, as shown in Figure 3a, consistent with a good connection. The union was rinsed in tap water, which readily removed the white deposits. As shown in Figure 3b, a ferrule was present in the union on the subject side. The subject compression nut was disconnected from the union, and the subject ferrule was found to have the correct orientation with respect to the union. A narrow band of bright metal on the outside surface of the ferrule and a similar band on the inside surface of the union, shown in Figure 4 and Figure 5a, indicated that there had been contact between the two sealing surfaces. No evidence of cracks or mechanical damage of the union, ferrule, or compression nut was detected.

The subject ferrule is shown in Figure 6. The outside surface was covered with a smooth, greenish colored oxide layer, except for the bright area of contact noted previously. A step in the inside diameter of the ferrule was noted. Corrosion was evident on the inside surface of the ferrule, as shown in Figure 7.

The end of the subject tube that had been inserted into the joint is shown in Figure 8. The end had geometry consistent with that formed by rotary tube cutters. In general, the outside surface of the tube had matte texture. Isolated, fine, longitudinal witness marks indicated axial sliding contact with the outside surface of the tube, consistent with pull out from the union. A circumferential band of etched metal, noted in Figure 8b, correlated to the step on the inside surface of the ferrule. The step likely formed a crevice and associated accelerated corrosion of the tube outside surface.

The subject tube was sectioned to remove the subject end and the opposite end. The inside diameter of the subject end was uniform from the cut face past the location of the compression nut. In contrast, the inside diameter of the opposite end was constricted in the vicinity of the ferrule, as shown in Figure 9. An exemplar tube assembly had been submitted for comparison to the subject. The inside diameter of the exemplar tube ends were constricted like the opposite end of the subject tube, as shown in Figure 10 and Figure 11. Inside diameters of the subject end, opposite end and exemplar tubes were measured using a snap gage and micrometer. The results are listed in Table 1. Lack of inside diameter constriction of the subject end indicated that the ferrule had not been completely crimped onto the tube.

2.2 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

The ferrule, subject end of the tube, and union were examined using a scanning electron microscope (SEM) and analyzed by energy dispersive X-ray spectroscopy[1] (EDS).

[1] The EDS analysis method used here detects the presence of elements from boron (B) to uranium (U), atomic numbers from 5 to 92 in the periodic table. EDS data alone are, however, insufficient to differentiate chemical compounds such as oxides, hydroxides, or carbonates or to characterize organic materials that consist of carbon (C), hydrogen (H), and nitrogen (N) only.

Representative SEM micrographs are shown in Figure 12 through Figure 16. The surface morphologies confirmed corrosion was active between the ferrule and the tube, consistent with insufficient mechanical seal. As shown in Figure 13, fine axial witness marks were caused by axial sliding contact. Likewise, the morphology shown in Figure 16 confirmed contact between the inside surface of the union and the outside surface of the ferrule.

Small areas on the subject tube, ferrule, union, and compression nut were ground flat with 400-grit silicon carbide paper and analyzed by semi-quantitative EDS. The results, listed in Table 2, were consistent with Type 316 stainless steel. As shown in Figure 5b and Figure 6a, the union and ferrule were stamped P316, a common designation for Type 316 stainless steel.

3.0 DISCUSSION

The physical condition of the subject tube end indicates that the tube pulled out of the compression joint. Corrosion between the subject tube and the ferrule indicated a lack of physical seal, and absence of tube inside diameter constriction indicated insufficient clamping force between the tube and the ferrule. Evidence of contact between the subject ferrule and the mating surface of the union suggests that enough clamping force to prevent leakage and immediate failure of the joint may have existed when the assembly was placed in service. However, insufficient clamping force was generated to crimp the ferrule onto the tube and produce a constriction of the tube inside diameter. A poor seal between the subject ferrule and tube allowed corrosion between the ferrule and tubing surfaces within the subject joint.

It was reported that the subject union was made by Parker. A product sheet obtained from the Parker website is shown in the Appendix. The subject union was consistent with Parker CPI single ferrule tube fittings. Parker installation instructions indicate the compression nut should be tightened 1 ¼ turns past finger tight.

Semi-quantitative chemical analysis, listed in Table 2, indicated the nickel concentration of the ferrule and union were slightly lower than the minimum for Type 316 stainless steel. However, the typical accuracy of EDS semi-quantitative analysis is around 0.5 to 1.0-wt%. Therefore, the results are consistent with Type 316 stainless steel. Much better accuracy could be obtained by quantitative analysis using other techniques, but the entire ferrule, much of the union, and a section of the tube would have been destroyed in the analysis. Because the semi-quantitative results were consistent with Type 316 stainless steel and none of the evidence indicated unusually aggressive corrosion or other degradation that could be attributed to small variations in chemical composition, quantitative chemical analysis was not performed.

4.0 CONCLUSIONS[2]

The following conclusions are based upon the submitted samples and the evidence gathered:

1. The immediate physical cause of the acid spill was insufficient clamping force between the tube and a compression union, which allowed the tube to be forced from the union, probably by internal pressure.

2. Semi-quantitative chemical analysis indicated the tube, ferrule, union, and compression nut were made of Type 316 stainless steel.

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[2] The conclusions in this report are based upon the available information and evidence provided by the client and gathered by Anamet, within the scope of work authorized by the client, and they are hereby presented by Anamet to a reasonable degree of engineering and scientific certainty. Anamet reserves the right to amend or supplement its conclusions or opinions presented in this report should additional data or information become available, or further work be approved by the client.

Table 1
Tube Inside Diameter, Average of Four Measurements

	Subject Tube Subject End (inches)	Subject Tube Opposite End (inches)	Exemplar Tube End 1 (inches)	Exemplar Tube End 2 (inches)
Uniform Diameter	0.655	0.655	0.613	0.614
Constricted Diameter	NA	0.596	0.587	0.587
Delta	NA	0.059	0.026	0.027

NA = Not Applicable

Table 2
Results of Semi-Quantitative Analysis by Energy Dispersive X-Ray Spectroscopy

Element		Tube (wt%)	Ferrule (wt%)	Union (wt%)	Nut (wt%)	Type 316 Stainless Steel (UNS S3160)	
						min	max
Carbon	(C)	ND	ND	ND	ND	-.-	0.08
Chromium	(Cr)	17.57	17.55	17.40	17.37	16.00	18.00
Iron	(Fe)	67.02	68.30	68.51	68.11	Major Constituent	
Manganese	(Mn)	1.83	1.44	1.40	1.67	-.-	2.00
Molybdenum	(Mo)	2.21	2.40	2.14	2.13	2.00	3.00
Nickel	(Ni)	10.78	<u>9.62</u>	<u>9.72</u>	10.06	10.00	14.00
Phosphorous	(P)	ND	ND	ND	ND	-.-	0.045
Sulfur	(S)	ND	ND	ND	ND	-.-	0.030
Silicon	(Si)	0.59	0.69	0.83	0.66	-.-	1.00

