STRESS CORROSION CRACKING OF BIOGLASS™
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by

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ABSTRACT

The objective of this study was to investigate the stress corrosion behaviour of Bioglass™ 45S5 in order to predict the lifetime of the glass in use as a load-bearing prosthetic device.

As part of this study, the development of Bioglass™ and the medical tests conducted to assess the glass's biocompatibility are reviewed. The results of implant tests in laboratory animals which indicate that stress corrosion cracking of the glass may be a prohibitive factor to its use are presented.

The theories of glass corrosion and stress corrosion cracking of silica based glasses are discussed and an extensive review of the literature presented.

The corrosion behaviour of the glass was analysed and found to be similar to that obtained by previous workers. The depths of the corrosion layers were found to be smaller. This was attributed to alumina contamination of the glass.

The fatigue parameters of the glass were measured by slow crack-growth studies and strength measurements in a corrosive solution simulating the physiological environment. The values of $A$ and $n$ in the equation relating crack velocity ($v$) and stress intensity ($K_I$) $v = AK_I^n$, were found to be $1 \times 10^{-173}$ and 30 respectively.

Lifetime predictions for the glass were performed. It was determined that the glass was suitable for use as a prosthetic device if the maximum tensile stress encountered in vivo did not exceed 15MPa.
ACKNOWLEDGEMENTS

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Thanks are extended to my fellow graduate students and researchers of the Department of Materials Science and Engineering who were a source of encouragement throughout the work.

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CHAPTER ONE

INTRODUCTION

Writings of ancient Greek and Egyptian civilizations outline attempts made to repair damage to the human body through the use of implants. Throughout the centuries the implant material has changed from grafts and simple materials to today's sophisticated compositions. Advances in medical science enabling a better understanding of the body's reactions to foreign substances coupled with rapidly changing materials technology has led to the development of modern prosthetic devices.

Limiting the discussion of prosthetic devices to those used in hard tissue replacement, i.e. bone, there are two requirements of a material to be used in medical applications. It must be biocompatible, that is have no adverse reaction to or with surrounding body tissue. It must also fulfill the strength requirements for the particular load bearing application of the prosthetic device. As examples, during walking, the force at a hip joint may reach as high as eight times the body weight, or the bending moment at the proximal end of the femur generated by the hamstring muscle can reach 72 Nm.

A popular material for implant use is AISI type 316 stainless steel because of its good strength, excellent corrosion resistance and availability in high quality. Co-Cr alloys have even better mechanical
properties and excellent corrosion resistance. Titanium and titanium alloys also find use in medical applications exhibiting good corrosion resistance and having low density (about half that of a wrought cobalt-chromium alloy). Other metals are employed but find limited use due either to poor mechanical properties, poor corrosion resistance, or restrictively high costs.

While metals satisfy the second requirement for an implant material, they fall short on the first, i.e. biocompatibility. Metals used in prosthesis belong in the category of "nearly inert" biomaterials. These materials under exposure to physiological environment show little or no chemical change. However, tissue reaction to the implant does occur. At the tissue-implant interface a fibrous membrane forms encapsulating the implant. This capsule prevents the formation of a chemical bond between the implant and surrounding tissue. Without this mechanical stability, deterioration of the interface with time occurs leading to slippage of the implant and subsequent injury to the patient. Research endeavouring to overcome this problem has followed two directions: improving the mechanical interlock between the host tissue and the implant, or developing new material which will chemically bond to the host tissue. The former has concentrated on porous implant surfaces allowing tissue ingrowth to improve mechanical fixation. Research on the latter was undertaken at the University of Florida in Gainesville. This research resulted in the development of a glass of composition such that exposure to physiological environment elicits a specific surface reaction which leads to the growth of bone directly to that surface. This direct bone bonding inhibits the formation of a fibrous
capsule around the implant and gives stable fixation of the prosthetic device.

The material developed at Florida is Bioglass™ 4555 and is the subject of this study. Composed of silica, soda, calcia, and phosphorous pentoxide, the glass undergoes a particular corrosive reaction at its surface which creates conditions conducive to bone growth.

In question now is whether this material satisfies the strength requirements for its application as an implant material.

Fracture of glass occurs by the growth of small surface flaws to a critical size precipitating catastrophic failure. The environment surrounding the glass has a major effect on the rate of growth of these flaws (so-called "static fatigue").

Studies show that a corrosive reaction at a highly stressed crack tip will accelerate crack growth leading to premature failure of the glass.

It is possible that the reaction which leads to Bioglass™'s excellent compatibility with bone, may also lead to its failure as a prosthetic material via accelerated static fatigue. The purpose of this study was to investigate this possibility by a quantitative study of the stress corrosion, or slow crack growth behaviour, of Bioglass™.
CHAPTER TWO
MEDICAL BACKGROUND AND LITERATURE REVIEW

2.1 BIOGLASS AS A PROSTHETIC MATERIAL

Bioceramics can be separated into three general classes; nearly inert, surface reactive and resorbable. The nearly inert bioceramics are used because of their resistance to change in the physiological environment and the minimal tissue response they elicit. Materials of this type include Al₂O₃ and LT1 Carbon. Resorbable ceramics, e.g. Ca₃(PO₄)₂ are used as temporary spatial fillers. They serve to maintain a form, slowly dissolving as natural tissue ingrowth occurs. Surface reactive bioceramics have controlled tissue implant responses which lead to a direct chemical bond across the interface. In this category of bioceramics is Bioglass™.

Bioglass™ was developed at the University of Florida, Gainesville, Florida by Dr. L. L. Hench and co-workers. Starting in 1969, the study program had two primary objectives, to develop a material that would form a direct chemical bond to bone and to fully characterize chemically, biologically and mechanically the interfacial bond. Hench summarized the requirements for model biomaterials in the following table. \(^{(51)}\)
TABLE 2.1

REQUIREMENTS FOR A BIOMATERIALS MODEL

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>CRYSTALLOGRAPHIC</th>
<th>MICROSTRUCTURAL</th>
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<tr>
<td>Vary type, concentration and rate of soluble ion(s) and pH</td>
<td>Provide variable substrate for protein and mineral epitaxy</td>
<td>Vary percentage and size distribution of porosity, interfacial area, and type of interfaces</td>
</tr>
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The degree of property control possible with a glass-ceramic material through variation of its composition and thermal treatment makes it an eminent model material.

2.2 BIOGLASS COMPOSITION

The bioglass composition most studied in clinical tests is 45S5.

TABLE 2.2

<table>
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<th>45S5 COMPOSITION</th>
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<tr>
<td>OXIDE</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Na₂O</td>
</tr>
<tr>
<td>P₂O₅</td>
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</table>

The composition was developed such that the leaching of component ions and the development of reactive surface layers leads to the nucleation of hydroxyapatite on the glass surface. The hydroxyapatite serves as the site of bone mineralization.
Favourable bone bonding behaviour is not restricted to the 45S5 composition. Through a series of in vivo tests Hench(56) determined the extent of the composition field of bone-bonding glasses in the Na2O-CaO-SiO2 system. The P2O5 content was maintained at a constant value of 6 wt % of the bulk composition. Bioglass samples 4x4x1 mm were implanted in the tibia of rats. After a given time period, the animals were sacrificed and the samples were subjected to a push-out proof test of 30N. Glasses which could be pushed out of the tibias at 30N or less were deemed to be non-bonding. The resultant composition boundary is plotted in Figure 2.1.

Tests have been done to determine the effects of altering the glass composition on its bone bonding capabilities.(49) It was found that K2O could be freely substituted for Na2O with no change in the bonding behaviour. B2O3 exchanged for SiO2 accelerates the reactions leading to bond formation. CaF2 substituted for CaO slows down, but does not inhibit, the release of ions necessary for the formation of the hydroxyapatite surface layer. MgO in place of CaO will inhibit bone bonding reactions. The presence of Al2O3 can also affect the formation of the surface calcium-phosphate layer, the site of hydroxyapatite nucleation. Leaching of phosphorous in the glass leads to the formation of this layer. However, it has been found that upon removal of the P2O5, bonding may still occur. The reactive glass can adsorb phosphorous from the physiological environment to combine with the leaching calcium to form the hydroxyapatite layer.

Controlled surface reactivity and, therefore, bone bonding capabilities appear to depend predominantly on the ratio of network
former (SiO$_2$) to network modifier (Na$_2$O + K$_2$O + CaO) in the glass. The larger the ratio, the more stable is the glass, i.e. the ion exchange processes necessary for the formation of the hydroxyapatite are restricted and the glass behaves as a nearly inert material.

2.3 IN-VITRO TESTING

With medical tests showing favourable results for the formation of a direct chemical bond of the implant to bone, in-vitro experiments were conducted to determine the sequence of reactions occurring on the Bioglass$^\text{TM}$ surface which promote this phenomenon.

Infra-red reflection spectroscopy and solution analysis show that, when exposed to simulated body solution, a SiO$_2$ rich layer forms on the glass followed by crystallization of a CaO-P$_2$O$_5$ rich layer on the surface$^{(69)}$ Clark, Pantano and Hench$^{(13)}$ used Auger spectroscopy combined with ion beam milling to determine surface compositional profiles for Bioglass$^\text{TM}$ in solution. A series of tests verified the sequence of corrosive reactions occurring on the Bioglass$^\text{TM}$ surface.

Samples of Bioglass$^\text{TM}$, cast and polished to 600 grit, were immersed in an aqueous solution (distilled water, HCl, tris-hydroxy-methyl-aminomethane to pH = 7.4) at 37$^\circ$C for times of 10, 20, 30, 40, 50, and 60 minutes. Surface analysis was performed on the samples. In addition a full corrosion profile was performed on the sample corroded for one hour. Results obtained by Clark et al are shown in Figure 2.2, and the results of Ogino et al in Figure 2.3.

Figure 2.2 illustrates the formation of a Ca-P rich layer on the surface overlying a SiO$_2$ rich layer. The Na$_2$O corrosion profile
could not be obtained due to migration of the Na ions from the electron and ion beam. Work by Pantano Jr. et al. (73) using low temperature Auger spectroscopy which allowed detection of Na, yielded the profiles shown in Figure 2.5. These results also show the presence of the Ca-P rich layer on the surface, enrichment of the surface by Na, and the underlying SiO₂ rich layer. Figure 2.4 gives an indication of the time necessary for the formation of the Ca-P surface layer.

The corrosive reactions leading to the formation of a surface conducive to bone growth on Bioglass™ are summarized as follows (14):

**STEP 1**: Immediately upon immersion in solution, stage 1 corrosion occurs with Na⁺ - H⁺ ion exchange.

**STEP 2**: Within 15 to 30 minutes of exposure to the aqueous solution SiO₂ is preferentially leached to a depth of 0.5 μm. Leaching of the SiO₂ causes the coincidental formation of the Ca-P rich surface film.

**STEP 3**: After the formation of the Ca-P rich film SiO₂ leaching stops. Alkali leaching continues with the resultant formation of a SiO₂ rich layer under the Ca-P surface.

**STEP 4**: Continued migration of Ca and P out of the glass leads to growth of the calcium phosphate film.

**STEP 5**: After approximately 1500 hours, crystallization of the Ca-P film into an apatite structure occurs.

**STEP 6**: In vivo, the apatite layer becomes the site for bone mineralization.

There is some discrepancy in Clark's paper for the depth of the Ca-P film between the value indicated on the figure of the corrosion profile and that referenced in the text. It is assumed after examination of the results obtained by Ogino et al that the value from the plotted corrosion profile (0.5 μm) is correct.

Hench proposes that the above corrosive reactions come as a result of the phase-separated microstructure of Bioglass™. The
phosphorous rich phase would tend to tie up the Ca ions in the glass. Research has shown that Ca increases the corrosion resistance of glasses. The SiO₂ rich phase would, therefore, be preferentially attacked in the initial stages of the glass corrosion. Diffusion of Ca, P and Na continues leading to the formation of the surface film. This film will protect the underlying silica network whilst also allowing migration of Ca and Na to the surface. The growth of the crystallized surface layer serves to protect the glass from further corrosion and allows bone bonding to occur.

2.4 IN-VIVO

Bioglass™, either alone, or as part of a composite has undergone extensive laboratory and clinical testing(49,113). Experiments have been performed to verify Bioglass™'s biocompatibility and to investigate the formation and properties of the bone-Bioglass™ bond.

A biocompatible material is defined as one which:

"Allows close contact of living cells at its surface, which does not contain leachables which produce inflammation and which does not prevent growth and division of cells in culture."(113)

In vitro tests performed showed normal growth of rat bone cells and a range of fibroblasts, including human, on Bioglass™ with no signs of toxicity. Toxicity to rat macrophages was also tested. Bioglass™ dust ingested by the cells caused 2 to 5% toxicity. Quartz, as a reference standard, yields 50% toxicity. In vivo tests showed no adverse effects of Bioglass™ implants on bone marrow, or soft tissue with intra muscular implantation.

The most extensive study of the formation of the bone-Bioglass™
bond was conducted by Hench and co-workers at University of Florida.\(^{(49)}\) In vitro tests have shown how collagen fibres become woven into and out of the hydroxyapatite surface of the Bioglass\(^{TM}\) (see Figure 2.6). Hench suggests that as Ca\(^{2+}\) and P\(^{5+}\) from body solutions are incorporated into the growing surface layer, the charges are balanced by inclusion of OH\(^{-}\) and CO\(_3^{2-}\) groups. These are characteristic of natural tissues (see Figure 2.7). As the layer grows and crystallizes (within a time of one to two weeks) organic metabolic constituents, such as collagen, mucopolysaccharides and glycoproteins, are incorporated into the glass surface. This graded inorganic-organic interface leads to the direct implant-bone bond.

The reactions between bone and Bioglass\(^{TM}\) have been studied extensively by Hench et al through implantation of Bioglass\(^{TM}\) in rats. After 6 weeks, implants in the femurs of rats were examined under SEM and showed intimate bonding between the bone and glass. Tetracycline, injected as a tracer for new bone in the rats for 3 days before sacrifice, was localized adjacent to the implant, showing that preferential formation of new bone occurred at the surface of the implant. Light microscope studies of the extracted bone showed that normal healing was taking place.

