

Reliability Investigation of piezoelectric Macro Fibre Composite (MFC) Actuators

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Abstract

Commercial Piezoelectric Macro Fibre Composite (MFC) actuators show high potential for vibration and noise reduction of flat mechanical structures like car roofs, windshields, and building facades. Within the European project "InMAR", the reliability of these devices has been investigated experimentally. The reliability assessment strategy of such complex material systems differs from the one applicable to monolithic materials. Failure modes different from the material immanent failures may occur randomly along the desired life span of the device. Therefore, a combined strategy of qualitative and quantitative methods as well as design weakness and accelerated testing techniques has been applied. Different test scenarios of combining the damage relevant parameters like electric field, mechanical strain and temperature were realized. It was found that the investigated devices exhibit a high reliability even on a lab scale production process. Cycles of more than 10^8 were survived without obvious degradation, despite high electromechanical cycling amplitudes and elevated temperatures. Microscopic investigations of cycled but still undegraded samples revealed intensive cracking all along the macro fibres, leading to the conclusion that this internal damage is tolerated as a system immanent procedure and does not affect the macroscopic performance. It is concluded that the MFC actuators show excellent reliability performance when applied within the specification range.

1. Introduction

Multi-functional materials are the key to integrated sensor and actuator functions which enable adaptronic systems to intelligently react on varying forces and environment [Her04, Han00]. The reliability of adaptronic systems has not extensively been investigated in the past, but it is evident that it strongly depends reliability of the functional material systems. The present study is a contribution to the reliability investigation of a special group of piezoelectric composite materials, the so called Macro Fibre Composite (MFC) patch actuators.

1.1 MFC actuators – design and properties

MFC actuators consist of rectangular uniaxially aligned piezofibers sandwiched between layers of adhesive and electroded polyimide films. Smart Material Corp. has commercialised the MFC – technology now offering a variety of different design forms [www.smartmaterial.com]. The device investigated here is a contracting MFC making use of the d_{31} effect (so-called P2 – type).

This device uses PZT fibers with top and bottom electrodes obtained by dicing metalized PZT wafers. All finger electrodes of each side connected together. Thus, the applied electric field is applied through the fibre thickness, see Fig. 1. The MFC assembly enables in-plane actuation and sensing in a sealed, durable, ready-to-use package.

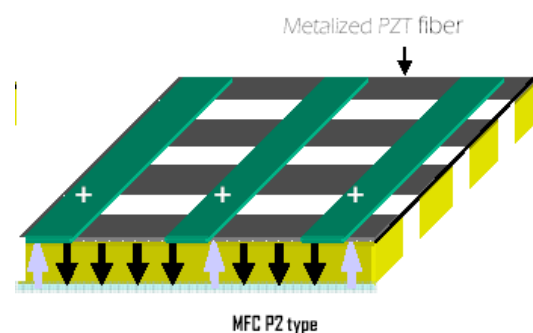


Fig. 1: Explanation of the 3-1 MFC with unipolar electrode structure on each side comprising a layered metallization on diced PZT fibers and unipolar finger electrodes.

The typical operational values of the device are summarized in the following table:

Properties of MFC P2- type		
Dimension active area	mm ²	85 x 28
Driving Voltage	V	-60 ... + 360
Specific Capacity	C/cm ²	4,5
Effective piezocoefficient d_{31}	pC/N	- 370
Effective Young's Modulus in actuation direction	GPa	30
Max. operation temperature	°C	80

1.2 Reliability investigations on PZT composites

The change of actuation and sensing performance of piezoelectric material is accounted to a variety of mechanisms, which depend on the design, application and loading conditions of the piezoelectric device.

Very little has yet been published on the degradation of Macro-Fiber-Composite (MFC) patches itself; one exemption is [Wil04].

Previous work on degradation in piezo patches in general includes the modelling of crack propagation in PZT material [Zha04, Zha04b]. The bending strength of PZT patches has been shown to depend on temperature and applied electric field [Fu00]. A number of mechanisms have been associated with fatigue, such as the ferroelectric fatigue of field induced polarization and strain [Pan92], the electrical fatigue [Kim96] due to microcracking and the electromechanical fatigue [Yoc03], which takes into consideration the interaction of mechanical and electrical loads. Thermal cycling of PZT patches has shown a significant influence on sensing and actuation performance [Bro96]. The performance of patches embedded in carbon fibre reinforced epoxy and their influence on the fatigue life of the laminate have been investigated extensively [Mal98, Mal00, Mal02]. Fibre composite patches have been cycled [Thi03] showing almost no degradation when loaded within their specified limits. The latter is the general impression when studying the available literature on cyclic damage in composites.