ND = None detected

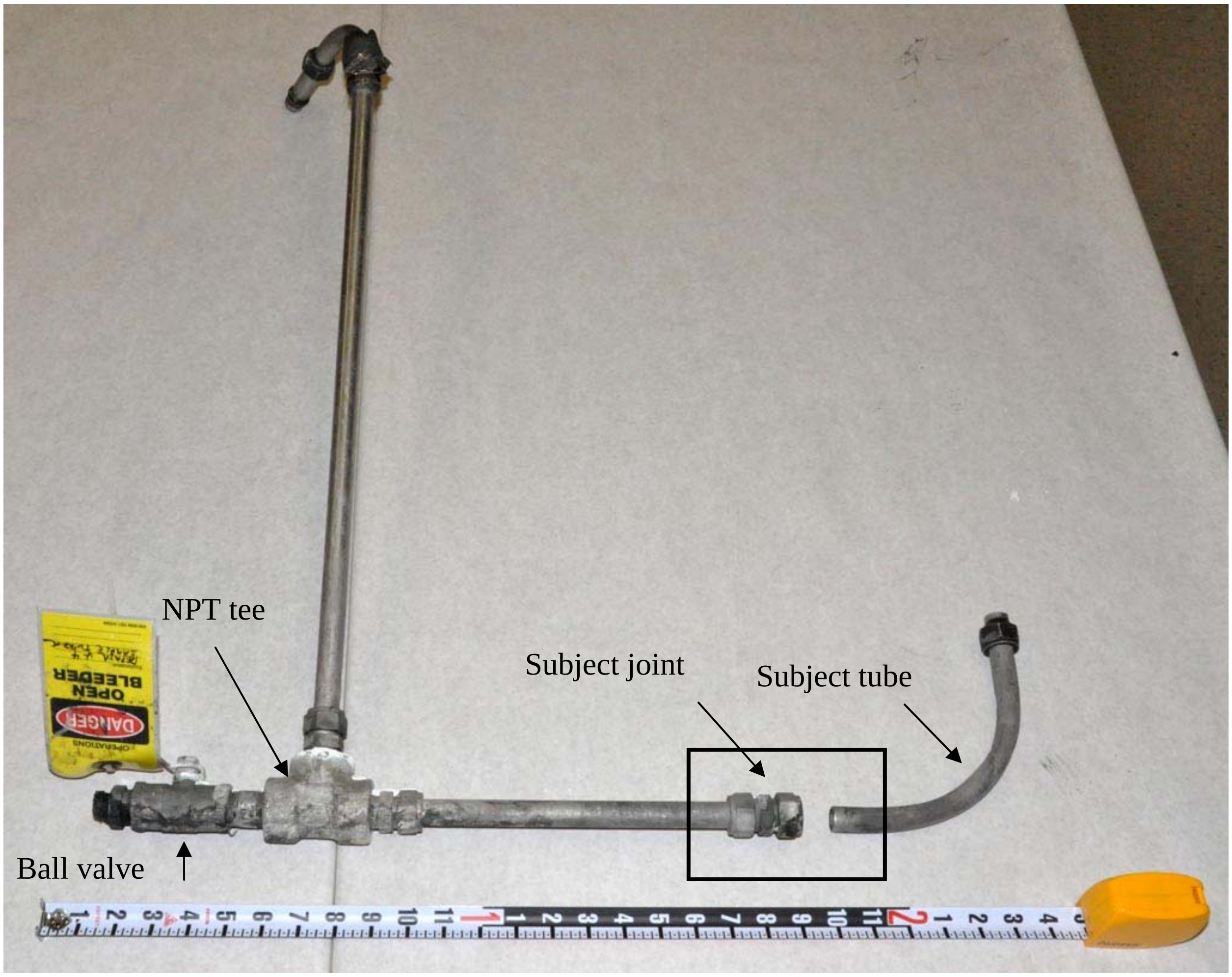
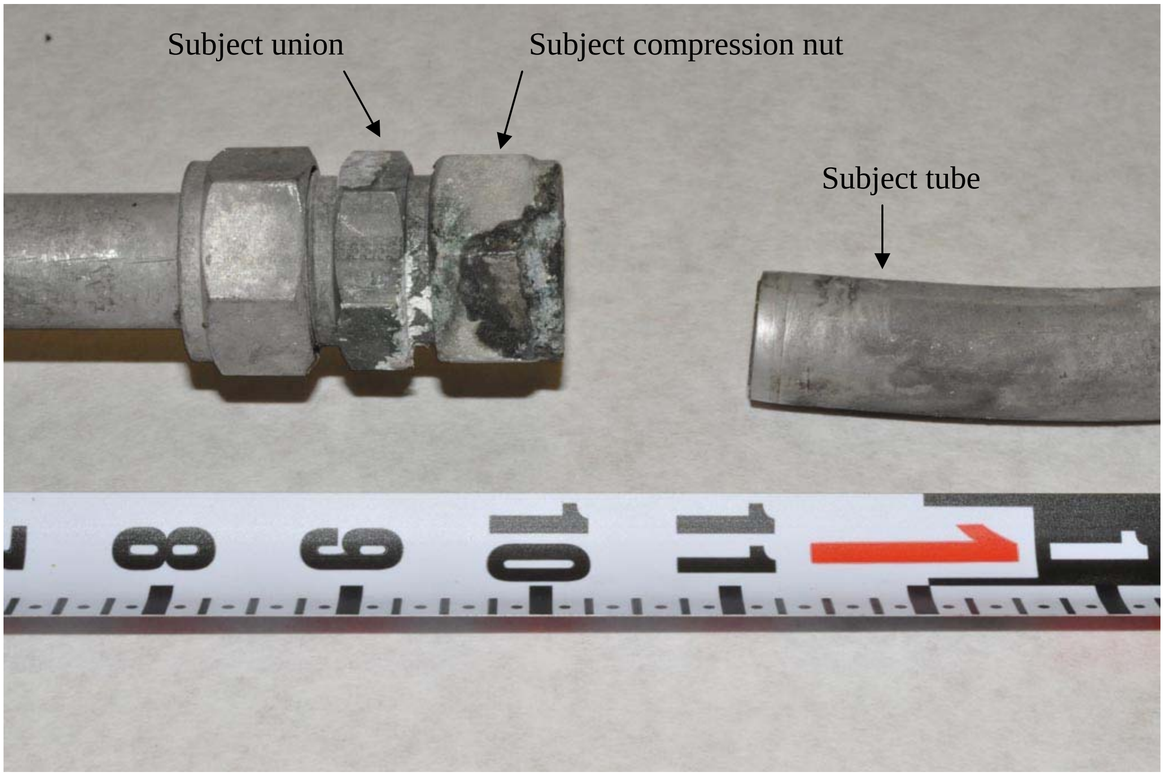
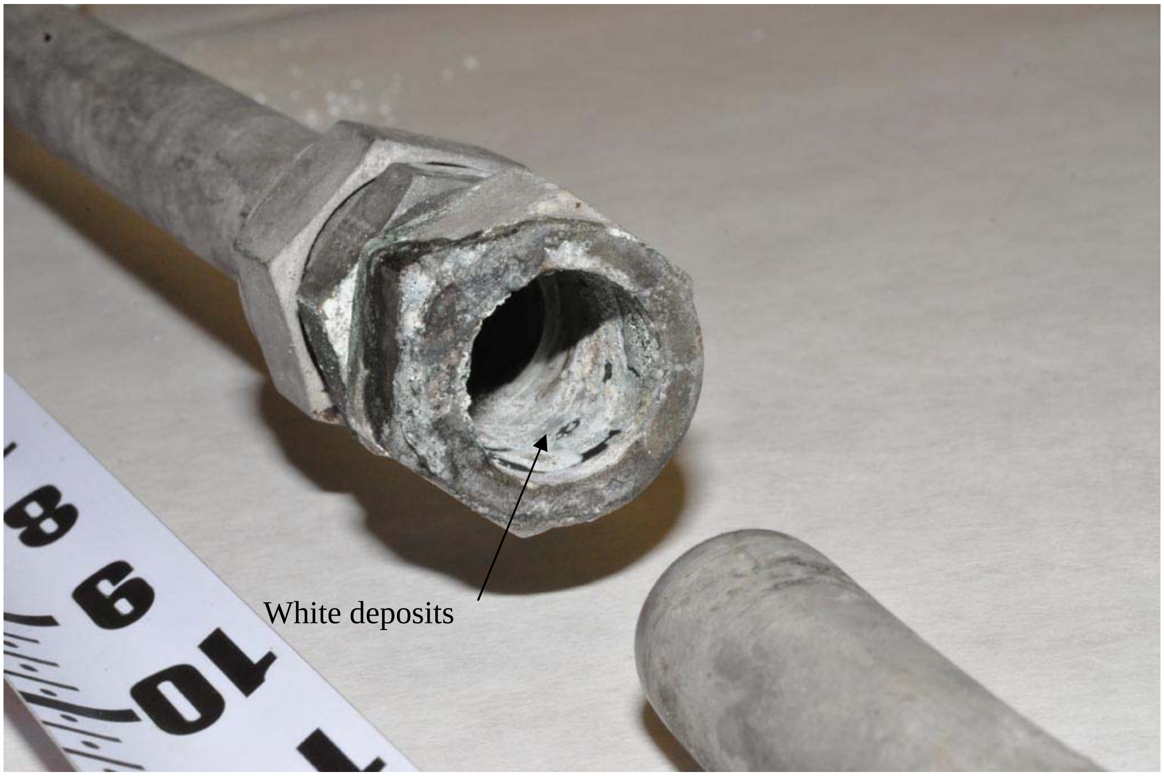


Figure 1 Tubing sub-assembly in the as-received condition. The boxed area indicates the subject joint.

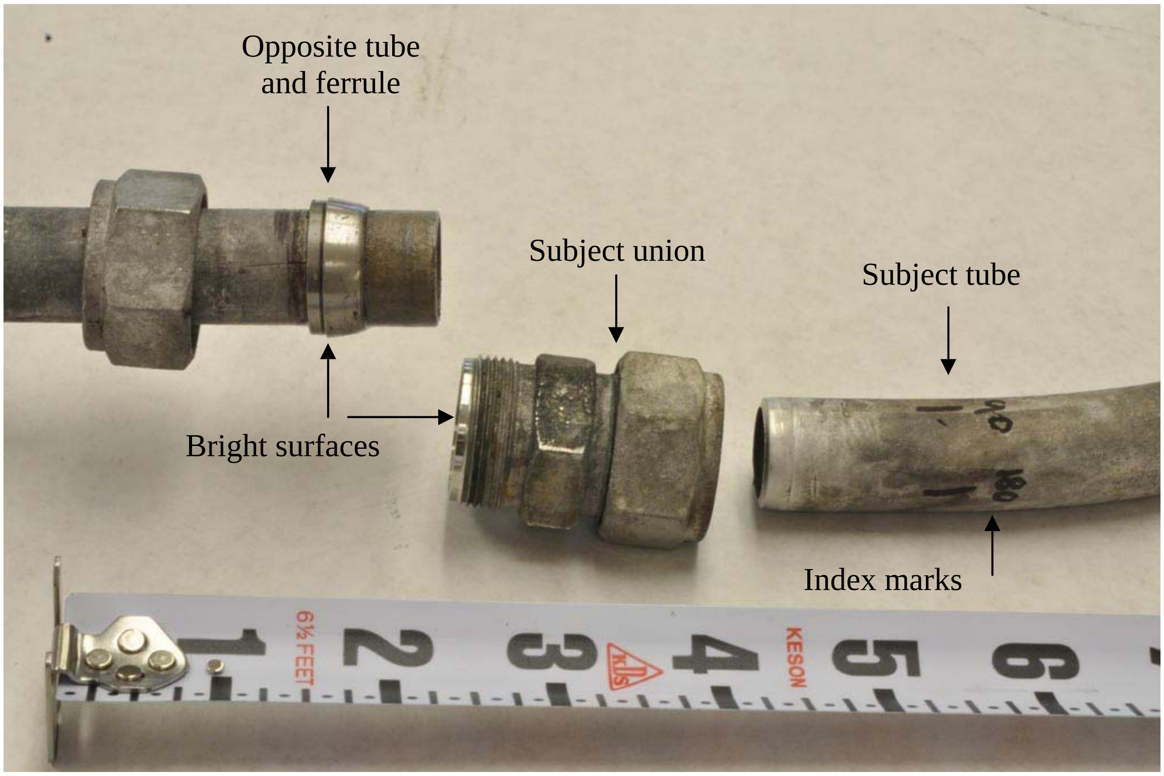


(a)



(b)

Figure 2 Two views of the subject joint in the as-received condition.



