



We are Nitinol.™

Corrosion Resistance of Oxidized Nitinol

Christine Trépanier, Lucy Zhu, Jennifer Fino, and Alan R. Pelton

Proceedings of SMST-2003, Monterey, CA, eds., A.R. Pelton and T.W. Duerig, 267-276
(2004).

2004

SMST-2003

Proceedings of the International Conference on

Shape Memory and Superelastic Technologies

5 May to 8 May 2003

Asilomar Conference Center

Pacific Grove, California, USA

Editors

Alan R. Pelton

Tom Duerig



© 2004 by SMST
All rights reserved.

No part of this book may be reproduced, stored in a retrieval system, or transcribed, in any form or by any means—electronic, mechanical, photocopying, recording, or otherwise—without prior permission of the publisher.

Published by:
SMST Society, Inc.
c/o SRI M/S AA287
333 Ravenswood Avenue
Menlo Park, California 94025
USA
Telephone: (650) 879-6476
E-mail: info@smst.org
Website: www.smst.org

Copies of this book may be ordered through the SMST website at www.smst.org or by calling the SMST office at (650) 859-6476, or through ASM International, Customer Service at (440) 338 5151 x5537 or at www.asminternational.org.

Printed and bound in the United States of America

Library of Congress Control Number: 2004102781

Publisher's Cataloging in Publication Data

SMST-2003: proceedings of the international conference on shape memory and superelastic technologies / edited by Alan R. Pelton and Tom Duerig.

xvi; 746 p.; 26 cm

Includes bibliographical references and index.

ISBN 0-9660508-3-5

1. Alloys—Congresses. 2. Alloys—Thermomechanical properties. 3. Shape memory effect. I. Pelton, Alan (Alan R.) II. Duerig, Tom (Thomas W.)

TN690.S675 2004
669'.94—dc20

Production Services by TIPS Technical Publishing, Inc.

CORROSION RESISTANCE OF OXIDIZED NITINOL

Christine Trépanier, Lucy Zhu, Jennifer Fino and Alan R. Pelton

Nitinol Devices & Components, 47533 Westinghouse Drive, Fremont, CA 94539

ABSTRACT

In the first part of this study, we showed that electropolished NiTi wires oxidized between 400°C and 1000°C form surface layers of mixed Ni₃Ti, Ni₄Ti, Ni, and TiO₂ phases. The present study investigates by potentiodynamic polarization tests the corrosion behavior of these oxidized wires with respect to the breakdown potential (E_{bd}). The E_{bd} dramatically decreases from 1000mV to below -100mV vs. SCE as the oxide thickness increases from less than 0.01 μ m to 10 μ m. Above 10 μ m, however, the oxide forms a protective barrier and the E_{bd} increases to 1000mV. Samples that had been deformed by up to 3% strain in bending developed cracks in the protective titanium layer and exposed the Ni-rich phases with a concomitant decrease in E_{bd} to below -100mV vs. SCE. These results will be discussed in terms of processing parameters for medical devices.

KEYWORDS

Corrosion, Oxidation, Strain, Nitinol, Polarization

INTRODUCTION

Nitinol is rapidly becoming the material of choice for several implant devices that rely on the superelastic properties of the material, such as self-expanding stents. Although several studies have demonstrated the good corrosion resistance and biocompatibility of Nitinol [1–3], recent studies have shown that in some cases Nitinol implants can corrode *in vivo* and release high nickel content [4, 5]. It has been shown that Nitinol corrosion resistance can be significantly improved by surface treatments such as electropolishing [1]. Electropolishing of Nitinol forms a protective uniform titanium oxide layer that protects the base material from corrosion. Still, since several Nitinol implants undergo several heat treatments to shape-set the devices or adjust transformation temperatures as

the final surface treatments, it's also important to assess the effect of Nitinol oxidation on its corrosion resistance.

Therefore, the goal of this study was to determine the effect of Nitinol oxidation on its corrosion resistance. Furthermore, since most implants are used under stress-strain conditions, the influence of strain on the corrosion resistance of oxidized Nitinol will also be assessed.