Similar results occurred for implantation in rat tibias. Micrographs of the bone-Bioglass\(^{TM}\) bond and the accompanying electron microprobe composition profiles of the interface are shown in Figures 2.8 through 2.12. Hench's experiments showed stabilization of the bone-Bioglass\(^{TM}\) bond by 3 months implantation whereafter it remained relatively unchanged for up to one year (to length of study).
The mechanical strength of the bond developed between Bioglass™ and bone has been measured by three separate methods. The canine femur push-out test measured the force necessary to dislodge a 6 mm diameter by 12 mm long cylindrical implant from the femur. A mean push-out force of 209N was measured for bulk Bioglass™. This compared to 12N for stainless steel, 13N for Co-Cr surgical alloy, and 19N for 99% fully dense Al₂O₃.

Secondly, segmental bone replacements of Bioglass™ implanted in femurs of monkeys were subjected to a rapid loading torsion test after a healing time of 30 to 50 weeks. The mean fracture stress of the femur with no implant was 150 MPa; that of the healed femur, 83 MPa. The loss of strength could be due to three contributing causes:

1. Lack of strength of the implant
2. Lack of strength of the interface
3. Decrease in strength of the bone due to retention of the Schneider nail used for alignment of the implant in surgery until just prior to testing.

The average value of the interfacial stresses during testing was 88MPa. Because few failures occurred at the interface, this value may be taken as a lower limit on the bond strength. From the tests it was seen that the interfacial strength was approximately 3/4 that of the host bone.

The third test was the pull-out of shafts of femoral head prosthesis. A force of 270N was required to remove the prosthesis. This force, equivalent to approximately 4X the body weight is unlikely to be encountered in vivo.

Studies have shown that a strong, direct chemical bond forms
between a Bioglass™ prosthesis and bone when proper fitting and initial (for first 2 weeks) immobilization of the implant is performed. Movement of the implant relative to the bone in the early stages of healing prevents bond formation.

The study of the mechanical strength of the bone-Bioglass™ bond in segmental replacements of monkey femurs brings to light a potential problem with the use of bulk Bioglass™ implants. The following passage is from Piotrowski’s report (78) on this study.

"Fractures in the femurs containing the bulk Bioglass™-ceramic segmental replacements occurred in various locations. Out of the 8 specimens tested, 2 fractured at the implant ... two of the eight specimens fractured at a site removed from the intact implant, while 4 implants fractured in vivo prior to sacrifice, presumably due to fatigue of the implant material."

It is apparent from this statement that static fatigue of the Bioglass™ could be a point of concern for use of this implant material and warrants further study.
Figure 2.1 Bioglass™ Bone Bonding Boundary (46)

- A: Bonding at 30 days or less
- B: Non bonding, reactivity is too low
- C: Non bonding, reactivity is too high
- D: Non bonding, non glass-forming
Figure 2.2 Bioglass™ Corrosion Profile (Clark) (14)
Figure 2.3 Bioglass\textsuperscript{TM} Corrosion Profile (Ogino) (69)
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2- Si-rich glass
3- Ca-P rich layer
4- bone
Figure 2.11 Electron Micrograph of One Year Bioglass™ Implant
B- bone
C- Bioglass™
Figure 2.12 Compositional Profile of Bioglass®/Bone Interface, One Year Implantation (49)
CHAPTER THREE
LITERATURE REVIEW

3.1 INTRODUCTION

From an extensive review of the literature, information was gained on the subject of stress corrosion in glass. The basic mechanisms of glass corrosion were reviewed with particular emphasis on the reactions of soda-lime-silica glasses. Methods of detecting and analysing glass corrosion were summarized. The various theories of stress corrosion were reviewed. Experimental techniques used in the study of stress corrosion of glass and the results obtained by several investigators were studied. The method of lifetime prediction for a glass from fatigue data and design diagrams for several glasses were reviewed.

This chapter will present the information gathered and a plan of study for the investigation of the stress corrosion of Bioglass™.

3.2 GLASS CORROSION

The reactions of Bioglass™ when exposed to a corrosive solution were outlined in Chapter Two. For a better understanding of the processes taking place it is necessary to review the basic mechanisms of glass corrosion and the effects of differing composition thereon. In particular the effects of varying alkali content, the presence of P2O5 and the presence of alumina in a soda-lime-silica glass must be addressed.

Several investigators have studied the basic mechanisms of glass corrosion. As a result of these studies, it was determined
that a silica based glass undergoes corrosion by two processes, termed Stage 1 and Stage 2 corrosion.

Clark\(^{(13)}\) gives an illustrative description of Stage 1 and Stage 2 glass corrosion. Using a 2-dimensional schematic representation of the 3-dimensional random network structure of glass, the basic mechanisms of glass corrosion are presented in simplified form. Clark's representation is given in Figure 3.1.

The initial stage of corrosion involves ion exchange between the alkali ions of the glass and hydrogen ions of solution.

\[
\text{SiONa(g) + H}_2\text{O} \xrightarrow{\text{====}} \text{SiOH(g) + NaOH}
\]

The second stage involves attack of the Si-O-Si bonds by OH\(^{-}\) ions.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O-Si-O-Si-OH} + 4\text{OH}^-\text{(sol'n)} & \xrightarrow{\text{====}} \text{O-Si-OH} + \text{OH-Si-OH} \\
\text{O} & \quad \text{O} \quad \text{(g)}
\end{align*}
\]

The leaching behaviour, (Stage 1 corrosion) of a number of differing glasses has been extensively studied. Considerable effort has been expended studying the kinetics of the alkali extraction and interpretation of the process mechanism.

In general it has been found that on initial exposure of an alkali-silica glass to water, the amount of alkali leached from the glass is proportional to \(\sqrt{t}\) \(^{(13)}\). Results of corrosion studies illustrating this behaviour are shown in Figure 3.2. The process of ion exchange between the glass and solution has been described as an inter-diffusion mechanism. In a study of the leaching of potassium silicate glasses, Boksay et al\(^{(13)}\) developed a theory to fit the observed profile (Figure 3.3) using a concentration independent diffusion
coefficient. The theory, however, could not be used to describe the profiles obtained for sodium and lithium silicate glasses.

Doremus\(^{(24)}\) used a concentration-dependent diffusion coefficient to generate steady-state diffusion profiles which were consistent with experimentally obtained profiles of the alkali ion, Figure 3.4. The interdiffusion coefficient used was of the form:

\[
\boxed{\mathcal{D} = D_{Na^+} D_{H^+} \left/ \left[ C_{Na^+} D_{Na^+} (1 - C_{Na^+}) D_{H^+} \right] \right.}
\]

where \(D_{Na^+}\) and \(D_{H^+}\) are the individual ionic diffusion coefficients. By assuming these were concentration independent, Doremus developed an approximation of the actual situation.

Das and Douglas\(^{(19)}\) studied the rate of alkali extraction from several binary and ternary alkali silicate glasses confirming the \(\sqrt{t}\) dependence of alkali extraction in the early stages of attack, Figure 3.5. They attempted to relate the chemical resistivity of the glass to electrical resistivity measurements on the assumption that both were determined by the rate of alkali ion diffusion through the glass. A correlation was not obtained, leading to the conclusion that the alkali extraction could not be described by a simple ion exchange reaction.

Das et al\(^{(13)}\), Doremus\(^{(23)}\) and other researchers proposed that a "gel layer" forms at the solution/glass interface which further complicates the leaching process.

Doremus\(^{(24)}\) suggested that the glass network is transformed to a loose gel structure through the reaction of water penetrating the glass with the silicon-oxygen bond.

\[
H_2O + Si-O-Si \rightarrow SiOH \text{ HO-Si}
\]
He suggested that water enters directly or is carried with hydrogen as H$_3$O$^+$ in the ion exchange process. By this process the gel/glass interface may move relative to the original glass interface. Doremus' model of the leaching of alkali silicate glass is shown in Figure 3.6. Diffusion through the leached layer plays an important role in the overall process. This diffusion cannot be represented by simple mathematical solutions due to the complicating factors of concentration-dependence of the diffusion coefficient and structural modifications influencing mobilities of species through the "gel layer".

Schafer and Schaeffer$^{(91)}$ suggest that it is not the migration of cations through the leached layer that is the rate controlling mechanism of corrosion, rather the controlling step is the reaction occurring at the leached layer/bulk glass interface by which the structural transformation to the more open network takes place.

Schafer proposed that the very poor chemical resistance of some glasses may be due to the microstructure of the leached layer. In a high alkaline glass the layer may have a channel-like microstructure composed of phase-separated regions of the water-rich gel phase and isolated glass islands. The channels provide routes for fast transport of cations and water molecules. The alkali leach rate under these conditions would show a linear time dependence. Schafer, however, does not provide any physical evidence of the microstructure suggested.

Researchers have determined that a wide range of alkali silicate glasses show linear time dependence of alkali extraction at longer corrosion times. The rate of silica extraction at these times also follows a direct time dependence (Figure 3.7). At this point Stage
2 glass corrosion, or network dissolution is occurring.

There is a gradual transition from Stage 1 to Stage 2 corrosion. The rate of alkali extraction throughout a corrosion process has been approximated by the empirical relation\(^{25}\)

\[
Q = a \sqrt{t} + bt \quad (3.2)
\]

At intermediate times ions exchange and network dissolution occur simultaneously.

The rate of silica extraction is influenced by the amount of alkali in the glass and solution and the pH of the solution. Evidence for this statement is presented below.

Douglas and El-Shamy\(^{25}\) found that the rate of silica extraction into acid media was very low. Their results are given in Figure 3.8. Increasing alkalinity of the solution increased the rate of silica extraction. This is explained by consideration of the following reactions for glass corrosion:

\[
\begin{align*}
-\text{Si-O-Si-OH(g)} &+ \text{OH}^-(\text{sol'n}) \rightarrow -\text{Si-OH(g)} + \text{O}^-\text{-Si-OH(g)or(sol'n)} \\
-\text{Si-O-M}^+(g) &+ \text{H}^+(\text{sol'n}) \rightarrow -\text{Si-OH(g)} + \text{M}^+(\text{sol'n})
\end{align*}
\]

By employing LeChatelier's Principle it is seen that as the hydroxyl ion activity in the solution is increased, removal of silica from the glass is favoured. Accompanying this is a decrease in activity of hydrogen ions, thereby reducing the leaching of alkali from the glass.

Douglas and El-Shamy present a theory to explain the pH dependence of silica extraction from the glass based upon occupancy of surface sites at the leached layer/solution interface.
The sites are represented as:

\[
\begin{array}{ccc}
\text{Empty} & \text{Occupied} \\
\begin{array}{c}
\text{ } \\
\text{O} \\
\text{O - Si - O}^-
\end{array} & \begin{array}{c}
\text{ } \\
\text{O} \\
\text{O - Si - O}^-\text{Na}^+ \text{ or } \text{O - Si-OH}
\end{array} \\
\begin{array}{c}
\text{ } \\
\text{O} \\
\text{O}
\end{array} & \begin{array}{c}
\text{ } \\
\text{O}
\end{array}
\end{array}
\]

A dynamic equilibrium of the above states is determined by the concentrations and solvation energies of the ions.

The occupancy of the sites is determined by the chemical potential of each ion in solution and the leached layer. The chemical potential is given by:

\[
\mu = \mu^0 + kT \ln C
\]

where \( \mu \) is the potential at infinite dilution, \( C \) is the species concentration (assuming that concentration \( \sim \) activity of species).

At equilibrium the chemical potentials of a species across the interface are equal. Thus:

\[
\frac{C_{\text{surface}}}{C_{\text{solution}}} = \exp \left( \frac{\mu^0_{\text{surface}} - \mu^0_{\text{solution}}}{kT} \right)
\]

Surface sites of the leached layer will be occupied by the ion of lowest chemical potential if the concentration of that ion in solution is great enough to give \( C_{\text{surface}} \) equal to fully occupied sites. When the concentration of the ion in solution is decreased, a fraction of the surface sites will be occupied by another ion species.

The equilibrium at the surface can be represented as equilibrium between silica and solutions of varying \( H^+ \) or \( pH \).

The equilibrium constant for the dissociation reaction
is equal to $10^{-9.8}$ at 30°C. Assuming that the constant applies to SiOH groups on a silica surface, it can be extended to include the SiOH groups at the leached layer/solution interface.

$$\frac{[\text{Si} - \text{O}]_{\text{surface}}}{[\text{Si} - \text{OH}]_{\text{surface}}} = 10^{-9.8} \quad (3.5)$$

or

$$\frac{[\text{Si} - \text{O}^-]}{[\text{Si} - \text{OH}]} = 10^{-9.8 + \text{pH}} \quad (3.6)$$

Using the above equation, the relative occupancy of surface sites by hydrogen can be calculated.

It is found that above $\sim \text{pH}9$, surface sites are increasingly occupied by alkali ions. This consequently retards transport of the alkali through the leached layer causing, in effect, a decrease in Stage 1 corrosion and an increase of Stage 2, or network dissolution. This is demonstrated by the results of Douglas and El-Shamy for a K$_2$O-SiO$_2$ glass shown in Figure 3.9.

Das$^{(20)}$ explains the higher durability exhibited by alumina glasses with this theory. The fraction of sites occupied by hydrogen on the alumina glass surface is given by

$$\frac{1}{10^{-10.635 + \text{pH} + 1}} \quad (3.7)$$

Network dissolution of the glass would predominate above $\sim \text{pH}=11$ as opposed to $\text{pH}=9$ for silica glass. Consequently the alumina glass is more insoluble over a wider pH range than the silica.
Shafer(91) concludes that the chemical resistance of an alkali silicate glass decreases with increasing alkali content or increasing radius of the alkali ion in the glass. His results are given in Figure 3.10. The latter arises from the higher field strength of the smaller ion making it more stable. The decrease of chemical durability of a glass with increasing Na⁺ has also been found by Clark et al(12).

In general, the durability of glass is determined by the nature of the surface film formed which in turn is controlled by the corrosive solution and the bulk composition of the glass.

Hench and Clark(48) identified five types of surfaces which form on silicate glasses during corrosive reaction. These are shown in Figure 3.11.

Type I surface films are formed through surface layer hydration with no significant alkali leaching or network dissolution occurring. This surface film would be found on vitreous silica under neutral pH conditions.