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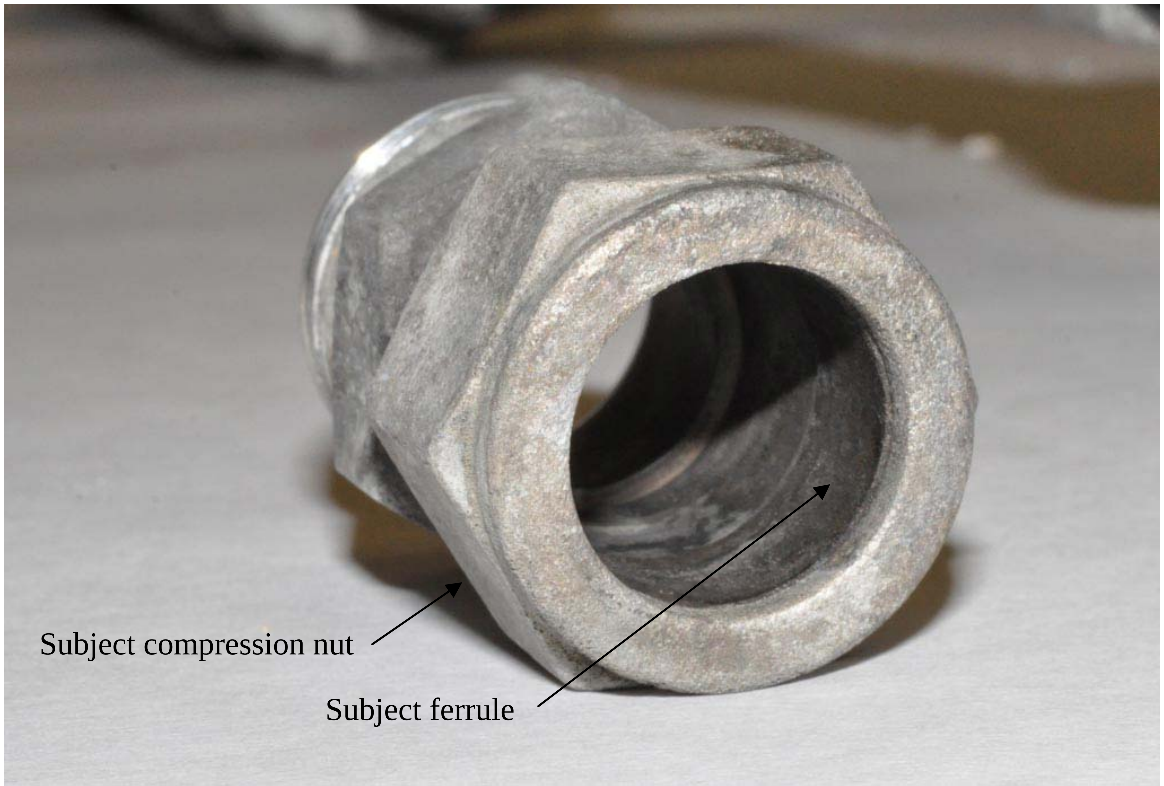
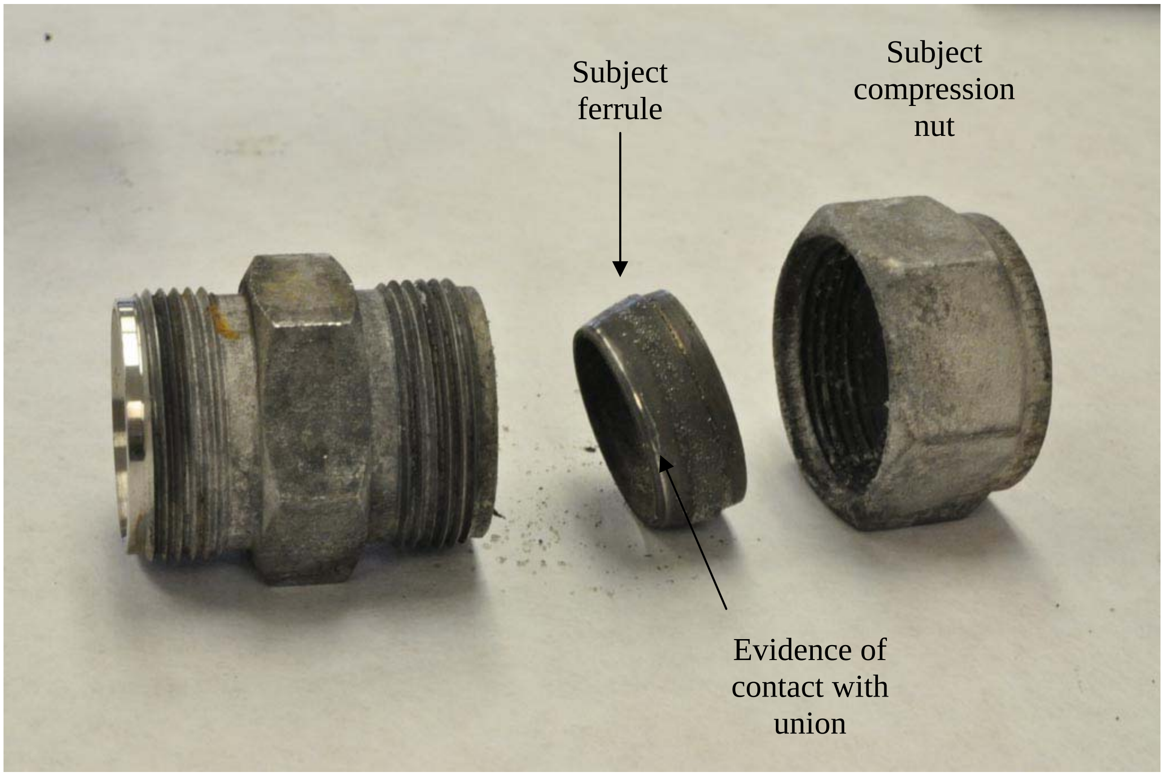


(b)

Figure 3 Subject union with opposite compression nut and ferrule disconnected. Photographs taken after rinsing in tap water.



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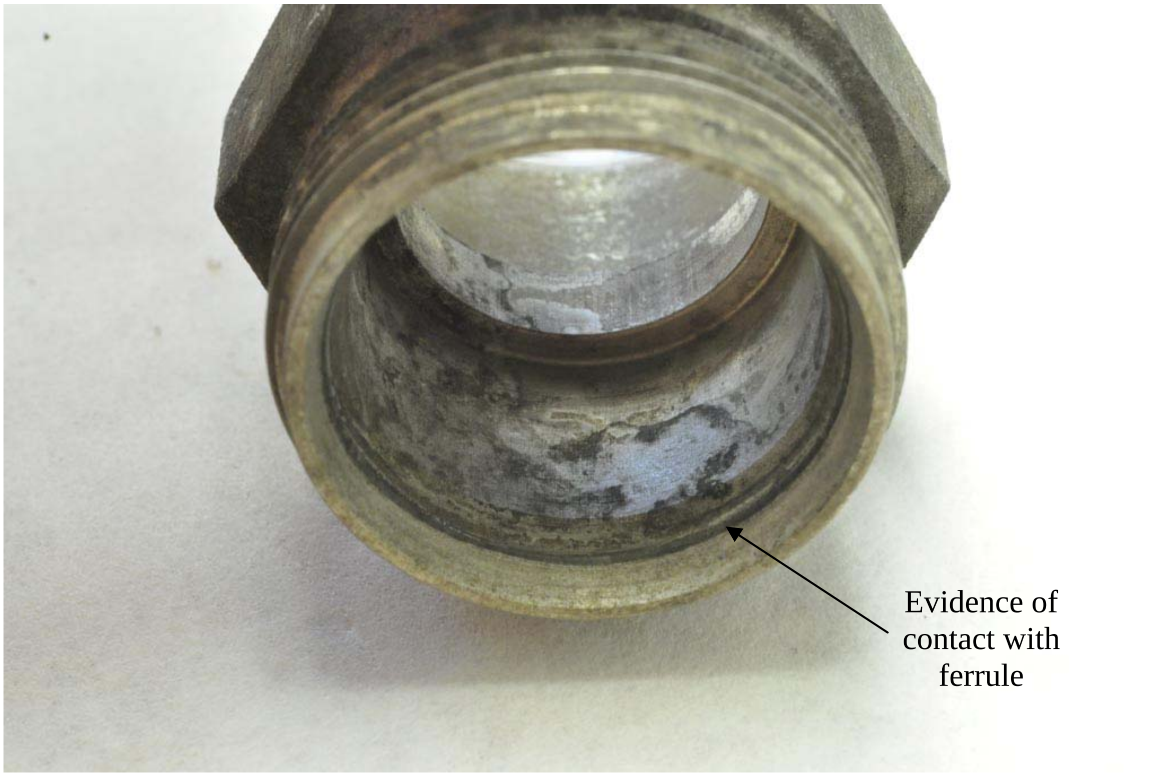