EXPERIMENTAL

Materials

Nitinol wire (50.8 at.%Ni) was fully annealed at 1000°C for 30 minutes, then centerless ground to remove the oxide that formed during the full anneal. Then, the wire was electropolished to achieve a passive titanium oxide layer before subsequent oxidation treatments in an air furnace at 400–1000°C in 100°C increments and at 3, 10, 30, 100, and 300 min.

Straight and bent (3% strain) wires were used to determine the corrosion resistance of the material. To simulate shape memory application, the wires were deformed to 3% strain in bending at a temperature below their martensitic transformation temperature and then allowed to recover at room temperature.

Corrosion Testing

In accordance with ASTM F2129, an EG&G Princeton Applied Research potentiostat model 273A was used to conduct the potentiodynamic polarization corrosion tests [6]. The potentiostat was controlled by a computer with 352 SoftCorrIII-DC corrosion test software. A saturated calomel electrode (SCE) was used as a reference electrode for the potential. Two platinum auxiliary electrodes were used as counter electrodes. Testing was conducted in an appropriate polarization cell as recommended in ASTM F2129. The solution was first de-aerated for 30 minutes prior to immersion of the test sample and then throughout the test. Then, the Open Circuit Potential (OCP) was monitored for 1 hour. The polarization of the test specimen was then started 100 mV vs. SCE below the OCP at a voltage scan rate of 0.167 mV/sec. The tests were conducted in Hank's simulated physiological solution at an initial pH of 7.4 ± 0.1 . The solution was maintained at $37 \pm 1^\circ\text{C}$ using a water bath. The corrosion resistance of the devices was characterized in terms of their breakdown potential (E_{bd}).

After testing, the samples were inspected with a JEOL JSM-5600 Scanning Electron Microscope (SEM) in both secondary electron imaging (SEI) and backscattered electrons imaging (BEI) modes. Composition of the oxide layer was analyzed by using Oxford Instruments Model 6587 Energy Dispersive X-Ray Spectroscopy (EDXS).

RESULTS AND DISCUSSION

Based on their breakdown potential, the corrosion resistance of the oxidized Nitinol specimens depended on the type of heat treatment (Figure 1 and Table 1). While some specimens did not show any localized corrosion, such as the electropolished sample, some specimens showed breakdown potentials as low as -140 mV vs. SCE (specimens heat treated at 500°C for 30 min.). Figure 2 illustrates the variation of the breakdown potential as a function of the oxide layer thickness (thickness of the oxide layer was assessed on heat treated specimens [7]).

As can be observed from Figure 2, there was a correlation between the breakdown potential and the oxide layer thickness. For oxide layer thickness between 0.01 and 0.05 μm , the breakdown

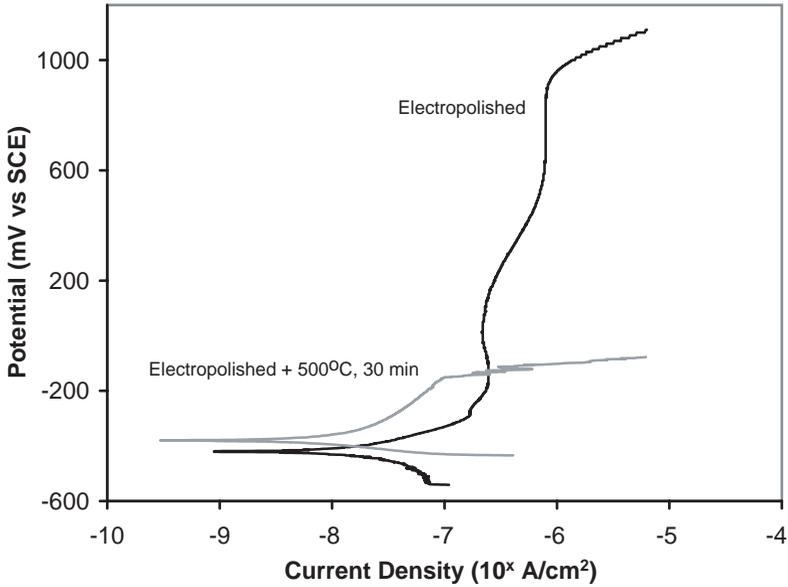


Figure 1 Polarization curves for electropolished and heat treated (500° C for 30 min.) specimens.

