Degradation of Engineering Materials – Implications to Regenerative Medicine

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Summary: Materials in general, to some degree are susceptible to environmental degradation. The degradation of biomaterials is one of the most relevant issues in the field of regenerative medicine. In industrial practice, the degradation is always a negative phenomenon. In bioengineering, the degradation may be undesirable (e.g. corrosion of metallic implants, wear of artificial joint implant) or desirable (biodegradable devices and tissue engineering). In both cases, the knowledge of the kinetics of degradation is crucial for safe use of biocomponents. The methods for predicting remaining life commonly used in industrial practice will be presented in the context of biomaterials. Non destructive techniques for monitoring degradation will be discussed and some ideas about their application to bio-environments proposed.

Keywords: biomaterials; degradation; mechanical properties; tissue engineering

Introduction

Degradation of engineering materials is manifested by deterioration of relevant properties which decide about performance of a given component. As any change in the properties of materials is governed by changes in their structure, in-service degradation of materials is inherently linked to specific processes taking place under the applied loads and stimulated by in-service environment, which is determined by the temperature, chemical composition, biological agents and physical stimuli (such as radiation).

Structure of modern engineering materials is designed at length scales ranging over more than 10 orders of magnitude (Figure 1). At atomistic scale, chemical composition and content of point defects, such as vacancies, determine elastic properties, chemical reactivity and thermal stability of solids. At a larger length scale, the atoms arrange themselves into linear (dislocations) and planar (interfaces) defects which control a basket of mechanical and physical properties, including resistance to plastic deformation and electrical conductivity. Properties of modern materials are also strongly influenced by a variety of particles, which again may differ in size ranging from 10^{-9} to 10^{-3} m. This plethora of structural elements is to a large extent in non-equilibrium state and undergoes significant changes under exposure to in- service conditions. Some of them are briefly described in the following section.

Degradation Mechanisms of Engineering Materials

Processes leading to degradation of materials can be broadly divided into volumetric and surface-type. Volumetric changes are driven by these agents which act over the entire volume of the component in question. Most frequently listed in this context are: (a) in service temperature, (b) mechanical loads, (c) electromagnetic radiation.

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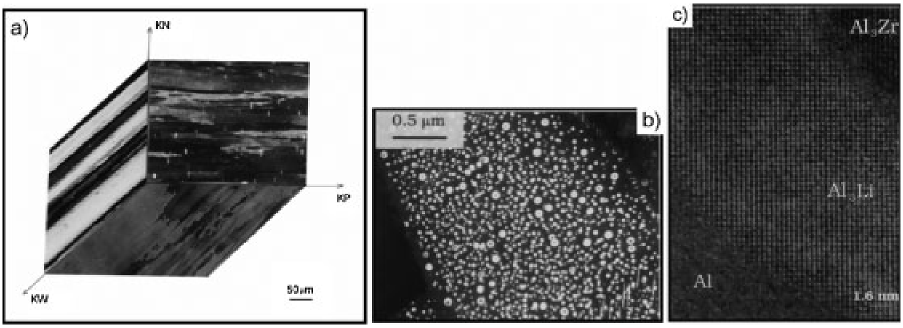

Figure 1.
Microstructure of an aluminium alloy observed at various scales: (a) grain size revealed by light microscopy, (b) nanoscale precipitates revealed by TEM and (c) atomic structure of precipitates revealed by High Resolution TEM.

In-service temperature determines in particular diffusion of atoms/point defects and the kinetics of phase transformations. Exposure to in-service temperature may result in segregation phenomena and coarsening of dispersed structures.[1,2] As rule of thumb, thermal activation becomes significant at temperatures approaching 0.2 of the melting point expressed in the Kelvin scale. From that point of view, the temperature of human body is relatively low for most of the metals. This is not true, however, for polymeric materials.

High mechanical loads cause plastic deformation and permanent distortion of the geometry. They may also bring about irreversible damage to the materials structures in the form of micro-cracks. Such cracks may also form at relatively low loads of cyclic nature (materials fatigue) or under combined effect of loads and corrosive environments. Figure 2 shows a schematic illustration of the influence of cyclic load and corrosive environment on mechanical properties of a material. At the low-scale length these phenomena are related to generation and movement of point and linear defects. Growth of micro-cracks depends on the balance between stress build-up and relaxation.