1.3. System reliability of complex materials

In the past, many publications appeared dealing with cyclic damage in monolithic piezoelectric materials [e.g. Nuf00 and references therein]. The aim was mainly to characterize the so called electric fatigue phenomenon which is characterized by a subsequent decrease of actuation perform-

ance due to microstructural processes within the material.

However, in a material composite not only these long term mechanisms will play a role for reliability. The failure behavior of such a material system will also be characterized by the interactions of the different materials and the interfaces between them. Possible failure modes will also be the delamination of materials as well as insufficient solder points or wiring. In other words, the pure material – immanent failures will be superimposed by those originating from improper manufacturing or design weaknesses.

As a first approach, we will assume that the failure behaviour of a *material system* will be similar to the one observed for *technical systems*. The failure behaviour thus is described by the well – known bath tub curve [Con01, Ber99] shown in Fig. 2.

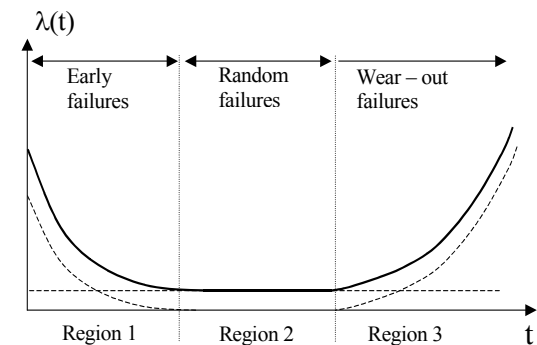


Fig. 2: The typical bathtub curve (thick line), as a superimposition of the three failure rates belonging to independent failure mechanisms dominating in the regions 1–3 (dashed lines).

The failure rate $\lambda(t)$ rate (number of failures per unit time) shows a characteristic time dependency, which is subdivided into three regions:

Region 1 exhibits a falling failure rate and covers the so-called early failures (“infant mortality”). The origin for those failures in most cases is not related to material properties, but rather to the quality of the manufacturing process of the whole device.

Region 2 is characterized by a constant failure rate and covers random failures that are not governed by a single failure mechanism. In this region, the device fails due to miscellaneous interactions with its environment, e.g. peak-like overloads, misuse, high temperatures and others.

Region 3 is the region where material-related failures start to dominate. The phrase “wear out failures” is commonly used. The failure modes in

this region are initiated by detrimental changes of the devices' material components, caused by the service loads applied to the device. The mechanisms leading to failures are called degradation mechanisms.

The failures of phase 1 and 2, in contrast to region 3, in general do not obey a statistical distribution of a basic population. These failures must be avoided by proper design of the device and/or by well controlled manufacturing processes. Therefore, the strategy is not to describe these failures by statistical means but to characterize the failures and then define adequate means of failure prevention.

2. Experimental investigations

The experimental test program aimed at investigation of possible failure modes along the whole life span of the device. Therefore, all three regions of the bath tub curve must be addressed.

The key elements of the investigations are:

- provoking of possible failure modes by different test scenarios
- Statistical treatment of the "phase 3 failures" expected in the high cycle range ($> 10^8$) of the material.
- identification of possible failure modes by means of microstructural investigation
- understanding failure origins as well as fault toleration mechanisms within the device by microstructural investigation

In the following sections, the different experimental approaches performed at the involved institutes are described.

2.1 Uniaxial cycling (free strain)

One part of the experimental examinations dealt with the operation of the MFCs without any mechanical load. Under these free strain conditions an unipolar electrical field (0-2kV/mm, 0-360V) with a constant frequency (120Hz) was applied to the MFC. Due to the electrical coupling the MFC alternates between no strain and the maximum strain (free strain) value. These test conditions apply a maximum movement on the ceramic, the packaging polymer and the electrode material. All material interfaces, esp. the interface between the ceramic and the packaging polymer have to withstand the free strain movement. The most expected failure mode is the delamination of the interface between the ceramic and the packaging. This results in an electrical debonding of the ceramic and the electrodes. The performance of the MFC under free strain conditions is a good

indicator of packaging reliability and endurance [Wil04]. The test setup is shown in Fig. 3.