Low alkali content silicate glasses undergoing selective leaching form Type II surfaces. At pH9, the surface silica layer serves as a protective film against further alkali leaching.

Researchers have found that the addition of Al₂O₃ to an alkali silicate glass leads to the formation of another surface layer on top of the silica. Dilmore(21) found that the addition of 2.5 mol% Al₂O₃ to a lithium silicate glass increased its corrosion resistance significantly. Dual protective films on the glass are characteristic of Type III surfaces.

Hench(14) proposes that addition of P₂O₅ to a soda-lime-silica
glass increases its corrosion resistance by the formation of a Type III surface. Hench argues that phosphorous is a network former in the glass of +5 charge existing in 4-fold co-ordination. Therefore, one of the P-O bonds is a double bond. Hench explains, with reference to McMillan's work (Glass Ceramics, 1964), that the double bond leads to phase separation of the phosphate and silica groups. In the glass, the alkali or alkaline earth oxides are more strongly associated with the P₂O₅. The silicate phase thus reduced in CaO content is consequently more susceptible to corrosion. As the silicate phase is attacked, a surface film rich in CaO and P₂O₅ is formed. This layer then serves to protect the silica from further network dissolution. Stage 1 leaching of Na⁺ and Ca²⁺ continues resulting in the formation of a silica rich layer. These two surface layers are typical of Type III surfaces. Therefore, addition of P₂O₅ to the glass, while initially decreasing the corrosion resistance serves to stabilize the corrosion reaction with time eventually retarding further corrosion.

An important assumption of this theory is that the CaO in the glass is associated with the phosphorous phase. Several investigators (12, 20, 75, 91) have noted the increased durability of alkali silicate glass with the addition of CaO. Results obtained by Clark et al (12) are given in Figure 3.12. In the early stages of corrosion the presence of Ca increases the coupling interaction between Si-O and non bridging Si-O bonds. The stronger structure retards leaching of the alkali. In the later stages of corrosion increased durability arises from the formation of a Ca-enriched zone in the Na-depleted leached layer. This zone acts to stabilize a SiO₂ rich surface layer by filling microvoids
and inhibiting further Na diffusion.

Type IV surfaces are similar to Type II with the exception that the silica rich film formed on the surface is not highly durable. Rapid Stage 1 and Stage 2 corrosion processes can occur. Alkali silicate glasses of high alkali content form Type IV surfaces.

Type V surfaces formed by homogeneous attack of the alkali and silica are found on silicate glasses under highly alkaline conditions with pH9.

The analytical techniques of identifying and analysing the surface layers formed on the corrosion of alkali silicate glasses are outlined in the following section.

3.3 ANALYTICAL METHODS FOR STUDYING CORROSION OF GLASS

Several analytical techniques are available for studying the process of glass corrosion. While the physics of each is beyond the scope of this work, the methods will be reviewed briefly outlining the application of each and the information that can be obtained.

Static or replenished corrosion experiments may be conducted on bulk or powdered glass samples. Studies have shown that the ratio of solid surface area (SA) to solution volume (V) strongly influences the corrosive reactions. Maintenance of a constant SA/V ratio is necessary for control of corrosion tests. Powdered samples undergo rapid increases in surface area as dissolution occurs and have a tendency to form agglomerates and localized corrosion cells. Therefore bulk samples, in which control of SA/V is much easier, are preferred for corrosion tests.
Detection of reaction layers and information on the processes occurring during glass corrosion is accomplished through solution analysis and/or the use of a number of surface analytical tools. Solution analysis may be used to determine the rate of surface attack and the types and amounts of leached ionic species.

Infra-red reflection spectroscopy (IRRS), electron probe micro-analysis (EPMA), scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDXA), secondary ion mass spectroscopy (SIMS), and Auger electron spectroscopy (AES) provide additional information on surface corrosion reactions. Each technique has limiting factors which govern its use in corrosion analysis.

One of these factors, important when studying the chemical composition of a corrosion layer, is the sampling depth of each technique. These are illustrated in Figure No. 3.13.

SIMS and AES have sampling depths of 5 to 50 Å, making these techniques useful for analysis of thin corrosion layers. Monitoring of the composition (through secondary ion of Auger electron emission) whilst ion beam milling gives a composition profile through the corrosion layer. SIMS has full elemental detection and isotopic characterization capabilities. This is a useful technique for determination of the extent of hydration of the corrosion layer. Sputtering effects pose a problem for quantitative composition analysis. Similarly, AES is semiquantitative. Users of the AES technique, as well as SEM/EDXA and EPMA analysis, experience problems due to charging of the glass sample under the incident electron beam causing subsequent changes in emitted x-ray intensities. The migration of alkali from the beam
is also a problem.

EPMA analysis has a greater sampling depth than SIMS and AES. Cross-sectional profiles are usually obtained on the EMP. The spatial resolution of the probe is approximately 2 μm, however, a value often larger than the full depth of the corrosion layers on glasses. The EMP shows very good compositional sensitivity (about 0.1%) but only a few species may be monitored at one time. EDXA, on the other hand, allows rapid total analysis of small areas. Surface heterogeneities less than 1 μm may be analysed. Sensitivity to compositional variations is poor though, being of the order of 5%.

Surface roughness causes error in the chemical analyses performed by the above mentioned techniques. Chemical analyses by IRRS is unaffected by surface roughness. Species are identified by IRRS from the wave number position of a peak indicating a specific bond vibration. IRRS may also indicate microstructural changes occurring due to the corrosion process.

Physical changes of the glass surface can be studied by SEM. High magnification (up to 20,000x) and a large depth of field allow identification of pitting, exfoliation or precipitation occurring as a result of the corrosion process.

3.4 STRESS CORROSION OF GLASS

3.4.1 THEORY

Stress corrosion cracking, or static fatigue of glasses is a phenomena that has been studied extensively. Several investigators have proposed theories to explain the propagation of cracks in glass
under the combined influence of stress and corrosion, the corrosive medium of prime consideration being water.

Static fatigue of glass is a term used to explain the time dependant behaviour of the strength of glass. Delayed failure of glass was discovered by Grenet in 1899 who found that glass could statically support a weight for a time and then fail. It is believed that, under load, microscopic cracks in the glass grow due to environmental interaction until the Griffith criteria for fracture (energy to create new surface < energy stored) is satisfied and abrupt failure occurs.

Orowan\textsuperscript{(102)} proposed that delayed failure was due to diffusion of water vapour or other species to the tip of a crack where they were adsorbed causing a reduction of the surface free energy. This in turn caused a reduction in the breaking strength of the glass (from the Griffith equation for strength, strength $\propto$ surface energy). This mechanism for delayed failure was discounted because the curves of existing data could not be explained by surface diffusion considerations.

Gurney\textsuperscript{(102)} determined that at a crack tip in glass under load, the bonds of the glass were severely stretched and more susceptible to corrosive attack than the bulk glass. Chemical erosion at the tip would cause the crack to grow to the critical failure size. Gurney's theory however did not fit the experimental data.

By studying the fatigue behaviour of sodium-silicate glass in the temperature range -170\degree C to 242\degree C Charles\textsuperscript{(100)} determined that static fatigue is an activated process. He obtained straight line plots for time-to-failure under constant load versus inverse temperature.
From the slope of the curve a value of 18.8 Kcal/mol was calculated for the apparent activation energy of the fatigue process. This was approximately equal to the value Charles obtained for glass corrosion, 20 Kcal/mol, and the value for the activation energy for Na⁺ diffusion in glass, 17-23 Kcal/mol. Charles reasoned therefore that static fatigue occurred by a chemical reaction at crack tips in glass in which diffusion of sodium ions was the rate determining step. This is an unlikely explanation as stress corrosion occurs in pure silica glass.

Charles and Hillig(102) developed the theory further assuming that the activation energy was stress dependent and the rate limiting step was the attack of the silicon-oxygen bonds of the glass by hydroxyl ions. The source of hydroxyl ions was water vapour present in the test environment. They proposed an equation for crack propagation which is given below.

\[ v= v_0 \cdot (OH^-) \cdot (A_{\text{glass}}) \exp\left(\frac{-\Delta E^* + \sigma \Delta V^*/3 - V_M \gamma/\rho}{RT}\right) \]  (3.8)

where
- \((OH^-)\) = hydroxyl ion activity at the crack surface
- \((A_{\text{glass}})\) = chemical activity of flat glass surface in corrosive environment
- \(\Delta E^*\) = activation energy for chemical reaction
- \(\Delta V^*\) = activation volume for chemical reaction
- \(V_M\) = molar volume of glass
- \(\gamma\) = interfacial surface tension
- \(\rho\) = radius of curvature of glass surface

From their equation, for a given glass and environment, crack motion is controlled by stress and crack curvature.

Charles and Hillig suggested that different changes to the crack geometry would occur from stress corrosion depending upon the magnitude of the stress. These are shown in Figure 3.14. Above a threshold stress level flaw sharpening occurs as the crack advances.
Below this "static fatigue limit" the crack tip becomes blunted. In the former case the crack grows to a critical size and geometry causing the stress at the tip to reach the critical level at which abrupt failure occurs.

Lawn(62) argues that the fundamental understanding of the chemical reactions causing static fatigue is limited by the approach taken by the researchers. He suggests that theories developed from reaction rates and crack tip geometry are phenomenological and are limited in capacity to explain and predict material behaviour. To understand the mechanism of static fatigue it must be approached at a molecular level.

Evidence gathered by electron microscope studies(62) showed that crack healing occurs in brittle materials. This suggests that the crack tip cannot be rounded but must be atomically sharp. Thomson et al(62) model the crack as a thin slit terminated by non linear linkage bonds. This representation is shown in Figure 3.15. Under the influence of high stress fields, the bond at the crack tip, represented as a spring element, is stretched beyond its linear response range.

Michalske and Freiman(67) developed a molecular model for stress corrosion in silica glass. A schematic representation of their model is shown in Figure 3.16.

The reaction between a water molecule and a crack tip occurs in three stages:

Stage 1: The strained crack tip bond adsorbs a water molecule. The lone pair of electrons on the oxygen of the water interacts with the silicon and the hydrogen proton forms a hydrogen bond with the bridging oxygen of the glass.
Stage 2: The cleaving of the Si-O and O-H bonds to form two hydrogen bonded silanol groups.

Stage 3: The cleaving of the hydrogen bond and consequent fracture at the crack tip.

The sequential rupturing of the freshly exposed crack tip bonds leads to crack growth and static fatigue of the glass.

Michalski and Freiman performed static fatigue experiments in other solutions and concluded that the model can be extended to include active species other than water. They found that species promoting stress corrosion in silica possessed at least one lone pair of electrons (Lewis base) opposite a proton donor site with the distance between the acid and base sites approximately equal to the Si-O bond distance. Figure 3.17 shows some of the active species identified in their study.

In further development of the atomistic model, Michalske and Bunker (65) performed molecular orbital calculations to estimate bond energies and electron distributions which would give information on bond strength and reactivity as a function of bond strain. From their calculations they drew the following conclusions:

1. Unstrained, the Si-O bonds are relatively inert.

2. Changes in O-Si-O or Si-O-Si bond angles create Lewis acid sites on Si and Lewis base sites on O thereby increasing their reactivity.

3. Chemicals known to dissociatively absorb on strained surface bonds have also been shown to cause stress corrosion. Strained bonds more readily adsorb molecules and are more susceptible to subsequent reactions that cause bond rupture than unstrained bonds.
Michalske uses these results to develop an atomistic fracture model. He represents the crack front as a line separating broken and unbroken bonds. For the crack to grow the bonds bordering the front must be broken. Michalske presents a model whereby a kinked front develops (see Figure 3.18) the kinks being highly strained and reactive bonds. Crack growth occurs with the rate being controlled by kink site nucleation and the rate at which the kinks move laterally across the front.

Research on the stress corrosion of glass has shown that, for a given environment, the crack velocity is a function of the applied load and crack length expressed as the stress intensity factor \( K_1 \).

Williams developed a relationship for the stress intensity at a crack tip starting from the Airy stress function equation:

\[
\nabla^2 (\nabla^2 \psi) = 0
\]

\[
\sigma_x = \frac{\partial^2 \psi}{\partial y^2}, \quad \sigma_y = \frac{\partial^2 \psi}{\partial x^2}, \quad \tau_{xy} = \frac{\partial^2 \psi}{\partial x \partial y}
\]

Williams argued that \( \nabla^2 \psi \) is harmonic and if \( \nabla^2 (\nabla^2 \psi) \) could be expressed as a function of two harmonics, \( f \) and \( g \), with \( \nabla^2 f = 0 \) and \( \nabla^2 g = 0 \), then \( \psi = r^2 f + g \) would be a solution to the stress function equation. Williams' coordinate system is diagrammed below.

\[
r^2 = x_1^2 + x_2^2
\]

From the fact that the stresses at the free surfaces of the crack must be equal to 0, the function must have imaginary solutions. Therefore, to traverse the crack tip an imaginary coordinate system
was chosen, $z = x_1 + ix_2 = re^{i\theta}$ ($\theta = \text{angle from } -x_1 \text{ to } -x_2$).

Williams expressed the two functions $f$ and $g$ as real parts of two polynomial series;

$$f = \sum \text{Re } z^{\lambda-1}$$

substituting $z = re^{i}$

$$f = \sum r^{\lambda-1} \cos(\lambda-1)\theta$$

and

$$g = \sum r^{\lambda+1} \cos(\lambda+1)\theta$$

giving

$$\psi = \sum r^{\lambda+1} f(\theta)$$

The stresses $\sigma_x, \sigma_y, \tau_{xy}$ were defined in terms of $\psi$ in polar coordinates, i.e. $\sigma_r, \sigma_\theta, \tau_{r\theta}$.

The equation was then solved for the boundary conditions:

1) $\sigma_\theta = 0$ when $\theta = 0$ and $2\pi$ (crack faces)
2) $\tau_{r\theta} = 0$ when $\theta = 0$ and $2\pi$ (crack faces).