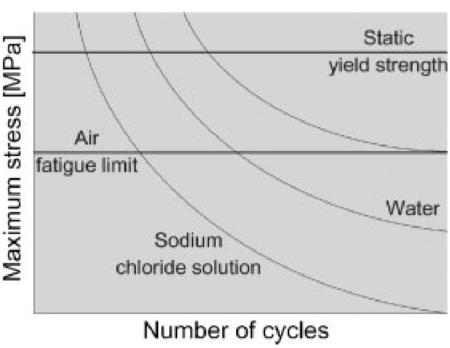

Figure 2.
Schematic illustration of the influence of cyclic load and corrosive environment on mechanical properties.

Exposure to electromagnetic and acoustic fields may cause significant changes in the structure of materials which absorb energy carried out by such waves. The response of different materials to a given type of radiation varies considerably. For example, metallic materials subjected to neutron radiation exhibit reduced ductility due to substantial increase of dislocation loop density.[3] Polymers are especially susceptible to ultraviolet radiation damage. In addition, materials (including polymers) intended to biomedical applications are usually subjected to radiation sterilization which may induce changes in their microstructure and properties. It is well known that UHMWPE have significantly higher stiffness after radiation sterilization[4] whereas radiation sterilization has a detrimental effect on mechanical properties of some polyurethanes.[5]

Surface-type degradation is primarily driven by "short-range" interactions between the material and surrounding environment. These interactions can be analyzed in terms of dissolution (homogeneous or preferential) of the solid and adsorption/ absorption of atoms from the surrounding. Hydrogen and oxygen are of particular interest in the context of atoms intake. On the other hand dissolution of metals and sulphur is known to "poison" liquid environments. Environmental surface-type degradation can be classified into one of three mechanisms: chemical, electrochemical or wear related.

The most common example of chemical degradation is oxidation, i.e. direct chemical reaction between the metal and atmospheric oxygen. There are various mechanisms of oxide scales formation on the metal surface.[6] These mechanisms determine their stability and protection properties. Porous oxide films through which the diffusion of molecular oxygen can occurs continuously are not protective whereas nonporous films provide good protection against further environmental attack.

In bioengineering, the most commonly used protective films are anodic oxides formed on austenitic stainless steels and titanium and its alloys. Figure 3 shows series of anodic oxide films formed on the surface of Ti-6Al-4V alloy at various conditions together with the compositional profiles of such a layers. For more detail see ref.[7]

Corrosion is the most common example of metallic material degradation. It is estimated that 25% of global steel production is used for replacement of structural parts which have been corroded. Corrosion processes may occur uniformly on the entire surface or locally - usually in places which differ in chemical composition or density of defects. They are stimulated/ affected by aggressive environments, which in turn are affected by metal dissolution. Corrosion is particularly dangerous when occurring in human body since it can lead to metallic ions accumulation. In fact, for biomedical applications only corrosion resistant materials such as austenitic stainless steels, titanium or cobalt alloys are used. However, one can expect that some

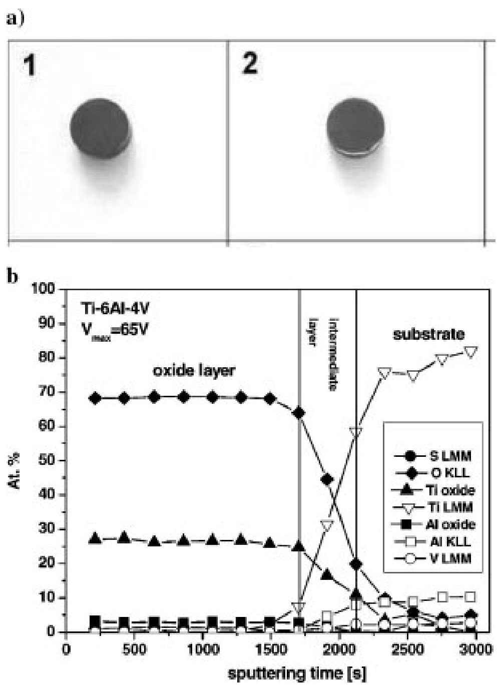

Figure 3.
Anodic oxide films formed on Ti-6Al-4V alloy (a) and their chemical characteristic (b).

