Conf-9205127--1

FINITE ELEMENT ANALYSIS OF MONOLITHIC SOLID OXIDE FUEL CELLS

ANL/CP--73835

DE92 010515

Anil Saigal
Department of Mechanical Engineering
Tufts University
Medford, Massachusetts 02155

and

Saurin Majumdar
Materials and Components Technology Division
Argonne National Laboratory
Argonne, Illinois 60439

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

For Presentation and Publication in Conference Proceedings
1992 ANSYS Technology Conference
Pittsburg, PA
May 4–7, 1992

*This work was supported by U. S. Department of Energy under Contract W–31–109–Eng–38.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

FINITE ELEMENT ANALYSIS OF MONOLITHIC SOLID OXIDE FUEL CELLS

Anil Saigal
Department of Mechanical Engineering
Tufts University
Medford, Massachusetts 02155

and

Saurin Majumdar
Materials and Components Technology Division
Argonne National Laboratory
Argonne, Illinois 60439

ABSTRACT

This paper investigates the stress and fracture behavior of a monolithic solid oxide fuel cell (MSOFC) currently under joint development by Allied Signal Corporation and Argonne National Laboratory. The MSOFC is an all-ceramic fuel cell capable of high power density and tolerant of a variety of hydrocarbon fuels, making it potentially attractive for stationary utility and mobile transportation systems. The monolithic design eliminates inactive structural supports, increases active surface area, and lowers voltage losses caused by internal resistance.

The fundamental building block for the MSOFC is a cell module comprising a cosintered corrugated anode, an anode/electrolyte/cathode three-layer composite, and a corrugated cathode. However, small differences in the coefficients of thermal expansion of the anode, electrolyte, and cathode give rise to large tensile residual stresses in the

anode and cathode during cool-down from sintering temperature to room temperature after firing. These tensile residual stresses often exceed the fracture strengths of the anode and cathode materials and result in failure and fracture of the cell module. The ANSYS finite-element code has been used to perform the stress and fracture analyses, to develop failure- and safe-zone maps, and to provide guidelines for selecting proper thicknesses of the electrodes and electrolyte to prevent failure of the fuel cells during fabrication.

INTRODUCTION

The monolithic solid oxide fuel cell (MSOFC), intended primarily for coal-based power generation, is currently under joint development by Allied Signal Corporation and Argonne National Laboratory (ANL). The MSOFC employs thin ceramic components in a honeycomb structure with very small cells, a design that permits fabrication into unique shapes unachievable in fuel cell systems using liquid electrolyte. The all-ceramic MSOFC is tolerant of a variety of hydrocarbon fuels, making it potentially attractive for stationary utility and mobile transportation systems. The monolithic design eliminates inactive structural support, increases active surface area, and lowers voltage losses caused by internal resistance. This results in an MSOFC with high efficiency, excellent performance, and power per unit mass or volume unequaled in any other solid oxide fuel cell configuration.

The fundamental building block for the ceramic monolithic solid oxide fuel cell stacks is a cell module comprising a cosintered corrugated anode, an anode/electrolyte/cathode three-layer composite, and a corrugated cathode. In this crossflow version, the fuel and oxidant channels are formed

by corrugated anode and cathode layers and positioned at right angles to each other. The anode/electrolyte/cathode three-layer composite is flat and is stacked between the corrugated anode and cathode. The present study was undertaken to analyze the stresses and fracture behavior in one cell module and to quantify the effects of fabrication variables (such as layer and corrugation thicknesses) on the failure of this module due to fracture and residual thermal stresses developed during cool-down from sintering temperature to room temperature.

Residual thermal stresses are generated in layered ceramic composites due to differences in the coefficients of thermal expansion of various layers; such stresses have been analyzed, for example, in a metal-ceramic two-layer system by Hsueh and Evans (1). They have also analyzed the stresses in a infinitely long work-hardening metal cylinder bonded to a ceramic that had a different coefficient of thermal expansion, and they compared their analysis with experimentally measured values of stresses at the surface for a copper-cordierite system (2). The measured stresses were significantly lower than the predicted values. The discrepancy was attributed to a difference between plane strain, which was assumed in the analysis, and plane stress, which is approximately the condition at the surface of the specimen, as well as to the porosity of the metal.

