JMEPEG (2012) 21:2638–2642
DOI: 10.1007/s11665-012-0396-8

Irradiation-Assisted Stress-Corrosion Cracking of Nitinol During eBeam Sterilization

Stuart A. Smith, Brock Gause, David Plumley, and Masao J. Drexel

(Submitted April 4, 2012; in revised form September 5, 2012)

Medical device fractures during gamma and electron beam (eBeam) sterilization have been reported. Two common factors in these device fractures were a constraining force and the presence of fluorinated ethylene propylene (FEP). This study investigated the effects of eBeam sterilization on constrained light-oxide nitinol wires in FEP. The goal was to recreate these fractures and determine their root cause. Superelastic nitinol wires were placed inside FEP tubes and constrained with nominal outer fiber strains of 10, 15, and 20%. These samples were then subjected to a range of eBeam sterilization doses up to 400 kGy and compared with unconstrained wires also subjected to sterilization. Fractures were observed at doses of >100 kGy. Analysis of the fracture surfaces indicated that the samples failed due to irradiation-assisted stress-corrosion cracking (IASCC). This same effect was also observed to occur with PTFE at 400 kGy. These results suggest that nitinol is susceptible to IASCC when in the presence of a constraining stress, fluorinated polymers, and irradiation.

Keywords eBeam sterilization, medical device fractures, stress-corrosion cracking

1. Introduction/Background

Medical device fractures during sterilization are not only costly but also give rise to fears of embrittlement and residual cracks which may later result in device failure. A search of the current literature does not provide any conclusive explanations for these fractures. This study sought to recreate these fractures and determine their root cause.

Stress-corrosion cracking (SCC) can be described as a synergistic material attack achieved by the combination of three factors: a tensile stress, a susceptible material, and a particular environment (Ref 1). Without any one of these three factors SCC will not occur. The concept of SCC is well illustrated by the Venn diagram shown in Fig. 1. The special case of irradiaiton-assissted SCC (IASCC) takes place when the presence of radiation alters the materials and/or environment to enable the SCC processes. Previous studies of IASCC are almost exclusively dedicated to the investigation of nuclear reactor materials where radiation can alter the distribution of alloying elements, damage the crystal lattice, and modify water chemistry (Ref 1, 2).

Previous studies of nitinol have shown that it is susceptible to chemical attack in halide-containing solutions such as bleach and fluoridated saliva (Ref 3, 4). Furthermore, several studies have gone on to show the susceptibility of nitinol to SCC when stress in fluoride-containing solutions (Ref 5, 6)

This study, and a concurrent study by Norwich (Ref 7), are the first to look at the attack on nitinol from halide-containing polymers while subjected to the energy provided during irradiation—in this case eBeam sterilization.

2. Experimental Set-Up

Nitinol wires covered with FEP were subject to bending and constrained to a calculated strain value. The wire used was superelastic, light oxide surface, with nominal diameter of 0.5 mm and active Af of 16 °C. Prior to straining, the wires were covered with unshrunk FEP heat shrink tubing. These constrained samples were subsequently eBeam sterilized. The following control samples were also subject to eBeam sterilization: straight with FEP cover and strained with no FEP covering (bare). For comparison of coatings, two additional groups of strained parts were exposed to 400 kGy: one coated with heat shrunk FEP and the other with PTFE tubing. Specimen quantities and treatment combinations are listed in Table 1.

The wire samples were covered with FEP tubing, bent to the desired radii, and constrained with nitinol wire to maintain their geometry, as shown in Fig. 2.

All sterilization was performed at Nutek Corporation. The equipment used is a state-of-the art LINAC linear accelerator. Samples were placed in envelopes and positioned on cardboard backing for even irradiation and subsequently placed on the belt that passes though the electron beam field. The exposure or dosage of radiation, measured in kilogray (kGy), increases with the time spent in the eBeam field. Since the belt speed is constant, multiple passes through the field are required to increase dosage level.

This article is an invited paper selected from presentations at the International Conference on Shape Memory and Superelastic Technologies 2011, held November 6-9, 2011, in Hong Kong, China, and has been expanded from the original presentation.

Stuart A. Smith, Metallurgical Solutions, Redwood City, CA; **Brock Gause**, Nutek Corporation, Hayward, CA; **David Plumley**, Fort Wayne Metals, Fort Wayne, IN; and **Masao J. Drexel**, Confirmd LLC, Redwood City, CA. Contact e-mail: ssmith@met1solution.com.