Table 1.
NDT techniques for monitoring degradation.

NDT technique	material feature monitored
spark spectrometry	chemical composition
hardness testing	mechanical properties
light microscopy	microstructure
Radiography	cracks and voids
thermography	thermally loaded elements
acoustic emission	cracks, voids, micro-strains, corrosion pits
eddy current	cracks and voids
ultrasonic	microstructure, cracks, voids
phased array	microstructure, cracks, voids, delamination

corrosion processes are inevitable after implantation of metallic materials into a human body.

Industry pays an enormous price for material degradation. Materials degradation problems are in particular important in marine environments, oil and gas production, energy conversion and generation (including fossil and nuclear energies). In response to these challenges the extensive research programmes have been carried out which resulted in a number of now well developed techniques for monitoring the degradation of materials of industrial installations.

Techniques for Monitoring Degradation

Degradation of materials of industrial installations is a serious challenge from the point of view of safety and economy of their operation. Un-detected degradation has been in the past a cause of serious industrial accidents. Based on this concern, a number of techniques have been developed which can be used for in-service monitoring of properties/structures of materials.[8] With the recent development in this area, most of them are now automated and well codified. Table 1 summarizes NDT techniques frequently used in industrial practice.

Visual examinations of various components are carried out using fibre-optics devices and digital images (Figure 4). Ultrasonic and eddy current measurements can be efficiently used to inspect surface and volumetric flaws in any type of engineering material.[9,10]

Acoustic emission is one of the modern techniques which provides information on type and position of active defects in in-service conditions.[11,12] It is based on digital analysis of acoustic signals generated from the structures exposed to mechanical loading and undergoing "environmental" degradation. With the modern technology

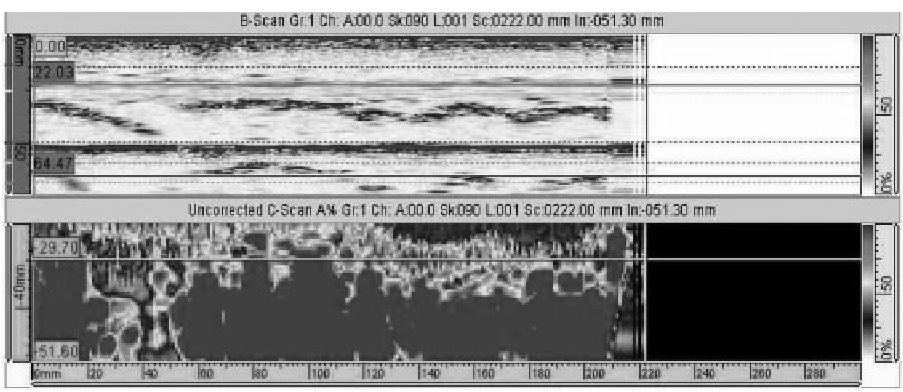

Figure 4.
Delaminations in a pipe of hydrogen plant.

for signal detection and processing, various processes taking place in the structure of materials can be identified and analyzed in terms of their impact on the properties. Current capacity of the systems used for acoustic emission allows for monitoring such subtle processes as corrosive dissolution of metals.

Engineering Approach

Over the years of experience with degradation of materials, the engineering community has developed specific methods for an efficient approach to this problem. This approach is based on the following paradigms:

- quantitative data are needed for quantitative predictions,
- in-service failures are important source of information,
- simulations and modelling are essential for predicting in-service life.

The engineering community in particular has been collecting enormous data obtained in vast number of time consuming experiments with various materials exposed to varied loadings. These data is usually collated into master plots, which can be used to predict time to failure of a given material under the specified in-service load and temperature. As an example one can use the data accumulated for creep and fatigue of metals in various environments.