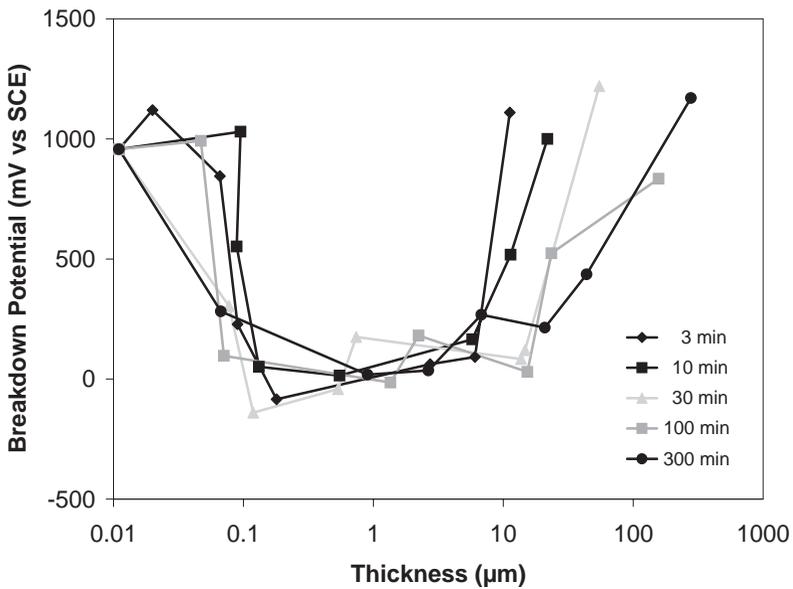


Figure 2 Breakdown potential as a function of oxide layer thickness.

potentials remained very high. Then, there was a sharp decrease in the breakdown potential starting from 0.1 μm to 10 μm thick oxide layer. An increase in the breakdown potential was observed for specimens with an oxide layer thicker than 10 μm . It is important to note that with such a thick oxide layer, the material was insulated from the test solution.

Table 1 Breakdown Potential as Function of Heat Treatment Time and Temperature^a

Time Temp.	3 min.	10 min.	30 min.	100 min.	300 min.
400° C	1120	1030	304	992	282
500° C	845	552	-140	97	18
600° C	228	51	-42	-14	36
700° C	-84	14	175	181	268
800° C	62	165	83	30	214
900° C	92	518	120	524	436
1000° C	1110	1000	1220	834	1170

a. Electropolished specimen's breakdown potential is 957 mV vs. SCE.

Deformation of the specimen (3% strain in bending) resulted in severe cracking of the oxide layer for specimens with a very thick oxide layer, which also greatly influenced the corrosion test results (Figure 3 and Table 2). As an example, the breakdown potential of the Nitinol specimens heat treated at 400° C for 10 min. decreased from 1030 mV vs. SCE to 417 mV vs. SCE. In general, a significant decrease in the breakdown potential was observed for the majority of the specimens (Figures 3 and 4).

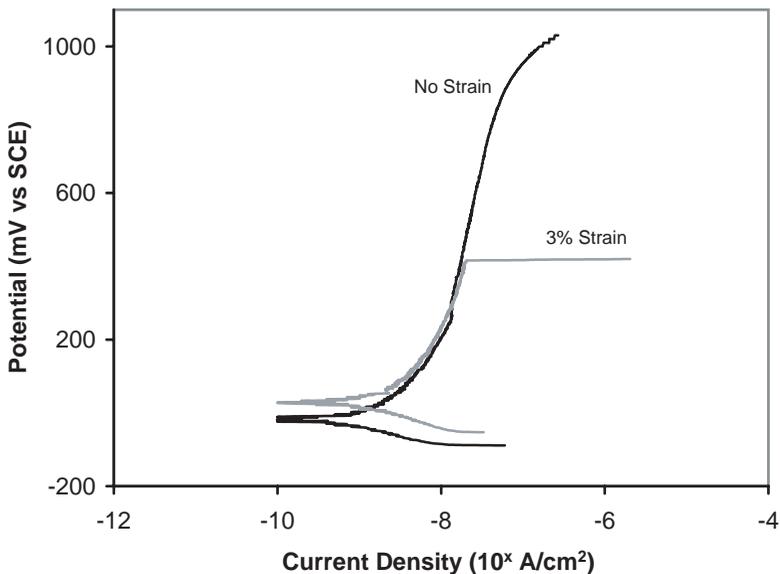


Figure 3 Effect of strain on Nitinol heat treated at 400° C for 10 min.