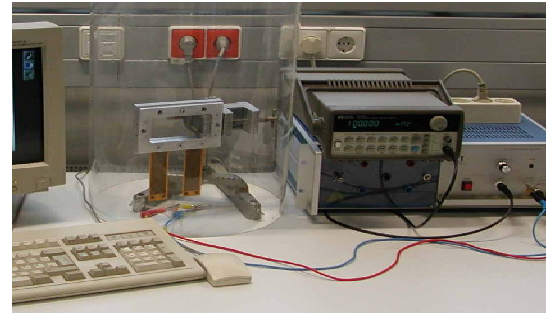


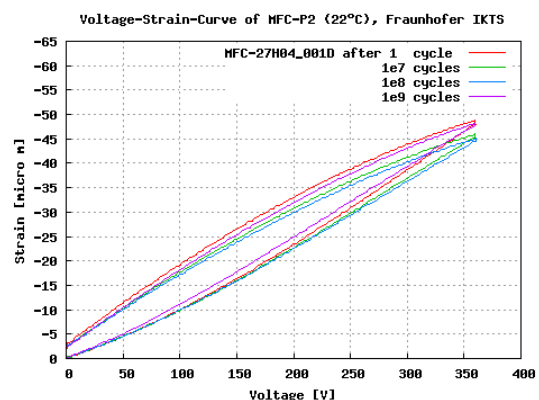
Fig. 3: setup of the experiments under no mechanical load conditions, room temperature

The environmental conditions (temperature, humidity, media exposure) have a not neglectable influence on the aging esp. of the polymer and therefore on the lifetime of the MFC device. One of the most important impacts in this context is the influence of the temperature. The conducted experiments were carried out at two temperature levels (22°C and 75°C) with two samples at each temperature.

The monitoring of the MFC performance was measured at the following cycle numbers: 1(initial), 1e6, 2e6, 5e6, 1e7, 2e7, 5e7, 1e8, 2e8, 5e8 and 1e9. The monitoring parameters are:

- voltage-strain curve
- small signal capacity and loss factor ($\tan \delta$)

As already stated above the main focus of the experiment is on the degradation of the device composition (packaging delamination). The measured parameters are indicating changes in the MFC device. To clearly separate according degradation mechanisms in addition micro structural investigations were performed (section 2.3)



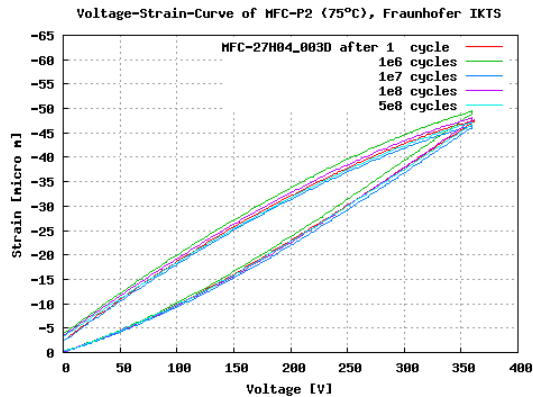


Fig. 4: voltage-strain-curve at increasing cycling numbers up to $1e9$ cycles.

Fig. 4 depicts the voltage-strain-curves from the 1st cycle (initial state) to the measurement values up to 10^9 cycles. The absolute value of the free strain at 360V of the four tested samples show a variation of about 4%. This is a common value for MFCs. Up to 10^9 cycles the free strain values at the check cycles are within a band of 10%. There is no difference in the results for the cycling temperatures of 22°C and 75°C.

Measurements of dielectric data reveal the high stability of MFC under free strain conditions. As shown in Fig. 5 a very limited reduction of capacity and tand was found. A drop in capacity would indicate local electrode debonding. The increase of tand is expected if a degradation in the ceramic occurs. Those effects have not been seen.

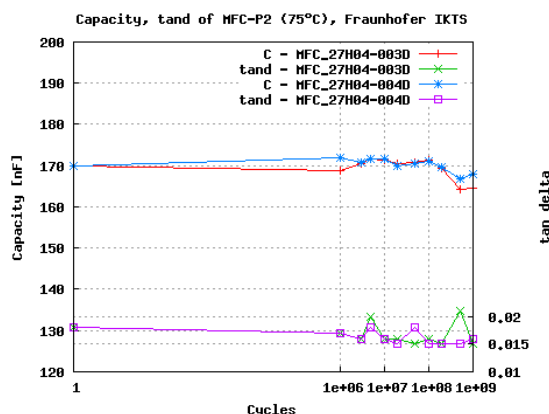


Fig. 5: measured dielectric data: small signal capacity and tand

2.2 Bending cycling

The second load scenario investigated was under application of the patch actuator to a steel beam.

In order to introduce mechanical cycling simultaneously to the electrical treatment.

Loss of performance through long duration use of PZT devices is a common observation. High-durability PZTs follow a time-dependent deterioration of displacement amplitude and also current leakage. In these cases degradation is displayed by a change in the hysteresis loop, showing a decrease in remanent and maximum achievable polarization and an increase in coercive field as the domain walls become more heavily pinned. The degradation mechanism, responsible for cyclic loading damage, is caused by changes in the coupling of mechanical-electrical parameters (mainly ageing and depoling) and by structural inhomogeneities (microcracking).