This yielded two solutions;

1) $\psi_1 = 0$
2) $\psi_2 = f(r, \theta)$

By replacing $\theta$ by $K$ ($K = \theta - \pi$), Williams developed an equation for $\sigma_y$:

$$\sigma_y = -\frac{a_1}{r^{\nu_2}} \cos \frac{K}{2} (1 + \sin \frac{K}{2} \sin 3\frac{K}{2}) + \ldots$$

$a_1 = \text{constant}$

Under an applied stress;

$$\sigma_y = \sigma_{app} \left(\frac{-a_1}{r^{\nu_2}} \cos \frac{K}{2} (\ldots)\right)$$

which can be reduced to;

$$\sigma_y = \sigma_{app} \sqrt{\frac{a_1}{r}} Y$$

were $Y$ is a geometric factor replacing the series function.

$K'$ was originally termed the stress intensity factor.

$$\sigma_y = \frac{K'}{\sqrt{r}}$$
The value of the constant $a_1$ is related to the crack length $2c$ so the stress intensity at a crack tip can be expressed as:

$$K = Y\sigma\sqrt{c}$$  \hspace{1cm} (3.9)

The fatigue behaviour of a glass is detailed by a plot of crack velocity versus stress intensity, a typical example of which is shown in Figure 3.19.

Figure 3.19 is representative of the behaviour of a silicate based glass in a water containing environment. Three distinct regions of crack growth behaviour are identified on the figure:

In Region I the crack velocity is exponentially dependent on the stress intensity factor. In this region the data can be fitted to an empirical relation $v = AK_1^n$ where $A$ and $n$ are constants for a given glass composition and test environment. For environments of lower water concentration the curve is shifted to lower velocities and higher stress intensities. This shift and the exponential behaviour of the curve can be explained by the Charles and Hillig theory of stress corrosion. Therefore, it is believed that the rate of crack growth for this region is controlled by the rate of the corrosive reaction of water at the crack tip.

The presence of a static fatigue limit, ie. $K_1 = K_{10}$ below which no detectable crack growth occurs, also supports the Charles-Hillig theory of stress corrosion cracking.

In Region II the crack velocity is independent of the stress intensity factor and a velocity plateau is observed on the curve.
The velocity at which the plateau is found depends on the water concentration in the test environment. Region II crack growth is due to stress enhanced chemical reaction between the glass and water with the rate of crack growth controlled by the rate of transport of water to the crack tip.

In Region III the crack velocity again increases exponentially with the stress intensity but with a slope that is usually higher than that found for Region I behaviour. At the high stress intensities of Region III crack growth occurs by purely mechanical failure. The rate of crack growth in this region is independent of the water in the environment and is controlled by the chemical composition and structure of the glass. The curve for Region III asymptotically approaches the value of $K_{IC}$ for the glass.

3.4.2 EXPERIMENTAL TECHNIQUES FOR STRESS CORROSION STUDY

Because stress corrosion is a process whereby subcritical flaws can be propagated to failure, the fatigue behaviour of a glass component is an important engineering design consideration. The lifetime of a glass piece in service is limited by the time needed for initial cracks in the glass to grow to critical size. A knowledge of the fatigue parameters $A$ and $n$ is necessary to calculate estimated lifetimes. A detailed analysis of the methods of lifetime prediction will be presented later. The following review details the experimental techniques used to quantify the static fatigue behaviour of glasses.

In general, there are two methods of studying stress corrosion in glass; direct and indirect. Direct methods employ fracture mechanics
type specimens containing macroscopic cracks. Accurate measurements of crack velocity and stress intensity can be made during testing from which crack growth parameters are directly determined. Indirect methods use strength measurements to infer the crack growth parameters. Direct methods offer the advantage that detailed information on fracture behaviour is obtained. The indirect method has the advantage that the crack growth parameters are determined for flaws similar to those naturally found in the glass component of concern. In the latter, the need for an assumption of identical fracture processes at the tip of a large artificial crack and natural cracks which occur in a typical glass piece is eliminated.

Of the number of sample geometries employed for direct determination of the stress corrosion parameters of a glass, the double cantilever beam (DCB) is most often used. This is because the specimens are easy to prepare, the crack front propagated in the sample approximates a straight line simplifying data analysis, and considerable lengths of stable crack growth can be maintained. The double cantilever beam configuration is shown in Figure 3.20.

Several investigators have determined expressions for the stress intensity factor for the DCB specimen. The detailed mathematics of their solutions will not be presented here. A comprehensive analysis can be found in the literature. The following table lists some of the expressions obtained and the range of crack lengths for which the solutions are valid. The variables are defined in Figure 3.20(a).
TABLE 3.1

\[ K_1 \text{ for DCB CONFIGURATION}^{(96)} \]

<table>
<thead>
<tr>
<th>FORMULA</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ K_1 = \frac{3.46}{b} \left( \frac{P}{h} \right) \left( \frac{c}{h} + 0.688 \right) ]</td>
<td>[ c/h \geq \frac{w}{h} - 2 ]</td>
</tr>
<tr>
<td>[ K_1 = \frac{3.467}{b} \left( \frac{P}{h} \right) \left( \frac{c}{h} + 0.68 \right) ]</td>
<td>[ 1.5 \leq \frac{c}{h} \leq 4 ]</td>
</tr>
<tr>
<td>[ K_1 = \frac{3.464}{b} \left( \frac{P}{h} \right) \left( \frac{c}{h^2 + 1.2 \left( \frac{c}{h} \right) = 0.693} \right) ]</td>
<td>[ c/h \geq 0.875 ]</td>
</tr>
<tr>
<td>[ K_1 = \frac{3.208}{b} \left( \frac{P}{h} \right) \left( \frac{c}{h - 0.4405} \right) \left( \frac{4.893}{(c/h)^2 - 4.71(c/h) + 5.345} \right) ]</td>
<td>[ 0.5 \leq \frac{c}{h} \leq 2.2 ]</td>
</tr>
</tbody>
</table>

To guide the movement of the crack down the centre of the DCB sample, a groove is often machined along either side. This is shown in Figure 3.20(b). For a side grooved DCB sample the stress intensity factor can be expressed as\(^{(108)}\):

\[ K_1 = \left( \frac{Pc}{bb_n} \right)^{0.5} \left( \frac{h^{0.5}}{h} \right) (3.47 + 2.32 \frac{h}{c}) \]  \hspace{1cm} (3.10)

Fatigue tests using DCB glass samples are usually conducted under fixed load, fixed displacement or constant applied moment conditions. During the fatigue tests the crack tip position is monitored optically using a travelling microscope. The time is recorded at each crack length measurement and the crack velocity is calculated from this data.

For fixed load conditions the stress intensity is calculated using Equation 3.10 with \( P \) being constant. Under fixed displacement conditions the load will vary, decreasing as the crack grows. Calculation of the stress intensity requires monitoring of the load with time, done by continuous chart recording of a load cell output. For a constant moment loading configuration the stress distribution in the beam is constant. The stress intensity for this configuration is independent.
of crack length and is determined from the applied moment.

Hibino et al\(^{(52)}\) developed a system for studying static fatigue of glass under dynamic loading conditions. The test geometry was an edge-cracked tensile specimen stressed in a tensile testing machine under fixed strain rate loading. The crack length was monitored using an ITV camera and video recorder. The crack tip position, time and load data were recorded for the duration of the test and analysed later to determine crack velocity and stress intensity.

Using the above methods, data of crack velocity and stress intensity are obtained from which the stress corrosion \(K_1-v\) diagram may be plotted. The fatigue parameters \(A\) and \(n\) may be determined directly from the resulting curves.

Indirect methods of studying fatigue behaviour offer simpler experimental techniques but involve more complicated data analysis to obtain values for \(A\) and \(n\).

Experiments measuring the loading rate dependence (\(\dot{\varepsilon} = \text{constant}\) or \(\dot{\sigma} = \text{constant}\)) of strength can be used to determine a glass' fatigue parameters.

Ritter developed equations for failure strength as a function of stress rate for dynamic fatigue tests. The details of the derivation are given below (the variables have their usual meanings).

The general equation for stress intensity at a crack tip is given by:

\[
K = Y\sigma\sqrt{c} \tag{3.11}
\]

The velocity of the crack can be expressed:

\[
v = \frac{dc}{dt} = \left(\frac{1}{2\sigma}\right)K_0t\left(\frac{\partial\sigma}{\partial t}\right) \tag{3.12}
\]
or

$$d\sigma = (\dot{\sigma}/\nu)\, \, dcr \quad (3.13)$$

From

$$\nu = AK^n \quad (3.14)$$

for Region I crack growth behaviour:

$$\nu = V_0 \left( K/K_0 \right)^n \quad (3.15)$$

So, from (3.11);

$$K = K_0 \left( C/C_0 \right)^{\frac{n}{2}} \left( \sigma/\sigma_0 \right) \quad (3.16)$$

Substituting for $\nu$ in (3.13) and integrating from initial conditions (indicated by subscript $o$):

$$\sigma = K_0 \left( \frac{(\pi C_0)^{1/2}}{\nu K_0 (n-2)} \right)^{1/(n+1)} \quad (3.17)$$

($\pi$ enters the equation from the assumption that $Y$ is a constant equal to $n^{1/2}$ for surface flaws).

Assuming very small initial cracks, i.e. $C \ll C$ and large values of $n$ (as for glass)

$$\frac{1}{C_0} (n/2)-1 \approx (1/C_0)(n/2)-1 \quad (3.18)$$

This reduces equation (3.17) to:

$$\sigma = K_0 \left( \frac{1+2\pi C_0^{3/2} \dot{\sigma} (n+1)}{(\pi C_0)^{1/2} V_0 K_0 (n-2)} \right)^{1/(n+1)} \quad (3.19)$$

Evans and Wiederhorn(33), used this derivation to obtain a simple equation for the stress rate dependance of strength;

$$\sigma = B \dot{\sigma}^{1/(n+1)} \sigma_{IC} (n-2)^{2/(n+1)} \quad (3.20)$$

where \[ B = 2/ (AY^2(n-2)K_{IC}n-2) \]

The equation for constant strain rate experiments has the
same form i.e.:

\[ B \dot{\varepsilon}^{1/(n+1)} \sigma_{\text{lc}}^{(n-2)/(n+1)} \]  \hspace{1cm} (3.21)

The fatigue parameter \( n \) may be determined from a plot of log failure-stress versus log strain rate for a number of different strain rates. The slope of the curve generated is equal to \( 1/(n+1) \). An example of this curve is shown in Figure 3.21.

Alternatively, by assuming equal failure probabilities for two sample populations of a glass i.e. \( \sigma_{\text{lc}1} = \sigma_{\text{lc}2} \), \( n \) may be determined from tests at two strain rates only. Equation (3.21) then becomes:

\[ \sigma_{1} / \sigma_{2} = (\dot{\varepsilon}_{1} / \dot{\varepsilon}_{2})^{1/(n+1)} \]  \hspace{1cm} (3.22)

or

\[ \log \sigma_{1} = \log \sigma_{2} + \frac{1}{n+1} \log (\dot{\varepsilon}_{1} / \dot{\varepsilon}_{2}) \]  \hspace{1cm} (3.23)

\( N \) strength measurements are made at each strain rate, with the values ranked in order of magnitude. Corresponding ranked strengths are plotted on logarithmic axes with the intercept of the curve giving the value of \( n \). The validity of the assumption of equal failure probabilities for the two sample distributions is verified by a slope =1 for the data curve. An example plot for this method of fatigue parameter determination is given in Figure 3.22.

The configuration commonly used for strength testing of glass is the four point bend sample. The sample configuration and loading pattern are shown in Figure 3.23. The expression for the bend strength can be developed from simple beam theory.

The stress in a beam is given by:

\[ \sigma = \frac{-My}{I} \]
where: \( M = \) applied moment
\( l = \) moment of inertia
\( y = \) distance from centroid

For the four-point bend sample the maximum tensile stress occurs at \( y = h/2 \),
and
\[
I = \frac{wh^3}{12}
\]

From the loading diagram of Figure 3.23, the maximum bending moment is between the inner spans and is equal to:
\[
M = PL/8
\]

Solving the equation for the maximum stress in the beam gives the expression for the four-point-bend strength:
\[
S = \frac{3PL}{4wh^2}
\]

where: \( P = \) load
\( L = \) lower span
\( w = \) sample width
\( h = \) sample height

3.4.3 REVIEW OF LITERATURE RESULTS

The stress corrosion behaviour of soda-lime-silica glass has been extensively studied. Results obtained for such glasses in a water containing environment are shown in Figure 3.24.

The crack velocity-stress intensity curve clearly shows the three regions of crack growth behaviour. For increasing water content in the test environment, the curves are displaced to higher velocities but maintain the same slope. This follows directly from the Charles-Hillig theory of stress corrosion and equation 3.8. For crack growth due to a chemical reaction, increasing the concentration of the reactive species will increase the rate of growth. The mechanisms of growth
are the same. The data points in Region III of the curve all lie along the line of a single curve verifying the hypothesis that in this region failure is purely mechanical and independent of the test environment.

Figure 3.25 shows the effect of test temperature on the stress corrosion of glass. The $v - K_1$ curves shift to higher velocities and the data fit a relationship of the form $v = A e^{Q/RT}$. These results agree with the Charles and Hillig theory of stress corrosion as an activated process.

$K_1-v$ curves obtained by investigators showing the effects of glass composition on stress corrosion behavior are shown in Figure 3.26.

The addition of alumina to a silica glass decreases the slope of the $v-K$ curve. This follows from the theory of glass corrosion presented earlier. Alumina-containing glasses form durable aluminosilicate surfaces with the Al-O bond being more resistant to OH$^-$ attack. The increased susceptibility of soda-lime silica glass to stress corrosion is shown in the figure. The curve for soda-lime-silica glass is displaced to much higher crack velocities, e.g. at $K_1=4 \times 10^5 \text{ N/m}^{3/2}$, $v=10^{-10} \text{ m/s}$ for silica and $10^{-6} \text{ m/s}$ for soda-lime-silica. Ion exchange at the crack tip causes an increase in the local pH of the solution. Ion exchange may cause changes in the electronic structure of the Si-O bond at the tip. Also, the differing sizes of the Na$^+$ and H$^+$ ions may induce tensile stresses during exchange. All three of these reactions may result in an increased crack velocity for the soda-lime-silica glass and the observed differences in slope for the two curves.
The effect of pH on the rate of crack growth is shown in Figure 3.27. Increasing the concentration of the reactive species in solution, e.g. replacing 1N NaOH by 6N NaOH causes a displacement of the crack growth curve to higher velocities. This follows from the Charles and Hillig equation for crack velocity and Equation 3.8 which directly relates velocity to OH⁻ concentration.

