

Invited Talk

Toward the Concept of Designing Smart Corrosion Prevention System

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ABSTRACT

The techniques that are applied for prevention of corrosion mostly rely on the logic of protecting the surfaces and not on providing the ways and means of promoting the processes that would not allow the course of corrosion to begin. The result is, we have a plethora of methods for different components of the same vessel, and for different environment and circumstances, for the same equipment. Sometimes we try on macrodesign, while at times we depend on material selection as remedy. Inhibitors are used in few cases whereas you find coatings being administered here and there and electrochemical protection employed somewhere else. This gives a look to the sea-going vessels as if they are coming out of an operation theatre with bandages and dressings all over. These specific solutions to specific corrosion at specific location for specific ambience have led to bulky systems with heavy penalty on payloads and still shrouded in uncertainty so far as prevention of corrosion is concerned. Different systems for protection for different situations have also led to the difficulties of monitoring as to the structural integrity of the equipment. This talk is intended to systematically analyse the total corrosion situation - the material, the environment and the circumstances, and propose a design of intelligent corrosion prevention system.

While the concept of designer material and nanotechnology and their application to design corrosion-resistant material systems are examined, extension of biological processes for molecular repair of materials and components is explored to firm up the concept of self-repairing systems. The idea of functional smartness as exemplified by functionally graded materials and smart coatings and skins are reviewed along with the design of electron cloud. An answer to the question whether materials could be adapted to meet the requirement of environment that causes corrosion without losing its integrity is probed. It is getting possible to integrate materials, sensors, actuators and control electronics and redefine the concept of material from a purely passive system to an active system with inherent self-sensing, diagnosis and self-repairing and control capabilities.

INTRODUCTION

Deterioration due to corrosion is often accepted as an unavoidable fact of nature, which has led to a lack of interest in fundamental investigation into the various aspects of corrosion and the basic prevention measures. Result is, 'standard' solutions are used while unexpected problems lead to catastrophic failures without any warning. We have tried to find solution to every symptomatic problems leading to bulky structures and entailing large maintenance headaches and costs.

Corrosion protection measures have in general been attempted as a post-corrosion measure, not as corrosion-process measures. Once the corrosion has taken place, we endeavour to make up for the damages. There are few measures which have been tried to control the corrosion process but we must examine them more minutely and design the processes that stop them.

Another weakness of the present corrosion protection techniques is that they have been sought more as a maintenance and retrofit remedy, not as designing the processes that would prevent corrosion and not as a material environmental design work against corrosion. Can we not, today, with the large volume of information available on material, environment and the circumstances with respect to corrosion employ an intelligent corrosion prevention system at the design stage itself?

CORROSION PROTECTION TECHNIQUES

It is said that under ideal service conditions the possibility of which is rare, corrosion can be completely avoided. Ideal service conditions can be created and maintained intelligently. The materials will remain absolutely uniform, with no heterogeneities in either composition or structure, and the environments will be entirely uniform. Such conditions are difficult to attain. Through examination of the techniques employed for corrosion we shall explore how such conditions can be created. There are three primary approaches to prevent corrosion: (1) the isolation of the electrolyte from the electrodes by means of protective surfaces (2) the avoidance of galvanic couples, and (3) the use of galvanic protection. The present techniques of corrosion protection using these methods can be broadly classified into five categories based on the application of good design practices, a scientific approach to material selection, the use of inhibitors, application of a protective coating and using cathodic or anodic protection.

GOOD DESIGN PRACTICES OR DESIGNING FOR ENERGY-EQUILIBRIUM?

Designing against corrosion is based on the premise that protection against corrosion can be designed into the product. Thus crevice corrosion, galvanic corrosion and mechanico-chemical types of corrosion namely stress corrosion cracking, corrosion fatigue and cavitation corrosion (Henthorne 1972, Pludek 1977, Anon 1978) are being handled to a large degree by applying good design practices. To avoid crevice corrosion, the technique is to avoid crevices into which oxygen or other oxidants won't have free access, which in case of deficiency in oxygen, gives rise to concentration cells and cause corrosion.