Another important source of information on performance of different materials in specific conditions is the failures reported by users/designers of similar installations. Failures in the industrial context are generating substantial losses and frequently causing fatalities. No wonder that the industry undertakes variety of special measures to reduce the risk involved in operation of costly and potentially dangerous installations. One of them is use of so called safety factors, which substantially decrease the load carried out by engineering components. Nevertheless, the risk of malfunction is almost never reduced to zero and various breakdowns are unavoidable. If they indeed take place, they should be always carefully investigated to avoid them in the future. The engineering community has learned that this, however, requires concentrated efforts of a larger group of interested parties who are willing to share the data collected at frequently very high price.

Experimental data are of extreme importance in any aspect of materials engineering. On the other hand, there is such diversity in specific in-service conditions that rather rarely one can find readily available data for a particular application. This rationalizes efforts for data generalizing based on modelling and simulations. Modern modelling is based on multi-length scales approaches (Figure 5). Currently available computational tools allow nowadays for such modelling with respect to

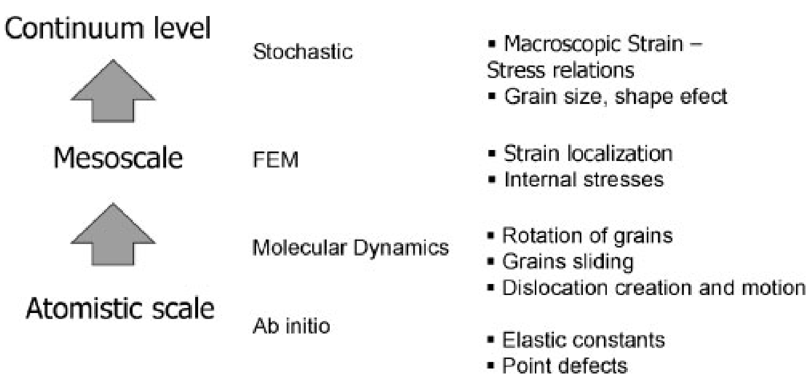

Figure 5.
Concept of multi-length scale.

engineering materials. For example, ab-initio methods can be used to predict properties of various crystallographic phases and their dependence on point defects. Methods of molecular dynamics offer possibility of modelling properties of large number of atoms under applied load in various in-service environments. At a macroscopic scale, Finite Element Method is an efficient tool for modelling behaviours of components made of materials with complex microscopic structures.

Degradation of Biomaterials

The degradation of biomaterials is one of the most relevant issues in the field of regenerative medicine. The biomaterials such as metals and alloys, polymers (synthetic or natural), ceramics and composites degrade and loose their original properties due to exposure to in-vivo strongly aggressive environments and body reaction.[13] The undesirable degradation takes form of wear, corrosion, deformation, creep, fatigue, fractures and oxidation of the biomaterials. Despite all the progress made in regenerative medicine these phenomena are recognized as major factors limiting the success of the total joint replacement (TJR). Although, millions of TJRs are performed annually to improve quality of life of the patients, the most of them fail after few years causing pain, reducing the joint range of movements, components loosening, and finally resulting in a revision operation.[14,15]

Abrasion, burnishing, pitting, erosion and delamination were found to be the most predominant modes of in vivo degradation (wear and cold fow) of polyethylene in TJR. From the scanning electron micrographs of the exposed surfaces of the retrievals it was found that fine multidirectional scratches were dominant in all retrievals (Figure 6). In addition to the scratches, flakes and rim erosion are also observed. Moreover, two implants revealed pitting areas and surface microcracks, which most likely result from subsurface fatigue. Polyethylene delamination was observed for metal backed component. Some of the implants were completely worn out to the metal backing in some places (Figure 7a).