The widely differing slopes of the curves for glass in NaOH and HCl suggest that a different process controls the rate of reaction at the crack tip in each case. At low pH values the primary corrosive mechanism is ion exchange of Na⁺ and H⁺. At higher pH values, the attack of the Si-O bond by OH⁻ ions becomes predominant. Both mechanisms cause weakening and rupture of the bonds at the crack tip. The slope of the curve for soda-lime-silica glass in water is approximately the same as that for the glass in NaOH, indicating that the localized solution pH at the crack tip is alkaline, a fact supported by findings of Weiderhorn (101). The high pH is induced by Na⁺-H⁺ ion exchange at the tip.

Michalske and Frechette (66) studied the stress corrosion of glass in the presence of water. In an environment of liquid water they observed that the velocity curve exhibited a bend, or plateau region for velocities of ~10⁻² m/s. The shape of the curves obtained are shown in Figure 3.28. Michalske explains that, for v=10⁻² m/s, water facilitates crack growth. As the velocity increases, drag of the water on the walls of the crack causes fine cavitation bubbles to form. The wetted sections of the crack front grow around the dry area joining on the other side forming a hackle step. The energy
used to generate the hackle steps and propagate them causes a decrease in the crack velocity. At higher velocities a stable cavitation bubble forms across the crack front separating the tip from the liquid. The crack growth then proceeds as for a dry environment. This is shown by a jump in crack velocity to approximately critical velocity.

The results obtained by various researchers for the fatigue parameters of several glasses in water are listed in Table 3.2. These results are taken from the accumulated data of Freiman, Baker and Wachtman(38).

3.5 LIFETIME PREDICTION

Fatigue parameters obtained from stress corrosion studies of a glass can be used to determine the lifetime of the glass under given service conditions.

An equation to determine the time-to-failure for a glass under constant load can be derived from the expressions for crack velocity, \( v = \frac{dc}{dt} \), stress intensity at a crack tip, \( K_I = \sigma Y \sqrt{c} \) and the empirical relationship \( v = AK^n \) which has been shown to hold for glass. Integrating \( v = \frac{dc}{dt} \) from the initial to the final conditions yields:

\[
t_f = 2K_{II}^{2-n}A \sigma a^2 Y^2 (n-2)
\]

where
- \( t_f \) = time to failure
- \( K_{II} \) = stress intensity for initial flaws
- \( \sigma_a \) = applied stress

assuming that for large values of \( n \) \( (K_{IC}^{2-n}K_{II}^{2-n}) \).

\( K_{II} \) is a parameter which is difficult to measure and so is replaced by:

\[
K_{II} = \frac{\sigma}{\sigma_{IC}} K_{IC}
\]
which follows from the linear relationship between applied stress and stress intensity. \( \sigma_{lc} \) is a measure of the critical fracture strength for the same glass in an inert environment determined from a series of strength measurements.

Using these substitutions, equation 3.25 becomes;

\[
t_f = 2\sigma_a^{-n} (K_{1c}/\sigma_{lc})^{2-n}/AY^{2(n-2)} \quad (3.27)
\]

Therefore, design diagrams for a glass can be calculated from the parameters obtained from \( K_{1-v} \) diagrams and the inert or pristine strength of the glass.

Statistical analysis of the strength of the glass can be used in conjunction with the above equations to determine the design stresses for specified failure probabilities.

Alternatively proof tests may be used to eliminate samples containing flaws larger than a maximum size and so ensure a minimum service life.

For a sample to survive the proof test

\[
K_{lp} = \sigma_p \sqrt{C_i} < K_{ll} \quad (3.28)
\]

where \( \sigma_p \) is the proof test stress and \( C_i \) is the maximum flaw size in the piece.

\[
K_{ll} = \sigma_a \sqrt{C_i} \quad (3.29)
\]

is the stress intensity at the beginning of service. This can also be expressed as:

\[
K_{ll} < (\sigma_a/\sigma_p) K_{lc} \quad (3.30)
\]

Substituting this into (3.27) the minimum time to failure results, i.e.,

\[
t_{min} = 2\sigma_a^{-2} (K_{lc}\sigma_a/\sigma_p)^{2-n}/AY^{2(n-2)} \quad (3.31)
\]
Using equation (3.31) design diagrams for a glass component can be obtained. Two examples are shown in Figures 3.29 and 3.30.

3.6 **BIOGLASS™ APPLICATIONS**

Researchers at the University of Florida have undertaken pre-clinical experiments and clinical trials to examine the potential for use of Bioglass™ as a prosthetic material in a series of applications. In a review paper on the research some of the potential applications are listed as follows:

1. tooth root replacement
2. orthodontic anchors
3. periodontal packing material
4. hip devices
5. spinal fixation
6. finger joint anchors
7. joint resurfacing
8. ossicular chain replacement

This list covers only the applications for which clinical or preclinical tests have been initiated. There are other possible applications for Bioglass™ as orthopaedic devices including various joint replacement devices, bone fixation or intramedullary devices.

To obtain a measure of the expected lifetime for Bioglass™ in these applications it is necessary to determine the stresses which would be acting on the material in service. Of particular importance is the maximum tensile stress, this being the stress which would act
at the flaw tips to cause stress corrosion cracking of the glass.

An exact determination of stresses in a prosthetic device requires detailed analysis of loading and boundary conditions and implant geometry. These parameters will vary for each case being dependant on the patient's skeletal structure, musculature and weight. However, approximate values for the maximum tensile stresses incurred can be used to obtain estimated lifetimes for the glass. Some values of these stresses are given in the following table.

| TABLE 3.3 | STRESSES IN PROSTHETIC DEVICES |
| PROSTHETIC DEVICE | MAXIMUM TENSILE STRESS | SOURCE |
| patella | 3-3.5 MPa | 44 |
| femoral head | 2.5 MPa | 4 |
| tooth (blade design) | 1 MPa | 17 |
| total hip: lateral neck | 70-120 N/mm² | 15 |
| total hip: distal lateral | 180-254 N/mm² | 15 |
| total hip: distal medial | 16-218 N/mm² | 15 |
| Freeman-Swanson knee | 19 MPa | 79 |
| fracture fixation: pin | 105,500 psi | 8 |
| bone plate | 20-50 ksi | 64 |

The prosthesis for which ceramics are most often suggested as a potential material is the total hip replacement device. An analysis of the stresses incurred on loading in the femoral component of the device is given in Figure 3.31.
3.7 PLAN OF STUDY

The overall objective of this study is to investigate the stress corrosion behaviour of Bioglass\textsuperscript{TM} 4555 with the aim of being able to predict the lifetime of the glass in use as a posthetic device. The plan of study undertaken to achieve this objective is outlined as follows.

Bioglass\textsuperscript{TM} of the composition developed by Hench will be prepared. Following the procedure used by Hench et al, the corrosion behaviour of the glass in a solution representing the physiological environment will be assessed. This experiment will yield information on the bone-bonding potential of the glass and will determine if the glass behaves similarly to that tested in-vivo and in-vitro by Hench.

The fatigue parameters $A$ and $n$, will be determined from slow crack growth studies of the glass. Crack growth in double-cantilever beam specimens under fixed strain rate loading and load relaxation will be monitored using an optical technique. The static fatigue behaviour of the glass will be analysed in solution and in air. Standard soda-lime-silica glass will also be tested for comparison and as a means of testing the experimental system.

Four-point-bend tests will be performed on the glass in solution. The fatigue parameter $n$ will be determined from the results of the tests at two strain rates. This value will be compared to that obtained from the slow-crack-growth studies.

The inert strength of the glass will be determined by four-point bend strength tests at rapid strain rates and in a liquid $N_2$
environment.

The values of $A$, $n$ and inert strength will be used to determine estimates for the lifetime of Bioglass$^\text{TM}$ used in several prosthetic devices. The potential application of the glass may then be assessed.
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Figure 3.1 Stage 1 and Stage 2 Glass Corrosion (13)
Figure 3.2 $\sqrt{t}$ Dependence of Glass Corrosion (81)

a) $15\%K_2O-85\%SiO_2$

b) $15\%K_2O-15\%CaO-70\%SiO_2$

c) $15\%Na_2O-85\%SiO_2$

d) $15\%Na_2O-10\%CaO-75\%SiO_2$
Figure 3.3 Glass Corrosion Profile of $K_2O-SiO_2$ Glass

+ Experimental data points
— Curve fitted by Boksay et al. (13)
Figure 3.4 Glass Corrosion Profiles by Doremus (24)
Profile of lithium ion in lithium-silicate glass.
- Experimentally measured values
- Fitted (calculated) curve
Figure 3.5 $\sqrt{F}$ Dependence of Alkali Extraction for Binary and Ternary Silicate Glasses (19)

(a) potassium-silicate glass
(b) sodium-cadmium-silicate glass
Figure 3.6 Model of Leached Alkali-Silicate Glass Surface (24)
Figure 3.7 Time Dependence of Glass Corrosion, Long t (19)
Figure 3.8 Silica Extraction as a Function of Solution pH\(^{(25)}\)
Figure 3.9 Corrosion of K₂O-SiO₂ Glass (25)
pH dependence of alkali and silica extraction from 15 K₂O-85 SiO₂ glass
Figure 3.10  Effects of Alkali Content on Corrosion Resistance

- Leaching of $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ glass in 0.01n HCl, 30°C
- N = Na$_2$O content, C = CaO content
Figure 3.11 Types of Glass Corrosion Surfaces\(^{(48)}\)
Solution Data for Glasses Corroded in Static Aqueous Solution at 100°C

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Figure 3.12 Effect of CaO Content on Glass Corrosion\textsuperscript{(12)}
Figure 3.13 Sampling Depths of Analytical Techniques Used in Studying Glass Durability (13)
Figure 3.14 Changes to Crack Tip Geometry by Stress Corrosion (13)

a) Flaw sharpening by stress corrosion
b) Flaw growth with tip rounding balanced by the lengthening of the flaw
c) Flaw blunting by corrosion
Figure 3.15 Thin Slit Model of a Crack Tip

- $P$: load on crack tip
- $u_0$: crack tip displacement
- $B\rightarrow B$: strained crack tip "linkage" bond
Figure 3.16 Molecular Model for Stress Corrosion of Glass

1. Strained crack tip bond adsorbs water molecule
2. Cleaving of Si-O and O-H bonds to form two hydrogen bonded silanol groups
3. Cleaving of hydrogen bonds and subsequent fracture at crack tip
Figure 3.17 Species Inductive to Stress Corrosion of Glass (67) - water and nonaqueous species with lone-pair orbitals opposite protons (— bond expected to cleave during crack tip interaction)
Figure 3.18 Kinked Front Model of Stress Corrosion Cracking (65)

a) two-dimensional model of crack front
   o broken bonds
   • unruptured bonds
b) * crack front kinks creating new broken bonds
Figure 3.19  Slow Crack Growth, K-v Diagram
Figure 3.20  DCB Sample Configuration
(a) regular
(b) side-grooved
Figure 3.21 Failure Stress vs Strain Rate for Silicate Glass (89)
Figure 3.22 Fatigue Parameter, \( n \), from Two Strain Rates\(^{(33)}\)

\[
\log(\sigma_1 / \sigma_2) = 1/(n+1) \log(\dot{\varepsilon}_1 / \dot{\varepsilon}_2)
\]
Figure 3.23 Four Point Bend Strength Test
Figure 3.24  K - v Diagram, Soda-Lime-Silica Glass in Moist Air (33)
Figure 3.25 Effects of Temperature on Stress Corrosion of Glass (100)
Figure 3.26 Effects of Glass Composition on Stress Corrosion (102)
Figure 3.27 pH Dependence of Stress Corrosion Cracking (108)
Figure 3.28 Stress Corrosion of Glass in Liquid Water (66)
Figure 3.29 Lifetime Prediction from Stress Corrosion Analysis (33)
Figure 3.30  Proof Test Design Diagram
Figure 3.31 Stresses on Loading of Hip Prosthesis
CHAPTER FOUR

EXPERIMENTAL

4.1 INTRODUCTION

A knowledge of the stress corrosion parameters of a glass in a particular environment allows the design engineer to determine the lifetime of a piece of the glass in service.

To this end, a study has been performed on the stress corrosion behaviour of Bioglass\textsuperscript{TM} in a simulated physiological environment. Crack growth parameters were determined using direct crack growth studies in DCB samples and indirect, 4-point bend strength, analysis methods.

The following sections of Chapter 4 detail the experimental procedures followed for fatigue testing of Bioglass\textsuperscript{TM}.

4.2 SAMPLE PREPARATION

The Bioglass\textsuperscript{TM} chosen for this stress corrosion study was 45S5. Samples for fatigue experiments were prepared from melts of the component oxides. Composition 45S5 is given in Table 4.1.

| TABLE 4.1 |
| Bioglass Composition |
| OXIDE | WEIGHT % |
| SiO\textsubscript{2} | 45.0  |
| CaO  | 24.5  |
| Na\textsubscript{2}O | 24.5  |
| P\textsubscript{2}O\textsubscript{5} | 6.0   |

91
Reagent grade $\text{Na}_2\text{CO}_3$, $\text{CaCO}_3$, and $\text{P}_2\text{O}_5$ were combined with -325 mesh $\text{SiO}_2$ in 100 gram lots and melted in covered fireclay crucibles at $1350^\circ\text{C}$ for two hours. Melting times were kept to a minimum to prevent extensive contamination of the glass by dissolution of the fireclay. Melts were stirred for homogenization of composition, and quench cast into graphite molds. Further homogenization of the glass batch was performed by ballmilling the cullet in polypropylene bottles with alumina milling media for 18 hours. The glass powder was remelted for fining in covered alumina crucibles at $1350^\circ\text{C}$. A firing cycle of 2.5 hours rise and 5 hour soak was employed. Blocks of glass were cast in a graphite mold preheated to $450^\circ\text{C}$ and placed immediately in an annealing furnace maintained at $450^\circ\text{C}$. The glass was held at this temperature for $\sim 15$ hours and then furnace cooled.