The oxidation cell accentuates corrosion, but it accentuates it where the concentration of electrolyte is lower. Thus the place of greater concentration of oxygen becomes cathode and the crevice with lesser concentration the anode which corrodes. To avoid corrosion, therefore, we may argue that an increase in the quantity of electrons between the anode and cathode may retard the anodic reaction or corrosion.

The galvanic corrosion has been categorized into composition cells, stress cells and concentration cells. A composition cell may be established between any two dissimilar materials, with material at higher electromotive level acting as anode-the corroding part. Thus zinc in the galvanized steel is the anode and steel the cathode. Even two phase alloys with different energy levels in each form galvanic couple. Thus in pearlite ferrite with higher energy level corrodes while iron carbide with lower energy level is protected. Heat treatment alters the micro structure of the metal. Thus tempering of the martensite produces many galvanic cells and grain boundaries of ferrite and carbides. The grain

boundaries serve as the anode because the boundary atoms have a higher potential. A fine grained metal with more anodic area therefore corrodes faster than a coarse grained metal. The grain boundary zone may be considered to be stressed, since the atoms are not at their positions of lowest energy. The effect of internal stress on corrosion is evident after a metal has been cold-worked. The cold-worked area serves as the anode and the stress-free area as the cathode. Again, the higher level of energy of the stressed part is the cause of corrosion.

One underlying theme of the galvanic corrosion mechanism is that it is caused by the setting up of galvanic cells and the accompanying electrical current. The two dissimilar electrodes may be provided by the differences in composition, or differences in the energy levels or the differences in the electrolytic environment concentration. In all cases the cause is the dis-equilibrium between the two sets of environment. And the energy must flow from higher to lower level to maintain the balance and that is what causes the corrosion. If this dis-equilibrium could be counteracted continuously in the other direction, say by balancing of energy levels, the corrosion won't begin, we can stop the corrosion. We can see from the above, the loss of electrons is the culprit. Keep enough supply of it so that the metal doesn't lose electron and therefore doesn't corrode.

MATERIAL SELECTION OR DESIGNING A MATERIAL?

You can't select the environment and the circumstances under which the material has to perform without corrosion. But you can intelligently create another environment and the circumstances which will be in equilibrium with the material. Or you can select a material that will perform and at the same time doesn't corrode in the environment and under the particular circumstances. The environment and the circumstances are the most varying parameters and must be intelligence-controlled. While selecting a material most of the times, a compromise is settled between the strength properties and the corrosion properties and thus what we get from the material is not the best performance parameters but the reduced one. Solutions are often found in having a metal for mechanical strength and a plastic coating for corrosion resistance. The initial and continued integrity of the coating then becomes critical. Perfect match between material and the environment has been missing and the task is not to select a material from the available heap of it but to design one which is meeting the strength and corrosion requirements both - the designer material. We can also think of adaptive material structure.

DESIGNER MATERIAL

We have not been able to exploit the full potential of materials because of corrosion. Recent advances in computing and-mathematics are making it possible to simulate the properties of materials without ever making them and scientists are deciding what properties they would like, not only mechanical, chemical, electromagnetic properties but also corrosion properties, and designing the material that will do the job including having the anti corrosion properties in whatsoever environment desired. The simulations begin with the rules of quantum mechanics governing the matter on the atomic and subatomic scale, quantum mechanics being the most accurate way of describing material theoretically in terms of Schrodinger equation. This equation gives the details of the desired system - the material. The solution is known as a wave function. This wave function gives everything that can be known about the system. And with a description of the arrangement of nuclei and electrons, scientist can calculate the forces between them and design the material. Supercomputers are fast becoming the crucibles of the future, forging a new generation of designer materials. (Mike May 1999).

COATINGS

A coating applied to a metal to prevent corrosion may offer a form of sacrificial protection, or act as an inhibitor or simply exclude the corrosion environment. To act by exclusion, a painted surface, of example, isolates the underlying metal from the corroding electrolyte. The sacrificial coatings are metallic coatings that act in the first place by exclusion. However if weak spots develop they form galvanic cell with the substrate in which they corrode in preference to the substrate material. More important, the corrosive products produced in this process plugs the weak spot and protects the substrate and the coating from further attack. The inhibitive coatings are mainly paints which contain inhibitive pigments.