(b) Inside surface of union, subject joint side

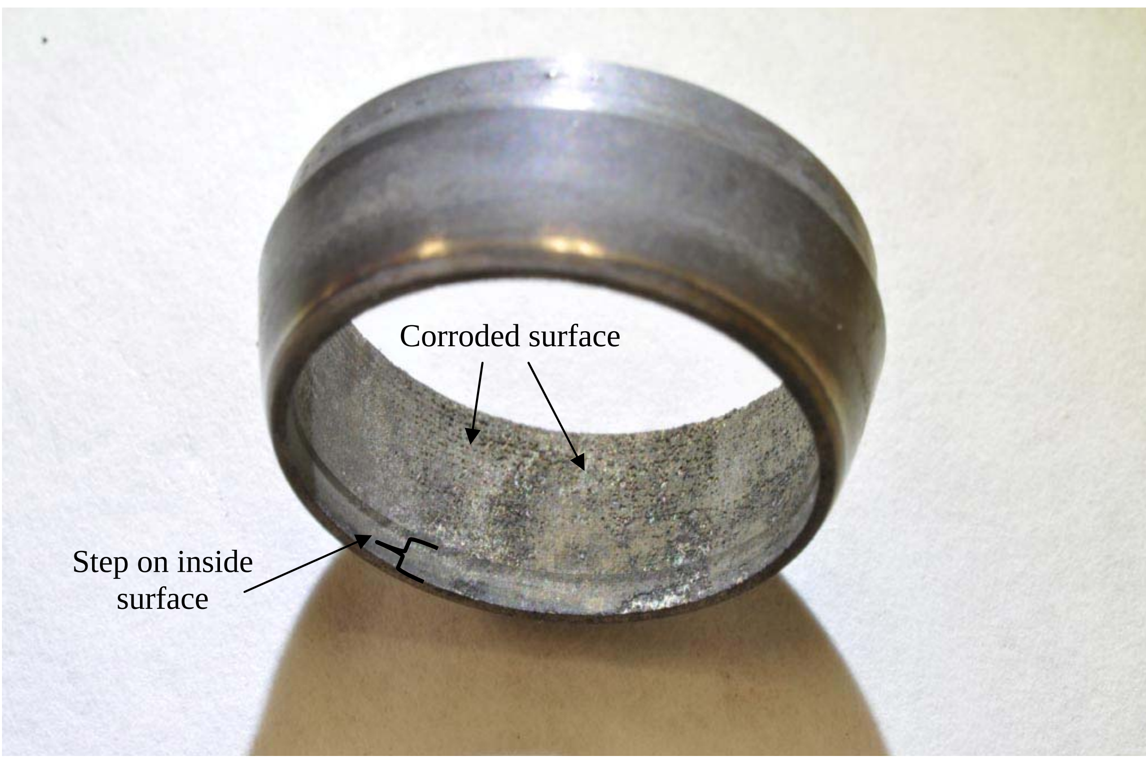
Figure 4 Subject union, ferrule, and compression nut after disassembly.

(a)

(b) Stamped wrench flat

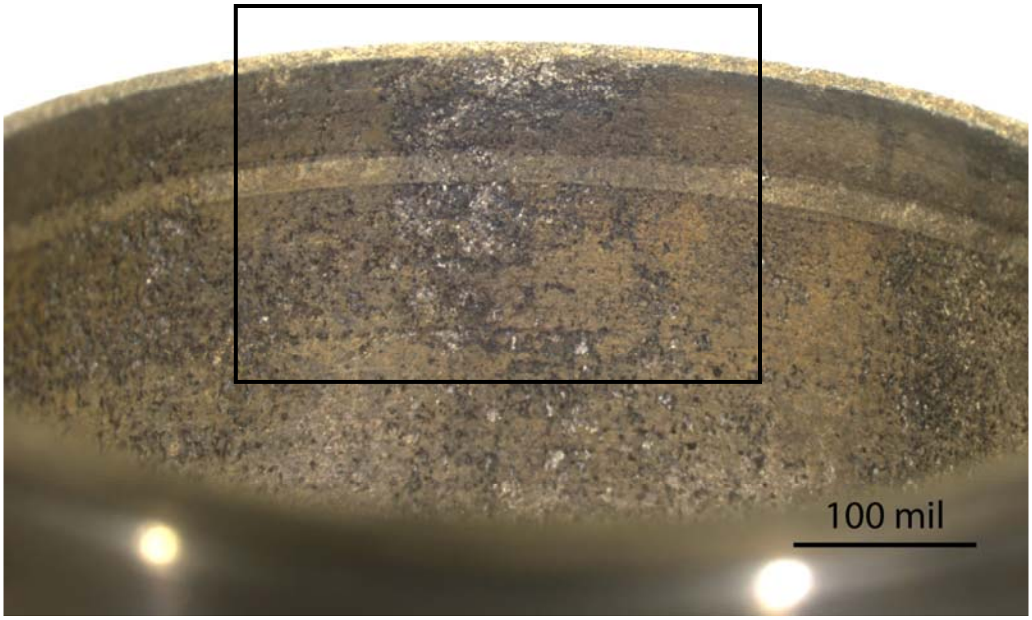
Figure 5 Macrographs of the subject union. The orientation shown in (a) is rotated 180 degrees from the orientation shown in Figure 4b.

(a) Outside surface



(b) Inside surface

Figure 6 Subject ferrule.



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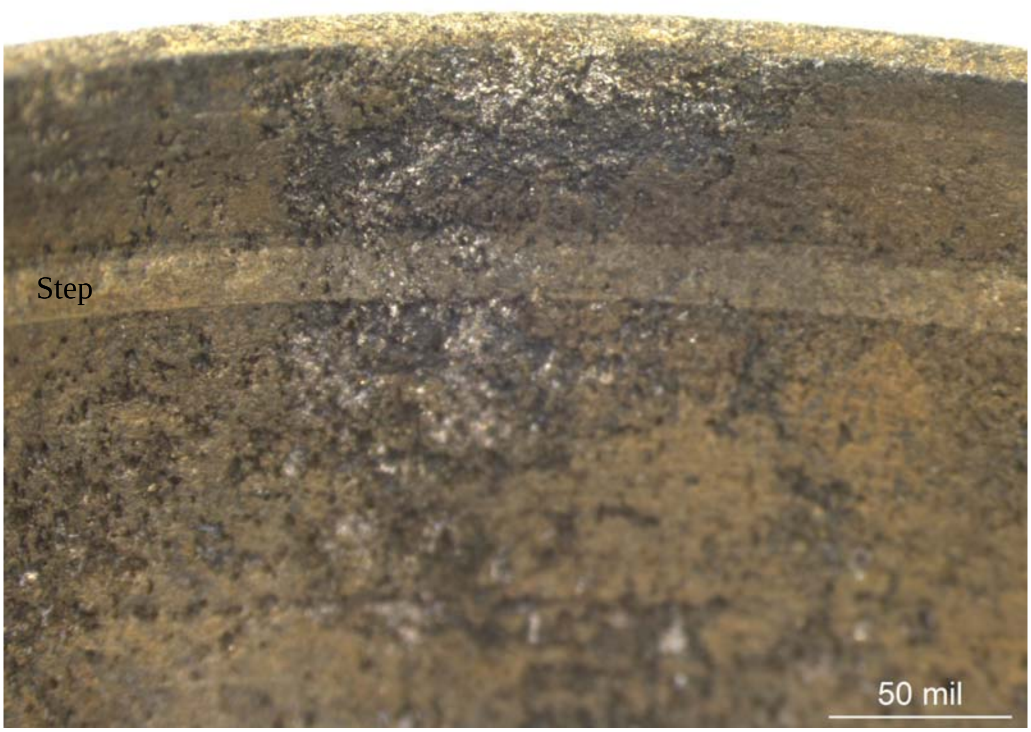
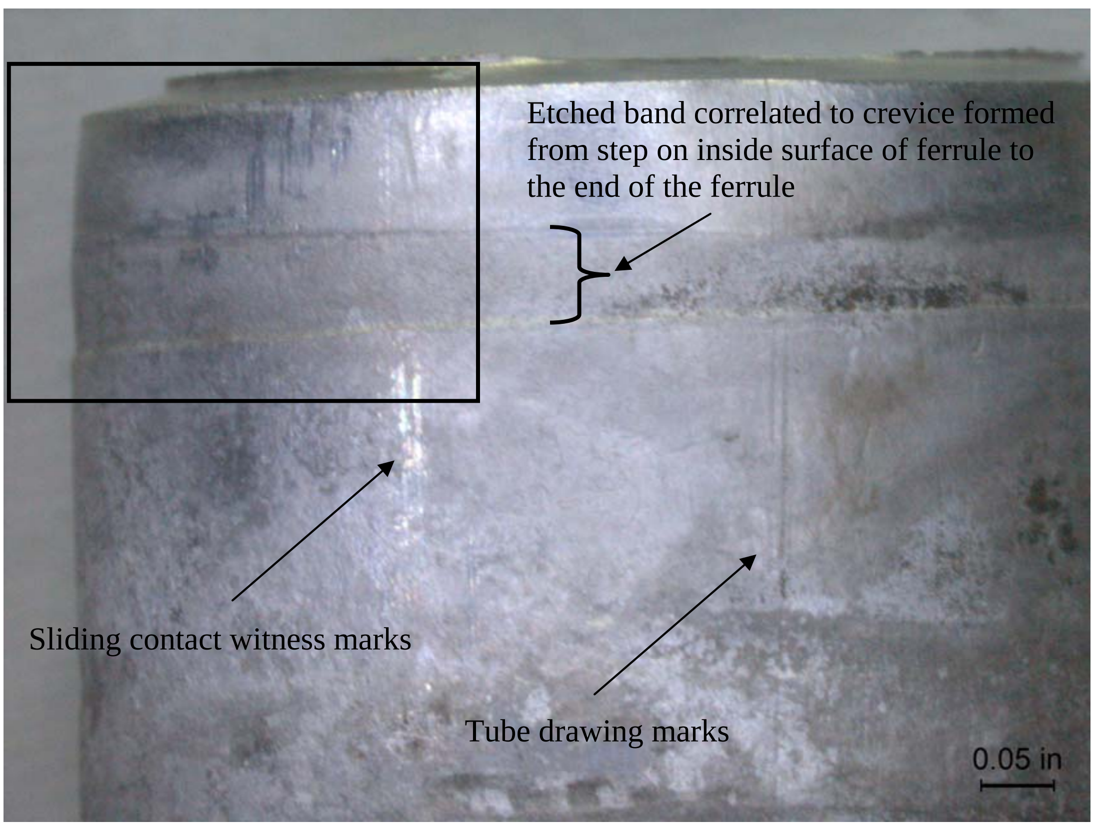