Several different mold sizes were tested in preliminary casting experiments. The mold dimensions were optimized with regards to available furnace size, melt size, the ease and quickness of casting and the cooling rate of the cast block. Pouring of the melt must be performed quickly and smoothly to prevent cords or high stress regions forming in the block as it casts. In addition, the casting system (glass/mold) must be dimensioned such that cooling of the glass through the crystallization temperature range occurs quickly. The dimensions of the mold used for the bulk of the sample preparation are given in Figure 4.1.

Double cantilever beam samples for slow crack growth studies were machined from the cast glass blocks. The rough surface produced on the base of the block from the casting mold was smoothed by lapping.
(Logitech) with 600 grit SiC powder/water grinding media. Once smooth, the block could be mounted on a sample holder for sawing. A high speed saw (Micromeretics) with a 0.015" thick diamond blade was used to slice the block into single sample pieces. The blocks were cut across their width to yield samples (6.0 cm x 1.3 cm x 0.6 cm). The individual samples were then lapped to size and parallelism. A groove was machined down the centre of the sample on both faces leaving a web of uncut glass approximately one third of the total sample thickness. This web provided a path for crack guidance during the fatigue testing. A 0.040" thick diamond saw blade mounted on a wafering machine was used to cut the side grooves.

The samples were then reannealed at 450°C for several hours to relieve stresses induced by the extensive machining. After annealing, the glass was examined under crossed polars and samples exhibiting regions of high stress concentration were discarded.

Sample dimensions were measured with a micrometer and a microscope vernier eyepiece. Typical final dimensions for the double cantilever beam samples are given in Figure 4.2.

Steel tabs with centre holes through their thickness were attached to the sample ends with a thermal setting wax. These tabs were used to mount the sample in the loading system. Problems with sample breakage and misalignment prohibited the drilling of holes for the loading pins directly in the samples. In the subsequent analysis, the tabs were treated as direct extensions of the cantilever arms.

Several methods of introducing sharp cracks in the samples were investigated. Tests using notches sawn by a diamond blade were
unsuccessful due to the high overloading necessary to initiate a crack at the blunt notch tip. A rig designed to initiate a crack by forcing a wedge into the sawn notch also proved unsuccessful. The best results were obtained by touching the hot tip of a soldering iron to a point on the glass approximately 1/8" along the side groove. Stresses induced from thermal expansion of the glass caused a crack to form from the sample end to the point of heat application. Some extent of crack healing was evident on removal of the heat source suggesting that the crack tip was atomically sharp.

4.3 CORROSION TESTING

Static corrosion tests were conducted on bulk samples of Bioglass™ 45S5 to verify the corrosion reaction occurring at the glass surface in-vitro. Corrosion profiles were compared with those obtained by Hench and others for the same glass.

Small samples of 45S5, 5mm x 5mm x 2mm were freshly abraded with 600 grit SiC polishing paper and immersed immediately in 500ml of test solution at room temperature. The solution, representative of the physiological environment, consisted of distilled water buffered to pH=7.4 by the addition of HCl and trishydroxymethylmethylamine. This test solution composition was used throughout the study. After one hour, the samples were removed and blown dry by a gentle air stream. The corrosion profiles were analysed by Auger and SIMS analysis.

4.4 FATIGUE TESTING

Fatigue tests were performed by fixed strain-rate and fixed-grips
load relaxation techniques. In the former, the DCB samples were loaded quickly to initiate crack opening and the crack then propagated at a slow strain rate (typically 0.0012mm/min). Measurements of crack velocity were taken for crack lengths in the range \( 2 \leq c/h \leq 10 \) (c=crack length, \( 2h=sample 
height \)) where the effects of the sample free ends on the crack tip stress field are low. The fixed- grips test method consisted of loading the sample under constant strain rate to initiate crack motion and when the crack had grown to \( c > 2h \) the machine was stopped and the crack motion continued under the steadily decreasing load. The load was continuously monitored by the millivolt output of a load cell. It was found during the course of testing that the system used for transmitting load to the piezoelectric load cell as designed by the manufacturers was unacceptable because of an unstable zero load reading. The drifting of the load was caused by a variable stress being transmitted to the cell from the threaded loading attachment. To overcome this problem a new loading arrangement was designed to transmit load by direct pressure on the active bearing surface of the load cell. This is shown in Figure 4.3. Prior to fatigue tests the load cell was calibrated in position on the tensile machine using weights suspended from the loading rod. All fatigue tests were performed on a Wykeham Farrance tensile machine. Rods, with universal joints at the ends, were attached to the stationary load cell at the top of the machine and to the moving piston at the bottom. The universal joints were used for sample fixation. The joint ends were cut to a channel shape and drilled to hold the loading pins which passed through the steel tabs attached to the arms of the glass DCB samples.
A schematic of the loading system is shown in Figure 4.4 and a photograph in Figure 4.6.

Stress corrosion tests were performed in air and in the test solution. A plexiglass box was constructed to contain the solution and allow complete submersion of the Bioglass™ sample whilst still allowing visual monitoring of crack growth. The box was mounted with silicone rubber fixed just below the lower universal joint hinge. A clamp holder fastened to the lower loading rod served to support the box when filled with solution.

To prevent unbalanced loading at the beginning of the fatigue tests (i.e. a moment introduced by the unsupported sample) from turning the crack from the grooved midplane, a sharpened screw threaded through the bottom of the plexiglass immersion box was used to level the glass. When the tensile load reached a level sufficient to support the glass horizontally the screw was retracted to non-contact. At this point, the downward moment due to the weight of the sample was considered negligible in comparison to the applied load and would therefore have no appreciable effect on the velocity of crack motion. The validity of this assumption was checked by considering the worst possible case, i.e. the total weight of the sample acting on the upper loading pin, and comparing the force of this load with the applied load. These values were found to be 0.1 N and 8 N respectively, supporting the above assumption.

To prevent moments being applied to the sample by hinging actions of the lower universal joint, the joint was fixed in an upright position. A dummy sample was loaded in the test rig to pull the joint
to the upright, aligned position. It was then secured by packing the joint with silicone seal. The experimental apparatus designed for testing the stress corrosion of Bioglass™ in solution is shown in Figure 4.5.

A novel system was designed to optically monitor crack motion during the fatigue tests. The traditional method of following the position of the crack front with a travelling microscope was replaced by a video recording system. A video camera with a macro lens was focussed on the sample crack and outputed to a television monitor and a video cassette recorder. Prior to testing, a grid was applied to the face of one arm of the DCB sample as can be seen in Figure 4.5. A travelling microscope was used to measure the positions of the vertical grid marks with reference to the point of load application, i.e., the centres of the holes in the attached tabs. This grid was used to calibrate the optical system and as reference for crack length measurements. The position of the crack tip was made visible to the camera lens by the reflection of oblique lighting from its surface. The digital millivolt meter reading the output from the load cell was placed behind the test chamber in the field of view of the camera and a 0.01 second stopwatch built into the camera was started at the beginning of each fatigue experiment. With this system a permanent record of each fatigue test consisting of simultaneous measurements of crack length, applied load and time was obtained. These values enabled direct calculation of stress intensity and crack velocity from the recorded data. A photograph of the system is shown in Figure 4.6. The images of the DCB sample, timer and millivolt meter readout
are clearly visible on the television monitor.

4.5 DATA ANALYSIS

Results of stress corrosion experiments are commonly presented in the form of crack velocity / stress intensity plots. In this study, a computer processed the data from the video tapes and presented the results on $K_I$-$V$ diagrams.

Several investigators have determined expressions for the stress intensity at the crack tip in a double cantilever beam specimen. (See literature review, section 3.3.) The formula given in the equation below will be used throughout this study, i.e.,

$$K_I = \frac{Pc}{2b(n)^{0.5}h^{1.5}}(3.47 + 2.32h/c)$$

(4.1)

where the variables are defined in Figure 4.7.

Crack velocity values were determined simply by the rate of change of crack length with time; $(V = \frac{dc}{dt})$.

Load values at any time during the fatigue tests were directly obtained from the millivolt meter readings recorded on videotape, corrected for the zero load output, and converted to newtons through a pre-calibration of the load cell.

Crack lengths were calculated from measurements taken from the television monitor using a travelling microscope. The position of the crack was determined by pausing the replay of the video tape and focussing the crosshairs of the microscope eyepiece on the crack tip. On advancing the video, the position of the crack tip was monitored at intervals of 0.1 seconds for rapid crack motion, longer time periods
were used for slower moving cracks.

To express the crack position measured by the travelling microscope in terms of actual crack length, the magnification of the complete optical system was determined. Included in this estimate were allowances for changes in magnification along the length of the sample due to image distortion from the curvature of the macro lens on the camera and the television screen. The grid applied to samples prior to testing was used for this purpose. The actual distance of the grid line from the loading points was measured with a microscope and a vernier eyepiece. By measuring the position of the grid marks on the television monitor with the travelling microscope a reference scale was developed for determining crack lengths. A magnification factor was calculated for each grid spacing by division of the actual distance by the distance between lines measured with the travelling microscope. Crack lengths were calculated by determining the distance as measured by the travelling microscope between the crack tip and the previous grid mark. This was converted to an actual distance on the sample using the corresponding magnification factor and added to the value measured for the distance of the grid mark from the point of load application. An example of this calculation is illustrated in Figure 4.8. Crack length calculations were performed within the computer program used to determine crack velocity - stress intensity values.

A modification of SMOOT, a program developed by Mr. F. Kus, McMaster University, was used for data analysis. The program reads a data set of \((X(I), Y(I))\) pairs with corresponding weighting factors \(W(I)\), and determines a smooth spline approximation fitting the data
to a curve. The degree of the spline and smoothness of fit are determined from parameters defined in the program. Also included in the program is the capability of determining the derivative of the fitted function at any point along the curve. A listing of the program utilized is included in Appendix 1.

Input to the program was in the form of a number of data files containing the information measured from the video tape. These are summarised in Table 4.2.

<table>
<thead>
<tr>
<th>FILE NAME</th>
<th>CONTENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRID (J)</td>
<td>Grid measurements taken on the sample</td>
</tr>
<tr>
<td>GRIDTM (J)</td>
<td>Grid measurements taken by the travelling microscope</td>
</tr>
<tr>
<td>CRAKTM (I)</td>
<td>Crack position as measured by the travelling microscope</td>
</tr>
<tr>
<td>TIME (I)</td>
<td>Time corresponding to crack position measurement</td>
</tr>
<tr>
<td>PMV (I)</td>
<td>Millivolt meter load reading</td>
</tr>
</tbody>
</table>

Entered also in the program were the sample dimensions H, B, and B_N, and the zero load reading from the millivolt meter, PMVO. From the input data, the actual crack length and applied load were calculated for each time entered. The values of crack length were fitted, using the spline approximation, to a function of time. The derivative of the function, taken for each time, gave a measure of the crack velocity at that particular time, v = dc/dt. Corresponding
values of stress intensity were calculated from the load and crack length data. Results obtained were written to a data file as crack velocity, stress intensity pairs. Plotting of the data file using a simple plotting routine yielded the $K - v$ diagrams used for interpretation of the stress corrosion behaviour of the glass.

### 4.6 STRENGTH TESTS

Strength measurement tests by four point bend were performed on samples of Bioglass™ 45S5 wetted with the same buffered corrosion solution used in the DCB sample fatigue tests. Dimensions of the samples and the four point bend rig are given in Figure 4.9. The samples were prepared from cast glass blocks by slicing and lapping to size. Final finishing on the glass was by 600 grit SiC slurry. Edges of the samples were rounded with 600 grit SiC polishing paper. Strength tests were performed on a Wykeham-Farrance compression machine at two strain rates, 0.001 and 0.600 mm/min. Prior to testing, the samples were immersed in the corrosion solution. The glass was kept wet for the duration of the strength test by the dropwise addition of the solution when necessary. To expedite the testing procedure, the samples were loaded rapidly to approximately one half the fracture load and then loaded to failure at the controlled strain rate. An estimate of the expected failure load was obtained by breaking three samples using controlled strain rate loading only. No difference in failure strength is expected for the two loading patterns (88). The output from the machine load cell during the bend tests as recorded on an x-y recorder, was used to calculate the applied load at failure.
Four point bend strengths were calculated using Equation 3.24.

A total of twenty-five samples were broken at each strain rate. Using Equation 3.23, a value of $n$, the exponent in the stress corrosion relation $V = AK^n$, was obtained. Strengths at each strain rate were ranked in order of magnitude, $\sigma_1^i$ and $\sigma_2^i$ for $i = 1$ to 25. Plotting the logarithmic values of the pairs yielded a curve of slope $=1$ with an intercept equal to $\frac{1}{(n+1)} \log \frac{\dot{\varepsilon}_{1}}{\dot{\varepsilon}_{2}}$.

Four point bend tests were also performed to determine the "inert" strength of the glass, i.e. the strength for failure in the absence of a corrosion medium. Two test methods were employed. In the first, the samples were cooled to the temperature of liquid nitrogen and broken at a strain rate of 0.600 mm/min. The extreme cold of the sample prevents water vapour from reacting at flaw tips. In the second test method very rapid loading (5 mm/min.) was used to fracture the specimens. At such strain rates, the contribution of slow crack growth is minimal and the magnitude of the strength is determined by the initial flaw distribution in the sample\(^{(29)}\).