The steel beams of dimensions 250 x 40 x 1 mm were prepared by gluing the patches to the beams by means of a 2 – component epoxy (3M DP 460). Fig. 6 shows the specimen as well as a sketch of the dimensions of the beams.

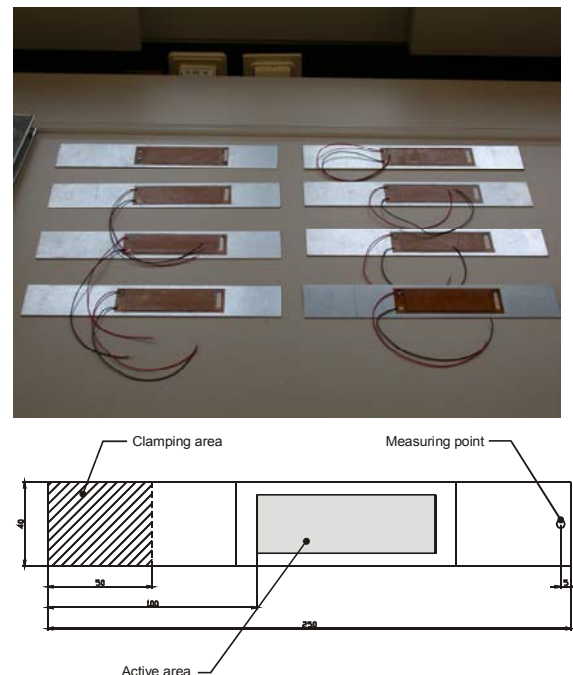


Fig. 6: Steel beams with attached piezo patches prepared for experimental testing (top), sketch of the beam geometries showing the positioning of the patch on the beam (bottom)

The beams were tested at IMM and ERAS with test stands described in the following:

2.2.1 Bending tests at IMM

The degradation of piezoelectric MFC patches, bonded on thin steel beams, was examined at resonance (~ 125 Hz), temperature range from 20° C to 150° C and long fatigue duration (up to 0,5 billion cycles).

The developed experimental set up and the associated peripheral units were capable to:

- Impose vibration at the second eigen-frequency (~ 125 Hz) of the MFC patch-steel beam. The structure is fixed at the one end and cycling electrical field form stationary waves
- Control the frequency in order the structure to remain at resonance as the eigen-frequency is slightly but continuously shifting.
- Heat the specimen uniformly from 20° C to 150° C and keep the temperature constant at the selected level.
- Measure instantly the following parameters : frequency, beam deflection, temperature, power, current, impedance, capacitance, coupling coefficient and $\tan\delta$.

A real time, high-speed hardware – software unit was designed and constructed, together with a chamber with environmental control. Beam deflection (during cycling) was measured by a laser displacement transducer ($0,2 \mu\text{m}$ accuracy, 50 Ksamples / sec). Four specimens could be independently tested at the same time (Fig. 7)



Fig. 7: The experimental set up for resonant testing of four PZT patches bonded on steel beams.

The evolution of resonant frequency, displacement against fatigue cycles and impedance, capacitance against fatigue cycles is presented in Figs. 8 and 9.

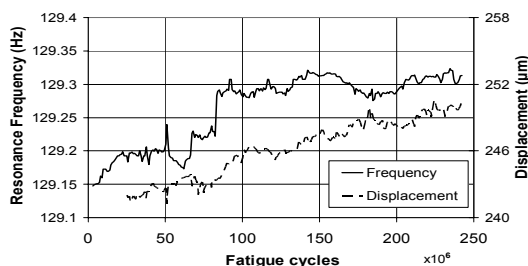


Fig. 8: Variation of resonant frequency and displacement against fatigue cycles.

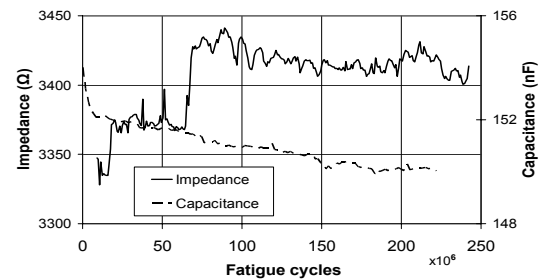


Fig. 9: Variation of impedance and capacitance as a function of fatigue cycles.

The results are summarized and interpreted as follows:

The effective power consumption presents a local maximum in the resonant mechanical frequency and therefore it can reliably replace the vibration amplitude as a measure for the estimation of the eigenfrequency shift.

Mechanical resonance, peak current and minimum impedance occur within 1 Hz frequency span.