73 specimens were prepared and tested. Four levels of strain were examined: 0, 10, 15, and 20%. Prior to exposure, strain levels were calculated by measuring the bend radii.

Each strain level was irradiated to levels of 25, 100, 200, 300, and 400 kGy. Higher irradiation doses were achieved by the accumulated effect of multiple exposures at lower levels.

To compare heat shrunk FEP to non-shrunk FEP, 3 of the specimens at 10% strain were heated to shrink the FEP tubing prior to 400 kGy irradiation.

To compare PTFE to FEP, three specimens were covered with PTFE and strained to 15% prior to 400 kGy irradiation.

Nitinol wires without a polymer covering were strained to 10% and exposed to 400 kGy.

Visual inspections of strained specimens were conducted to determine if fracture occurred. Fracture surfaces were inspected under magnification, SEM and EDX. Tension tests were performed on 0% strain samples.

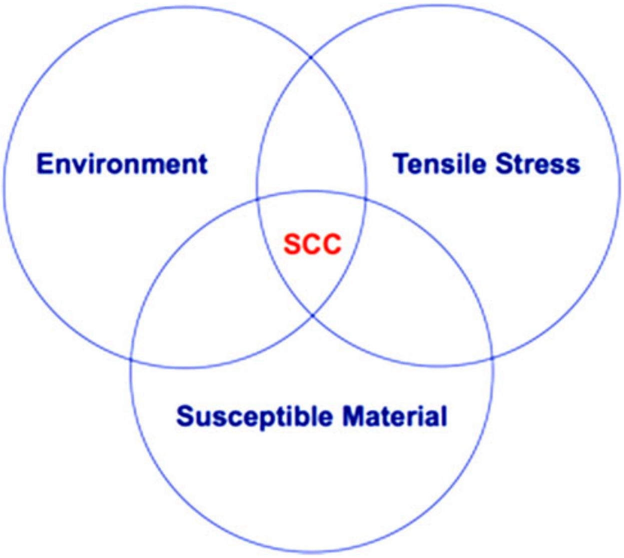

Fig. 1 Venn diagram illustrating the required factors for inducing SCC

Table 1 Details of specimen treatments

Dosage, kGy	Coating	Strain level, %	Quantity of specimens
25	FEP	10	5
25	FEP	20	5
100	FEP	10	5
100	FEP	20	5
200	FEP	10	5
200	FEP	20	5
300	FEP	10	5
300	FEP	20	5
400	FEP	10	5
400	FEP	20	5
400	FEP	Unconstrained	5
400	None	10	5
400	None	Unconstrained	5
400	PTFE	15	5
400	FEP*	10	3

*Prior to irradiation, the FEP coating was heated to shrink the tubing

3. Results

3.1 Fractures

Fractured specimens were completely broken into two pieces often breaking through the coating as seen in Fig. 3. Further examination of unbroken samples did not lead to the discovery of any partially fractured wires.

Fractures occurred in samples at all strain levels. Unconstrained samples showed no fractures. For complete fracture count, see Table 2.

3.2 Unrecovered (Unshrunk) FEP Coating

Fractures were observed only in the groups of samples exposed to 200, 300, and 400 kGy. There were no breaks in groups exposed to 25 and 100 kGy and no fractures evident with unstrained Nitinol.

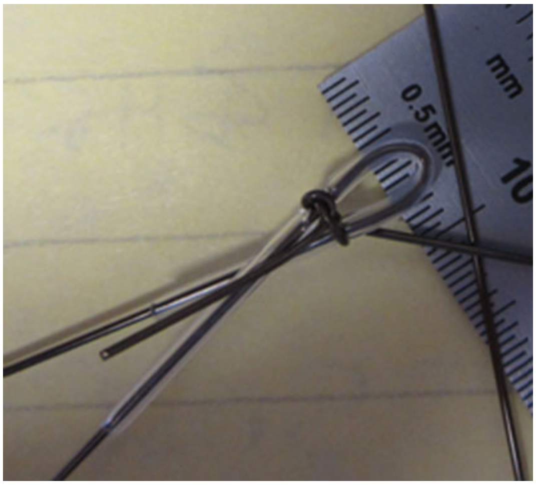

Fig. 2 Example of constrained coated nitinol wire

Fig. 3 Example of fractured sample-PTFE coated shown

Table 2 Fracture count of nitinol specimens exposed to eBeam sterilization

Dosage, kGy	Coating	Strain level, %	Fracture count
25	FEP	10	0 of 5
25	FEP	20	0 of 5
100	FEP	10	0 of 5
100	FEP	20	0 of 5
200	FEP	10	5 of 5
200	FEP	20	4 of 5
300	FEP	10	5 of 5
300	FEP	20	3 of 5
400	FEP	10	5 of 5
400	FEP	20	5 of 5
400	FEP	Unconstrained	0 of 5
400	None	10	0 of 5
400	None	Unconstrained	0 of 5
400	PTFE	15	5 of 5
400	FEP*	10	0 of 3

*Prior to irradiation, the FEP coating was heated to shrink the tubing

At 200 kGy, 5 of 5 samples of the 10% strained samples broke and 4 of 5 samples of the 20% strained samples broke.