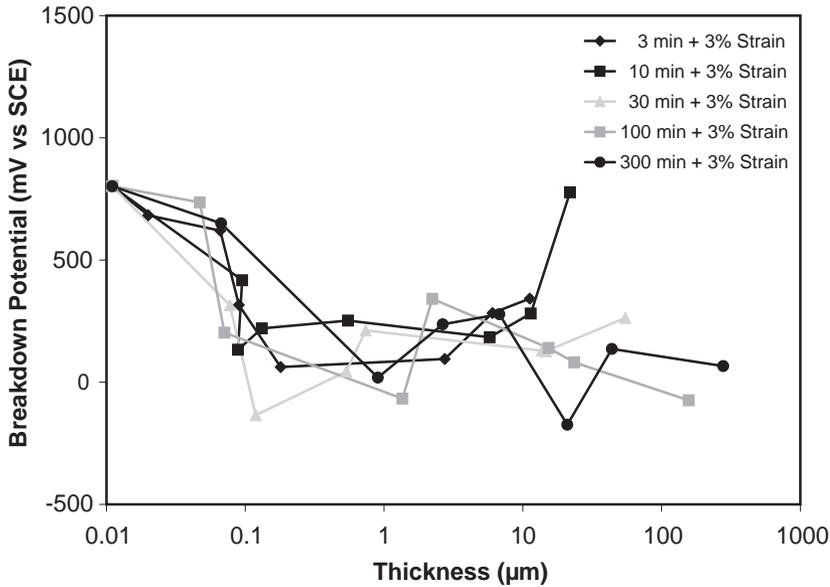


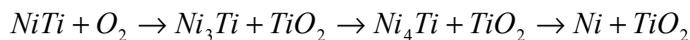
Figure 4 Breakdown potential as a function of oxide layer thickness after 3% strain.

Table 2 Breakdown potential as a function of heat treatment time and temperature after 3% strain^a

Time Temp.	3 min.	10 min.	30 min.	100 min.	300 min.
400° C	683	417	315	736	650
500° C	620	133	-135	203	19
600° C	316	220	44	-67	237
700° C	62	252	212	341	278
800° C	95	184	129	140	-174
900° C	283	281	127	81	136
1000° C	342	777	263	-74	66

a. Electropolished specimen's breakdown potential is 802 mV vs. SCE after 3% strain.

In the first part of this study, Zhu *et al.* explored the kinetics and phase transformations of oxide formation in NiTi [7]. Using the same material and heat treatments time and temperature as was used in this study, it was observed that the oxidation appears to follow a chain of reactions as follows:



The presence, amount, and distribution of these phases depend on time and temperature. Since nickel and nickel compounds have poor corrosion resistance, the presence of nickel-rich phases in the oxide layer in Nitinol can be detrimental to the corrosion resistance of the material if exposed to the environment. It is likely that the significant decrease in the corrosion resistance of the specimens with an oxide layer thicker than $0.1\mu\text{m}$ is due to defects or breaks in the protective titanium oxide layer that was illustrated by Zhu [7]. Deformation of the specimens up to 3% strain had a similar effect. These observations are in agreement with the results from our visual inspection of the wires after corrosion testing. SEM and EDXS analyses clearly showed that localized corrosion (pitting) initiated in the Ni-rich phase (Figure 5), where the nickel-rich phase appears light gray and the titanium oxide layer appears darker gray.