(b) Boxed area in (a)

Figure 7 Macrograph and SEM micrographs of the subject ferrule inside surface. Note the step which slightly increases the inside diameter at the end of the ferrule.

(a)



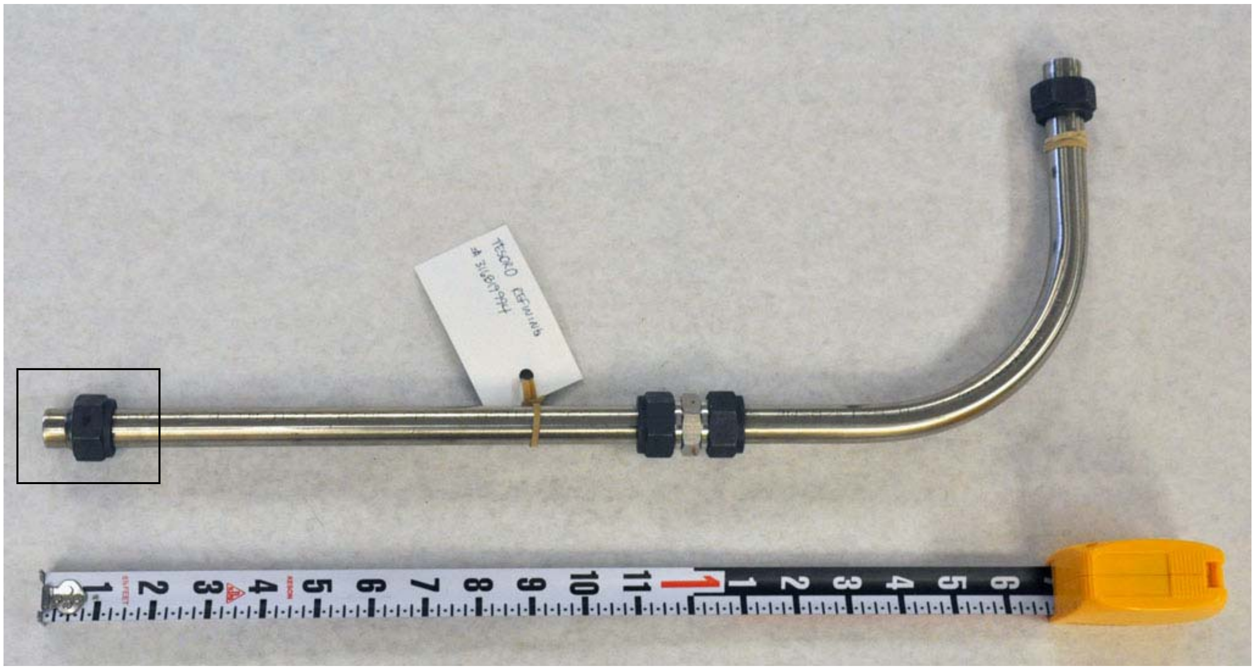
(b)

Figure 8 Subject tube end.

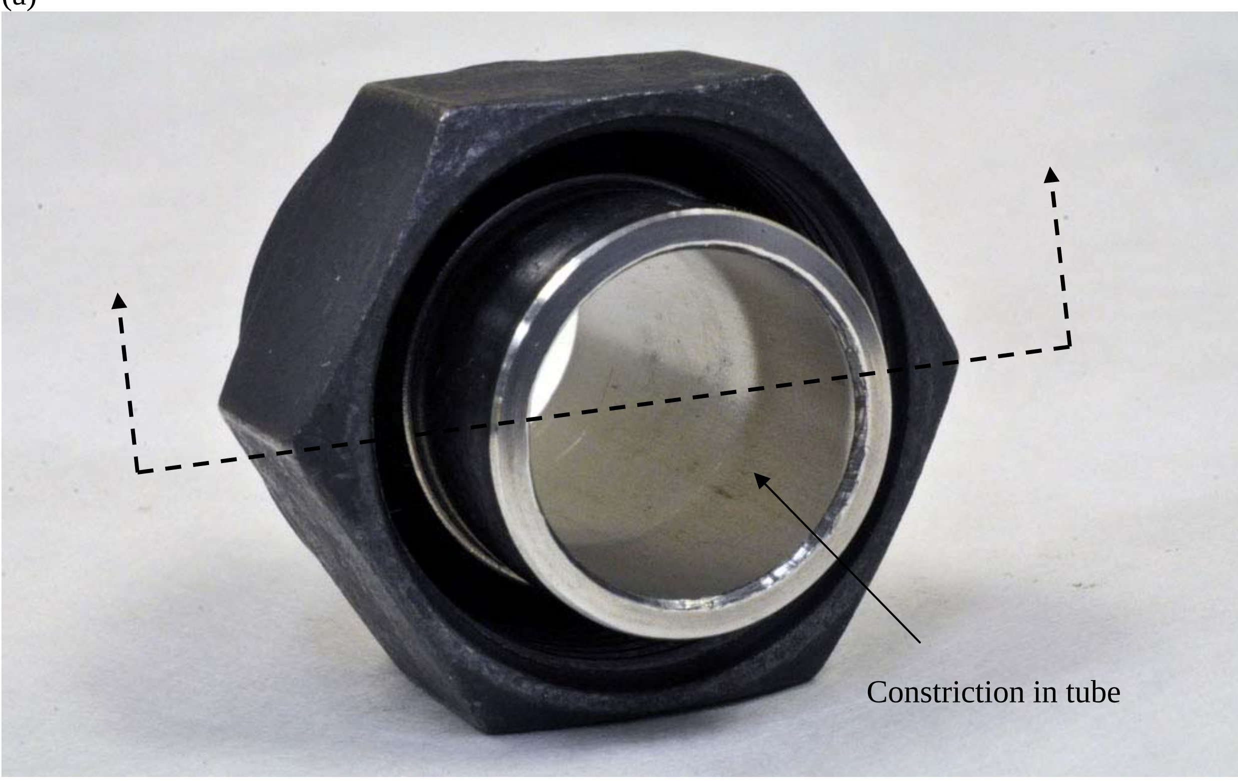
(a) Subject end

(b) Opposite end

Figure 9 Photographs of the subject tube ends. No constriction of the failed end of the subject tube (a) was visible, but constriction of the opposite end of the failed tube (b) was visible.

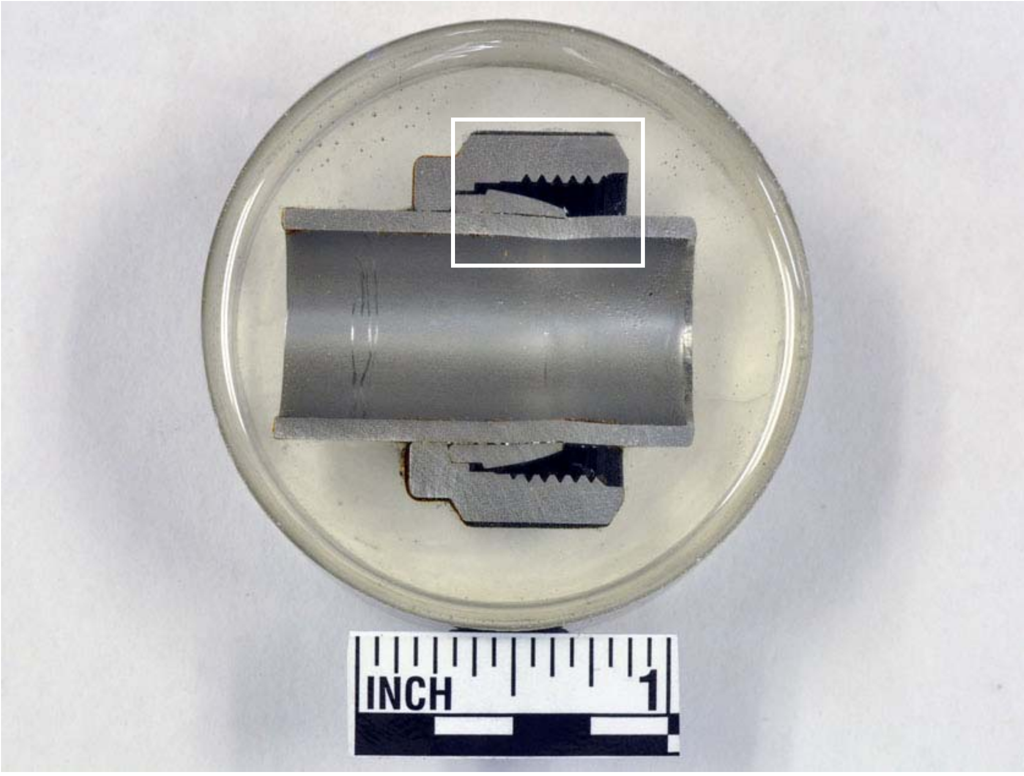


(a)



(b) End sectioned from boxed area in (a)

Figure 10 Photographs of the exemplar assembly. The dashed lines in (b) indicate an axial section prepared to show the tube constriction caused by clamping force between the nut and the ferrule.