At 300 kGy, 5 of 5 samples of the 10% strained samples broke and 3 of 5 samples of the 20% strained samples broke.

At 400 kGy, 5 of 5 samples of the 10% strained samples broke and 5 of 5 samples of the 20% strained samples broke.

3.3 PTFE Coating

All five samples exposed to 400 kGy were fractured during irradiation.

3.4 Recovered (Heat Shrunk) FEP Coating

No fractures were evident after exposure to 400 kGy.

3.5 Fracture Surface Examination

Upon examination of the broken samples, the fracture surfaces of each exhibited discoloration consistent with a progressive oxidation which worked its way from the outside wire surface into the wire as shown in Fig. 4 and 5. The surface markings are similar to beach marks found in fatigue failure except the propagation field has been chemically attacked during the stages of crack growth. The samples were not mechanically cycled. Surrounding the crack growth area was the uniform final fracture surface. This surface morphology is consistent with SCC (Ref 8).

3.6 SEM and EDX

The outer wire surfaces and fractured surfaces of select specimens were examined under scanning electron microscopy (SEM) and analyzed using energy-dispersive x-ray spectroscopy (EDX) to determine chemical signatures associated with specific locations.

SEM examination showed a fracture surface with clear origin of crack initiation, SCC fracture propagation region, and the ductile failure region. Figure 6 shows the contrast between the SCC region and the ductile failure region. Figure 7 shows the outer surface of nitinol exposed and not exposed to FEP and irradiation. The non-exposed sample is smooth, while the exposed sample is rough and scaly.

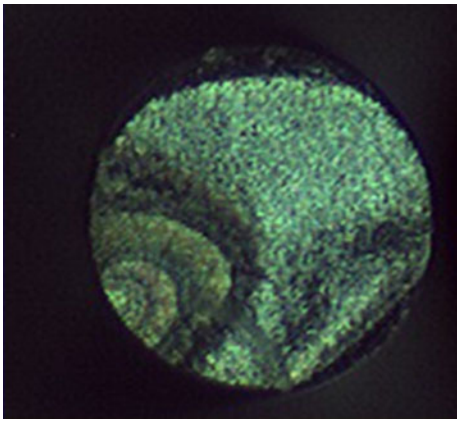

Fig. 4 Fracture surface of specimen showing signs of SCC

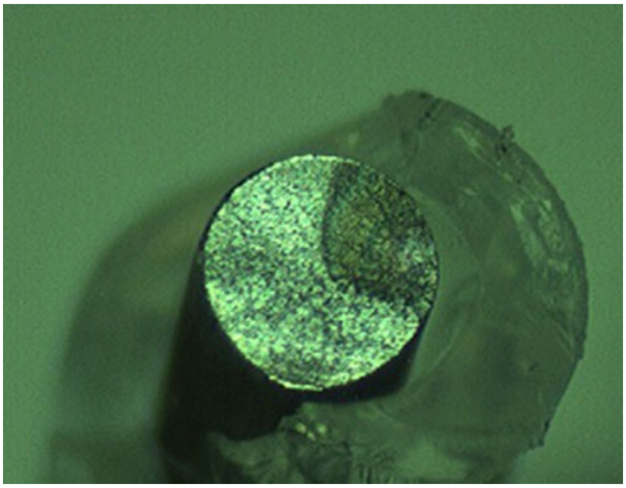

Fig. 5 Fracture surface of specimen showing signs of SCC

Using EDX, the fractured surfaces and outer wire surfaces showed elevated levels of fluorine, shown in Fig. 8. This verifies the presence of a fluorine-rich coating on the wire as a result of irradiation through the FEP tubing. A similar film was observed on wire irradiated in PTFE tubing.

3.7 Unstrained Specimens

As a control, unstrained samples with and without FEP coating were subject to eBeam sterilization and then tensile tested. The accumulated exposure was 400 kGy. Also tested was nitinol directly from the spool, with no exposure to FEP or irradiation. In Fig. 9, the tensile curves of these three samples were superimposed to show how little difference there is in the tensile characteristics of these wires. All the values are well within the normal variation for tensile tests and any differences are considered negligible.