FABRICATION OF FUEL CELLS

The electrolyte is a dense layer of yttria-stabilized zirconia (YSZ) that allows mass transport of oxygen ions through the cell. The anode is a cermet consisting of nickel (NiO in the "green" and air-fired states) dispersed in a matrix of YSZ, and the cathode consists of strontium-doped lanthanum

manganite. These electrodes are electronically conductive and contain inter-connected porosity to facilitate mass transport of reactant gases to the electrode/electrolyte interfaces.

The approach to fabrication of the monolithic fuel cell is based on the process of ceramic tape casting, which is ideally suited for forming the thin (25 to 100 μm) flat ceramic layers required in the monolithic design. Multilayer tapes consisting of anode/electrolyte/cathode structures are made by several techniques, including multilayer casting, lamination under heat and pressure, and electrode spraying. The technical challenge is to cofire and cosinter the cell modules, each of which comprises a corrugated anode, an anode/electrolyte/cathode three-layer composite, and a corrugated cathode. The MSOFC is fabricated by forming thin ceramic components as green (unfired) layers, incorporating them into the monolithic structure, and cofiring the structure at elevated temperatures to form the required sintered body. The firing schedule consists of a controlled heat-up to 400°C, further heating to the sintering temperature of about 1200–1350°C, and finally, cool-down from the sintering temperature to room temperature. Because fabrication of the fuel cell requires only a single high-temperature processing step, the MSOFC has the potential for low-cost manufacturing.

Although the coefficients of thermal expansion of the cathode and the electrolyte are closely matched, the NiO–containing anode has a slightly higher coefficient of thermal expansion. Cracking was experienced in the cell modules in the anode/electrolyte/cathode three-layer composite during cool-down from sintering temperature to room temperature after firing.

The fabricated cell modules had a 10-mil corrugation thickness, 1-mil-thick electrodes (anode and cathode), and an electrolyte thickness of 5 mils.

MODELS FOR STRESS AND FRACTURE ANALYSES

The finite-element model of one cell module of the MSOFC is shown in Fig. 1. ANSYS, a commercial finite-element code from Swanson Analysis Systems, Inc., was used in this study (3). An eight-noded layered shell element (STIF 91) was used to model the anode/electrolyte/cathode three-layer composite, with each layer capable of having different thermal and elastic properties. A quadrilateral shell element (STIF 43) was used to model the corrugated anode and cathode. Because there are two planes of symmetry, only one-quarter of the cell module model was analyzed. The cell module is assumed to be stress-free at the sintering temperature when cool-down begins; the stress-free temperature is assumed to be 1200°C.

The thermal and elastic properties used in the analysis are shown in Table 1, and the strength values reported in Table 1 were measured at ANL. Toughness of the anode/ electrolyte interface for this study is assumed to be 1.5 MPa $m^{1/2}$ (4). Residual elastic thermal stresses are generated in the externally unconstrained cell module during cool-down and reach a maximum at the end of cool-down when the cell module is at a uniform temperature. In the linear elastic fracture mechanics analysis, a through crack parallel to the anode corrugation at the anode/electrolyte interface is assumed to preexist. Strain energies (W) are calculated at two different crack lengths, and from that the strain energy release rate per unit extension of the crack area, G, is computed:

$$G = -\frac{\delta W}{\delta A_c}$$

The stress intensity factor, K, a measure of toughness, which is related to G, is given by

$$K = \left(\frac{E G}{1 - \nu^2}\right)^{1/2}$$

where E and ν are the elastic constants of the electrolyte.

It is known that the stresses near the tip of a crack between two dissimilar materials have an oscillatory singularity, and therefore the strain energy release rate and the stress intensity factor cannot be defined in the conventional sense (5). However, in many models of interfacial cracks, strain energy release rates are computed by ignoring the oscillatory singularity. A study by Delale et al. has also provided some basis for calculating strain energy release rates by simplified beam or plate analyses or by finite-element analyses, ignoring the oscillating character of the singularity (6).