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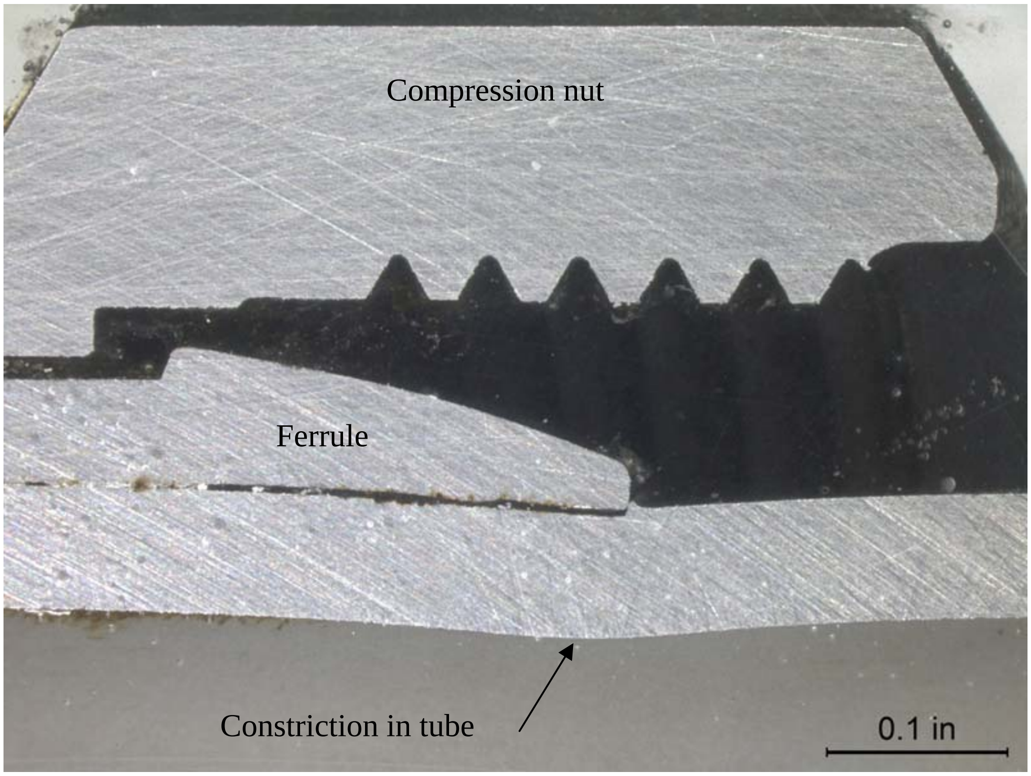
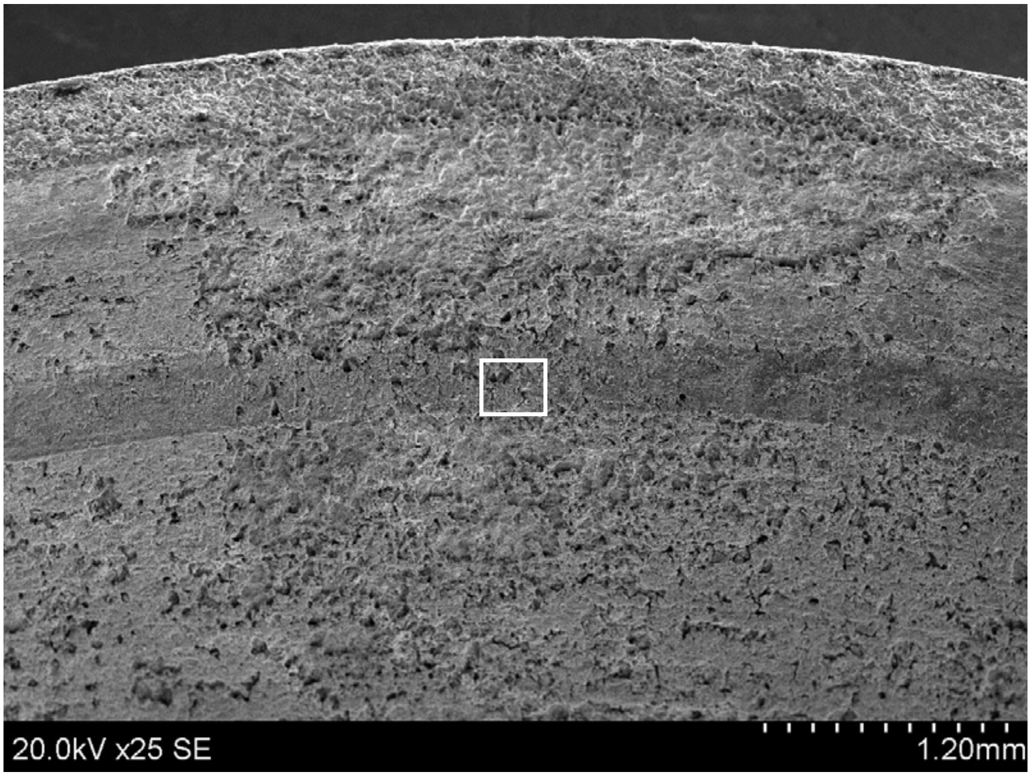
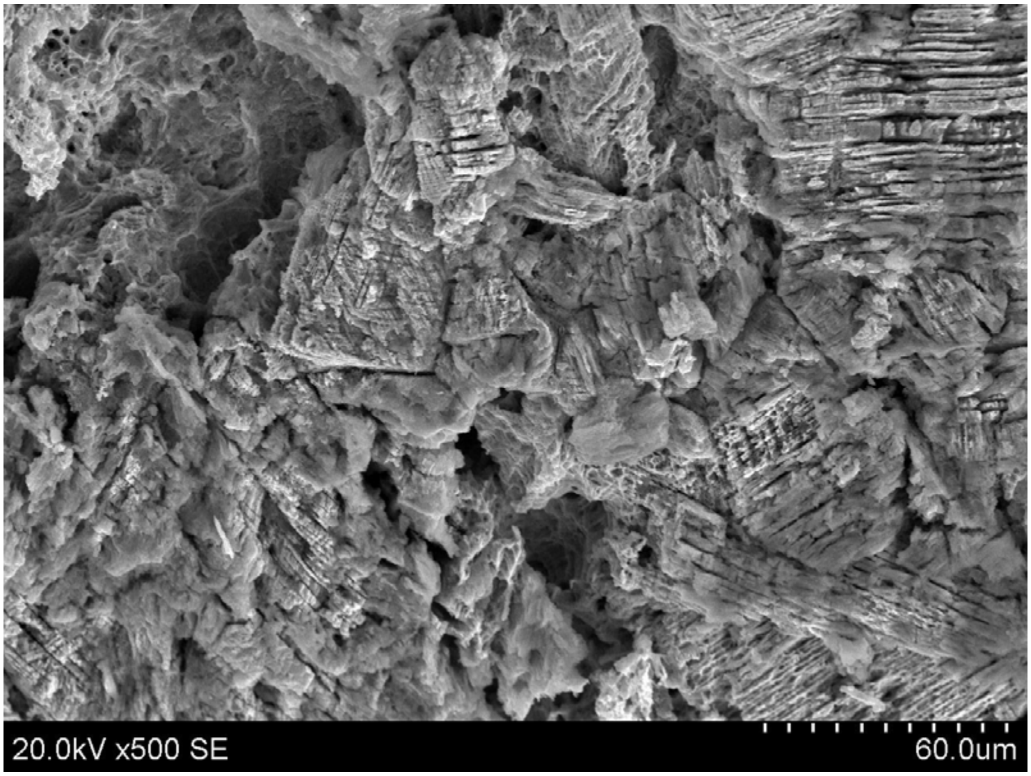


(b) Boxed area in (a)

Figure 11 Axial section of the exemplar tube end shown Figure 10.