As shown in Fig. 10, the breaks were all typical ductile failures with normal tensile properties for nitinol. This and the tensile characteristics indicate that there is no detrimental effect of the sterilization process to unstrained nitinol with or without FEP coating.

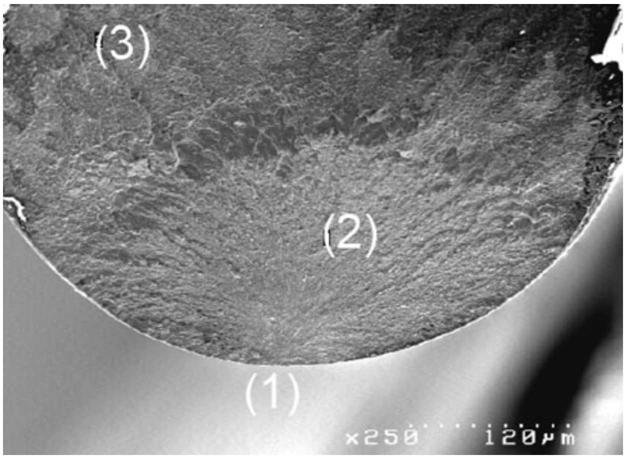

Fig. 6 SEM of fractured sample. (1) Origin of fracture, (2) SCC region, and (3) ductile failure region

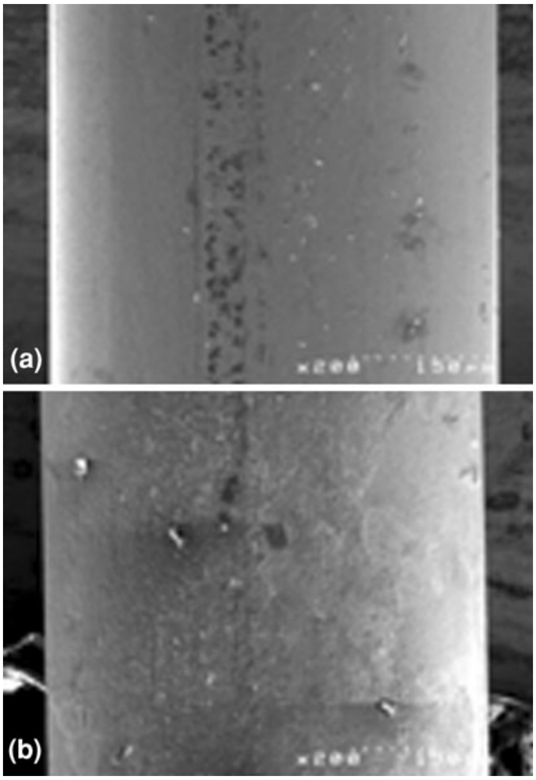

Fig. 7 SEM of outer surface of nitinol wire. Top: not exposed to FEP and irradiation shows the surface as smooth and not scaly, bottom: fluorine-rich coating, indicated by arrows, from exposure to FEP and irradiation shows as white, rough, and scaly surface

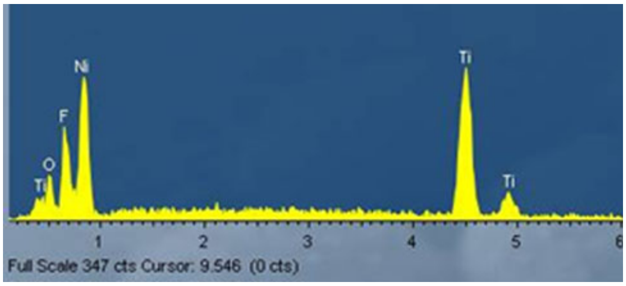

Fig. 8 EDX analysis of fracture surface showing the presence of fluorine

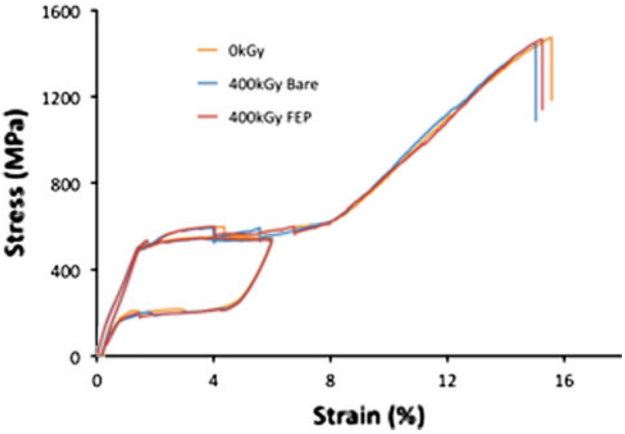

Fig. 9 Tensile curves for nitinol wire, irradiated nitinol wire, and irradiated FEP-coated nitinol wire