RESULTS

Cell modules with several anode/electrolyte/cathode (A/E/C) thicknesses were analyzed. The fuel cell currently being fabricated had an A/E/C ratio of 1:5:1 and 10-mil-thick corrugations. Based on finite-element analysis, the maximum tensile stresses in the anode and cathode were 168 and 94 MPa, respectively. These values far exceed the measured strengths of the anode (100 MPa) and cathode (65 MPa). The stresses in the electrolyte are compressive. This is to be expected because the coefficients of thermal expansion of the anode and cathode are greater than that of the electrolyte. Thus, based on the analysis, it is reasonable to conclude, as has been

observed, that the fuel cells will crack and fail due to residual thermal stresses generated during cool-down from sintering temperature to room temperature during fabrication. It was also found that the slope of the corrugations did not significantly change the anode and cathode stresses.

A parametric study was conducted to obtain a better understanding of the effects of A/E/C thickness ratio and corrugation thickness on the stresses in the anode and cathode and to develop failure- and safe-zone maps. The maximum tensile anode and cathode stresses occur in the anode and cathode, which form part of the three-layer composite. Figures 2 and 3 show the maximum tensile anode and cathode stresses, respectively, as a function of electrode (anode and cathode), electrolyte, and corrugation thicknesses. Anode thickness is equal to cathode thickness, and anode stresses are found to decrease with increase in electrode thickness and with decrease in electrolyte thickness (Fig. 2). Similarly, cathode stresses decrease with increase in electrode thickness and with decrease in electrolyte thickness (Fig. 3). However, as corrugation thickness was decreased from 10 mils to 5 mils, the anode stresses decreased while the cathode stresses increased.

Figure 4 shows the stress intensity factor as a function of electrode thickness and electrolyte thickness for 10-mil-thick corrugations. The factor increases with increasing electrolyte thickness but tends to increase, reach a maximum, and then decrease as a function of electrode thickness.

The failure- and safe-zone maps for corrugation thicknesses of 5 and 10 mils are shown in Figs. 5 and 6. For small electrode thicknesses, anode fracture is the dominant mode of failure. As electrode thickness increases,

cathode fracture becomes the dominant mode. In addition, as corrugation thickness increases, the probability of anode failure increases while that of cathode failure decreases. Over the range of electrode and electrolyte thicknesses studied, the cell module will fail because of cathode or anode fracture rather than anode delamination due to crack propagation at the anode/electrolyte interface. It appears that for a reasonably thick electrolyte, i.e., minimum thickness of 3 mils, the electrodes should be atleast 6 mils thick. Thus, the cell module should comprise a 10-mil-thick corrugated anode, an anode (6 mils)/electrolyte (3 mils)/cathode (6 mils) three-layer composite, and a 10-mil-thick corrugated cathode.

CONCLUSIONS

The ANSYS finite-element analysis code has been used to predict the residual thermal stresses developed in one cell module of a monolithic solid oxide fuel cell during final cool-down from sintering temperature to room temperature.

The failure mode of the monolithic solid oxide fuel cell during cool-down after firing depends on the mismatch of the coefficient of thermal expansion of the anode and the other layers, the fracture toughness, and the thickness of the various layers.

The analysis predicts, as has been observed, failure of the cell module with a 1:5:1 ratio of the anode/electrolyte/cathode thickness due to high tensile residual stresses that develop in the anode and cathode during fabrication.

Failure- and safe-zone maps have been developed to provide guidelines in selecting the proper thicknesses of electrodes and electrolyte to prevent failure of the fuel cells during fabrication.

A cell module comprising a 10-mil-thick corrugated anode, an anode (6 mils)/electrolyte (3 mils)/cathode (6 mils) three-layer composite, and a 10-mil-thick corrugated cathode is recommended for future fabrication and study.

ACKNOWLEDGEMENT

This work was supported by U. S. Department of Energy under Contract W-31-109-Eng-38.

REFERENCES

1. C. H. Huesh and A. G. Evans, "Residual Stresses in Metal/Ceramic Bonded Strips," J. Am. Ceram. Soc., 68 [5], 1985, pp. 241-48.