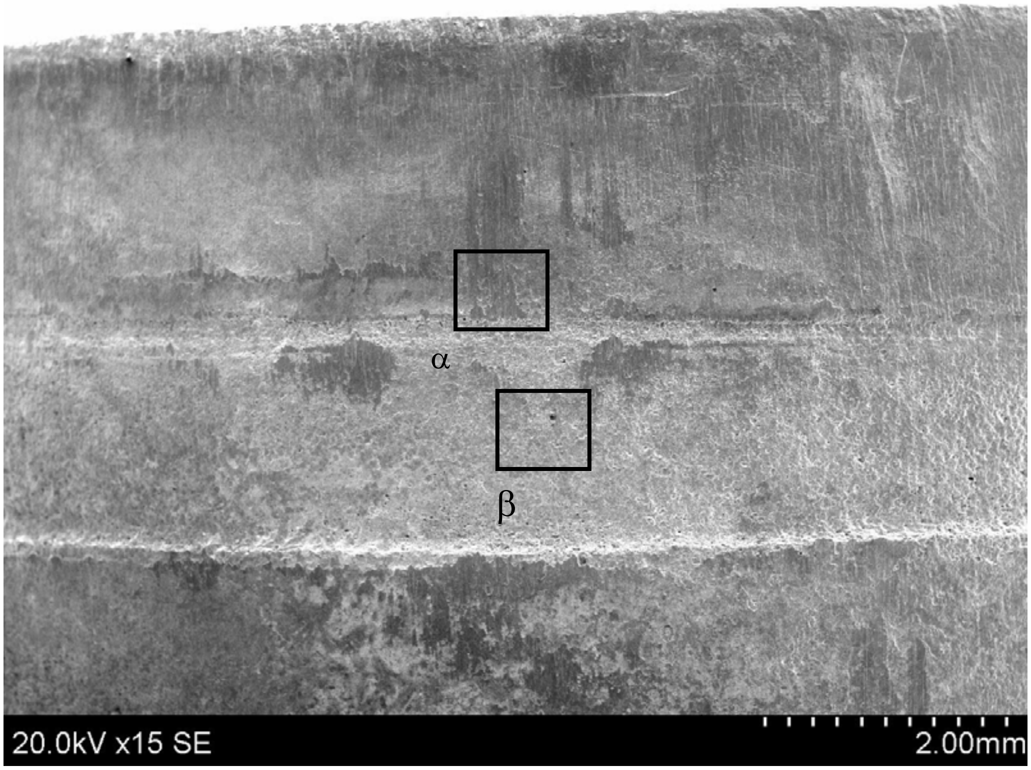


(a) Location shown in Figure 7b

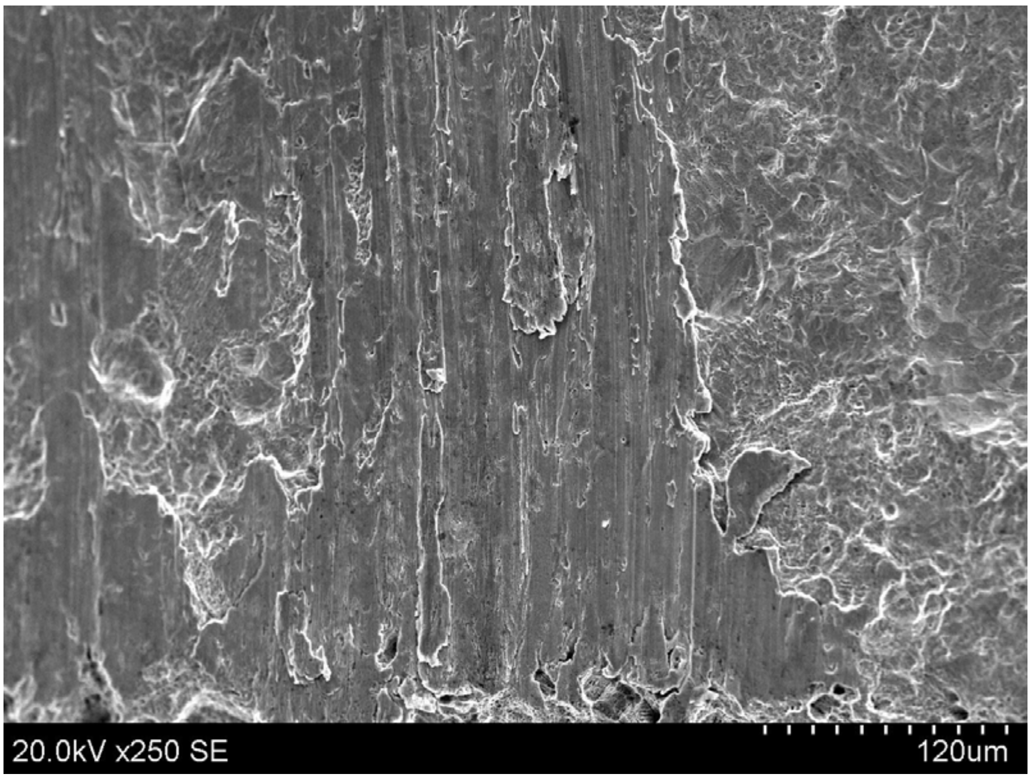


(b) Boxed area in (a)

Figure 12 SEM micrographs of the inside surface of the subject ferrule.

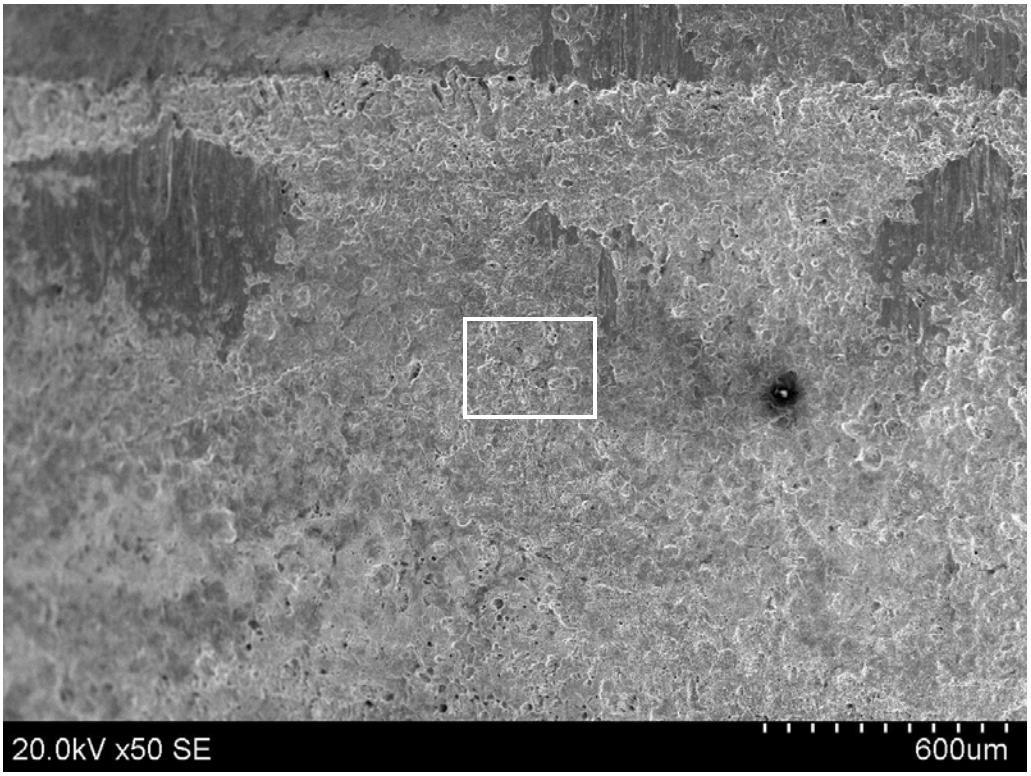


(a) Boxed area in Figure 8b

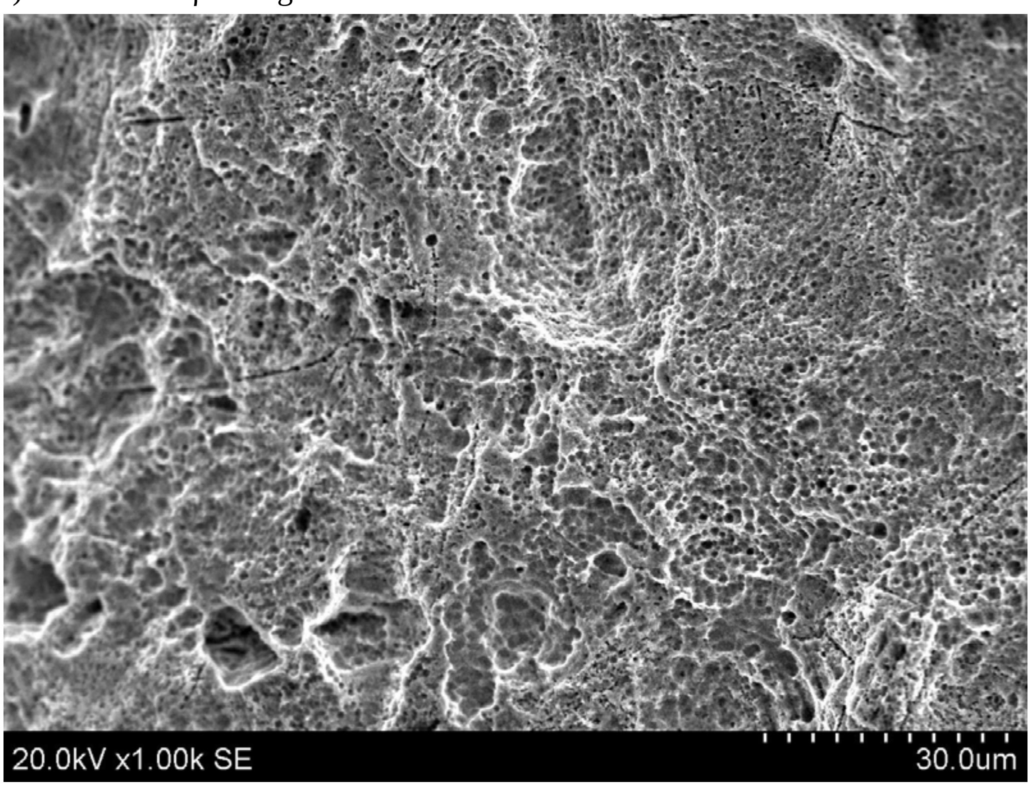


(b) Boxed area α in (a)

Figure 13 SEM micrographs of the subject tube end outside surface. Sliding contact deformation was likely caused when the joint separated during the incident.