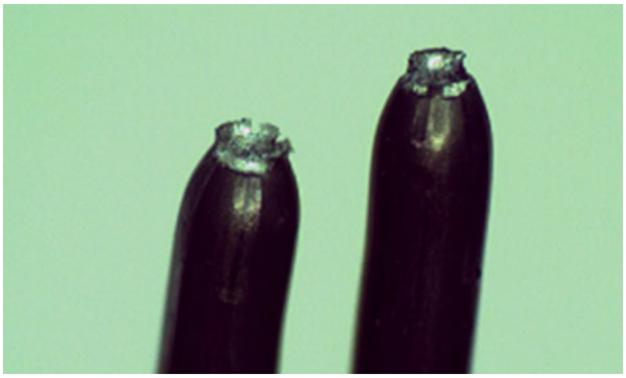

Fig. 10 Typical ductile failures for nitinol in tension—irradiated FEP-coated nitinol shown

4. Discussion

It is believed that fluorine ions in the FEP and PTFE polymer chains are liberated to interact with the high tensile stress regions of the nitinol. At these locations, IASCC progresses and ultimately results in the wire fracture.

Although IASCC can cause complete fractures of wires at the higher levels of strain, the beginning stages of IASCC may be evident upon further examination of wires with lower exposure levels. There were no partial fractures discovered in this study.

In comparison to FEP, when exposed to the same high levels of eBeam radiation, PTFE exhibits the same catastrophic results. Further investigation is warranted to determine if PTFE and FEP have comparable susceptibility to IASCC at lower levels of radiation.

Unlike hydrogen embrittlement, IASCC cannot be "repaired" with heating and or a vacuum.

5. Future Work

Further studies needed:

Detailed study of surface influence
Surface area of coating to wire ratio
Polymer proximity to surface
PTFE
Lower irradiation levels
Strain cycles
Heat shrink tube recovery versus unrecovered.

6. Conclusions

1. The combination of FEP or PTFE, constrained nitinol, and eBeam sterilization can produce IASCC resulting in catastrophic fracture.
2. Both constrained and unconstrained nitinol showed no change in appearance or tensile properties when exposed to eBeam sterilization without the presence of FEP.
3. Fluoride-rich films were deposited onto the nitinol wires during sterilization within FEP or PTFE tubes.
4. The presence of post-heat shrunk FEP with constrained Nitinol during eBeam sterilization did not result in observable IASCC and did not result in catastrophic fracture.
5. The occurrence of IASCC increased with irradiation dose.

Acknowledgment

The authors would like to thank Neeru Jhingan of Milestone Technology for her support with the SEM/EDX analysis.

References

1. R. Jones, *Stress-Corrosion Cracking,* ASM International, Materials Park, OH, 1992, p 1, 2, 180, 181
2. M.B. McNeil, *Irradiation Assisted Stress Corrosion Cracking. Nuclear Engineering and Design*, Elsevier, Amsterdam, 1998
3. C. Lasley, M. Mitchell, B. Dooley, W. Bruchman, and C. Warner, The Corrosion of Nitinol by Exposure to Decontamination Solutions, *SMST*, 2003, p 375–384
4. N. Schiff, B. Grosgogeat, M. Lissac, and F. Dalard, Influence of Fluoride Content and pH on the Corrosion Resistance of Titanium and Its Alloys, *Biomaterials*, 2002, **23**, p 1995–2002
5. J. Wang, N. Li, G. Rao, E. Han, and W. Ke, Stress Corrosion Cracking of NiTi in Artificial Saliva, *Dent. Mater.*, 2007, **23**, p 133–137
6. X. Li, J. Wang, E. Han, and W. Ke, Stress Corrosion Cracking of NiTi Orthodontic Wires in Sodium Fluoride solution, *Adv. Mater. Res.*, 2008, **32**, p 79–82
7. D. Norwich, Fracture of Polymer Coated Nitinol During Gamma Sterilization, *SMST* 2011, ASM International, Materials Park, OH
8. D. Wulpi, *Understanding How Components Fail*, American Society for Metals, Materials Park, OH, 1985, p 221