In spite of careful procedure to prevent excessive contamination of the glass, some impurities are introduced through the various processing steps. Of particular importance is the alumina contamination. X-ray fluorescence measurements were performed to determine the glass composition and the level of Al$_2$O$_3$ contamination therein. A series of strength measurements were also performed on glass melted in a platinum crucible to avoid alumina dissolution. The fatigue parameter, $n$, measured for this glass was compared with that obtained for the glass melted in fireclay and alumina. In this way the influence of the dissolved
impurities, particularly $\text{Al}_2\text{O}_3$, on the stress corrosion behaviour of the glass was assessed.
Figure 4.1 Graphite Casting Mold
Figure 4.2 Double-Cantilever Beam Sample- Dimensions

- L Sample Length: 4.7 cm
- C Crack Length: —
- b Sample Thickness: 0.6 cm
- b_n Web Thickness: 0.2 cm
- h Beam Height: 0.6 cm
- T_L Tab Length: 0.4 cm
- T_H Tab Height: 0.5 cm
Figure 4.3 Load Cell Apparatus
Rig designed for transmittance of load to active bearing surface of load cell
Figure 4.4 Loading System Schematic
Figure 4.5 Water Containment System for Fatigue Tests
Figure 4.6 Test System for Slow-Crack-Growth Study
Figure 4.7 DCB Specimen Configuration
Crack Length = \( \frac{(C_{TM} - G_{TM1})(G_{A2} - G_{A1}) + G_{A1}}{G_{TM2} - G_{TM1}} \)

Figure 4.8 Crack Length Calculation

\( G_A \) = actual grid position

\( G_{TM} \) = position of grid measured by travelling microscope

\( C_{TM} \) = position of crack tip measured by travelling microscope
Figure 4.9 Four-Point Bend Test

- $b$  Sample Width  
  0.45 cm

- $d$  Sample Thickness  
  0.25 cm

- $L_1$  Inner Span  
  1.27 cm

- $L_2$  Outer Span  
  2.54 cm
CHAPTER 5

RESULTS AND DISCUSSION

5.1 INTRODUCTION

Analysis of the stress corrosion behaviour of Bioglass\textsuperscript{TM} 45S5 was performed in three experimental stages:

1) determination of corrosion reactions,
2) slow crack growth studies in a corrosive environment,
3) 4-point bend strength measurements in a corrosive environment.

The results of these experiments and discussion of how they affect the lifetime of Bioglass\textsuperscript{TM} in the body will be covered in the following sections of this chapter.

5.2 CORROSION PROFILE

Corrosion reactions occurring on the surface of Bioglass\textsuperscript{TM}, while possibly detrimental to the long term mechanical behaviour of the glass, are essential to the development of conditions conducive to bone attachment. Experiments to determine the in-vivo bonding behaviour of glass 45S5 prepared for this study are beyond the facilities of the Materials Science laboratories at McMaster University. In-vitro testing was therefore performed to verify that the glass utilised in the study is comparable to that produced by Hench et al and exhibits the behaviour necessary for bone bonding. Ogino\textsuperscript{(63)} states that formation of a "calcium-phosphate rich film on the bioglass surface in-vitro corresponds closely to the capability of the material to bond to living
Experiments to determine the depth composition profile of surface corrosion layers formed in-vitro on Bioglass™ were performed by Ogino et al and Clark et al. (See Literature Review, Section 2.3, Figures 2.2 and 2.3.) Employing experimental techniques similar to those used by Clark and Ogino, the corrosion profile of the Bioglass™ of the present study was measured.

Difficulty was encountered in attempts to obtain a depth profile using the AES technique. Despite coating the sample with gold and maintaining a beam current 0.5 μA, unstable charging of the glass occurred during analysis. Various procedures were employed in analysis in efforts to overcome this problem. These included alternate milling and spot analysis of the bottom of the milled crater, use of a raster instead of spot analysis to reduce the concentration of the electron beam, and line scan analysis across the edge of a deep crater milled in the glass. All efforts were unsuccessful. As a result of the charging, the Auger signal peak heights were seen to change quickly and, apparently randomly, giving meaningless data. A sample output showing the composition versus sputter time as measured by Auger peak to peak heights is given in Figure 5.1.

The SIMS method of analysis yielded results which could be taken as a semi-quantitative analysis of the composition profiles through the corrosion layers. Shielding effects from the profile crater and matrix effects prevent the results from being fully quantitative.

The electron-optics facilities of Western University were
used for analysis. Measurements were done on a Cameca Ion Microscope. The primary beam was oxygen ions at a current of 79 nanoamps. A 11.5 kilovolt high voltage source was used. The secondary ions monitored were Si$^{4+}$, Al$^{3+}$, P$^{5+}$, Na$^+$ and Ca$^{2+}$. 

Output in the form of intensity of counts of secondary ions versus time was collected. The data obtained for the depth profile is shown in Figure 5.2. The secondary ions monitored are identified by their atomic mass. Analysis of a second sample yielded a depth profile identical to that of the first.

A printout of count intensity and time at 15 second intervals was also obtained for the species monitored. Intensities were normalized via division by the average values measured for each species in the bulk glass. Using an estimated value of the profiling rate, 5Å/s (based on known rates for other glasses), plots of relative concentration (% of bulk) through the corrosion layer were calculated. These are given in Figure 5.3 and Figure 5.4.

Examination of these figures yields information on the glass's reaction with the corrosion solution. SiO$_2$ is depleted from the immediate surface of the glass behind which is a layer enriched in this oxide. The other glass components P$_2$O$_5$, CaO and Na$_2$O exhibit the opposite behaviour, enrichment at the glass surface and depletion behind. These reactions are the same as those found by other researchers of Bioglass$^\text{TM}$ corrosion$^{(12,63)}$. Clark and Hench proposed a theory of the corrosion procedure which can be successfully applied to explain the results presented here. On exposure to the corrosion solution leaching of the surface glass begins. It has been well documented
that the presence of CaO in alkali silicate glasses improves their corrosion resistance. (See Section 3.2) In Bioglass\textsuperscript{TM} the CaO is strongly associated with the P\textsubscript{2}O\textsubscript{5}. SEM examination of Bioglass\textsuperscript{TM} has shown that it has a phase separated microstructure, the P\textsubscript{2}O\textsubscript{5} dissociating from the SiO\textsubscript{2} network.\textsuperscript{(51)} As a consequence of the CaO partitioning, the SiO\textsubscript{2} phase is preferentially attacked by the corrosive solution leading to its depletion at the surface. As the silica is removed, a surface layer enriched in CaO and P\textsubscript{2}O\textsubscript{5} is formed. (See Figure 5.3.) This corrosion resistant layer then serves to protect the silica from further attack. Leaching of the Na\textsuperscript{+} and Ca\textsuperscript{2+} from the depth of the glass continues causing the formation of the silica rich region. (See Figure 5.4) The results also show that the glass contains an amount of alumina, (the percentage of alumina could not be quantitatively determined from the SIMS analysis) the profile of which was similar in pattern to that of silica.

The individual corrosion results were combined and expressed as weight percent vs depth in the profile of Figure 5.5. Comparison of this plot to those of Ogino and Clark shows agreement in the pattern of response of the glass components, the profiles obtained being acceptably described by the corrosion mechanisms determined by Clark et al. These results indicate that the glass studied exhibits behaviour which would promote bone bonding in-vivo.

There is however, a discrepancy between the experimental results for the depth of the corrosion layers and the literature values. The results are summarized in Table 5.1.
TABLE 5.1

DEPTH OF CORROSION LAYERS

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>Ca-P FILM</th>
<th>Si-RICH LAYER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clark et al</td>
<td>0.5 µm</td>
<td>3.0 µm</td>
</tr>
<tr>
<td>Barry &amp; Nicholson</td>
<td>500 Å</td>
<td>3000 Å</td>
</tr>
</tbody>
</table>

These results indicate a corrosion layer one-tenth the thickness of that measured by Clark.

Two simple explanations for the discrepancy could be (1) error in the estimate of the profiling rate on the SIMS, or (2) error in the value obtained from Clark's paper for the profile (as outlined in Chapter 2, two values are given in the reference for the profile depth). Of these, the latter was considered improbable on comparison to similar results obtained by Ogino. The former was discounted because of the magnitude of the difference. Another possible explanation is that the discrepancy arises from differences in the glass affecting the corrosion behaviour. While there are possible differences in the densities or stress states of the glasses, the major difference can be found in the composition of the glass.

X-ray fluorescence analysis was used to determine the composition of the glass after melting in fireclay and alumina crucibles. These results are given in Table 5.2.
TABLE 5.2
CHEMICAL ANALYSIS

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>WT % AFTER FIRECLAY MELT</th>
<th>WT % AFTER FINING MELT</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>46.6</td>
<td>45.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td>22.3</td>
<td>19.8</td>
</tr>
<tr>
<td>CaO</td>
<td>22.3</td>
<td>21.2</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>5.2</td>
<td>10.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>MgO</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

There is some error associated with the measured compositions, especially in the P₂O₅ content, due to the lack of an appropriate standard for the analysis.

The important result from these analyses is that the glass contains approximately 2 wt % Al₂O₃, the source being dissolution of the crucibles during glass melting. Researchers of glass corrosion have found that the addition of alumina to an alkali-silica glass increases its corrosion resistance by the formation of a resistant alumina-silicate surface layer. (See Literature Review, Section 3.2.) It is suggested that the contamination of the Bioglass with 2 weight % Al₂O₃ leads to the formation of such a layer which then acts to reduce the leaching of the glass constituents. The enrichment of the surface of the glass in both alumina and silica as shown in the
corrosion profile, Figure 5.5, supports this theory. This would effectively reduce the depth of the corrosion layers formed. The effects of the thin surface layers on the in-vivo behaviour of the glass could not be determined in this study. However, the influence of alumina contamination on the fatigue behaviour of the glass was assessed and will be presented later in this chapter. Other factors may also contribute to the difference in depth profiles. These include the temperature and SA/V ratios of the test. The corrosion testing was performed at 25°C, not 35°C as in Clark's study. This was done to maintain the same temperature for the corrosion test as utilised in the slow crack growth studies. It is not expected that this small temperature difference would cause significant differences in the corrosion profiles. This assumption is based upon results in the literature\(^{(102)}\) for the dependence of glass corrosion on temperature.

The fatigue behaviour of Bioglass\(^{TM}\) 45S5 as dictated by the corrosion reactions identified is analysed in the following sections.

5.3 SLOW CRACK GROWTH STUDIES

The stress corrosion behaviour of Bioglass\(^{TM}\) 45S5 was investigated by studying slow crack growth in DCB samples. The samples had a density of 2.77 g/cm\(^3\) and a Youngs modulus of 81 GPa (determined ultrasonically). A typical sample contained less than 2% volume as bubbles or inclusions. The chemical composition of the glass is listed in Table 5.1. The studies were performed using the testing system outlined in Chapter 4.

Results obtained for the slow crack growth of Bioglass\(^{TM}\) in
air are shown in Figure 5.6. Identified in the figure are the three distinct regions typical of stress corrosion crack growth.

Region I exists for stress intensities below $\sim 4 \times 10^5 \text{ N/m}^{3/2}$. Crack velocities as low as $10^{-8} \text{ m/s}$ were measured therein. At this velocity corresponding to $K_1 = 3 \times 10^5 \text{ N/m}^{3/2}$ there is no evidence of a stress corrosion threshold. The testing system design did not allow extended testing at lower stress intensities, the load being insufficient to maintain the sample's horizontal position.

Region II crack growth extends over the range of stress intensity of $4 \times 10^5$ to $7 \times 10^5 \text{ N/m}^{3/2}$. The crack velocity plateau is at $v = 2 \times 10^{-5} \text{ m/s}$. The position of this plateau is governed by the humidity of the test environment. While the value varied daily, the relative humidity of the air was typically 60-65%.

At stress intensities above $7 \times 10^5 \text{ N/m}^{3/2}$ the curve of $\log(v)$ versus $K_1$ starts to rise. Controlled velocities over $10^{-3} \text{ m/s}$ could not be obtained, therefore only the initial portion of Region III behaviour is plotted. Extrapolation of the curve gives an estimated value of $K_{IC}$ of $\sim 9 \times 10^5 \text{ N/m}^{3/2}$. This value is within the range of data for $K_{IC}$ found in the literature (see Section 3.4).

Figure 5.7 shows the results for the stress corrosion testing of Bioglass\textsuperscript{TM} in solution. While there is no distinct separation of the curve into three regions of crack behaviour as was seen for Bioglass\textsuperscript{TM} in air, there is a change of slope in the curve at a crack velocity of $\sim 10^{-4} \text{ m/s}$. From the basic theory of stress corrosion, the data is expected to follow a straight line curve from the lowest velocities to the value corresponding to critical failure. According
to the theory of Charles and Hillig, Region II crack growth should be eliminated because of the infinite availability of the corrosive species at the crack tip. The results obtained are better described by the theory put forward by Michalske. (See Section 3.4) At the higher crack velocities, the tip "outruns" the movement of the solution. Cavitation at the tip can result from viscous drag of the solution on the crack walls. The net effect is a delay in the reaction of the solution at the tip similar to that which occurred in Region II for the glass tested in air. This causes a displacement of the curve to a lower velocity at a given stress intensity, or a change of slope of the $K_1$-v curve as seen in the results.

Figure 5.8 shows the data obtained at the slower crack velocities for Bioglass™ tested in solution. The lifetime of a glass will be predominantly controlled by Region I behaviour. At the higher crack velocities of Region II and Region III, the time for the crack to grow to critical size is very short and contributes little to the total time to failure. In Region I the crack growth data can be fitted by a logarithmic plot to a straight line curve satisfying the relationship $v = AK^n$. The results yield a value of $n = 30 \pm 5$, $\log A = -173 \pm 25$. Glass with a fatigue parameter $n = 30$ has been described in the literature as having only moderate corrosion resistance.(87)

Sources of error in the experiment were the errors of measurement in the optical monitoring system and the dimensioning of samples. Of these, the latter are of greater magnitude. The travelling microscope used for crack length measurements allowed measurement to 0.001 cm, or 0.0002 cm actual crack length. The accuracy was however limited
by the resolution of the image on the television monitor. (Figures 5.9 and 5.10 are photographs taken at high magnification from the television monitor showing how the crack tip image appears through the travelling microscope). Image clarity usually restricted measurement to \( \pm 0.01 \text{ cm} \), or \( \pm 0.002 \text{ cm} \) actual crack length. The same error is found in the grid marker position causing, therefore, the total error in crack length to be approximately \( \pm 0.004 \text{ cm} \).

The estimated error of the other variables in the equation for the stress intensity are given in Table 5.3.