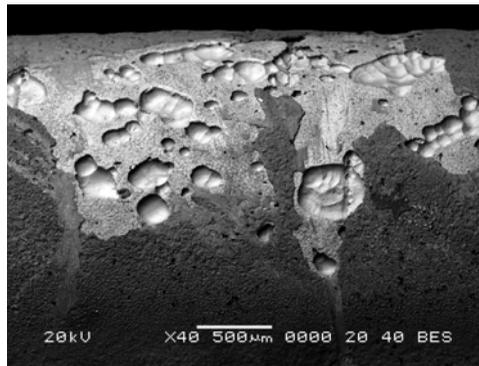


Figure 5 Pit initiation site on 1000°C , 300 min. specimen (3% strain).

These results are consistent with the results from a previous study conducted on oxidized Nitinol which showed that the uniformity and composition of the oxide layer are the determinant factors in the corrosion resistance of Nitinol [1].

Furthermore, because of its superelastic properties, it is likely that Nitinol implants will undergo significant deformation during their use. For example, the physiological strain range for implanted Nitinol stents is about 1–2% [8]. It is also not unusual for self-expandable Nitinol stents to be deformed up to 8% strain when constrained in the delivery system before their deployment. As was shown in the present study, when oxidized Nitinol is deformed, the oxide layer might crack and expose the nickel-rich phases, which can significantly lower the corrosion resistance of the material. Since the oxide layer on Nitinol is not superelastic, a thin oxide layer is preferable since it can flex and sustain the large deformations of the underlying Nitinol material without cracking.

Finally, based on these results, if Nitinol implants go through several heat treatments to shape-set or adjust the transformation temperatures of the devices, it is preferable that the implants undergo a final surface treatment to remove the thick oxide layer and passivate the surface. Furthermore, it is important to point out that unlike thermally-grown oxide that promotes the growth of mixed titanium oxide and nickel-rich phases, chemically and electrochemically grown oxide promotes pure titanium oxide formation. During chemical polishing and electropolishing, process nickel is preferentially removed.

CONCLUSIONS

This study investigated the effects of oxidized Nitinol on the corrosion resistance of the material. Our results show that

- The breakdown potential dramatically decreases from 1000mV to below -100mV vs SCE as the oxide thickness increases from less than $0.01\mu\text{m}$ to $10\mu\text{m}$. It is likely that the significant decrease in corrosion resistance of specimens with an oxide layer thicker than $0.1\mu\text{m}$ is due to defects or breaks in the protective titanium oxide layer. These superficial cracks expose Ni-rich phases that grow during the oxidation of Nitinol. Above $10\mu\text{m}$, however, the oxide forms a protective insulating barrier and the breakdown potential increases to 1000mV vs SCE.
- Samples deformed up to 3% strain in bending developed cracks in the protective titanium oxide layer and exposed the Ni-rich phases with a concomitant decrease in breakdown potential to below -100mV vs SCE.

REFERENCES

1. C. Trépanier, M. Tabrizian, L.H. Yahia, L. Bilodeau, and D.L. Piron, *J Biomed Mat Res* **43** (*Appl Biomater.*, 1998), p. 433.
2. R. Venugopalan and C. Trépanier, *Min Invas ther & Allied Technol* **9** (2) (2000), p. 67.
3. J. Ryhänen, *Min Invas ther & Allied Technol* **9** (2) (2000), p. 99.
4. G Riepe, C. Heintz, E. Kaiser, N. Chakfé, M.Morlock, M. Delling, and H. Imig, *Eur J Vasc Endovasc Surg* **24** (2002), p. 117.
5. A. Gimenez-Arnau, V. Rimbau, E. Serra-Baldrich, and J.G. Camarasa, *Contact Dermatitis* **43** (1) (2000), p. 35.
6. F2129-01, *Annual Books of ASTM Standards, Medical Devices and Services* **13.01** (2001).
7. L. Zhu, J. Fino, and A.R. Pelton, in *SMST-2003: Proceedings of the International Conference on Shape Memory and Superelastic Technologies* (Pacific Grove, Calif.: International Organization of SMST, 2003, in press).
8. T. Lopes, X. Gong, and C. Trépanier, in *SMST-2003: Proceedings of the International Conference on Shape Memory and Superelastic Technologies* (Pacific Grove, Calif.: International Organization of SMST, 2003, in press).