The electromechanical coupling coefficient was used as a measure of the ageing of the PZT material. The coupling coefficient was found to have a nominal increasing trend.

The experimental data indicate that the piezoelectric material does not exhibit considerable degradation operating at a temperature up to 150°C (IMMG please check: is the temperature correct?), at its resonant frequency of ~ 125 Hz and for 0,5 billion cycles.

2.2.2 Bending tests at ERAS

The tests executed at ERAS aimed for a statistical treatment of “phase 3” failures. For this purpose, it is important to test as many specimen as possible simultaneously. The procedure of statistical treatment will be examined during the following section.

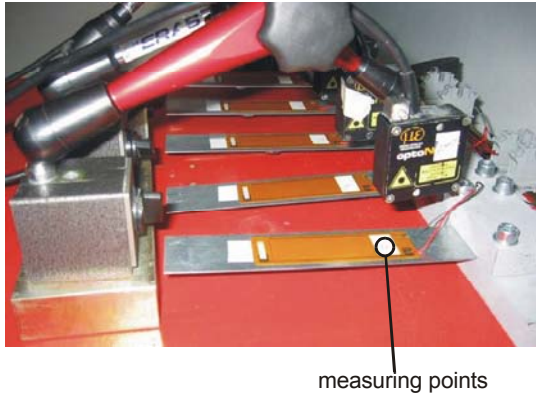


Fig. 10: Test-stand for degradation tests. The images show the beams with clamping unit and the laser sensors for the acquisition of the deflection.

The test stand developed at ERAS is shown in Fig. 10. In order to stiffen the set-up, the entire clamping unit was fixed to a massive steel plate.

The piezo actuators are excited in the first bending resonance by a sine signal via a frequency generator. The deflection signals are acquired by laser sensors. In the present experiments, 5 beams were cycled up to approx. 2×10^8 cycles. The measurement and evaluation was carried out with a multi channel measuring system which acquires the deflection of the bars daily. During the measurement the piezo patches are triggered with a sweep from 0...250 Hz. The measuring time is 180 s. The diagrams in Fig. 11 show the transfer functions at the start and the end phase of the measurements.

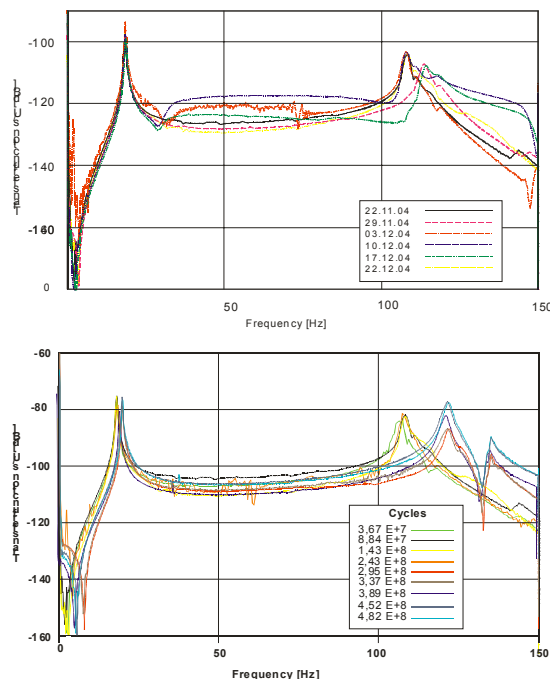


Fig. 11: Transfer function 0-150Hz at the beginning (top) and at the end (bottom) of the test period

Success run analysis

The comparison between the transfer functions before and after cycling reveals that there is no change in the performance of the device. All $n = 5$ specimen survived the degradation test without any substantial indication of a reduction in performance within $t_{\text{test}} = 2 \times 10^8$ cycles. This is the basis for the success run analysis.

Due to space constraints, the full explanation of the success run test theory is not presented here. For a better understanding, the interested reader may consult the literature [Nuf06, Mey03].

In many practical cases, a lifetime (or cycle number) L_{dem} is demanded. While metallic components often are designed to lifetimes of $L_{\text{dem}} = 10^6$ cycles, in case of piezoelectric devices a cycle number of $L_{\text{dem}} = 10^8$ is frequently regarded as a reasonable value.

The aim of the investigation is to calculate a *least guaranteed probability of survival* R_{min} until $L_{\text{dem}} = 10^8$ cycles.