Smart Coating Systems

Smart coatings are structured coating systems that provide an optimum response to some external stimulus. They react to outside conditions, such as temperature, stress, strain or the environment, in a selective way. Conceptually, it is possible to design surface coatings with variable intrinsic responses to external stimuli. Material interface between corroding parts and the environments need to be developed that could maintain electronic and ionic equilibrium between corroding material and the environment. The intelligent combination of material and novel processing technologies is being used to manufacture numerous coating systems that embody smart concepts. Active and passive sensors and actuators are being manufactured using nano engineering in conjunction with coating technology. In the scientific literature there are many materials that offer 'Smart Properties'. Such materials require a change in property that can be easily stimulated by change in the local environment, such as temperature, stress, strain and chemical potential.

Functionally graded Coatings employing Smart Concept

The composition and structure of a functionally graded material (FGM) varies in a specific manner with position in the material imparting a controlled change in the properties of an FGM with position. FGMs are classified into three main categories which are called interface, surface and bulk FGMs (Rawlings 1995). An interface FGM is a layer of graded material situated at the interface between two materials with different properties, the interface thus avoids the corrosion between the two materials. Often the properties required at the surface and the interior of a component are not the same. Thus a hard, wear and corrosion resistant surface may be needed whereas it would be desirable for the interior to be ductile. Surface FGMs whose progressive change in composition and structures eliminate the significant discontinuities in properties that occur across well-defined interface have been proposed as an alternative to conventional coating systems. The aim of a bulk FGM is to give the different property requirements at the surface, over a reasonable volume beneath the surface and at the core of a component. Although still at the research stage, it appears that the bulk FGMs could lead to the development of a series of novel materials with unique service performance including anti-corrosive performance.

An adaptive coating structure against corrosion

Functionally graded materials can be used to fabricate smart, environmentally tolerant coatings. The concept of the manufacture of smart overlay coatings for industrial gas turbines, under the 'Link Surface Engineering' initiative, is the development of functionally graded coatings, that can adaptively respond to the mode of corrosion attack within the industrial gas turbine. This is achieved by designing a graded coating system that forms alumina scales for high temperature protection (900-1200°C), but chromia and/or silica scales to combat type II hot corrosion at lower temperature (650-800°C). It is

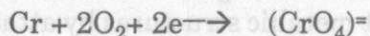
the mode of corrosion attack, plus the graded coating structure, that permits this adaptive response (John Nichols, 1996). Optimal design requires that the coating composition profile vary through the coating to provide alloys that grow stable alumina scales at the coating surface. Beneath these the composition changes to alloys more resistant to type II corrosion. It is the mode of type II corrosion attack that permits this functionally graded coating to exhibit smart concepts.

PROTECTION BY PASSIVATION

The production of ions and electrons build up an electrical potential, called the electrode potential, which depends on the nature of the metal the environment. The dissociation of metals into solution, the environment produces ions. The electrons produce electrode potential. In the presence of other ions, say Cr^{++} ions, in the electrolytes, the oxygen-or an oxidizing agent such as nitric acid, may combine to form a protective film on the cathode



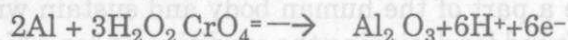
With the accumulation of the chromate ions on the cathode, the cathode is isolated from the electrolyte retarding further reaction. Under such conditions, the metal is said to be passivated. This effect can be accentuated if certain easily oxidized elements are added to the metal. Stainless steel, for example, always contains chromium which oxidizes easily. Although it is above iron in the electromotive series, the chromium-oxygen combination provides a passive surface film of $(\text{CrO}_4)^=$ by the reaction



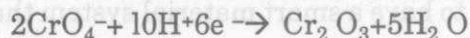
However, because the film is removed when the stainless steel is placed in non-oxidizing electrolyte, stainless steel is subject to corrosion in HCl , HF , or other oxygen-deficient solutions.

Corrosion inhibition or self repairing systems?