2. C. H. Huesh and A. G. Evans, "On Residual Stresses and Cracking in Metal/Ceramic Systems for Microelectronics Packaging," Mechanical Aspects of Interfaces and Surfaces in Ceramic Containing Systems, Annual Report to Office of Naval Research, Contract N00014-81-K-0362, Department of Materials Science and Mineral Engineering, University of California, Berkeley, Dec. 31, 1984, pp. 242-82.

3. ANSYS Users Manual, Swanson Analysis Systems, Inc., 1990.

4. S. Majumdar, T. Claar, and B. Flandermeyer, "Stress and Fracture Behavior of Monolithic Fuel Cell Tapes," J. Am. Ceram. Soc, 69 [8], 1986, pp. 628-33.

5. F. Erdogan and G. Gupta, "The Stress Analysis of Multilayered Composites with a Flaw," Int. J. Solids Struct., 7, 1971, pp. 39-61.

6. F. Delale, A. S. D. Wang and W. Binienda, "On Strain Energy Release Rate for a Crack at the Interface of Two Bonded Materials," Advances in Aerospace Sciences and Technology, AD-08, Eds. J. Yuceoglu and R. Hesser, ASME, 1984, pp. 113-19.

Table 1 Mechanical Properties of Anode, Electrolyte, and Cathode Used in the Finite Element Analysis

Property	Anode	Electrolyte	Cathode
Young's Modulus (MPa)	1.38×10^5	1.80×10^5	1.23×10^5
Poisson's Ratio	0.26	0.32	0.27
Fracture Strength (MPa)	100	185	65
Thermal Expansion Coeff. (/°C)	11.38×10^{-6}	10.53×10^{-6}	10.89×10^{-6}

LIST OF FIGURES

Figure 1 Typical Geometry of One Cell Module in a Monolithic Solid Oxide Fuel Cell.

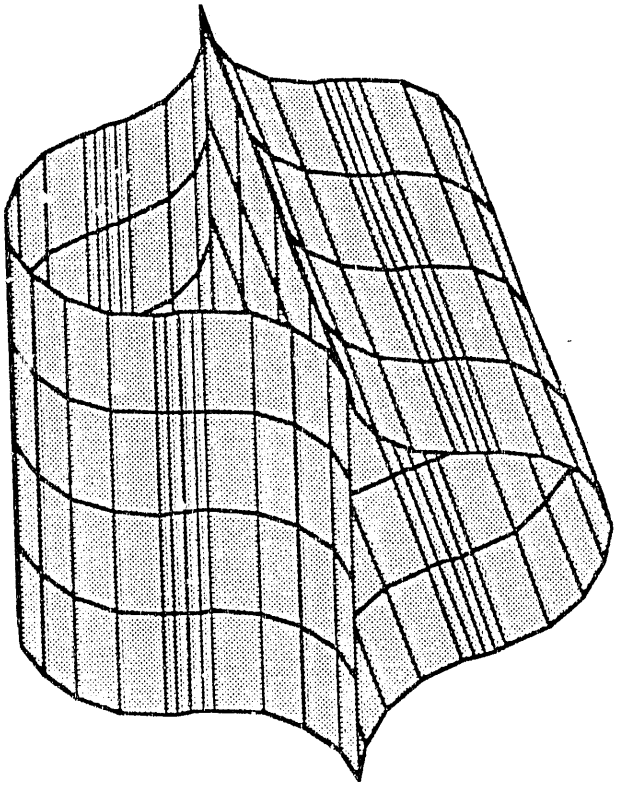
Figure 2 Maximum Tensile Anode Stress as a Function of Electrode (Anode and Cathode), Electrolyte, and Corrugation Thicknesses. (MOR=modulus of rupture)