The analysis is only valid if the basic population obeys a distribution function. Since the analysis is applied here to material immanent failures (phase 3 – failures) like electrical fatigue of the piezo material only, it is reasonable to assume that the probability of survival R follows a weibull distribution. Another assumption is that the weibull parameter β is associated with a degradation process and is reasonably chosen in the range $\beta \in [2,5 \dots 3,5]$. Together with a confidence level of $\alpha = 90\%$, the success run formula (Eq.1)

$$R_{\text{min}}(L_{\text{dem}}) = (1 - \alpha)^{\frac{1}{n \left(\frac{t_{\text{test}}}{L_{\text{dem}}} \right)^{\beta}}} \quad (1)$$

results in a least guaranteed survival probability of

$$R_{\text{min}} \approx 93\% \quad (2)$$

The general relation between the so – called life time ratio $t_{\text{test}} / L_{\text{dem}}$, which indicates how much longer than the demanded lifetime the test specimens survived, the number of tested specimen, and the achievable survival probability ins shown in Fig. 12.

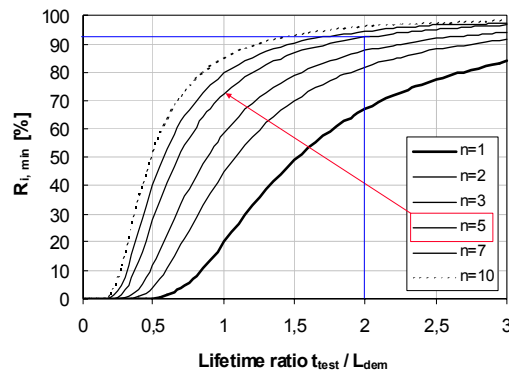


Fig. 12: Dependency of R_{min} on the lifetime ratio and the number of test specimen

The interpretation of the result is that the MFC actuators exhibit a very small probability to fail (ca. 7%) due to degradation processes. Note that this analysis is only valid for the given test parameters and is not valid for failure origins different from degradation which have been discussed in the theoretical background.

2.3 Microstructural investigation

The metallographic samples were prepared considering the structure of the MFC. Two samples were taken in the longitudinal direction and another one in the transverse direction in different areas along the patch. To keep the different materials in the MFC safe the sample preparation was done shaping the three cuts together using a resin (epoxy) so the process was performed under room temperature.

Firstly, the cuts were carefully located in the mould. Then the shaping process was made using the epoxy resin in a liquid stage and mixing it up with a commercial hardener. The sample was afterwards cured for 24 hours at room temperature. This way the resin was kept under environment conditions and no contractions or dilatations happen to the metallographic sample and so, no crack appeared due to the sample preparation.

Optical and SEM microscopy were considered for microstructural characterization of the material. Electromechanical failure effect on material was aimed in this part of the study, so cracking and microstructure changes were the target of the study. Consequently samples with and without etching were considered for complete characterization.

Etching is used to reveal the microstructure of the material to be studied. The PZT material etching recommended in the literature (Ceramography) was used in this study, a mixture of distilled water, chloride acid and fluorhydric acid. By means of chemical etching the domain and grain boundary structure were revealed.

Microscopic study was carried out on samples tested under material specifications (maximum cycles 10^9 and temperature 75°C).

PZT fibers are ceramic materials and consequently fragile. Due to their low resistance they are susceptible to crack during cycling (samples are submitted to bending at each cycle and consequently, the embedded PZT fibres are stressed). The investigation on cycled but still undegraded samples revealed different damage stages in the material, see Fig. 13.

At the initial stage (no testing) pores of different sizes and some cracks due to samples manufacturing process appeared in the PZT fibres. But the longer took the cycling the higher the cracking of the material (from the point of view of both, dimension and quantity). In some cases the origin of the cracks were located in previously existing damages (like pores), and in other cases they were due to failure of the material itself.

Regarding the influence of cracking on the electromechanical behaviour of the MFC system, it seemed not to be affected while kept under MFC specifications.

In order to study electromechanical features from the microstructure point of view, domain structure was revealed by means of chemical etching. In most cases it was necessary to use SEM microscopy due to the small grain size (between 140 and 200 μm). Although in certain cases, when samples showed considerable grain size (between 400 and 300 μm), it was possible to see the domain structure using optical microscopy, see figure 14. Slight depolarization has been observed in the domain orientation of the PZT material after cycling. In the raw material, polarization domains were continuous among the different grains and oriented in the main polarization direction. After cycling, domains were slightly reoriented due to the electric fields applied during cycling, but there remained the main polarization direction (MFC polarization direction), as can be seen in the figures 14 and 15.