One method of corrosion control is to modify the environment. It is possible in principle to remove the aggressive agent, but this will normally be inconvenient or impossible. Alternatively, a chemical can be added (necessarily in small amounts) which produces a marked decrease in the rate of corrosion of the metal - such a chemical is called a corrosion inhibitor. This has been capitalized by adding rust inhibitor to decrease corrosion in radiators, steam boilers and other containers. Inhibitors for aqueous corrosion may be inorganic or organic, the former may be subdivided into oxidizing and non-oxidizing. The oxidizing inhibitors e.g., chromate ions act by keeping the natural passive film **in good repair**. Chromate ions promote oxidation (an anodic reaction) of iron or aluminium at the weak spots in the film:



Whilst being themselves simultaneously reduced (a cathodic reaction)



It will be seen that in each half reaction a solid product (Al_2O_3 and Cr_2O_3) is formed which serve to keep the film **in good repair**.

The non-organic inhibitor e.g., benzoate, which is an organic ion, but is more conveniently classified along with the inorganics keeps the film **in good repair** as the result of promoting the oxidation of the metal to oxide (by oxygen) and allowing local precipitation of the ferric salts of the inhibitive ion. In view of the mechanism by which the inorganic inhibitors act, the protective oxide film must be potentially stable in the corrosive

environment containing the inhibitor. This is a condition favoured by a neutral or alkaline pH.

Modifying the environment is not restricted to aqueous environment. For example, in enclosed spaces it is possible to protect against atmospheric corrosion using vapour phase inhibitors. In an enclosed space, they enter the atmosphere, to a limited extent, find the metal surface and absorb there and are used to avoid atmospheric corrosion in enclosed spaces, e.g., in packaging during shipment and storage. To have a self-controlled addition of inhibitors, a system can be devised to monitor the content of inhibitor in the electrolyte and add the inhibitor when it falls below a particular value. This way total system of inhibition can be made self-repairing, self-organizing and self-learning.

ELECTROCHEMICAL PROTECTION - BALANCING THE ELECTRON FLOW

We know that aqueous corrosion requires the oxidation of a metal in an anodic reaction :-



If electrons are supplied to a corroding structure then the above reaction is inhibited. Since, if it were to continue, it would contribute to the surfeit of electrons already entering the structure. This supply of electrons, which inhibits the anodic reaction, and thereby reduces, or stops, the corrosion is the basis of cathodic protection. The more noble metal in the galvanic couple is protected from corrosion, while the more base metal dissolves sacrificially. Electrons are transferred to the noble metal through the metallic circuit from the base metal. This phenomenon is used to protect metallic structures by attaching to them a more base metal that is known as a sacrificial anode.

An alternative method of supplying electrons to the structure is to use a dc rectifier and an auxiliary electrode-called the impressed current technique. The structure is connected to the negative terminal of the rectifier and the positive terminal to the auxiliary electrode.

Cathodic protection and impressed current techniques both use the process of supply of electrons to the component that has to be protected from corrosion. It is very close to the smart concept of preventing corrosion. The only thing that is lacking is the achievement of equilibrium between corrosion and supply of electrons, the impressed voltage, which is caused by the changes in environmental and circumstantial conditions.

TOWARD SMART NON CORRODING BIOMATERIAL SYSTEMS

Biomaterials have to work with the intelligent human systems and therefore have to be intelligent. Their corrosion too has to be avoided intelligently. The work on finding a compatible biomaterial that can become a part of the human body and sustain without corrosion is in progress. Ways are being found for designing the condition under which the material won't corrode. This search for biomaterial and the adjoining material environment around it is leading to indicate that it is possible to have a smart material system that can resist corrosion.

Surface modification

Despite the potential harm of metallic ion release, metals continue to be used because of their strength, particularly their toughness, but their corrosion resistance and hard-to-issue compatibility with human system must be improved. Their surface should be modified to improve corrosion resistance, wear resistance, and bone conductivity. This may be

realized by a recent progress of ion-beam technology. Surface modification techniques in aqueous solutions and with ion beam are applied to biomaterials.

Surface modification of titanium

The easiest way to increase the corrosion resistance of titanium is anodic oxidation in an acidic solution or high-temperature oxidation in air. Sputter-deposition of thin TiO_2 film is also effective in improving corrosion-resistance. Nitrogen ion is implanted to improve wear resistance and bone conductivity of titanium, and to improve corrosion resistance of Ti-6Al-4V. The most important reason of surface modification of titanium is the improvement of bone conductivity, through formation of calcium phosphate film.