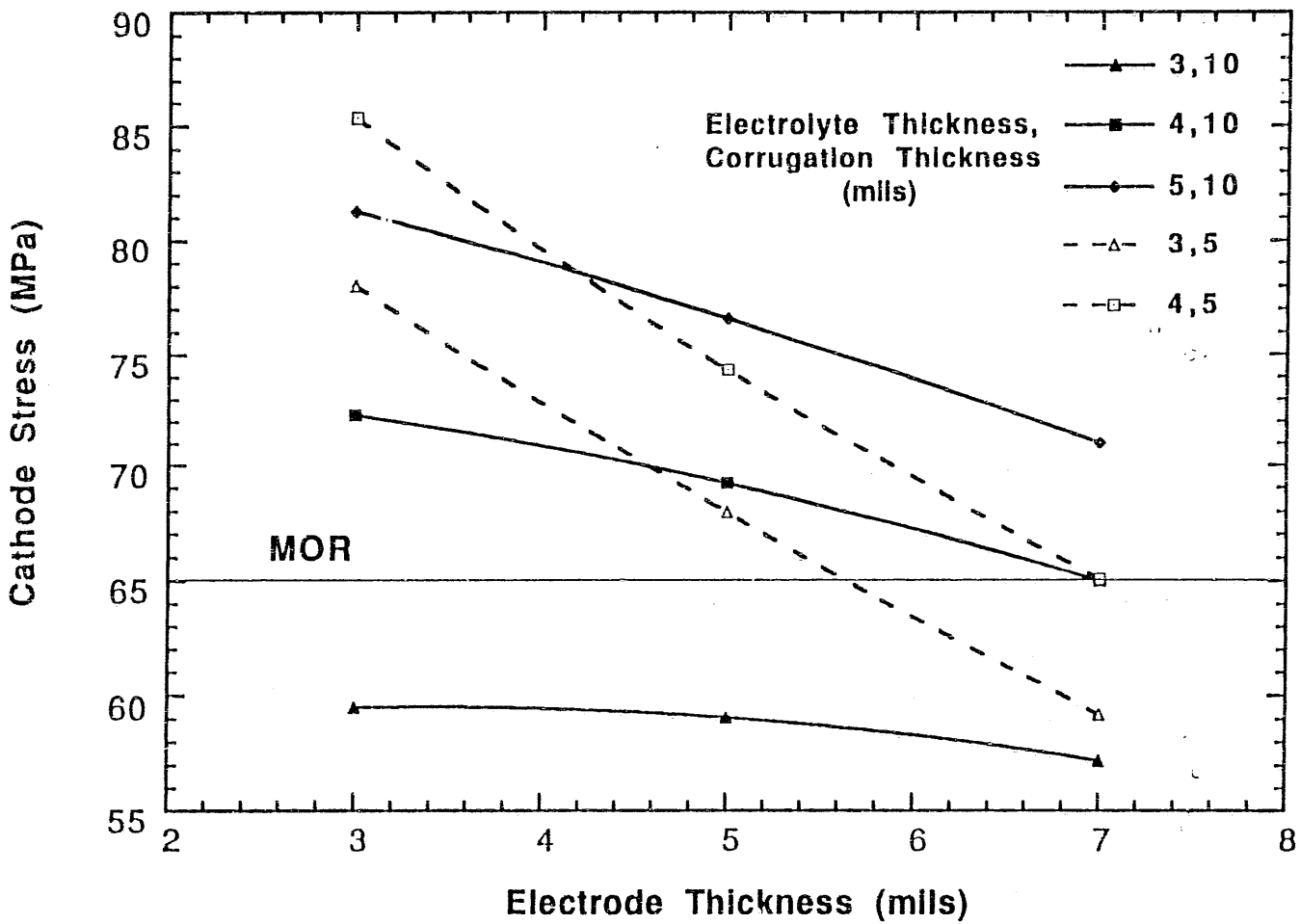
Figure 3 Maximum Tensile Cathode Stress as a Function of Electrode (Anode and Cathode), Electrolyte, and Corrugation Thicknesses. (MOR=modulus of rupture)