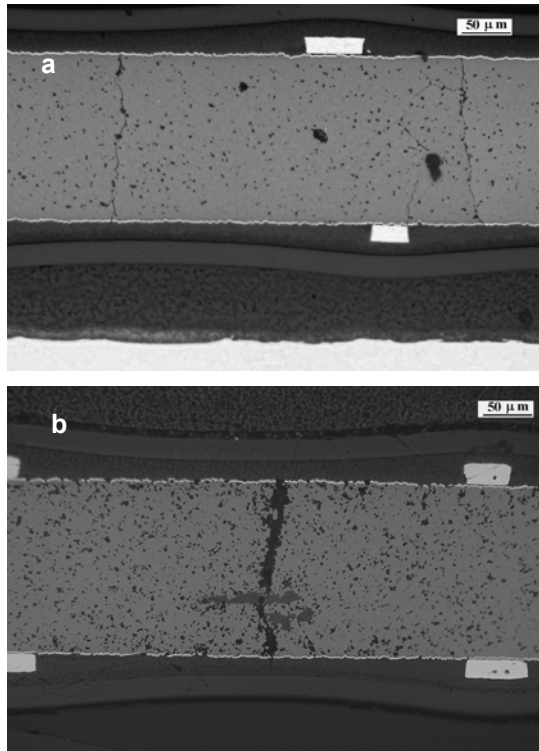


Fig. 13: cracking of PZT fibres cycled at 75°C, a) tested up to $160 \cdot 10^6$ cycles and b) up to 10^9 cycles.

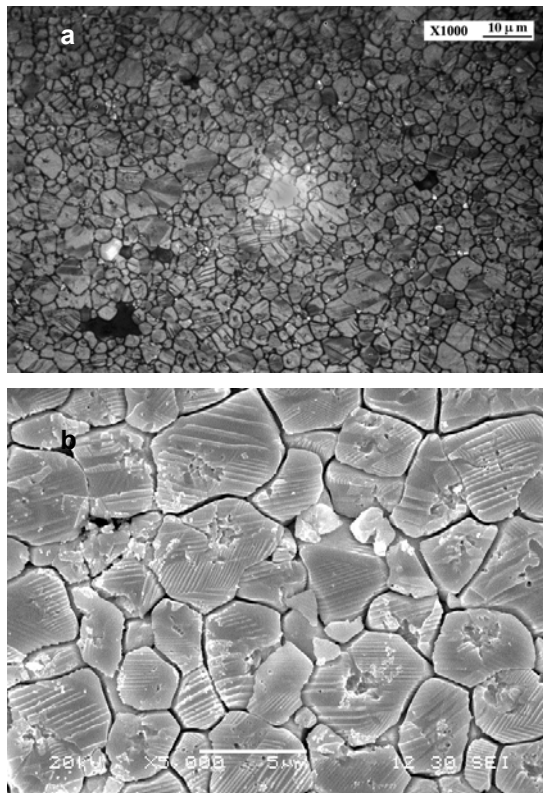


Fig.14: Domain structure visualized by a) optical microscopy and by b) SEM

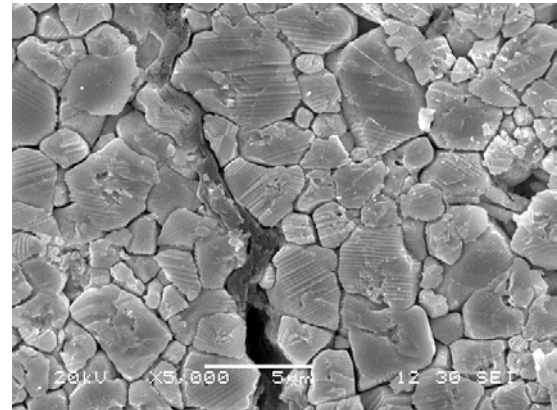


Fig.15: Domain structure around cracks visualized by SEM microscopy.

The study showed that indeed cracking of the fibres is observed. However, the presence of cracks do not necessarily lead to a decrease of the performance, what is documented in the sections before. Therefore, it is concluded that the cracking is a system – immanent feature which is tolerated by the material design.

3. Conclusion

Piezoelectric MFC material systems have been investigated with respect to their reliability. The experimental studies covered electromechanical cycling at different test scenarios along the whole desired life span. For the degradation mechanisms, especially electric fatigue, a success run analysis showed that failure due to degradation is an unlikely scenario, at least up to 10^8 cycles. During all tests, no other failure mechanisms like electroding problems or destruction of the resin matrix etc. occurred. However, this does not mean that those failures may not appear in the field. Those so-called phase 1 or phase 2 – failures are strongly dependent on the real application conditions defined by the end – user as well as the quality of the manufacturing process. For the latter, different methods of assessment are necessary including qualitative methods like FMEA.