In vivo degradations products such as particulate and ionic wear and corrosion debris cause aggressive biologic response that can lead to synovitis, periprosthetic bone loss, and aseptic loosening of the implants.[13] The polyethylene wear particles migrate into the periprosthetic spaces and stimulate the activity of the macrophages by the release of cytokines, which activate the osteoclasts and these osteoclasts lead, in the long term, to the bone resorption around the prosthesis.[14] Increased concentrations of circulating metal-degradation products of fretting corrosion of the metallic implants may also induce the bone resorption, and have deleterious biological effects over the long term.[16] Additionally to these negative biological effects, deformation and damage of the implant

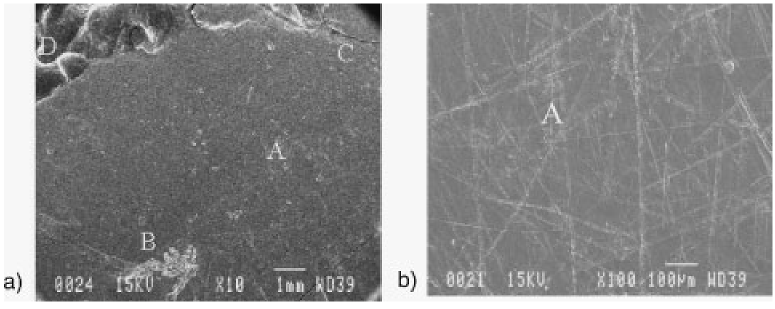

Figure 6.

SEM images of the peripheral (a) and central (b) parts of the polyethylene glenoid retrieval showing: multidirectional scratches (A), flakes (B), cracks (C) and rim erosion (D).

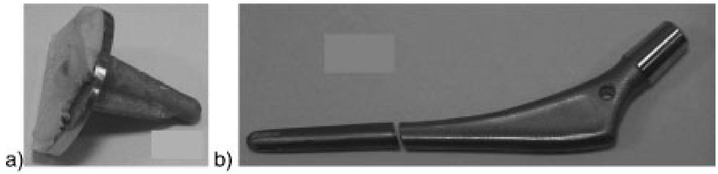

Figure 7.
Wear and fracture of the tibia component (a) and fracture of the hip stem (b).

materials disturb the stabilising function of the implant. It was found, for instance, that glenohumeral instability after arthroplasty was associated with the wear of the glenoid component.[17]

There are many factors which influence the material degradation in total joint replacements. Design-manufacturing ones include geometry of the prostheses, surface roughness, loading characteristics, and lubrication condition. Among the material factors material properties are crucial, however, details of manufacturing process, sterilization and handling may profoundly alter these properties. Design of the artificial joints is of paramount importance. Insufficient thickness of the polyethylene component influences wear of the total joint replacements.

Bartel et al.[18] indicated that to minimize wear a minimum thickness of eight to ten millimeters should be chosen for tibial components and six to eight millimeters for acetabular components. Contact surface geometry described by radial clearance (or degree of conformity) between the radii of curvatures of the articulating surfaces of components is another geometrical factor affecting the wear of implants. Low joint conformity might result in high contact stresses and could contribute to faster implant wear and failure. Swieszkowski et al. ,[19] reported that the peak stress generated in non-conforming glenoid components under conditions of normal living can be as high as 25 MPa; since this exceeds the polyethylene yield strength deformation and wear of the components can be expected.

The major factor responsible for the polyethylene implants failures is oxidative degradation of polymer induced by sterilisation with γ-irradiation. The irradiation results in generation of free radical in polyethylene. These free radicals may react with the oxygen that could diffuse into polyethylene during shelf storage and/or in vivo, causing the polymeric chain scission, in turn, this will lower the molecular weight of PE, increase the density, stiffness and brittleness, and reduce the fracture strength and elongation to failure. Any of these changes could dramatically affect the wear resistance.[14,20]

Material fatigue could be the reason of the subsurface cracking in the polyethylene components of the knee implants. These cracks very often propagate to the surface of the implants causing the fracture of the polymeric components. The fatigue and structure defects of the biomaterials may result in the fracture of the metallic stem in the total hip replacements (Figure 2b). Aggressive fatigue loading of cemented artificial joints is responsible for formation of micro-cracks in bone cement and stem/bone micro-motions.[21]