Corrosion of metallic biomaterials in body fluid and surface modification has been studied by Hanawa et al (2001). Surface oxide films on metallic materials act as an inhibitor of corrosion as well as aid in biocompatibility. The film inhibits the dissolution of metal ions, but is not always stable in human body.

Bio Dur® 108 alloy is a nickel-free austenitic stainless alloy developed by Carpenter Technology Corporation. Beside austenitic stability, the high nitrogen content of one percent also contributes to high levels of corrosion resistance and strength. The strength of such alloys tends to be dominated by nitrogen content, while corrosion resistance is strongly related to the content of chromium, molybdenum and nitrogen. (Ge bean, et al, 2001). The Nitrogen ion implantation has been carried out on titanium alloy for medical implant to improve corrosion resistance in pseudo physiological solution (Fukumoto et al 2001). The corrosion resistance was more improved by multi energy implantation.

THE CONCEPT OF SMART SKIN : CLOSE ADHERING CLOUD OF ELECTRONS

The concept of supplying externally electrons to the corroding structure may be used to prevent corrosion. That this is a feasible solution can be gauged from the Unitel's Smart Skin design which contains layers of niobium supporting a close adhering cloud of electrons. This is a proven technology. In 1967, a design was offered to NASA by AVCO of Everett, NJ, with the ability to screen out harmful particles and radiation, including heat, during re-entry into the earth's atmosphere. A close adhering cloud could permanently prevent the corrosion of the surface by maintaining a surplus of electrons in the outer circuit.

SMART DUST

Packed full of sensors, lasers and communication transceivers, particles of 'smart dust' are being designed to communicate with one another. They could be used for a range of applications from monitoring of weather to spying. These tiny 'motes' are being developed at the University of California, Berkeley, to produce the smallest possible devices that have a viable way to communicate with each other. Each mote is made up of a number of micro electromechanical system (MEMS) wired up to form a very simple computer (Duncan Graham, Rowe, 1999). It is expected that in future smart dust could be used to monitor and control corrosion in adverse conditions.

NANOTECHNOLOGY, BIOTECHNOLOGY AND INFORMATION TECHNOLOGY

When products are fabricated out of iron, steel or other metals it is natural for them to return to their original state. This process is called corrosion, and may be the only time when a 'natural process' can cause a tremendous concern. This indicates something wrong,

something 'unnatural' with the engineering processes through which we process materials, taking them to higher energy level, placing them in unstable state. Materials try to find their natural state.

The very necessity of macroprocesses has arisen because of high demands on the performance of materials-mechanical, chemical and others requiring higher energy. Against this we have biological processes that proceed in infinitesimal steps and remain in equilibrium with the nature. There has been a thinking in this direction that macro processes in modern engineering could be oriented in biological fashion. Nanotechnology and biotechnology seem to provide answer to this problem of meeting the modern day requirement of high energy and that of equilibrium with the environment.

If you can design materials with the properties and behaviour you desire, nanotechnology shows the possibility of manufacturing them. K Eric Drexler (1987) argues that the old style of technology is bulk technology, where we handle atoms in unruly herds. Nanotechnology, on the other hand, will allow us to handle individual atoms and molecules, so we can build complex structures, one atom at a time. He says, nanotechnology will completely transform information technology, biotechnology, and material science, enabling us to build self-replicating engines. Nanoscale science and engineering will allow us to work directly with the building blocks of matter where all properties and functions are defined - and can be changed including corrosion properties in an environment.

"Once we have the software to direct them, replicating assemblers can build almost anything, including more of themselves, including the possibility of corrosion - resistant materials. Just as trees do, systems of replicating assemblers can construct big, complicated structures, even extremely large pieces of hardware - cars, ships and aircrafts" (Drexler 1987). The artificial intelligence applied to engineering will give the ability to quickly design enormously complex systems embracing a corrosion proof system. With this sort of design ability, molecular machines with the ability to repair living tissue and corroded parts could be built.