The microstructural investigations showed cracking of the piezo fibres at all cycle numbers from the very beginning. Although the cracking seems to become more intense (more cracks per unit area or by number of fibre segments) with increasing cycle number, a correlation between the cracking and a macroscopic parameter related to the devices' performance was not found. We therefore assume that the cracking is a system – immanent property which is tolerated by the system as a whole. It is plausible that the electrical contacting of the single broken fibre pieces is not affected by the cracking. The (macroscopic) stiffness of the device, which accounts for the actua-



tion properties, is mainly defined by the matrix material which showed no obvious damage. With these two main arguments it is obvious that the macroscopically observed actuation performance does not show a significant reduction.

To sum up, the presented results show that the MFC material systems show a high reliability if used within the given specifications.

4. References

- [Ber99] B. Bertsche, G. Lechner: Reliability in Mechanical Engineering, 3rd Edition. (Springer, Berlin, Heidelberg 1999) (in German)
- [Bro96] Allen J Bronowicki, Lori J McIntyre, Robert S Betros, George R Dvorsky: Mechanical validation of smart structures, *Smart Mater. Struct.* 5 (1996) 129–139
- [Con01] P. D. T. O'Connor: Practical Reliability Engineering, 4th Edition (John Wiley & Sons Inc. 2001)
- [Fu00] Ran Fu, Tong-Yi Zhang: Influences of Temperature and Electric Field on the Bending Strength of Lead Zirconate Titanate Ceramics, *Acta mater.* 48 (2000) 1729–1740
- [Han00] H. Hanselka, B. Vogl, D. Mayer, Active Structural Acoustic Control as a Part of the German Industrial Research Project ADAPTRONIK, Publication in Smart Materials Bulletin, Elsevier Advanced Technology, Oxford, U.K. (2000)
- [Her04] S. Herold, D. Mayer, H.: Hanselka, Transient Simulation of Adaptive Structures, *J. Intel. Mat. Syst. Str.*, 15 (2004) 215–224
- [Kim96] Sang-Joo Kim, Qing Jiang: Microcracking and electric fatigue of polycrystalline ferroelectric ceramics, *Smart Mater. Struct.* 5 (1996) 321–326
- [Mal00] S Mall, T L Hsu: Electromechanical fatigue behavior of graphite/epoxy laminate embedded with piezoelectric actuator, *Smart Mater. Struct.* 9 (2000) 78–84
- [Mal02] S Mall: Integrity of graphite/epoxy laminate embedded with piezoelectric sensor/actuator under monotonic and fatigue loads, *Smart Mater. Struct.* 11 (2002) 527–533
- [Mal98] S Mall, J M Coleman: Monotonic and fatigue loading behavior of quasi-isotropic graphite/epoxy laminate embedded with piezoelectric sensor, *Smart Mater. Struct.* 7 (1998) 822–832
- [Mey03] A. Meyna, B. Pauli: Handbook on Reliability and Safety Engineering (Hansa Verlag, München Wien 2003) (in German)
- [Nuf00] J. Nuffer, D. C. Lupascu, J. Rödel, Damage Evolution in Ferroelectric PZT Induced by

Bipolar Electric Cycling. *Acta Mater.* 48, 3783 – 3794 (2000)

[Nuf06] J. Nuffer, H. Hanselka, Characterization of Reliability. In: Czichos, H.: Springer Handbook of Materials Measurement Methods. Berlin : Springer, 2006, Chapter 16.4, S.891–912

[Pan92] W Y Pan, S Sun, B A Tuttle: Electromechanical and dielectric instability induced by electric field cycling in ferroelectric ceramic actuators, *Smart Mater. Struct.* 1 (1992) 286–293

[Thi03] Bäbel Thielicke, Thomas Gesang, Peter Wierach: Reliability of piezoceramic patch sensors under cyclic mechanical loading, *Smart Mater. Struct.* 12 (2003) 993–996

[Wil04] W. Wilkie, D. Inman, J. High, R. Williams: Recent developments in NASA piezocomposite actuator technology, ACTUATOR 2004, 9th International Conference on New Actuators, 14 – 16 June 2004, Bremen, Germany

[Yoc03] M Yocum, H Abramovich, A Grunwald, S Mall: Fully reversed electromechanical fatigue behavior of composite laminate with embedded piezoelectric actuator/sensor, *Smart Mater. Struct.* 12 (2003) 556–564

[Zha04] X P Zhang, S Galea, L Ye and Y W Mai: Characterization of the effects of applied electric fields on fracture toughness and cyclic electric field induced fatigue crack growth for piezoceramic PIC 151, Technical Note, *Smart Mater. Struct.* 13 (2004) N9–N16

[Zha04b] T.Y. Zhang, C.F. Gao: Fracture behaviors of piezoelectric materials, *Theoretical and Applied Fracture Mechanics* 41 (2004) 339–379

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