Bio-degradable Materials

In bioengineering the degradation may also be a desirable process (e.g. biodegradable devices and tissue engineering). There are many examples of the biodegradable materials application in medicine, such as absorbable sutures, bone fixation materials, adhesives, temporary substitutes for tissues, medical devices for guided tissues regeneration, or scaffolds for tissue engineering.[22] They are also used in drug delivery systems. Modern materials used in these applications are not only degradable but also bioresorbable, what means, that the degradation products are not stored in situ, but can be eliminated from the body through natural pathways.[23]

Biodegradation is defined as the gradual breakdown of a material mediated by a specific biological activity.[24] While natural materials, such as, e.g. collagen are degraded in tissues by enzymes, the degradation of synthetic degradable materials is mostly by hydrolysis. This is the case for the most commonly used synthetic aliphatic polyesters, which are often based on Poly (glycolic acid), Poly (lactic acid), Poly (ε caprolactone) and their copolymers. Thus, the term biodegradation, which is widely applied to these materials, is not strictly adequate, as the hydrolysis is not specific for biological environment. On the other hand, hydrolytic reactions may be catalysed by enzymes and also by pH of the liquid.[24] In this way, it can be controlled in specific tissues. The degradation rate may vary from weeks to years dependent on the chemical composition, material structure, shape and size of the implant and the particular temporary biological state at the implantation site. Thus, our abilities to predict of behaviours of degradable materials in tissues are limited and there is a burning need of new experimental systems both in vitro and in vivo in this respect.

At the very early stages of their development implantable materials were expected to be chemically inert and highly stable.[25] As it was becoming more and more evident that human body is able to accept a wide range of different materials, the growing interest in materials which interact chemically with the host tissues could be observed. This was mainly in order to improve the contact between the material and tissues. While the inert materials were usually encapsulated by a dense connective tissue, the active ones were expected to become at least partially incorporated in the host tissue. These, second-generation biomaterials were designed to be either resorbable or bioactive.

The third and the most advanced generation of materials are the bioactive one used for reconstructive surgery of tissues. They are expected to combine resorbability and bioactivity, with the healing effects.[25]

This leads to the tissue engineering and tissue engineered product (TEP), usually consisting of artificial scaffold seeded with living cells, serving as a support for self-regeneration of the tissue.[26] Candidate materials for scaffolds, such as polymers and calcium salts- based ceramics, are biodegradable. In the most wanted scenario the scaffold degradation should be followed by the host tissue deposition. This idea, described in details by Dietmar Hutmacher,[27] is schematically represented in the Figure 8. Although the direction is very promising, the problems with the controlling the material degradation are even more challenging in such applications. This is due to the adverse effect of the degradation of the support in cell culture, which is accompanied by the pH changes. The buffer system in vivo is much more effective, so it happens that biodegradable materials, which may serve as implantable devices, cannot be used at the first stage of TEP preparation (cannot be put in the contact with cells in vitro). This problem may be overcome by using the dynamic systems for a culture (so called bioreactors), however, it should be stressed once again here, that the successful medical applications of degradable materials strongly dependent on the improvements in controlling the degradation/resorption processes in biological systems.

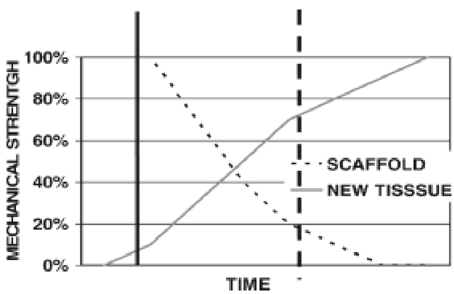

Figure 8.
Schematic representation of the idea of gradual disappearing of the scaffold while replacing by the host tissue which is expected to regenerate. Vertical lines represent the possible implantation time point.

Summary

Materials have been and are decisive for development of civilization. As a result a broad knowledge have been accumulated by the materials science and engineering community. This knowledge proved to by extremely useful for a whole range of industrial sectors, including such an aerospace (air transport) and power generation (nuclear power plants) which require a long lasting continuous operation under high safety standards. As similar requirements are typical of medical applications of the engineering devices, an exchange of information and best practises should prove to be mutually beneficial. In this context, a suggestion is put forward, that some of the current NDT techniques might find their applications in monitoring degradation of the materials used in bio-medical functions.

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