Purdue University research led by chemist Hicham Fenniri are using the same principle that makes DNA strands link together to create tiny structures that may someday be used to manufacture molecular wires and other components for use in nanometer-sized electronic device. They have created molecules designed automatically using self-assembly techniques to develop nanoscale structure with specific dimensions and chemical properties. The beauty of this system is that, by designing the molecules that make up the system, you have perfect control over every part of the system (Goldein 2000).

Self- repair capability on biomolecular lines and nanotechnology

The design of inhibitor systems, electrochemical protection and coating systems need changes in the processes to make it self-repairable. One approach is the biological one. Engineers in the macroscopic world typically build rigid structures that stoically resist the forces of nature. Nature has, however, taken a different approach, developing machines that flex over the course of their action. The question is, does it require a totally rigid nano-structure or whether it is desirable at all? In fact, biological molecules take advantage of flexibility for many aspects of their functions. Can we design a flexible system for corrosion prevention? This process is easy for evolution but far more difficult for biotechnological design. We design our machines in one step, instead of through many small random optimization steps, and we expect to get it right with a minimum of redesign.

Biological molecules are examples of solved problems in nanotechnology-lessons from nature that may be used to inform our design of nanoscale machines. The entire discipline of biotechnology has emerged to harvest this rich field of biological wealth. The

information in DNA is routinely edited and rewritten and build custom proteins tailored for a given need. Why not for corrosion prevention, today, for instance, bacteria are engineered to produce hormones, genes for disease resistance are added to agriculture plants, and cells are cultured into artificial tissues?

There are powerful overlays among nanotechnology, biotechnology and information technology. For example, the idea of nanotechnology came from applying an engineering perspective to the discoveries of molecular biology and one path to nanotechnology lies through further advances in biotechnology. The study of the inherent structures within biological information and biological systems led to the emergence of the bioinformatics. This synergistic coupling of nano, bio and info wherein nanotechnology offers the possibility of engineering structures with well-defined properties that are in tune with the environment and applying biological processes of self-assembly and self-repairing capabilities for repairing corroding parts and components and the use of information technology for flawless communication and control is expected to pave the way for an intelligent corrosion prevention material system.

AFTERWORD

While there are broad theories that help to determine a particular metal for a particular purpose, its actual corrosion behaviour can be very variable, because corrosion depends upon so many factors. Such **variability** can be tackled better by designing intelligent corrosion prevention systems. While the approaches to corrosion protection are empirical, they lack in exactness. The paper suggests that with adequate knowledge of corrosion, a reliable intelligent system for avoiding corrosion is feasible to attain.

If 'rust never sleeps', how can ever the corrosion prevention system sleep? A continuous monitoring of basic parameter of corrosion and continuous repairing/filling/replacement/equilibrium of the electron-ion is a must, not at few locations, but at all the places, throughout the material surfaces and at all the time, in all the conditions with varying environment and operational conditions. This would be the smart system that would keep the material structures always in 'as if new' condition. This will automatically keep things in equilibrium - the materials, the environment and the circumstances.

One takes the posture that corrosion can be prevented only in a few cases and what one attempts is to control it within limits, which itself reduces the life of the structure. It has been proposed that by having a system that maintains the equilibrium between materials, environment and circumstances, corrosion can be prevented altogether. This needs the identification and definition of each of the parameters, their interplay, their monitoring and appropriate feedback action.

The concept of designer material with the synergistic integration of nanotechnology, biotechnology and information technology is the possible answer to provide an intelligent, active and adaptive corrosion prevention system. Corrosion control is basically a design problem, using the term in its widest sense. It is not just a question of choosing corrosion resistant materials or very durable coatings, it is a matter of fitting together all the different elements to prevent corrosion. Going further, it is a matter of designing materials including the environment such that they are in harmony with the varying circumstances and with each other so that they are in total equilibrium with each other in sustainable manner, the way other natural systems are. This means designing corrosion - resistant systems that include the corroding material, the environment under the existing and the impending circumstances in such a way that they aid in the sustainability of the eco system, in such a way that they become a part of the eco-generation, degeneration and regeneration system. For this to happen it is important that we understand the natural processes, the biological processes and modify our macro engineering processes to align them with the biological world.

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