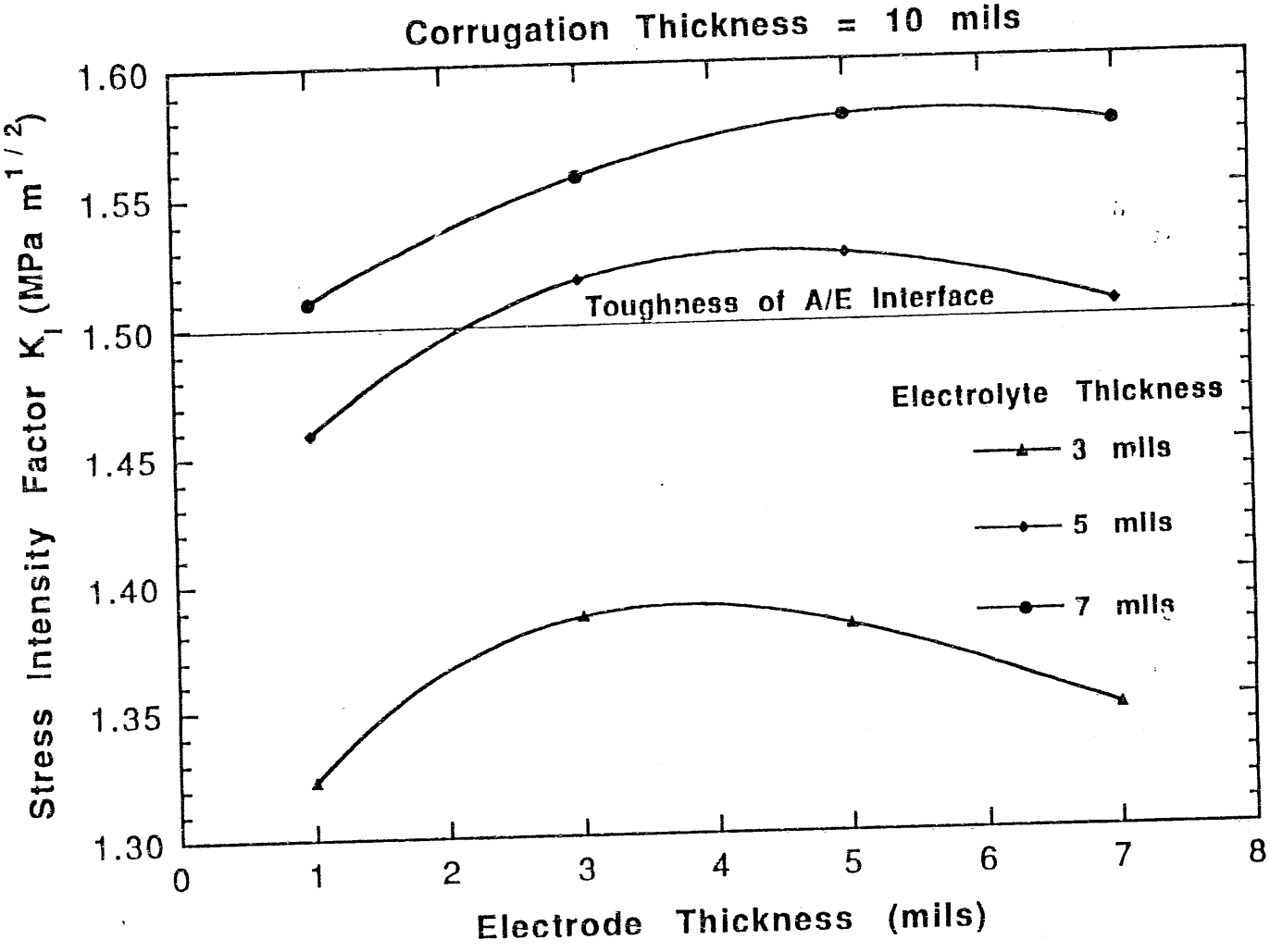
Figure 4 Stress Intensity Factor as a Function of Electrode and Electrolyte Thickness for 10-mil-Thick Corrugations.