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<tr>
<th>VARIABLE</th>
<th>ERROR ±</th>
<th>RELATIVE ERROR (%)</th>
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</thead>
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<td>Load, ( P )</td>
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</tr>
<tr>
<td>Crack Length, ( c )</td>
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<td>0.5</td>
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<tr>
<td>Sample Thickness, ( b )</td>
<td>0.01 cm</td>
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</tr>
<tr>
<td>Web Thickness, ( b_n )</td>
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<td>5.0</td>
</tr>
<tr>
<td>Sample Height, ( h )</td>
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<td>0.5</td>
</tr>
<tr>
<td>Stress Intensity, ( K_1 )</td>
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<td>5.0</td>
</tr>
</tbody>
</table>

The major contributor to the estimated error in the stress intensity is the uncertainty in the value for the web thickness. This error arises in part from poor control of cutting depth during grooving of the samples. Other factors in this error are the asymmetry of the groove as shown in Figure 5.11 and the tendency for the crack
glasses is shown in the superimposed plots of Figure 5.16. Bioglass™ is more susceptible to stress corrosion cracking than the common soda-lime-silica glass. The curve for Bioglass™ is displaced to higher velocities at a given stress intensity and is of larger slope. The differences in the stress corrosion behaviour arise because of the compositional differences of the glasses. (See Section 3.2,3.4.) A typical glass for microscope slides has ~25% alkali and alkaline earth, Bioglass™ contains 49% total. It has been documented that increased alkali content increases the susceptibility of glass to corrosive attack. As mentioned previously, Bioglass™ has a phase separated microstructure with the calcium dissociated from the silica phase. Corrosion studies have shown that on exposure to an aqueous solution the glass is attacked resulting in leaching of silica from the surface. This will cause a weakening of the glass structure at crack tips thereby enhancing stress corrosion. In the standard soda-lime-silica glass used for microscope slides, the Ca remains associated with the silica increasing the glass's resistance to static fatigue. The influence of alumina on the stress corrosion of silicate glasses was discussed in Section 3.4. Alumina was found to increase the corrosion resistance of the glass. The effects of alumina on the stress corrosion of the present Bioglass™ will be detailed in Section 5.4.

An interesting observation from Figure 5.16 is that the scattering of data is much less for the commercial glass than for the present Bioglass™. This can be attributed to a more uniform stress state and homogeneity in the commercial glass. The sample preparation used for the present Bioglass™ induced residual stresses which could have
caused the irregular crack motion observed at points during the test. An example of this irregular crack growth is shown in the output from the curve fitting routine, Figure 5.17.

5.4 STRENGTH MEASUREMENTS

Four point bend strength tests were performed on samples of Bioglass™ in an experiment to determine a value for the stress corrosion parameter, n, with flaw conditions similar to those of a finished glass piece (i.e. for small surface cracks rather than a macroscopic crack as in the slow crack growth studies). Data obtained from the tests are given in Table 5.4.

Distributions of the strength values are shown in Figures 5.18 and 5.19. Both distributions are Gaussian with the distribution for the slower strain rate displaced to lower strength values, as is expected from static fatigue theory.

The strength values obtained were ranked in order of increasing magnitude and the logarithms plotted to give the results of Figure 5.20.

Fitting a straight line, slope = 1, to the data, a value of $n = 27$ was obtained from the intercept using Equation 3.23. A variance of $\pm 7$ is associated with this value from the scatter of the data and the experimental uncertainty associated with them.

Within the estimated limits, this value of n agrees with that obtained from slow-crack-growth studies, $n = 30 \pm 5$. From this, it can be concluded that the same fracture mechanisms are occurring at the tip of the macroscopic flaw of the DCB sample as at the tips of
the surface flaws of the strength samples.

Therefore, supported by this verification, the detailed results for the stress corrosion behaviour of 45S5 obtained from the slow crack growth studies can be applied with confidence to failure analyses or lifetime predictions of the glass in a load bearing application.

It is known that alumina in Bioglass™ has detrimental effects on the bone-bonding properties of the glass\(^{(49)}\). Any prosthetic device would therefore be made of Bioglass™ free from alumina contamination. Consequently, before the measured stress corrosion parameters can be used in lifetime analysis for a prosthetic device, the effects of the 2 wt % alumina contained in the glass on the fatigue behaviour must be assessed.

This was accomplished by repeating the 4 point bend tests with a series of Bioglass™ samples prepared from glass melted in a platinum crucible. The glass composition as determined by X-ray fluorescence analysis is given in Table 5.5.

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<th>XRF ANALYSIS OF BIOGLASS™</th>
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</table>
The results of the strength measurements therefore support the use of the fatigue parameters obtained for the alumina-contaminated glass in the calculation of lifetime predictions for pure Bioglass™.

5.5 LIFETIME PREDICTIONS

The time to failure for Bioglass™ under constant load is given by the equation;

$$t_f = B S_i n^{-2} \sigma_a^{-n}$$

where:

$$B = \frac{2}{(A \gamma^2(n-2)K_{lc}^n n^{-2})}$$

The values of $A, n, K_{lc}$ and $S_i$ were determined to be $10^{-173}$, 30, $9 \times 10^5$ N/m$^{3/2}$ and 70 MPa respectively. Substituting these values into the lifetime equation and assuming $\gamma \approx 1$ yields;
The estimated lifetimes for Bioglass\textsuperscript{TM} used in several prostheses are given in Table 5.7. The lifetimes are calculated for a constant stress, the magnitude equal to the maximum stress encountered by the device under normal loading. (See Table 3.3)

\begin{table}[h]
\centering
\caption{Lifetime Predictions}
\begin{tabular}{ll}
\hline
Prosthetic Device & Estimated Lifetime \\
\hline
Tooth (blade design) & $2 \times 10^{37}$ yr \\
Total hip: femoral head & $< 1$ s \\
Total hip: femoral stem & $< 1$ s \\
Fixation device: pin & $< 1$ s \\
Fixation device: plate & $< 1$ s \\
Freeman-Swanson knee & 1 month \\
\hline
\end{tabular}
\end{table}

The results presented in Table 5.7 indicate that for all but the tooth prosthesis, Bioglass\textsuperscript{TM} is unsuited for use as a prosthetic material in these applications due to its inherent low strength and stress corrosion behaviour. The glass may be suitable however for use in applications where the prosthetic device is subjected to lower tensile stresses, such as in ossicular bone replacement. No value of these stresses were found in the literature to allow a lifetime prediction to be made.

A plot of the lifetime of Bioglass\textsuperscript{TM} as a function of applied load is given in Figure 5.23. Figure 5.24 is a design diagram for the allowable stress levels to ensure a 50 year lifetime of the glass.
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## TABLE 5.6

### 4-POINT BEND TESTS: PLATINUM CRUCIBLE MELT

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### Notes
- \( P \) (N) refers to the load in Newtons.
- \( \sigma \) (N/m²) represents the stress in Newtons per square meter.
- LOG \( \sigma \) indicates the logarithm of the stress value.
Figure 5.1 Bioglass™ Corrosion Profile by AES - Raw Data
Figure 5.2 SIMS Analysis of Corrosion Profile - Raw Data
Figure 5.3 Corrosion Profile by SIMS - % Bulk Composition (P, Ca, Na)
Figure 5.4 Corrosion Profile by SIMS - % Bulk Composition (Si, Al)
Figure 5.5 Bioglass™ Corrosion Profile
Figure 5.6 K-v Diagram; Bioglass™ in Air
Figure 5.7  K-v Diagram; Bioglass™ in Solution
Figure 5.8 Region 1 Crack Growth, Bioglass™ in Solution
Figure 5.9  Slow Crack Growth of Bioglass™, Crack Tip Image
Figure 5.10 Crack Tip Image as Through Travelling Microscope
Figure 5.11 Sample Cross-Section
Figure 5.12  Slow Crack Growth, $t=t_1$
Figure 5.13  Slow Crack Growth, $t = t_2$
Figure 5.14 Slow Crack Growth, $t = t_3$
Figure 5.15  K-v Diagram, Soda-Lime-Silica Glass in Water
Figure 5.16  K-v Diagram, Bioglass™ and Soda-Lime-Silica Glass
Figure 5.17 Sample Output from Data Analysis Program
Figure 5.18 Strength Distribution, \( \dot{\varepsilon} = 0.600 \text{ mm/min} \)
Figure 5.19 Strength Distribution, $\dot{\varepsilon} = 0.001$ mm/min
Figure 5.20  Four Point Bend Strength at Two Strain Rates  
$\dot{\varepsilon}_1=0.600 \text{ mm/min}, \dot{\varepsilon}_2=0.001 \text{ mm/min}$
Figure 5.21 Four Point Bend Strength for Pure Bioglass™
\[ \varepsilon_1 = 0.600 \text{ mm/min}, \ \varepsilon_2 = 0.001 \text{ mm/min} \]
Figure 5.22 Combined Plot of Four Point Bend Strengths
Figure 5.23 Bioglass™ Lifetime Prediction under Constant Stress
Figure 5.24 Bioglass™ Design Diagram for 50 Year Lifetime
CHAPTER SIX
CONCLUSIONS

6.1 SUMMARY

The stress corrosion behaviour of Bioglass\textsuperscript{TM} 45S5 was studied in a series of three experiments with the objective of assessing the material's suitability in a load-bearing prosthetic application through lifetime analysis.

The surface reactions of the glass to a corrosive environment were identified by SIMS analysis. It was determined that, on exposure, a Ca-P rich film formed on the glass surface overlying a Si-rich region. The thickness of the corrosion layers were measured as 500Å and 3000Å respectively. It was found that the same corrosion mechanisms occurred on the surface of the glass as did on the glass used in the bone bonding studies of other researchers. The corrosion layers formed were an order of magnitude thinner than those detailed in the literature. It is proposed that Al\textsubscript{2}O\textsubscript{3} contamination of the glass explains this discrepancy by causing the formation of a resistant surface layer which inhibits further corrosion thereby reducing the depth of the layers formed.

Slow crack growth studies were performed to determine the fatigue parameters of Bioglass\textsuperscript{TM}. The results can be expressed

\[ v = AK^n \]

where:

\[ n = 30 \pm 5, \quad A = 1 \times 10^{-173} \pm 25 \]

for Region I crack growth behaviour. \( K_{IC} \), estimated from extrapolation
of the data in Region III, was determined to be $-9 \times 10^{5} \text{N/m}^{3/2}$.

The value of $n$ obtained from four-point bend strength tests, $n = 27 \pm 7$, was in agreement with the results of the slow crack growth studies. This test served to verify that the parameters obtained through fracture mechanics tests may be applied in the analysis of the propagation of micro-cracks or subcritical flaws in a service piece.

It was also determined from strength tests on Bioglass$^{TM}$ containing no alumina that its contamination of the glass, while affecting the depth of the surface corrosion layer, has no detectable effect on the measured stress corrosion parameters.

The inert strength of Bioglass$^{TM}$ was determined to be $70 \pm 5$ MPa as measured by four-point bend strength tests.

Lifetime prediction diagrams were plotted using the measured fatigue parameters. Calculations for the lifetime of the glass used in several prosthetic devices showed the glass to be unsuitable for use (i.e., lifetime less than 50 years) where maximum stresses of over 15 MPa would be encountered.

6.2 RECOMMENDATIONS FOR FUTURE STUDY

In the course of this study several areas have been identified as warranting further study.

1. Researchers$^{(71)}$ have shown that the fatigue parameters, $A$ and $n$, for a glass may change with time due to interaction of the glass with its environment. It is suggested that a study of the time dependence of the fatigue parameters in conjunction with the stress
dependence of the chemical reactions of Bioglass\textsuperscript{TM} be performed to determine if aging of the glass will influence lifetime predictions.

2. Bioglass\textsuperscript{TM} in the amorphous state has a large value of $n$ and inherently low strength. The material is suitable for low load applications, however, methods of improving its toughness must be found if the material is to be used for a load bearing prosthetic device. Several methods are available for increasing the strength of glass. Crystallization of the glass or the inclusion of second phase particles for toughening are two such methods. Future work should include study of the effects of crystallization on the fatigue parameters and strength of the glass. A means of increasing the glass's toughness by second phase toughening also warrants study. The effect of the second phase on glass biocompatibility and fatigue behaviour should also be addressed.
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APPENDIX I

PROGRAM SPACK
... (Program code continues here)

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GIVEN THE SET OF DATA POINTS \((x_i, y_i)\) AND THE SET OF POSITIVE NUMBERS \(\lambda_1, \lambda_2, \ldots, \lambda_p\), SNOOT determines a smooth spline approximating a degree \(k\) for the interval \(X_B = x_{1-k}\) to \(X_E = x_{n+k}\)

The smoothness of this spline is achieved by minimizing the sum of the discontinuity jump of the \(k\)th derivative at each data point.

The size of \(\lambda_i\) is determined by the condition that \(\lambda_i > \kappa \| y \|_{\infty}\)

The spline is given in its B-spline representation, and the coefficients \(c_j\) \((j = 1, \ldots, n - k + 1)\) can be evaluated by means of the function general.

**Calling Sequence**

```fortran
CALL SNOOT\(x, n, \lambda, y, x_{
in}, \lambda_{\in}, y_{\in}, \lambda_{\in}, \alpha, m, n_{\out}, c\).
```

**Input Parameters**

- \(x\) array, input - length \(n\), containing the data positions \(x_i\).
- \(n\) int, input - the number of data points.
- \(\lambda\) array, input - length \(n\), containing the data values \(\lambda_i\).
- \(y\) array, input - length \(n\), containing the data values \(y_i\).
- \(\alpha\) double precision, input - the degree of smoothness.
- \(m\) int, input - the number of knots.
- \(n_{\out}\) int, output - the number of knots.
- \(c\) double array, output of length \(n_{\out}\), containing the B-spline coefficients.

**Output Parameters**

- \(n_{\out}\) int, output - the number of knots.
- \(c\) double array, output of length \(n_{\out}\), containing the B-spline coefficients.

**Restrictions**

- \(n_{\out} > 2k\).
- \(x_B < x(1) < x(2) < \ldots < x(n) < x_E\).
- \(n_{\out} > 1\).
- \(n_{\out} > 2k + 2\).

**Other Subroutines Required**

- CHC, INTC1, RNCT, INTC2, RNCT2, RNCT3, RNCT4, RNCT5.

**DATA Initialization**

- The number of iterations \(N\) is set to the smallest of the number of knots \(n_{\out}\), the distribution of the knots, and the size of the output array \(c\).

**DATA Initialization Statement to Specify**

- The number of iterations \(N\) is set to the smallest of the number of knots \(n_{\out}\), the distribution of the knots, and the size of the output array \(c\).