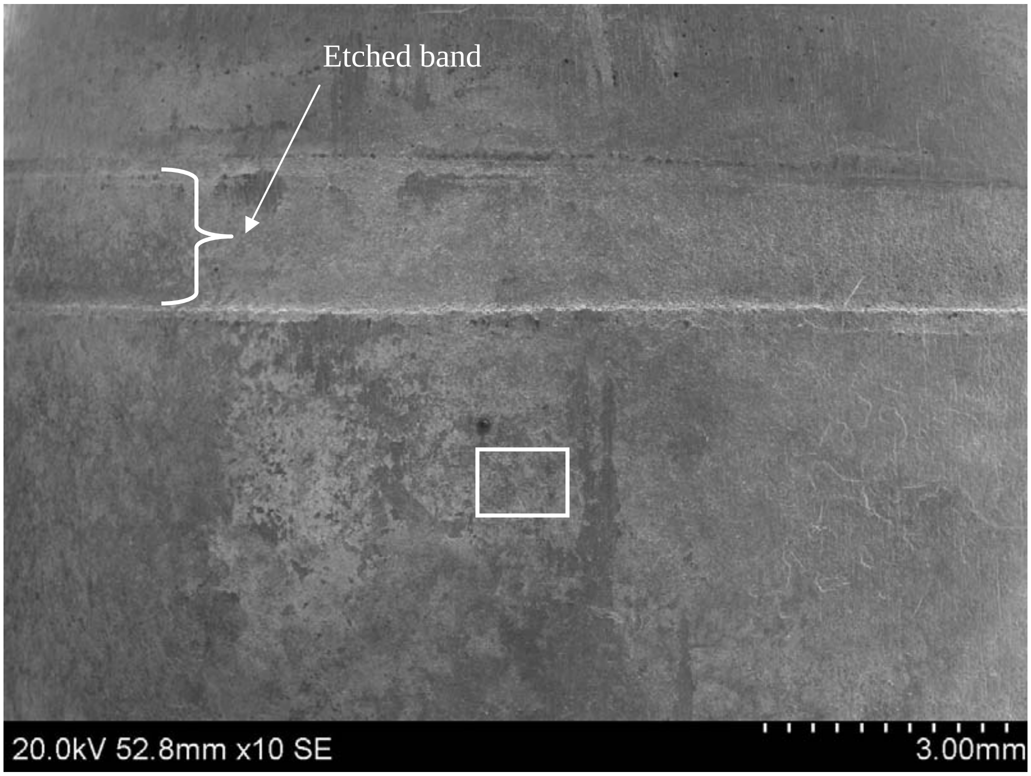


(a) Boxed area β in Figure 13b

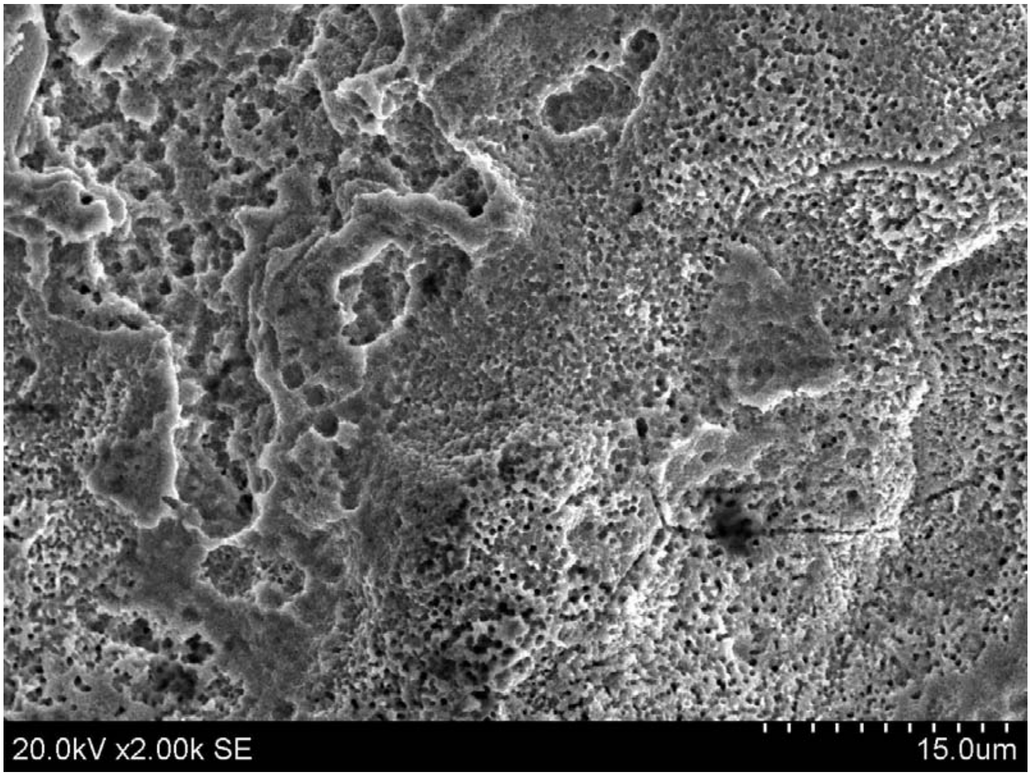


(b) Boxed area in (a)

Figure 14 SEM micrographs of the subject tube end outside surface.



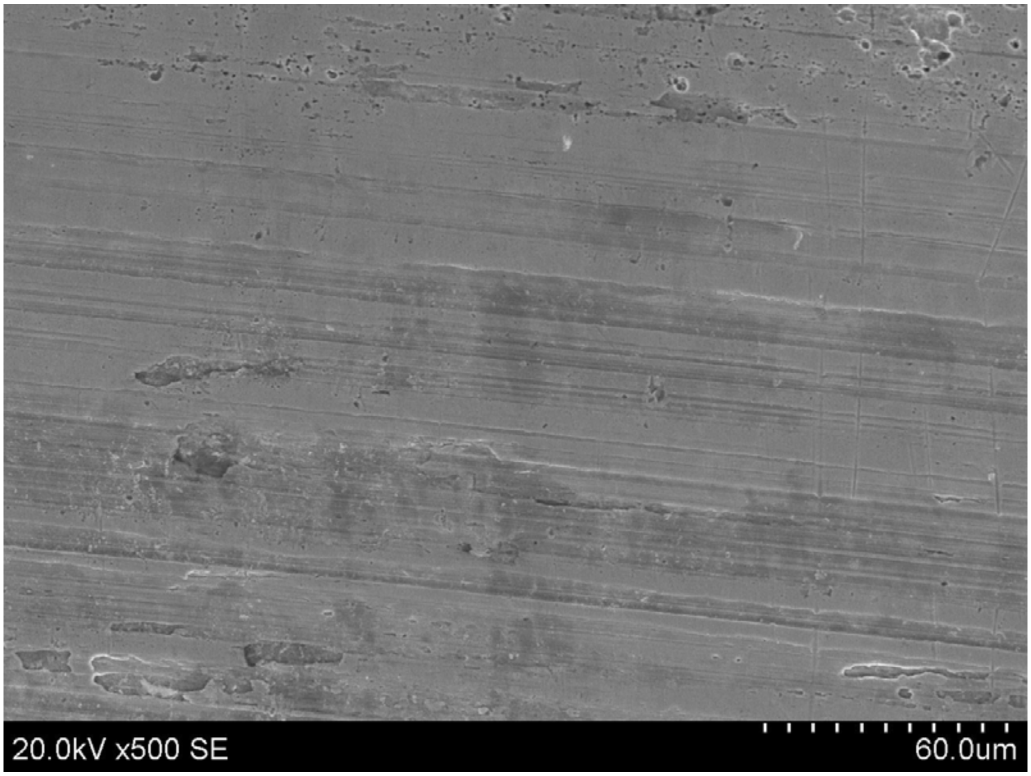
(a)



(b) Boxed location in (a)

Figure 15 SEM micrographs of the subject tube outside surface at the etched band.

(a)



(b) Boxed area in (a)

Figure 16 SEM micrographs of the inside surface of the subject union from the boxed area in Figure 5a.

Appendix

CPI™ Single Ferrule Tube Fittings

For use on instrumentation, process and control systems, analyzers, and environmental equipment

Problems with incorrectly installed tube fittings ?

CPI™ tube fittings are designed to provide three easy components for the installer-nut ferrule and body, You simply insert the tube, bottom it out, turn the nut 1 ¼ turns from finger tight and the CPI™ is properly made up. No extra ferrules, no different make up instructions, no extra places to seal.

Product Features:	Product Benefits:
•Single Ferrule	•Excellent vibration and temperature compensation and the integrity of two seal points
•Suparcase Technology	•Corrosion resistant ferrule
•Superior Seat Finish	•Enhanced body to ferrule seal
•Nut Lubrication	•Molybdenum Disulfide coated nut reduces make up torque and provides consistent remakes
•Heat Code traceability	•All stainless steel components are fully traceable with the chemical and physical documentation of the material
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