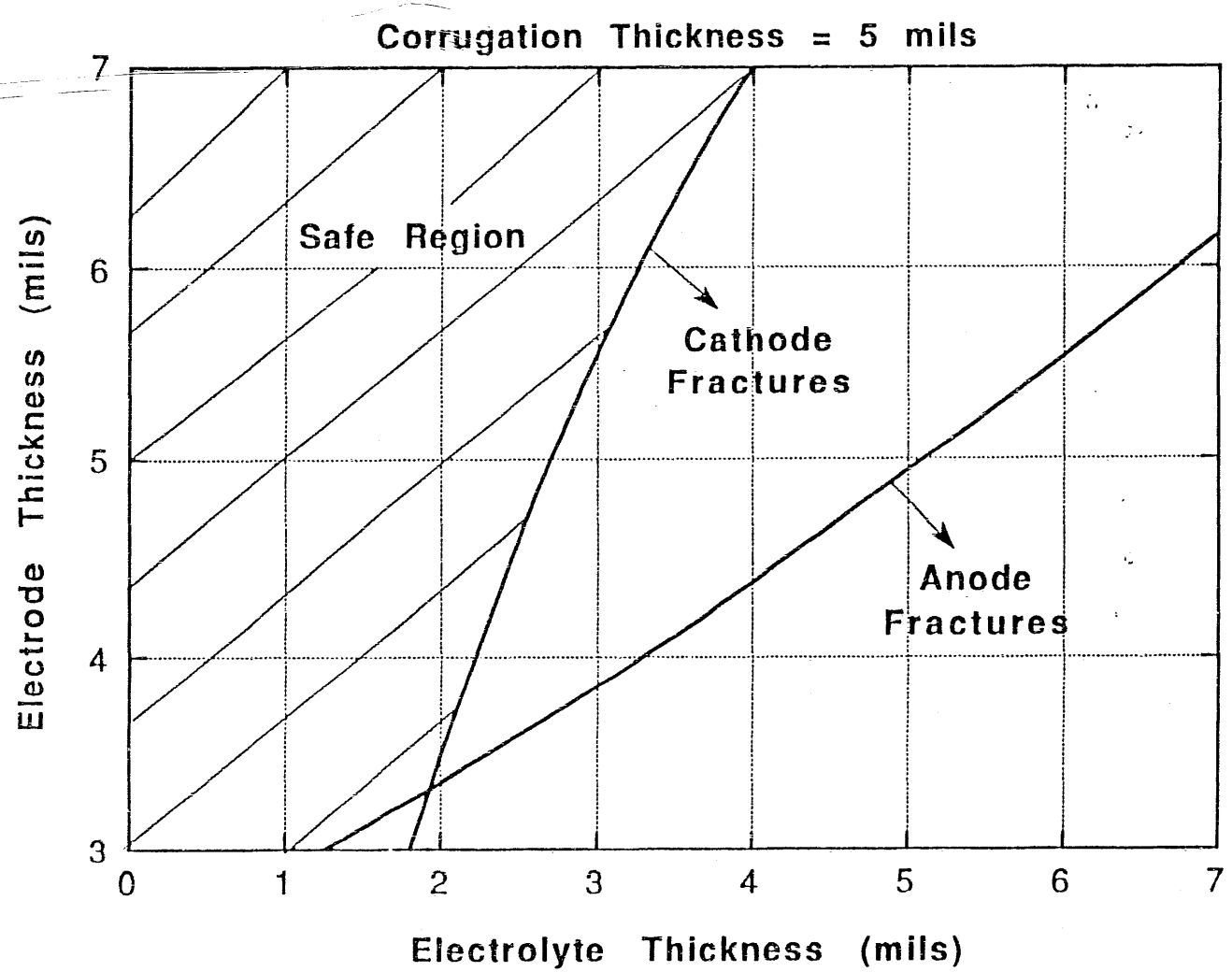
Figure 5 Failure- and Safe-Zone Map for 5-mil-Thick Corrugations.

Figure 6 Failure- and Safe-Zone Map for 10-mil-Thick Corrugations.



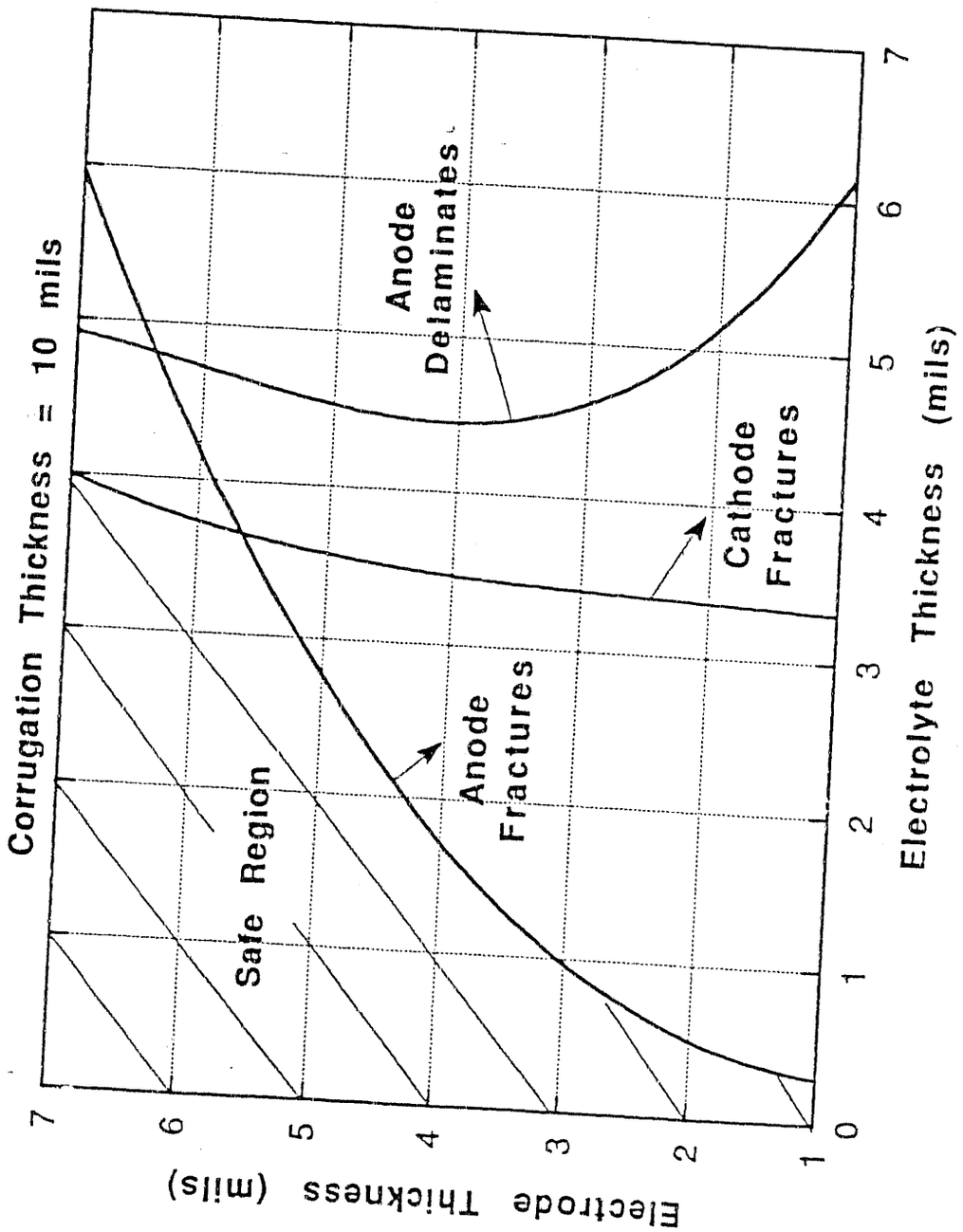

Cathode Stress (MPa)
90
85
80
75
70
65
60
55
2
3
4
5
6
7
8
Electrode Thickness (mils)
Electrolyte Thickness, Corrugation Thickness (mils)
3,10
4,10
5,10
3,5
4,5
MOR


Corrugation Thickness = 10 mils
Stress Intensity Factor K_I (MPa $m^{1/2}$)
1.60
1.55
1.50
1.45
1.40
1.35
1.30
Toughness of A/E Interface
Electrolyte Thickness
3 mils
5 mils
7 mils
0
1
2
3
4
5
6
7
8
Electrode Thickness (mils)


Corrugation Thickness = 5 mils
Safe Region
Cathode Fractures
Anode Fractures
Electrode Thickness (mils)
Electrolyte Thickness (mils)
7
6
5
4
3
0
1
2
3
4
5
6
7

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.



END

DATE
FILMED
5/13/92